ALLEN'S
COMMERCIAL ORGANIC ANALYSIS

FIFTH EDITION, REWRITTEN, REVISED, RESET

The organic chemicals and products employed in the arts, manufactures, commerce, medicine, science, etc. It treats upon the properties, modes of analysis, proximate analytical examination; methods for detection and estimation of impurities, adulterations, products of decomposition, etc.

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NOTE: Volume II enlarged over previous edition by 286 pages and 10 illustrations.

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NOTE: Volume III enlarged over previous edition by 96 pages and 11 illustrations.

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Strychnos Alkaloids. By C. Ainsworth Mitchell, M. A., F. I. C. Strychnos Plants; Nux Vomica; Assay of Nux Vomica; Preparations of Nux Vomica; Alkaloids of Curare; Strychnine, Strychnia; Salts of Strychnine; Analytical Reactions of Strychnine; Toxicology of Strychnine; Preparations of Strychnine; Brucine, Brucia; Analytical Reactions of Brucine.

The Tropine Alkaloids: Atropine and Its Allies Tropeines and Scopoleines. By Francis H. Carr, C. B. E., F. I. C., London. Properties of Atropine, and its Allies; Tropic Acid; Atropic Acid; Isatropic Acid; Constitution of Tropine; Scopine; Scopoline; Atropine; Hyoscyamine; Noratropine; Norhyoscyamine; Atropamine; Hyoscine; Scopolamine; Mandragornie; Artificial Tropines; Detection and Estimation of Tropeines; Toxicological Detection of Atropine and its Allies; Plants yielding Mydriate Alkaloids; Assay of Belladonna; Belladonna Plaster; Hyoscyamus; Datura; Scopolia; Bibliography.

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Volume VIII and IX will follow as quickly as the articles can be prepared and printed. These volumes will include the following important sections: Putrefaction Bases; Glucosides; Animal Bases; Meat and Meat Products; Vitamins; Proteins; Non-glucocidal Bitter Principles; Animal Acids; Cyanogen.

It is proposed to issue a tenth volume, which will include recent advances and a complete index to the whole series.

Each volume of Allen is sold separately.

ALLEN'S
COMMERCIAL ORGANIC ANALYSIS

VOLUME II

CONTRIBUTORS

TO VOLUME II

C. Ainsworth Mitchell, m. a. (Oxon.), f. i. c. London, England.

E. R. Bolton, London, England.

George A. Reitz, b. sc., ph. c. Philadelphia, U. S. A.

Glenn H. Pickard, Minneapolis, U. S. A.

H. E. Cox, m. sc., ph. d., f. i. c. Newport, England.

Elbert C. Lathrop, a. b., ph. d. Philadelphia, U. S. A.

J. W. Lawrie, ph. d. Wilmington, U. S. A.

Augustus H. Gill, ph. d., sc. d. Boston, U. S. A.

John Addyman Gardner, m. a., f. i. c. London, England.

ALLEN'S COMMERCIAL

ORGANIC ANALYSIS

A TREATISE ON

THE PROPERTIES, MODES OF ANALYSIS, AND PROXIMATE
ANALYTICAL EXAMINATION OF THE VARIOUS
ORGANIC CHEMICALS AND PRODUCTS
EMPLOYED IN THE ARTS, MANU-
FACTURES, MEDICINE, Etc.

WITH CONCISE METHODS FOR

THE DETECTION AND ESTIMATION OF THEIR IMPURITIES,
ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION

VOLUME II

Fixed Oils, Fats and Waxes, Special Characters and Methods, Butter
Fat, Lard, Linseed Oil, Higher Fatty Acids, Soap, Glycerin,
Wool-fat, Cloth Oils, Sterol Alcohols

BY THE EDITORS AND THE FOLLOWING CONTRIBUTORS

E. R. BOLTON	H. E. COX	J. A. GARDNER
A. H. GILL	E. C. LATHROP ·	J. W. LAWRIE
C. A. MITCHELL	G. H. PICKARD	G. A. REITZ

FIFTH EDITION. REVISED AND IN PART REWRITTEN

EDITORS

SAMUEL S. SADTLER, S.B.
MEMBER AMERICAN INSTITUTE OF CHEMICAL
ENGINEERS, CONSULTING CHEMIST,
PHILADELPHIA

ELBERT C. LATHROP, A.B. Ph.D.
MEMBER AMERICAN INSTITUTE OF CHEMICAL
ENGINEERS, AMERICAN SOCIETY FOR
TESTING MATERIALS, CONSULTING
CHEMIST, PHILADELPHIA

C. AINSWORTH MITCHELL, M.A., F.I.C.
EDITOR OF "THE ANALYST," CONSULTING CHEMIST, LONDON

PREFACE

This volume has practically the same scope as it had in the fourth edition, but due to the large amount of new and important methods that have been introduced, it has been found necessary to enlarge this book considerably. The tendency of authors in recent times is to be more explicit and detailed in writing up analytical methods. This promotes uniformity in the results arrived at by analysts who might otherwise be in serious conflict.

The Revisers and Editors have been careful to give prominence to the best and generally accepted methods, while retaining earlier methods that are still being used. In many cases earlier and briefer methods are more available for routine work, if properly standarized by the most exact methods.

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LARD

GEORGE A. REITZ

LINSEED OIL

GLENN H. PICKARD

HIGHER FATTY ACIDS

Revised by H. E. Cox

SOAPS

ELBERT C. LATHROP

GLYCERIN

J. W. LAWRIE

WOOL-FAT, WOOL-GREASE, SUINT, DEGRAS

Augustus H. Gill

STEROL ALCOHOLS

John Addyman Gardner

FIXED OILS, FATS AND WAXES

By C. AINSWORTH MITCHELL, M. A. (Oxon.), F.I.C.

GENERAL PROPERTIES AND ANALYTICAL METHODS

Under the names of fixed oils, fatty oils, fats, and waxes are classed many substances occurring in animal and vegetable structures.

The term fixed or fatty oil is generally used for such members of the group as remain liquid at ordinary temperatures. Those having this character contain a relatively large proportion of olein or other compounds of low m. p., but beyond this there is no absolute distinction between fixed oils and fats.

The waxes possess well-defined physical characters, and differ in chemical composition from the true fats. They are, however, in many respects closely related to them, and are conveniently described in the same division.

The following are the general properties characterising the true fats and fixed oils:

1. When pure, most of them are colourless or pale yellow. Impure and commercial oils vary in colour from light yellow to red, and even to brown and black. Many vegetable oils have a distinct shade of green from the presence of chlorophyll, and show absorption spectra, which is never the case with oils of animal origin.

2. Their smell and taste are often peculiar, and are characteristic of their origin. As these characters become less perceptible the more completely the oil is purified, they may be due to the presence of associated foreign matters not readily removed, rather than to the constituents of the oil.

3. If dropped in a liquid condition on paper they leave a permanent grease-spot, unless they are crystalline and hard enough to be rubbed off.

4. They are not fluorescent and, as a rule, have but little rotatory action on a ray of polarised light. Castor and croton oils, however, are dextrorotatory.

5. The sp. gr. is less than that of water, ranging between the limits of 0.875 and 0.970; but if certain anomalous oils from marine animals be excluded, the lowest density is about 0.912 at a temperature of 15°. In the fluid state, at the temperature of boiling water, the sp. grs. range from 0.850 to about 0.910. The waxes and allied substances are still lighter in the melted condition, their sp. gr. ranging from 0.808 to 0.845.

6. The fusing or melting points range within wide limits, and are liable to modification in an obscure manner by special treatment.

7. They are practically insoluble in water, but dissolve to some extent in absolute alcohol or strong spirit, especially when hot, and are readily soluble in ether, chloroform, carbon tetrachloride, carbon disulphide, benzene, petroleum spirit,[1] turpentine, and other volatile solvents. They are readily miscible with one another.

8. The fixed oils and fats are composed of carbon, hydrogen, and oxygen, the nitrogen, sulphur, phosphorus, and iron present in many of them being due to foreign matters, which often cannot be completely removed.

9. They do not emit inflammable vapours at the ordinary temperature, but may be burnt by means of a wick. They are not capable of being distilled at the ordinary atmospheric pressure without decomposition. When heated alone they darken and evolve acrid offensive vapours; and when further heated to about 315° carbon dioxide is evolved, together with the peculiarly irritating vapours of acrolein, C_3H_4O, various volatile organic acids, and gaseous, liquid, and solid hydrocarbons. The temperature at which this decomposition occurs has been improperly called the "boiling point" of the oil, the phenomenon of apparent ebullition being really due to the escape of the gases formed by the decomposition.

10. On distillation with superheated steam, they undergo a simpler decomposition, with formation of glycerol and fatty acids. This change may also be effected by acting on them with sulphuric acid or a strong base. The action is known as "saponification" or hydrolysis and its analytical application is discussed in another section.

11. If air is excluded, the fixed oils may be preserved unchanged for a lengthened period, but, on exposure to air, many of them

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[1] This solvent is called *petroleum ether* or *gasoline* in the U. S. Petroleum spirit is a name given commercially to a petroleum solvent intermediate between gasoline and kerosene or burning oil, Amer Eds.

thicken owing to absorption of oxygen, and are ultimately converted (if exposed in sufficiently thin layers) into a yellowish transparent skin or varnish.[1] Such oils (*e. g.*, linseed, walnut, hempseed, and poppy-seed oils) are called *drying oils*.

12. The *non-drying oils* behave in a different manner on exposure to air. They gradually become *rancid;* that is, lose their colour (and to a certain extent their fluidity), and acquire an acrid, disagreeable taste, and acid reaction to litmus-paper. This alteration is primarily an oxidation process brought about by the action of air and light, and is accompanied by the liberation of free fatty acids, aldehydes and other substances. It may be accelerated by the presence of foreign matters, such as the cellular substance of the animal or plant from which the oil was extracted. These substances furnish nourishment for bacteria, which probably cause further changes when once the decomposition process has begun. By agitating such rancid oil with hot water, and subsequently treating it with a cold and dilute solution of sodium carbonate, the products of decomposition may often be removed and the fat restored to its original state.

EXTRACTION AND PURIFICATION OF FIXED OILS AND FATS

The method of extraction and subsequent treatment have considerable influence upon the analytical characteristics of the product. For the *extraction* of oils and fats from animal tissues it is often sufficient to allow the material (*e. g.*, cod liver) to become somewhat putrid, when some of the oil drains from it, or may be obtained by slight pressure. A further quantity can be extracted by warming or boiling the tissue with water, as is done with blubber. In the case of lard and tallow, it is merely necessary to heat the substance alone, and strain the melted fat away from the membranous matter. From compact tissue, such as bone, the whole of the fat can be extracted by means of a solvent only.

The extraction of the fat or oil from vegetable tissue may be effected by boiling the crushed substance with water or by subjecting it to powerful pressure, either at the ordinary temperature or between

[1] Under certain conditions, as when cotton-waste, shoddy, or hemp is moistened with oil and exposed to the air, the oxidation of the oil becomes so energetic as to lead to considerable elevation of temperature, and even actual ignition (see p. 45).

plates heated to slightly above the m. p. of the fat.   The product obtained in the last manner will usually contain more "stearin" or solid fat than the "cold-drawn" oil.   In either case a certain quantity of the fat is mechanically retained by the tissues, and hence a larger yield can be obtained by the use of carbon disulphide or petroleum spirit, which, on being distilled off, leaves the fat behind.

The proportion of oil or fat yielded by any particular material depends on many conditions.

Tables of the yields usually obtained from different seeds, nuts, etc., are given in Schaedler's *Untersuchungen der Fette, Oele und Wachsarten*, and in Wright and Mitchell's *Oils, Fats and Waxes*.

Oils obtained by the use of solvents are more likely to contain impurities than those obtained by pressure.

Estimation of Oils and Fats.—In the laboratory, the estimation of the oil in solid animal and vegetable matters is effected by treating the finely divided and previously dried substance[1] with a suitable solvent under such conditions as to ensure complete extraction. Carbon disulphide or petroleum spirit may be employed for the purpose, but ether or carbon tetrachloride is, as a rule, preferable.

Grimme (*Chem. Rev. Fett. Ind.*, 1912, 19, 191) has made comparative estimations in which fat was extracted with various chlorohydrocarbons and with ether.   The following average percentage results were obtained:

Ether	$CHCl_3$	CCl_4	$C_2H_2Cl_2$	C_2HCl_3	C_2Cl_4	$C_2H_2Cl_2$	C_2HCl_5
7.45	8.58	7.43	8.13	7.46	7.79	7.71	9.62

Only in the case of carbon tetrachloride and trichlorethylene did the results agree with those obtained with ether.

Complete extraction of the fat from cottonseed was not obtained with less than 100 c.c. of either cold solvent, but 45 minutes' extraction was sufficient with carbon tetrachloride and 30 minutes' with trichlorethylene.

With proportions below 10% of fat the weight of the residue left on evaporating 50 c.c. of the extract may be accepted as sufficiently accurate, but an addition of 0.2% should be made for amounts between 10 and 15%, and of 0.4% for amounts between 15 and 20%. Preliminary drying of the material was found by Grimme to be unnecessary.

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[1] In the case of linseed and other substances containing drying oils, the desiccation must either be omitted or conducted in an atmosphere of hydrogen or illuminating gas.

Gowing-Scopes (*Analyst*, 1914, **39**, 4) confirms the suitability of cold trichlorethylene for the extraction of fat, but points out that it is advisable to dry the solvent to prevent the formation of hydrochloric acid, which would act upon the fat.

He recommends for the extraction a modification of the apparatus devised by Beadle and Stevens (*Analyst*, 1913, **38**, 143).

The physical properties of the solvents are shown in the following table of Gowing-Scopes (*Analyst*, 1914, **39**, 5).

Chlorohyrocarbon	B. p., deg.	Freezing point, deg.	Sp. gr. at 25°	Coefficient of expansion	Heat of vaporisation, calories	Refractive index	Viscosity at 25°	Specific heat
Chloroform........	61.5	.....	1.4791	0.001257	....	1.449 (15°C.)	.....	.....
Carbon tetra-chloride........	76 7	.....	1.5835	0.001227	....	1.464 (15°C.)	.....	.....
Dichlorethylene, Cis.	48.8 (at 763 mm.)	.....	1.3328	0.001360	6930	....	0.457	.....
Dichlorethylene, trans.	59 8 (at 763 mm.)	.....	1.3545	0.001270	7268	....	0.510	.....
Trichlorethylene...	87.5	− 73	1.4542	0.001193	7436	1.47914 (17°C.)	0.615	0.223
Tetrachlorethylene	121.0	− 19	1.6080	0.001078	8554	....	0.940	0.216
Tetrachorethane...	147.2	− 36	1.5881	0.000998	9134	1.49559 (17°C.)	1.808	0.268
Pentachlorethane..	159.1	− 22	1.6712	0.000909	8829	......	2.432	0.266
Hexachlorethane...	185.5 (at 776.7 mm.)	−187	2.01(?)	......	....	......	.....	.....

The *exhaustion* of seeds, bones, shoddy, oil-cakes, milk residues, etc., by simply digesting the substance with the solvent at the ordinary temperature, with frequent agitation, in a closed flask, is unsatisfactory, as it requires a considerable quantity of the solvent, of which a notable proportion is likely to be lost. The apparatus devised by (Soxhlet) Szombathy (see Vol. 1) obviates these drawbacks. The substance to be exhausted of oil is enclosed in a plaited filter or cylinder of filter-paper or a prepared "thimble," or if it is coarse, it is sufficient to place it loose in a large test-tube having an aperture at the bottom closed by a plug of glass-wool.

A very simple and convenient form of exhauster, adapted either for extraction or re-percolation, has been described by Dunstan and Short (*Pharm. J.*, [3], 1882, **13**, 664).

A form of exhauster, suitable for the extraction of very small quantities of material, was devised by West-Knights (*Analyst*, 1883, **8**, 65).

Other forms of exhauster have been contrived by Church, Drechsel, Angell, Thoms, Thresh (*Pharm. J.*, [3], 1884, **15**, 281); Frühling (*Zeit. angew, Chem.*, 1889, 242). (See also Vol. 1.) Various modifications of the Soxhlet apparatus for the extraction of fat at the boiling point of the solvent have also been devised, such as that of Stock (*J. Soc. Chem. Ind.*, 1897, 107), and that of Twiss and McCowan (*J. Soc. Chem. Ind.*, 1917, **36**, 692), in which there is only one aperture, through which the vapour passes into an inner compartment, this restriction being sufficient to raise the temperature and keep the solvent gently boiling.

To *recover* the oil from its solution in the ether or other liquid employed, the solvent should be distilled off at a steam-heat, and the last traces of it removed by placing the flask on its side and heating it in the water-oven until constant in weight. In some cases the complete removal of the solvent is best effected by blowing a gentle stream of air, previously filtered through cotton-wool, through the flask while it is maintained at a temperature of 100°.

Large quantities of material may be readily extracted in the apparatus (Fig. 1), which is constructed on the principle of the Szombathy extractor.
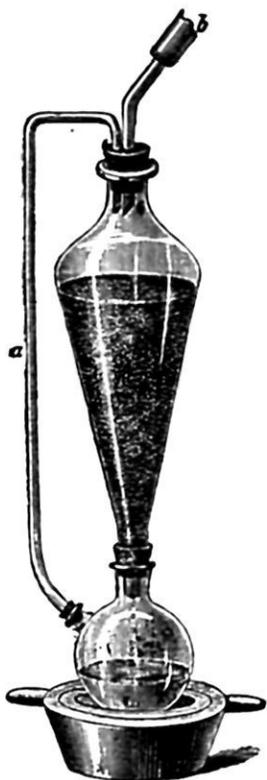
Fig. 1.

In the case of *liquids* containing oil in the form of emulsion a separation may often be effected by agitation with ether. For the extraction of unsaponifiable matter Förster has devised an apparatus which is figured and described in Vol. 1, page 84.

Purification of Oils.—The methods used in the refining and purification of crude oils have often considerable influence upon the analytical characteristics of the final products.

Action of Heat.—Simple application of heat may effect coagulation of protein impurities in an oil.

Mechanical Attraction and Filtration.—Substances such as Spanish clay, fuller's earth and the like, are used as mechanical precipitants

of the suspended matter in oils. The clarified oil, which is not chemically altered by this treatment, is subsequently decanted or passed through a filter.

Treatment with Acids.—Rape, linseed, and some fish oils are frequently refined by treatment with a small proportion of sulphuric acid, which chars the impurities and causes them to subside without materially attacking the oil itself. The objection to the process is that traces of free mineral acid may remain, even after the subsequent washing with water, and, if the oil is used as a lubricant, may lead to corrosion of bearings, etc., or to charring of the wick in the case of lamp oils. Treatment with sulphuric or hydrochloric acid is also employed in the removal of the lime which is present in bone fat.

Treatment with Alkalis.—Certain oils, notably cottonseed, olive, and sperm oils, are frequently purified by treatment with a solution of caustic soda, the quantity of which depends upon the amount of free fatty acids and impurities to be removed. Cottonseed oil contains a notable proportion of a resin-like substance which gives a blue coloration with the alkali. Ammonia, sodium carbonate, magnesium carbonate, milk of lime, and sodium peroxide are also employed in certain refining processes. Oils which have been treated with alkali usually contain a much smaller amount of free fatty acids than even the freshly-expressed crude oils, and cottonseed oil used for cooking purposes is often practically neutral.

Treatment with Oxidising Agents.—Fish oils are purified, and to some extent deodorised, by treatment with a current of steam followed by a current of hot air. Excessive treatment of this kind will alter the character of the oil itself, so that it becomes heavier and more viscous, and acquires other characteristics of "oxidised" or "blown" oils (*q. v.*). Palm oil is bleached by hot air in a similar fashion. Of chemical oxidising reagents mention may be made of dichromate and mineral acid (used in the purification of palm oil), manganese dioxide and hydrochloric acid, and hydrogen peroxide. Wax bleached by chlorine is apt to contain chlorine fatty compounds, which are decomposed with the liberation of hydrochloric acid when the wax is subsequently burnt in the form of candles.

Treatment with Reducing Agents.—Oils are not only hardened in the process of hydrogenation (*q. v.*), but also bleached and deodorised. Even nascent hydrogen in the absence of a catalyst will effect deodorisation.

Chemical Precipitants.—Protein impurities in fish oils and other oils may be chemically precipitated by means of tannin or solutions of metallic salts capable of combining with them.

For details of these and similar methods of clarifying, bleaching, and deodorising oils see Alder Wright and Mitchell's *Oils, Fats, and Waxes*.

Purification by Pressure.—Hydraulic pressure is widely employed for separating the solid from the liquid constituents of oils. The solid fats thus separated are commercially known as "stearine," though, as a rule, they are far from approximating in composition to the triglyceride of stearic acid. Similarly, the liquid expressed oils are conveniently termed "oleines," though of very complex composition. The following are some of the chief instances in which commercial fats and oils are separated by pressure into solid and liquid portions.

Original oil	Liquid product	Solid product
Olive oil.	Purified olive oil.	Olive oil stearin.
Cottonseed oil.	Purified cotton oil.	Cotton oil stearin.
Coconut oil.	Coconut olein.	Coconut stearin.
Tallow.	Tallow oil.	Tallow stearin.
Lard.	Lard oil.	Lard stearin.
Whale oil.	Purified whale oil.	Whale stearin.
Sperm oil.	Purified sperm oil.	Spermaceti.

CONSTITUTION AND CHEMICAL PROPERTIES OF FATS, OILS, AND WAXES

The fats, fixed oils, and waxes are esters of a series of acids mostly monobasic and called, from their sources, the fatty acids. The natural fats and fixed oils are all esters of the triad radicle, $CH_2.CH.CH_2$. Their composition may be expressed by the general formula $C_3H_5A_3$, in which A is a radicle of some acid. From the fact that the radicle C_3H_5 occurs in glycerol, it is generally called *glyceryl* or *glycyl*, and the esters are usually called *glycerides*.

The fatty acids most commonly forming esters with the glyceryl radicle in natural fats and oils are those belonging to the series with the general formulæ, $C_nH_{2n}O_2$ (acetic or stearic acid series); $C_nH_{2n-2}O_2$

(oelic acid series); $C_nH_{2n-4}O_2$ (linolic acid series); $C_nH_{2n-6}O_2$ (linolenic acid series), and $C_nH_{2n-2}O_3$ (ricinoleic or hydroxyacrylic acid series).

Glyceryl stearate, $C_3H_5(C_{18}H_{35}O_2)_3 = C_{57}H_{110}O_6$, is known as tristearin, or stearin; it is a constituent of beef and mutton tallow. In like manner olein is probably the principal component of almond, olive, and lard oils, and palmitin of palm oil. Esters of linolic acid are main constituents of cottonseed and maize oils, whilst the esters of linolenic and isolinolenic acid form an important part of linseed oil, and that of ricinoleic acid of castor oil. Olein, linolin, and linolenin, being liquid, predominate in oils, while stearin and palmitin, probably in combination with glycerides, are more abundant in solid fats.

The view formerly held that the natural esters rarely contain more than one acid radicle requires modification, since it has been shown that *mixed glycerides*, in which the acid radicles are not all of the same kind, are present in numerous fats. Thus Heise (*Arbeit a. d. Kaiserl. Gesundheitsamt*, 1896, 540) and subsequently Henriques and Künne (*Ber.*, 1899, **32**, 387) isolated oleo-distearin from the fat of the seeds of the East African tallow tree (*Stearodendron Stuhllmanni*), and the bromides of mixed glycerides were separated by Hehner and Mitchell (*Analyst*, 1898, **23**, 317) from linseed oil, walnut oil, and marine animal oils. The separation and behaviour of these bromides is a valuable test for distinguishing between different classes of oils, as is shown in a subsequent section. More recently, tests for distinguishing between lard and beef fat have been based upon the fact that the fats contain mixed glycerides of different composition (see p. 442).

The waxes proper contain the esters of higher alcohols of the methyl series. Thus spermaceti consists chiefly of cetyl palmitate, $C_{16}H_{33}C_{16}H_{31}O_2$, whilst Chinese wax, beeswax, and carnauba wax contain still higher radicles. Sperm oil and bottlenose oil are chiefly composed of fluid compounds having a constitution similar to that of the waxes.

In addition to the esters which constitute the essential portions, most natural fats, oils, and waxes contain more or less of free fatty acids, and small proportions of colouring, odorous, resinous, and other matters, to which the characteristic colours, smells, and tastes are mostly due. Small proportions of cholesterols or phytosterols

are also present, and their separation affords a means of distinguishing between oils of animal and of vegetable origin.

Free fatty acids in natural fats and oils are usually products of decomposition, accelerated by the presence of mucilaginous or protein matters. Ordinary butter, which contains casein, readily turns rancid and then contains free butyric acid; but if all casein and water are removed by melting and filtering the butter, the butter-fat may be kept unchanged for a much longer time. Over-treatment with sulphuric acid in the process of refining oils often results in the formation of free fatty acids. Commercial oils which have been refined by this process are apt to retain traces of free mineral acid.

Acid Value.—The proportion of free fatty acids is best ascertained by shaking a weighed quantity of the fat with warm alcohol and titrating the solution with a standard alkali solution, with phenolphthalein as indicator.

An accurately weighed quantity of the sample, ranging from 5 grm. of fatty acids to 50 grm. of an ordinary oil, is introduced into a flask or bottle furnished with a glass stopper, and from 50 to 100 c.c. of pure neutralised alcohol containing a little phenolphthalein in solution is added and raised to the boiling-point by immersing the bottle in hot water. The contents are thoroughly agitated to effect as complete a solution of the fatty acids as possible. If the sample of oil is wholly free from acid, the pink colour of the alcohol will remain unchanged, but otherwise it will disappear. In the latter case, a $N/2$ solution of sodium hydroxide is added in small amounts to the warm contents of the flask, which is shaken thoroughly after each addition until the pink coloration persists. The reaction is as well defined and the neutralisation point as easy to perceive as in the titration of mineral acids; but owing to the very high combining weights of the fatty acids, great care is necessary. Thus 1 c.c. of $N/2$ alkali used corresponds to 0.128 of *palmitic*, 0.142 of *stearic*, or 0.141 grm. of *oleic acid*. For estimating small proportions of free acid, it is desirable to employ decinormal alkali, whilst in the case of samples containing much free acid the quantity taken for the estimation should be correspondingly reduced. The result is usually expressed in terms of the number of mg. of potassium hydroxide neutralised by 1 grm. of the fat, and is termed the *Acid Value*.

If the mean equivalent weight of the free fatty acids is known, their percentage may readily be calculated from the acid value. For

this purpose it is often assumed that the free fatty acids in oils consist solely of oleic acid, and since 282 parts of oleic acid are equivalent to 56.1 parts of potassium hydroxide, the percentage of free fatty acids (expressed as oleic acid) is obtained by multiplying the acid value by the factor 0.502.

The amount of free fatty acids in commercial oils is often very considerable. Thus in palm oil the free acid, calculated as palmitic acid, usually ranges from 12 to nearly 80%. In 89 samples of olive oil intended for lubricating use, Archbutt (*Analyst*, 1884, 9, 171) found from 2.2 to 25.1 of free (oleic) acid, the mean being 8.05%. In the superior grades of olive oil the proportion of free acid is much smaller. In rape oil the percentage of free acid is generally from 1.5 to 6%; but cottonseed oil, which is refined by means of alkali, is generally free from any trace of acid.

The influence of free acid in an oil upon its tendency to act upon metal is considered in the section on "Lubricating Oils."

In the case of fats of a dark colour sharper readings may be obtained by the use of the indicator, known as *Alkali blue* 6 B (red with alkalis) in place of phenolphthalein. About 2 c.c. of a 2% alcoholic solution are added. It has been shown by Steele and Sward (*J. Ind. Eng. Chem.*, 1922, 14, 57) that the use of a solvent composed of equal parts of alcohol and benzene gives higher and more accurate results, especially in the case of tung oil, than when alcohol alone is used. The end-point of the titration can also be observed more sharply.

In estimating the acid value of artificially coloured fats the dyestuff must, if possible, be removed before the titration by treatment with a suitable solvent, such as 80% alcohol or petroleum spirit, which in some cases dissolves the fat and leaves the dyestuff (*e. g.*, nigrosine in leather fats). Sometimes the dyestuff may be removed by shaking an ethereal solution of the fat with dilute hydrochloric acid, and washing the residual fat solution with water. Or the petroleum spirit solution of the fat may be thoroughly shaken with a measured quantity of N/10 alcoholic sodium hydroxide solution, and the aqueous layer subsequently titrated with standard hydrochloric acid until colourless to phenolphthalein. Attention has been directed by Ware and Christman (*J. Ind. Eng. Chem.*, 1916, 8, 996) to the fact that the presence of metallic linoleates and residues in a

boiled oil will cause the acid value to appear too high, owing to the hydrolysis of the metallic soaps by the potassium hydroxide.

Saponification of Fixed Oils.—*Fatty oils* heated with water under a pressure of 8 to 12 atmospheres or distilled with superheated steam are hydrolysed into fatty acids and glycerol. This method of decomposing fats is employed in the industrial production of fatty acids and glycerol.

Many natural oils and fats are partly hydrolysed into fatty acids and glycerol probably by the action of air and light, and possibly bacterial action, in presence of traces of albuminous or other foreign matter. The free fatty acids often present in commercial palm oil, olive oil, and tallow are due to this cause.

The lipoclastic enzymes present in castor and other oil seeds are also capable of effecting the hydrolysis of fats in the presence of dilute acid and water, as was shown by Connstein, Hoyer, and Wartenberg (*Ber.*, 1902, 35, 3989).

Hydrolysis occurs when a fatty oil is heated to 110°, with about 8% of concentrated sulphuric acid. On washing the product with hot water, the sulphuric acid and glycerol are removed, and the fatty acids separate in the form of an oily layer.

An analogous action takes place when a fat or oil is treated with basic oxides or hydroxides. The change occurs more readily with some oils than with others, and is promoted by heat and by using alcohol or glycerol as a solvent for the alkali. A salt (soap) of the fatty acid is produced, glycerol being likewise formed. The soaps produced by potassium, sodium, or ammonium hydroxide are soluble in water, but most other soaps are insoluble.

Waxes yield soaps and a monatomic alcohol, instead of glycerol. The decomposition is usually difficult.

When an ester is split up into an acid and an alcohol, the change is usually called "saponification," no matter whether the agent effecting the change is water, an acid, or a base. The term is even extended to the decomposition of esters that do not yield fatty acids. It is evident, therefore, that the saponification of fixed oils is a definite chemical action, precisely analogous to the decomposition of the ordinary salts.

The table on page 13 gives the molecular weights and proportions of fatty acids and glycerol theoretically obtainable from pure triglycerides and other esters of common occurrence.

Hence it appears that the majority of fats and oils yield, on saponification, from 95 to 96% of fatty acids, and about 10% of glycerol. The esters of butyric, valeric, or lauric acid contained in butter-fat, porpoise, and coconut oils, respectively, yield a larger proportion of glycerol, whilst rape oil, containing an ester of erucic acid, yields a smaller proportion.

The waxes yield much smaller proportions of fatty acids, and, instead of glycerol, give large proportions of alcohols of the C_nH_{2n+1} series, as solid substances insoluble in water. The nature and proportion of the products of saponification sharply distinguish sperm and bottlenose oils from all other fixed oils of commercial interest.

Esters	Chief sources	Formula	Molecular weight	Products of saponification of 100 parts	
				Fatty acid	Glycerol
Glycerides					
Tributyrin............	Butter-fat	$C_3H_5(C_4H_7O_2)_3$	302	87.44	39.46
Trivalerin............	Porpoise oil, whale oil	$C_3H_5(C_5H_9O_2)_3$	344	88.96	26.77
Trilaurin............	Coconut oil, palmnut oil	$C_3H_5(C_{12}H_{23}O_2)_3$	638	94.04	14.42
Tripalmitin..........	Palm oil, lard	$C_3H_5(C_{16}H_{31}O_2)_3$	806	95.28	11.41
Tristearin............	Tallow, lard, cacao butter	$C_3H_5(C_{18}H_{35}O_2)_3$	890	95.73	10.34
Triolein..............	Olive oil, almond oil, lard oil	$C_3H_5(C_{18}H_{33}O_2)_3$	884	95.70	10.40
Trierucin............	Rape oil	$C_3H_5(C_{22}H_{41}O_2)_3$	1052	96.39	8.75
Trilinolin............	Maize oil, cotton-seed oil	$C_3H_5(C_{18}H_{31}O_2)_3$	878	95.67	10.48
Triricinolein..........	Castor oil	$C_3H_5(C_{18}H_{33}O_3)_3$	932	95.92	9.88
Trilinolenin..........	Linseed oil and drying oils	$C_3H_5(C_{18}H_{29}O_2)_3$	872	95.64	10.55
					Monatomic alcohol
Cetyl palmitate..	Spermaceti	$C_{16}H_{33}.C_{16}H_{31}O_2$	480	53.33	50.42
Myricyl palmitate. ...	Beeswax	$C_{30}H_{61}.C_{16}H_{31}O_2$	676	37.87	64.79
Ceryl cerotate.....	Chinese wax	$C_{27}H_{55}.C_{27}H_{53}O_2$	788	52.03	50.25
Dodecyl oleate...	Sperm oil	$C_{12}H_{25}.C_{18}H_{33}O_2$	450	62.67	36.88
Dodecyl doeglate	Bottlenose oil	$C_{12}H_{25}.C_{19}H_{35}O_2$	464	63.79	35.78

The nature of the fatty acids produced on saponification is of importance in distinguishing the various fixed oils, as is shown in the description of their individual characteristics.

Theory of Saponification with Alkali.—Geitel (*J. pr. Chem.*, 1897, **163**, 429; 1898, **165**, 113) concluded from mathematical considerations that in the saponification of triglycerides with alkali,

diglycerides and *monoglycerides* were formed as intermediate products. Thus where R represents a fatty acid radicle these stages may be represented:

Normal triglyceride	Diglyceride	Monoglyceride
$CH_2.OR$ $\|$ $CH.OR$ $\|$ $CH_2.OR$	$CH_2.OR$ $\|$ $CH.OR$ $\|$ $CH_2.OH$	$CH_2.OR$ $\|$ $CH.OH$ $\|$ $CH_2.OH$

This view was opposed by Henriques (*Zeit. angew. Chem.*, 1898, 697). Subsequently Lewkowitsch (*Ber.*, 1900, **32**, 89; 1906, **39,** 4095; *J. Soc. Chem. Ind.*, 1903, **22**, 596) brought experimental evidence in support of Geitel's view, whilst the opposite view was maintained by Fanto (*Monatsh.*, 1904, **25**, 919; 1907, **28**, 383; *Annalen*, 1907, **351**, 532) and by Marcusson (*Ber.*, 1906, **39,** 3466). On the other hand, experiments in which triolein was fractionally saponified with alcoholic alkali led Fortini (*Chem. Zeit.*, 1912, **36**, 1117) to the conclusion that saponification takes place in three distinct phases. The acetyl values of the fractions also supported the views of Lewkowitsch.

Experiments described by Fryer (*Analyst*, 1921, **46, 87**) have indicated that the velocity of saponification, from the point of view of the amount of free alkali removed from the reacting solution, is in inverse ratio to the saponification equivalent or to the mean molecular weight of fatty acids of the glycerides composing natural fats or oils.

In saponification with alcoholic alkali the ethyl esters of the different fatty acids in a fat are formed as intermediate products, and their separation by distillation affords a means of distinguishing between different oils and fats.

Alcoholysis of Fats.—When glycerides are subjected to the action of an alcohol containing a small quantity of an acid they are decomposed in a manner analogous to the hydrolysis effected by water in the presence of acid. A useful method of estimating the composition of fats has been based on this reaction by Haller (*Compt. rend.*, 1906, **143,** 657) who describes the process as "alcoholysis."

About 100 grm. of the dried fat are heated on the water-bath with 200 grm. of, e. g., methanol to which has been added 1 or 2% of dry hydrochloric acid, fresh additions of acidified methanol being made, if required, until the mixture appears homogeneous. It is then treated with a large volume of water or salt solution, which retains the excess of methyl alcohol and the glycerol from the fat, while the methyl esters of the fatty acids rise to the surface. These may then be separated by fractional distillation and the fatty acids in the distillates separated and identified. In the case of the methyl esters of butyric, caproic, and caprylic acids the distillation may be carried out at the ordinary temperature but from 194° (the b. p. of methyl caprylate) upwards reduced pressure is necessary. The method gives good results up to lauric acid, but the separated esters of myristic, palmitic, and stearic acids always retain some methyl oleate. This may be separated by chilling the fractions with ice and draining the crystals on a porous tile with the aid of a pump.

By this method Haller and Youssoufian (*Compt. rend.*, 1906, **173**, 803) found coconut oil to contain caproic, caprylic, lauric, myristic, palmitic, stearic, and oleic acids; whilst Meyer (*Chem. Zeit.*, 1907, **31**, 793) found cottonseed oil to consist chiefly (up to 70%) of palmitin, with the glycerides of oleic, linolic, and probably stearic and arachidic acids. The method has also been applied to the examination of castor and linseed oils by Haller (*J. Soc. Chem. Ind.*, 1907, **26**, 328; 1908, **27**, 234) and of japan wax by Tassily (*ibid.*, 1911, **30**, 907).

Elsdon (*Analyst*, 1913, **38**, 8) has submitted the process to critical examination and has shown that, although it determines the nature of the fatty acids contained in a fat, it is too tedious for ordinary laboratory work, and is only roughly quantitative. The results obtained may show the relative amounts of the constituents, but are probably not within 5 to 10% of the true values.

Saponification in Analysis.—The most convenient method of saponifying oils, etc., for the further examination of their constituents is by treatment with an alcoholic solution of potassium hydroxide and subsequent evaporation of the alcohol:

An alcoholic solution of alkali is prepared by dissolving 80 grm. of potassium hydroxide in 1000 c.c. of strong alcohol, which has been previously redistilled with a little alkali. It is desirable to dehydrate the spirit by keeping it over a large excess of dry potassium carbonate. About 5 grm. of the clarified fat or oil are weighed in a 4-oz.

wide-necked flask, treated with 25 to 30 c.c. of the solution of alkali in spirit, and the flask closed with a cork fitted with a long tube. The flask is heated over boiling water, and as soon as the spirit boils the contents are mixed by circular agitation. In most cases the whole of the oil will rapidly disappear, forming a clear solution of soap, which may be further heated for a short time with occasional agitation to ensure complete saponification of the fat. The cork is then removed and the alcohol evaporated. In the presence of unsaponifiable oil the contents of the flask should be allowed to boil until nearly dry, and the residue treated with 25 c.c. of spirit, and again boiled down. When there is no danger of loss of hydrocarbon oils or esters of lower fatty acids by incautious treatment, the saponification and subsequent evaporation may be satisfactorily conducted in a hemispherical porcelain basin, placed over a small naked flame. The mixture is well stirred with a glass rod, and kept gently boiling until the alcohol is nearly driven off and the residual liquid froths strongly. By this time the whole of the oil should have disappeared, but, if incomplete saponification is suspected, 10 c.c. of alcohol may be added, and the evaporation repeated.

To ensure the saponification of butter fat, codliver oil, the waxes, and other substances difficult to decompose, it is better to place the sample and alcoholic solution in a strong 200 c.c. bottle, closed by a rubber stopper firmly fastened by wire. The bottle is then kept at 100°, and frequently agitated during half an hour, or until no globules of oil can be seen, after which it is opened, and the contents rinsed into a basin and evaporated over boiling water till the alcohol is expelled. Special precautions for ensuring the saponification of waxes are described in the section on "Beeswax."

Saponification Values of Oils. *Koettstorfer's Process.*—The saponification of fatty oils being a perfectly definite reaction, not only can the proportions of fatty acid and glycerol produced from any particular ester be calculated, but the proportion of alkali required for the saponification can be similarly ascertained from the general equation: $C_3H_5\bar{A} + 3KHO = C_3H_5(OH)_3 + 3K\bar{A}$. Conversely, if the proportion of alkali required to effect the saponification of a particular oil be accurately determined by experiment, the nature of the ester present can be inferred. From the above equation it appears that 1 molecule of a glyceryl ester requires 3 molecules of alkali for saponification. The number of parts saponified by 1

molecule of alkali will therefore be $\frac{1}{3}$ of the molecular weight; but in the case of the ester of a monatomic alcohol, the number will be identical with the molecular weight. This figure, which really represents the number of grm. of an oil saponifiable by one equivalent in grm. of any alkali, or, in other words, the number of grm. of an oil which would be decomposed by 1000 c.c. of a normal solution of any alkali, is conveniently designated the "saponification equivalent" of an oil, and may in all cases be found by dividing the percentage of potassium hydroxide required for saponification into 5610, or the percentage of sodium hydroxide into 4000.

It is now customary, however, to express the results of this test in terms of the number of mg. of potassium hydroxide required for the complete saponification of 1 grm. of a fat or wax, this being known as the *saponification value.*

The estimation of the saponification value of an oil is conveniently effected in the manner described by Koettstorfer (*Zeit. anal. Chem.,* 1879, 18, 199), who applied it originally to the analysis of butter:

From 1.5 to 2 grm. of the sample, accurately weighed, are treated with 25 c.c. of approximately N/2 solution of potassium hydroxide in alcohol,[1] in a flask fitted with a long vertical tube. The flask is heated on the water-bath for about $\frac{1}{2}$ hour, or until complete solution of the fat takes place, and the saponification is judged to be complete. The operation is greatly expedited by subjecting the contents of the flask to frequent agitation. 1 c.c. of 1% alcoholic solution of phenolphthalein is then added, and the liquid titrated with N/2 hydrochloric acid; 25 c.c. of the potassium hydroxide solution, very carefully measured, should then be similarly treated without addition of fat, and titrated with hydrochloric acid in the same way as before. The difference between the volumes of standard acid used in the two estimations gives the number of c.c. corresponding to the alkali neutralised in saponifying the oil. Each c.c. of N/2 hydrochloric acid (= 18.25 grm. HCl per 1000 c.c.) thus employed represents 0.02805 of KOH, whence the *number of mg. of potassium hydroxide* required to saponify 1 grm. of the oil can readily be ascertained.

The *saponification equivalent* of the oil is found by dividing the weight of the sample employed, expressed in mg., by the number of c.c. of N/1 (not N/2) acid corresponding to the alkali neutralised by

[1] The alcohol employed for making the solution should be previously dehydrated by keeping it over an excess of dry potassium carbonate. Methanol may be used if it is first distilled with a little potassium hydroxide.

the oil.   If the percentage of potassium hydroxide required is known, the saponification equivalent can be found by dividing this percentage into 5610.

It is essential that the alcoholic alkali should be as free as possible from any colour, since any brown or yellow tint affects the sensitiveness of the acid reaction with phenolphthalein.   The saponification and titration should be conducted with as little access of air as possible, since the action is influenced by the presence of carbonic acid.

It is absolutely necessary to ascertain the strength of the alcoholic alkali from day to day, as such solutions rapidly alter, and the mere heating is liable to cause a slight change in the neutralising power. Standard sulphuric acid cannot be conveniently substituted for the hydrochloric acid recommended for the titration, as its employment causes a precipitation of sulphate, which masks the end-point.

In the case of waxes the nature and amount of unsaponifiable matter renders saponification more difficult, and it is necessary to boil the substance for at least an hour over a flame protected by wire-gauze with an excess of 2N. alcoholic alkali prepared with alcohol of 96 to 98% strength.   To prevent dissociation it is advisable to add 20 c.c. of neutral alcohol to the liquid before titration.

Cold Saponification.—The method of cold saponification devised by Henriques (*Zeit. angew. Chem.*, 1891, 721) may sometimes be found of use for oils and fats, though it is not satisfactory in the case of waxes.   From 3 to 4 grm. of the fat are dissolved in 25 c.c. of light petroleum and treated with 25 c.c. of N/1 alcoholic alkali solution, a blank estimation being simultaneously made.   Both flasks are closed, shaken, and allowed to stand for 12 hours at the ordinary temperature, after which the excess of alkali is titrated with standard hydrochloric acid.

The following table gives the saponification values and saponification equivalents of the chief esters occurring as constituents of the natural fats and oils.

As already stated, the saponification equivalents of the monatomic esters are identical with their molecular weights, while those of the glyceryl esters are one-third of their molecular weights.

Since the natural oils met with in practice do not consist of a single ester in a state even of approximate purity, the saponification values of ordinary oils and fats are the resultants of the values of their con-

stituents, and therefore show less pronounced differences than do the pure esters.

Substance	Chief sources	Saponification value	Saponification equivalent
Butyrin.................	Butter-fat............	557.3	100.67
Valerin.................	Porpoise, dolphin, and whale oils....	489.2	114.67
Laurin.................	Coconut and palm-nut oils..........	263.8	212.67
Palmitin................	Palm oil; lard.........	208.8	268.67
Stearin.................	Tallow; lard; cacao butter..........	189.1	296.67
Arachidin..............	Arachis oil...........	172.7	324.67
Olein..................	Olive, almond, and lard oils.........	190.4	294.67
Erucin.................	Rape oil.............	160.0	350.67
Linolin...............	Cottonseed, maize oils.	212.0	264.67
Linoleinin Isolinolenin }	Linseed oil...........	191.7	292.67
Ricinolein.............	Castor oil...........	180.6	310.67
Cetyl palmitate..........	Spermaceti...........	116.9	480
Myricyl palmitate........	Beeswax.............	83.0	676
Ceryl cerotate..........	Chinese wax.........	71.2	788
Dodecatyl oleate.....	Sperm oil......... ...	124.7	450
Dodecatyl doeglate..... ...	Bottlenose oil........	120.9	464

Nevertheless, the peculiarity of constitution of many of the natural fats and oils is indicated by the results of this test. Thus rape oil and similar oils containing erucin have low saponification values, whilst, on the other hand, butter fat, containing butyrin and other glycerides of lower fatty acids, gives high values.

The probable saponification values of oil and fats of commercial importance will be found in the tables on pp. 109 to 113. From the figures there given it will be seen that glyceridic oils and fats may be roughly classified into 3 groups in accordance with their saponification values: 1. Those with low values (169 to 181, usually about 175), such as castor oil and members of the rape-oil group. 2. Those with medium values (183 to 196), such as the majority of fats and oils, and 3. Those with high values due to the presence of lower fatty

acids, such as members of the coconut-oil group, butter-fat, and certain marine-animal oils (group X). The waxes (Group XII) and sperm oil have exceptionally low saponification values indicative of their peculiar composition.

Since hydrocarbon oils do not interact with alkali the proportion of such oils in admixture with fatty oils may be deduced from the saponification value of the mixture. Thus if a sample of so-called linseed oil has a saponification value of only 9.5 instead of about 190, it may be assumed to contain approximately 95% of hydrocarbon oil.

Separation of the Products of Saponification.—The solution of soap, freed in the foregoing manner from alcohol, should then be diluted with warm water till it measures 70 to 80 c.c A perfectly clear solution will usually be obtained if a pure oil has been used and the process has been successfully conducted, but *waxes* and mixtures containing *hydrocarbons* and other foreign matters will give a solution containing solid matter or oily globules in suspension. These admixtures may usually be removed and estimated by agitating the soap solution in a glass separator, with an immiscible solvent, ether being the most generally suitable for the purpose.[1] The ethereal layer is then separated, evaporated, and the residue weighed. The best method of manipulation is described later. Cholesterol and other unsaponifiable substances are present in small proportion, even in the purest fatty oils.[2]

If ether has been employed, it should be removed by keeping the soap solution at a gentle heat for some time. On then treating the solution with an acid, dilute sulphuric acid being generally preferable, a milky precipitate is produced, which, on warming the liquid, will collect into globules and form an oily layer on the surface. This layer consists of the *fatty acids* produced from the oil. These acids differ from the original esters in being soluble in alcohol, the solution having an acid reaction, and decomposing the carbonates of the alkali metals, liberating carbon dioxide and forming soaps.

[1] Owing to the limited solubility of myricyl alcohol in most solvents, the method described in the text is attended with practical difficulties in the case of beeswax and carnauba wax, though it is admirably adapted for the analysis of spermaceti. If the removal of the separated higher alcohol by an immiscible solvent is found impracticable, the solution of the soap should be treated with acetic acid in quantity just sufficient to destroy the pink coloration produced by phenolphthalein, and the solution treated with lead acetate. The precipitate should be washed, dried, mixed with sand, and the wax-alcohol dissolved in boiling petroleum spirit.

[2] In rigidly accurate experiments it is desirable to treat the unsaponified residue in the same manner as the original oil, as traces of fat are liable to escape saponification by a single treatment. If the residue left on evaporating the ethereal solution be treated with a little hot alcohol, the solution filtered hot, and the filtrate cooled, and, if necessary, allowed to evaporate spontaneously, crystalline plates of cholesterol will often be deposited.

The higher fatty acids are almost wholly insoluble in water and not sensibly volatile at 100°, but from butter-fat, coconut oil, palm-nut oil, porpoise oil, and some others a notable amount of the lower fatty acids is obtained, and hence the acids from these sources are partially soluble in water and capable of distillation with water at 100°.

For obtaining these *soluble* or *volatile acids* from oils, the soap solution is acidified with sulphuric acid in the manner already described, the aqueous liquid separated from the layer of fatty acids, and the latter boiled several times with a considerable quantity of water in a flask furnished with a long tube or inverted condenser. The liquids resulting from these operations are separated from the *insoluble fatty acids*, which it is desirable to boil again with a moderate quantity of water, a current of steam being passed meanwhile through the flask in which they are contained, and the distillate collected and treated like the washings.[1] The acidified aqueous liquid first separated from the layer of fatty acids is then distilled to small bulk and the distillate exactly neutralised with a standard solution of sodium or barium hydroxide, phenolphthalein being used as an indicator. The first washings from the insoluble fatty acids are next added to the contents of the retort, and the liquid again distilled to a low bulk, the process being repeated with the succeeding washings. The different distillates obtained should be titrated separately with N/10 standard alkali and phenolphthalein, as, in this manner, with but little extra trouble, the progress and completion of the washing, etc., can be followed, and useful information obtained as to the probable nature and relative proportions of the *lower fatty acids* present.

The several neutralised distillates may now be united and evaporated gently to dryness, the residue being dried at 100° until constant in weight. It consists of the sodium or barium salts of the acids which passed over in the preceding distillation. If the total volume (in c.c.) of N/1 sodium hydroxide solution employed for the neutralisation be multiplied by 0.022, or the volume of N/1 barium hydroxide solution by 0.0675, and the number so obtained be subtracted from the gross weight (in grm.) of the dry residue, the difference will be the weight of the *volatile fatty acids*. Their mean combining equivalent will be found by dividing their

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[1] When coconut or palm-nut oil is treated in this manner, the distillate will be found to contain lauric acid, which, though almost insoluble in water, is volatile in a current of steam. It may be separated from the more soluble volatile fatty acids by filtering the distillate.

weight by the volume (in c.c.) of normal alkali required for their neutralisation.

A further examination of the volatile fatty acids can be made by distilling the barium or sodium salts with phosphoric or diluted sulphuric acid, and examining the distillate as indicated in Vol. 1, p. 306. In Reichert's method (see below) an aliquot portion of the acidified solution of the saponified fat is distilled, and the distillate titrated with standard alkali.

Hehner Value.—In cases in which the oil under examination is known not to contain any appreciable quantity of esters of the lower acids, the treatment for their isolation may be wholly omitted, and the *insoluble fatty acids* are then practically identical with the *total* fatty acids liberated on adding a dilute mineral acid to the aqueous solution of the soap. The oily layer thus obtained should be shaken several times with warm water, or until, after separation, the aqueous liquid is no longer acid to litmus. The subsequent treatment of the insoluble fatty acids will depend on the nature and extent of the information required. In some cases it will be sufficient to add alcohol and titrate with standard alkali, with phenolphthalein as indicator.

If the fatty acids are to be weighed, it is best to run them from the separator into a small paper filter previously wetted with hot water. The funnel containing the filter is placed in the mouth of a small dry beaker, and the whole heated in the water-oven. As the filter dries, the greater part of the fatty acids will pass through the paper into the beaker. When no more drops through, the funnel is removed to a small dry flask, and the acids adhering to the separator or other vessels removed by means of ether, carbon tetrachloride, or petroleum spirit. The solution thus obtained is poured into the filter and caught in the flask below. A fresh quantity of the solvent is used to effect complete solution and removal of the fatty acids from the filter, these washings also being allowed to run into the flask. The solvent is then distilled off by immersing the flask in hot water, and the residual fatty acids further dried by blowing a current of air through the flask till they begin to lose weight, or until all odour of the solvent has disappeared. The weight of fatty acids thus estimated is added to that of the main quantity contained in the beaker, and the sum gives the *insoluble fatty acids* in the amount of fat employed for the analysis.

The result expressed in percentage of the fat is commonly termed the *Hehner value*. It usually ranges from about 95.5 to 96% in the case of fats containing only minute quantities of soluble fatty acids.

In most cases the estimation of the *total* insoluble fatty acids is sufficient, but, if desired, a further proximate analysis may be made by the methods indicated in the section on "Higher Fatty Acids."

The acidified aqueous liquid remaining after the isolation of the insoluble fatty acids and the removal of any volatile fatty acids by distillation, contains *glycerol*, which may be isolated by exactly neutralising the free acid with potassium hydroxide, evaporating the solution to dryness on the water-bath, and exhausting the residue with alcohol. On filtering and evaporating the alcoholic solution, the glycerol is obtained as a sweet syrupy liquid, which may be further purified by treatment with a mixture of alcohol and ether and evaporation of the filtered solution. Although glycerol resulting from the saponification of oils may be readily isolated in this manner, the results obtained are only very roughly quantitative, owing to loss during the evaporations. The estimation of the glycerol produced by saponification is most accurately effected by the methods described in the section on "Glycerol."

The following table shows in a condensed form the general process, just described, for the separation of the products of saponification of genuine fixed oils. The method of estimating *foreign additions* to fixed oils is described in a separate section.

Saponify the oil, evaporate off the alcohol, dissolve the residual soap in water, and agitate the solution with ether:				
Ethereal Solution contains *cholesterol, phytosterol,* hydrocarbons, *unsaponified oil, and higher alcohols* (f r o m waxes, sperm oil, etc.).	**Aqueous Layer.** Acidify with dilute sulphuric acid, and wash the liberated fatty acids with boiling hot water:			
	Oily Layer consists of *insoluble fatty acids,* which may be converted into lead salts and partially separated by treatment with ether:		**Aqueous Liquid** on distillation gives—	
	More Soluble in Ether. Lead compounds of *oleic, ricinolic, linolic, l i n olenic, hypogæ'c acids,* etc.	**More Insoluble in Ether.** Lead compounds of *myristic, palmitic, stearic, arachidic, cerotic a c i d s,* etc.	**In Distillate** *lower fatty acids,* such as *butyric, valeric, caproic, lauric, etc.;* estimated by titration with standard alkali, and further examined by fractional distillation, etc.	**In Retort,** an aqueous liquid, which, when neutralised, carefully evaporated to dryness, and the residue treated with ether-alcohol, gives a solution of *glycerol,* left as a sweet syrupy liquid on evaporating the solvent, b u t which is more accurately *estimated* in a separate portion by oxidation.

Reichert Value.—This term is applied to the number of c.c. of N/10 alkali solution required to neutralise the distillate obtained from the acidified solution of a fat saponified under definite empirical conditions.   It was devised by Reichert (*Zeit. anal. Chem.*, 1879, **18**, 68), and, though practically superseded by later modifications, is still used in some laboratories, and is the method by which the earlier recorded values were obtained.

As the process is an arbitrary one, only about $\frac{4}{5}$ of the entire volatile fatty acids obtainable from butter being found in the distillate under the conditions of operation, it is necessary to adhere to the following directions: Saponify 2.5 grm. of the fat with 25 c.c. of approximately N/2 alcoholic potassium hydroxide by heating it in a closed bottle or flask fitted with a long tube.   Transfer the product to a porcelain basin, and evaporate off the alcohol *completely* at a steam heat.   Dissolve the residual soap in water, add dilute sulphuric acid in slight excess, dilute the liquid with water to 75 c.c., add some fragments of pumice (preferably coiled round with platinum wire), and distil gently until 50 c.c. have passed over.   Filter the distillate, if not quite free from white flakes or oily globules, wash the filter with a little hot water, and titrate the clear solution with N/10 alkali, using phenolphthalein as an indicator

The following table gives typical Reichert values thus obtained:—

Substance	C.c. of N/10 alkali required	Observer
Butter- or milk-fat, cow's.........	12.5–15.2	Reichert, Cald-well, Moore, Allen, etc.
Butter- or milk-fat, ewe's.........	13.7	Schmitt.
Butter- or milk-fat, goat's.. ..	13.6	Schmitt.
Butter- or milk-fat, porpoise's.....	11.3	Allen.
Coconut oil....................	3.5–3.7	Reichert, Moore, Allen.
Palmnut oil....................	2.4	Allen.
Palm oil......................	0.8	Moore.
Cacao butter.................. ..	1.6	Moore.
Margarine....................	0.2–1.6	Caldwell, Moore, Allen.
Whale oil.....................	3.7	Allen.
Whale oil.....................	12.5	Allen.
Porpoise oil...................	11–12	Allen.
Sperm oil.....................	1.3	Allen.
Bottlenose oil..................	1.4	Allen.
Menhaden oil...	1.2	Allen.
Codliver oil...................	1.1–2.1	Allen.
Sesame oil........	2.2	Allen.
Cottonseed oil.........	0.3	Moore.
Castor oil.....................	1.4	Allen.

Reichert-Meissl Value.—In Meissl's modification of Reichert's process (*Dingler's Polyt. J.*, 1879, **233**, 229) double the quantity of fat (5 grm.) is used, and the resulting values are about 2.2 times as great. His modification is in common use, with the additional precautions indicated by Wollny (*Analyst*, 1887, **12**, 203, from *Milch Zeit.*, 1887, Nos. 32–35) to ensure complete saponification of the fat, and to obviate errors due to absorption of carbon dioxide and variations in the form and size of the distillation apparatus and the rate of distillation.

The special form of apparatus and method of distillation official in England are described in the section dealing with "*Butter.*"

The following official process of the A. O. A. C. is essentially the method as recommended by Wollny:

Apparatus and Reagents.

Sodium Hydroxide Solution.—100 grm. of sodium hydroxide are dissolved in 100 c.c. of distilled water. The sodium hydroxide should be as free as possible from carbonates, and be preserved out of contact with the air.

Alcohol, of about 95%, redistilled with sodium hydroxide.

Acid.—Solution of sulphuric acid containing 25 c.c. of strongest sulphuric acid in 1000 c.c. of water.

Barium Hydroxide.—An accurately standardised, approximately N/10 solution of barium hydroxide.

Indicator.—1 grm. of phenolphthaleïn in 100 c.c. of alcohol.

Saponification flasks, of from 250 to 300 c.c. capacity, of hard, well-annealed glass, capable of resisting the tension of alcohol vapor at 100°.

Pipette graduated to deliver 40 c.c.

Distilling Apparatus.

Burette.—An accurately calibrated burette, reading to tenths of a c.c.

Estimation.—Weighing the fat.—The butter or fat to be examined should be melted and kept in a dry, warm place, at about 60° for 2 or 3 hours, until the water and curd have entirely settled out. The clear, supernatant fat is poured off and filtered through a dry filter-paper in a jacketed funnel containing boiling water. Should the filtered fat, in a fused state, not be perfectly clear, it must be filtered a second time.

The saponification flasks are prepared by thoroughly washing with water, alcohol, and ether, wiping perfectly dry on the outside, and heating for 1 hour at the temperature of boiling water. The flasks should then be placed in a tray by the side of the balance and covered with a silk handkerchief until they are perfectly cool. They must not be wiped with a silk handkerchief within 15 or 20 minutes of the time they are weighed. The weight of the flasks having been accurately determined, they are charged with the melted fat in the following way:

The pipette with a long stem, marked to deliver 5.75 c.c., is warmed to a temperature of about 50°. The fat, having been poured back and forth once or twice into a dry beaker in order to mix it thoroughly, is taken up in the pipette, and 5.75 c.c. of fat allowed to flow into the flask. After the flasks have been charged in this way they should be re-covered with the silk handkerchief and allowed to stand 15 or 20 minutes, when they are again weighed.

Saponification.—10 c.c. of 95% alcohol are added to the fat in the flask, and then 2 c.c. of sodium hydroxide solution. A soft cork stopper is now inserted in the flask and tied down with a piece of twine. The saponification is then completed by placing the flask upon the water- or steam-bath. During the saponification, which should last 1 hour, the flask should be gently rotated from time to time, care being taken not to project the soap for any distance up its sides. At the end of an hour the flask, after having been cooled to about the temperature of the room, is opened.

Removal of the Alcohol.—The stopper having been laid loosely in the mouth of the flask, the alcohol is removed by dipping the flask into a steam-bath. The steam should cover the whole of the flask except the neck. After the alcohol is nearly removed, frothing may be noticed in the soap, and, to avoid any loss from this cause or creeping of the soap up the sides of the glass, the flask should be removed from the bath and shaken to and fro until the frothing disappears. The last traces of alcohol vapor may be removed from the flask by waving it briskly, mouth down, to and fro.

Dissolving the Soap.—After the removal of the alcohol the soap should be dissolved by adding 100 c.c. of recently-boiled distilled water, and warming the flask on the steam-bath with occasional shaking until solution of the soap is complete.

Liberation of the Fatty Acids.—When the soap solution has cooled to about 60° or 70°, the fatty acids are separated by adding 40 c.c. of the dilute sulphuric acid solution.

Melting the Fatty-Acid Emulsion.—The flask should now be stoppered as in the first instance, and the fatty-acid emulsion melted by replacing the flask on the steam-bath. The time required for the fusion may vary from a few minutes to several hours, according to the nature of the fat examined.

Distillation.—After the fatty acids are completely melted, forming a transparent oily layer on the surface of the water, the flask is cooled to the temperature of the room, and a few pieces of pumice-stone added. The pumice-stone is prepared by throwing it, at a white heat, into distilled water, and keeping it under water until used. The flask is now connected with a glass condenser, is slowly heated with a naked flame until ebullition begins, and then the distillation is continued by regulating the flame in such a way as to collect 110 c.c. of the distillate in, as nearly as possible, 30 minutes. The distillate should be received in a flask accurately marked at 110 c.c.

Titration of the Volatile Acids.—The 110 c.c. of distillate, after thorough mixing, are filtered through perfectly dry filter-paper, 100 c.c. of the filtrate poured into a beaker holding from 200 to 250 c.c., 0.5 c.c. of the phenolphthalein solution added, and N/10 barium hydroxide run in until a red colour is produced. The contents of the beaker are then returned to the measuring flask to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red colour produced remains apparently, unchanged for 2 or 3 minutes. The number of c.c. of N/10 barium hydroxide required should be increased by one-tenth.

The following typical Reichert-Meissl values have been recorded by different observers:

Oil or fat	Reichert-Meissl value	Oil or fat	Reichert-Meissl value
Almond.............	0.5	Maize oil............	4 to 4.5
Arachis.............	0.5	Palmnut oil..........	5 to 6.8
Butter fat...........	21.0–33.4	Porpoise oil..........	0.8 to 1.9
Castor..............	2.5	Palm oil........	0.0 to 0.7
Croton.............	12–13.5	Rape...........	46 to 56
Cottonseed..........	0.7–0.9	Sesame oil......... . .	1 to 2
Coconut oil..........	6.6–8.4	Whale oil........	0.7 to 2.0
Codliver oil.........	0.2	Wheat oil............	2 to 3
Doegling oil.........	1.4		
Dolphin oil..........	5–6		

Leffmann and Beam's modification (*Analyst*, 1891, **16**, 153; 1896, **21**, 251) in which a solution of sodium hydroxide in glycerol is used for the saponification is the official German method for the examination of fats and cheese, the estimation being made as follows: 5 grm. of the fat are cautiously heated with constant shaking over a small flame in a 300 c.c. Erlenmeyer flask with 20 c.c. of glycerol of sp. gr. 1.26, and 2 c.c. of sodium hydroxide solution (prepared by dissolving 100 grm. of sodium hydroxide in 100 c.c. of water). After evaporation of the water, which usually takes from 5 to 8 minutes, the liquid becomes clear, and is then completely saponified. It is now allowed to cool to about 80°, and treated with

90 c.c. of water at 80° to 90°. This solution is acidified with 50 c.c. of dilute sulphuric acid (50 c.c. of strong acid in 1000 c.c. of water) and the volatile fatty acids distilled and titrated as in the Reichert-Meissl process.

BROMINE AND IODINE ABSORPTIONS

Another method of differentiation based on the chemical constitution of the fats and oils is the estimation of the amount of bromine or iodine taken up under conditions intended to ensure the formation of additive compounds only. The fatty acids of the acetic series are saturated compounds, and do not form additive compounds with iodine or bromine, whilst the acids of the acrylic series combine with 2 atoms and those of the propiolic series with four atoms, as expressed by the following equations:

Stearic Acid. $C_{18}H_{36}O_2$. No addition compound with bromine or iodine.

Oleic Acid, $C_{18}H_{34}O_2$, forms $C_{18}H_{34}Br_2O_2$, and $C_{18}H_{34}I_2O_2$.

Linolic Acid, $C_{18}H_{32}O_2$, forms $C_{18}H_{32}Br_4O_2$, and $C_{18}H_{32}I_4O_2$.

Linolenic Acid, $C_{18}H_{30}O_2$, forms $C_{18}H_{30}Br_6O_2$, and $C_{18}H_{30}I_6O_2$.

The esters of the acids of these series behave similarly, so that an estimation of the percentage of bromine or iodine assimilated gives some idea of the proportion of olein as compared with palmitin and stearin in a fat, and of the linolin and linolenin of a drying oil as compared with the olein of a non-drying oil, although the fact must not be lost sight of that many solid fats contain esters of linolic and even linolenic acid, whilst drying oils contain olein in addition to the more unsaturated glycerides.

Bromine Value.—The earliest methods of estimating the amount of bromine absorbed by oils and fats were those of Mills and Snodgrass (*J. Soc. Chem. Ind.*, 1883, **2**, 435) and Mills and Akitt (*ibid.*, 1884, **3**, 366), but for most purposes these and similar methods have now been practically superseded by Hübl's iodine method and Wijs' iodine chloride method.

A considerable amount of bromine enters into combination by way of substitution as well as by addition, and McIlhiney (*J. Amer. Chem. Soc.*, 1894, **16**, 275; 1899, **21**, 1084) has based a useful test for the detection of rosin or turpentine in drying oils upon a determination of the *bromine substitution value.*

The solution of the weighed quantity of the oil in 10 c.c. of carbon tetrachloride is treated in a stoppered bottle with 20 c.c. of N/3 solution of bromine in the same solvent. After the lapse of 2 or 3 minutes 20 to 30 c.c. of a 10% solution of potassium iodide are introduced, the bottle thoroughly shaken, and the liberated iodine titrated with standard thiosulphate solution, and calculated into the corresponding bromine addition value. An addition of 5 c.c. of a neutral 2% solution of potassium iodate is then made, and the liberated iodine, corresponding to the hydrobromic acid formed in the substitution, titrated and calculated into the bromine substitution value.

Loss of bromine or hydrobromic acid is prevented by fixing a piece of wide rubber tubing round the neck of the bottle, so as to form a well into which the potassium iodide solution is poured. The bottle is then cooled in ice-water to create a partial vacuum before slightly withdrawing the stopper.

The bromine substitution value of ordinary fats and oils usually ranges from about 0.3 to 3.6, whilst rosin and turpentine show values of 50 and upwards.

Vulté and Logan (*J. Amer. Chem. Soc.*, 1901, **23**, 156) made comparative estimations of the bromine value by this method and of the iodine value by Hübl's method, and showed that the ratio between the iodine value as estimated and as calculated from the bromine addition value might afford useful indications in the detection of marine animal oils in linseed oil, etc. They found rosin to have a bromine substitution value of 102.3.

Comparative results obtained by Wijs' iodine chloride method and McIlhiney's bromine method are also given by Williams (*J. Soc. Chem. Ind.*, 1900, **19**, 300). A gravimetric bromine method was devised by Hehner (*Analyst*, 1895, **20**, 49; *J. Soc. Chem. Ind.*, 1897, **16**, 88) and was discussed by Lewkowitsch (*J. Soc. Chem. Ind.*, 1896, **15**, 859), Williams (*Analyst*, 1895, **20**, 277), and Jenkins (*J. Soc. Chem. Ind.*, 1897, **16**, 193).

The main advantages of this method, where applicable, are its simplicity and speed, but both are possessed in greater degree by the bromine thermal process (*q. v.*).

Insoluble Bromide Test.—Hehner and Mitchell found (*Analyst*, 1898, **23**, 315) that on treating an ethereal solution of certain oils with a slight excess of bromine an insoluble precipitate was obtained, the

amount of which could frequently give valuable indications as to the purity of an oil.

These precipitates appear to be the bromides of mixed glycerides containing one radicle of linolenic acid or (in the case of marine animal oils) clupanodic acid. The bromide from linseed oil melts at 143.5 to 144° and contains about 56% of bromine. The similar bromides from marine animal oils decompose before melting, and this affords a means of detecting even a small amount of such oils in linseed and other drying oils.

The precipitate may be collected either in a Soxhlet tube, if the quantity taken is small, or on a counterpoised filter, but the method employed for the estimation of stearic acid in mixtures of fatty acids (see page 535) is the most satisfactory, the best filtering material in this case being thin, flexible chamois leather tied over the end of the small thistle funnel, from which any adhering precipitate can afterwards readily be removed by washing.

From 1 to 2 grm. of the sample are dissolved in 40 c.c. of ether, to which a few c.c. of glacial acetic acid are added, the precipitate formed being more granular from such a mixture than when ether alone is employed. The solution is cooled in an ice-chest and bromine added, the flask being preferably left all night in the ice. This, however, is not essential for ordinary working. The liquid is filtered off by the suction funnel attached to a pump, the flask washed out with four successive portions of ether at 0°, and the residue dried in the flask to constant weight. Even when ether at ordinary temperatures is used, no considerable error is introduced.

Various samples of pure linseed oil were examined by this method, with the following results:

Sample	Oil taken, grm.	Weight precipitate, grm.	Percentage of deposit
A..........................	1.3226	0.3156	23.86
A..........................	3.1005	0.7573	24.42
B..........................	0.6792	0.1765	25.8
C..........................	1.0000	0.2480	24.8
C..........................	1.0000	0.2500	25.0

A sample of walnut oil gave, in two determinations, 1.9 and 1.42% of bromide. Poppy oil gave no deposit, nor did Brazil nut oil, maize

oil, cottonseed oil, olive oil, Japanese wood oil, or almond oil. Mixtures of linseed oil and other oils gave percentages of bromide in proportion to the percentage of linseed oil, as will be seen from the following table:

Oils used	Linseed oil, %	Insoluble bromide, %	Linseed oil, calculated from bromide, %
Linseed A and walnut.	69.0	16.6	69.0
Linseed A and walnut.	38.2	9.3	38.1
Linseed A and maize oil	52.0	12.4	50.8
Linseed A and maize oil	50.5	12.2	50.0
Linseed A and maize oil	51.7	12.6	51.6

The following values were obtained in this way by Walker and Warburton (*Analyst*, 1902, 28, 237): Linseed oil, 23.14; 23.52; tung oil, nil; candlenut oil, 8.2; 7.28; Japan fish oil, 21.14; 22.07; fish oil (deodorised) 49.0; 52.28; codliver oil, 35.33; 33.76; cod oil, 32.68; 30.62; shark-liver oil, 21.22; 19.08; seal oil, 27.54; 27.92; whale oil, 15.54; 16.14; and sperm oil, 2.61; 2.42% (and after 48 hours' standing, 3.72; 3.69).

As a rule linseed oil yields about 25% of insoluble bromide, but Mitchell has met with a specimen yielding over 30% and Lewkowitsch with one giving 37.72%. Other insoluble bromide values for marine animal oils are given by Procter (*J. Soc. Chem. Ind.*, 1906, 25, 798). Sutcliffe (*Analyst*, 1914, 39, 28, 338) recommends the following modification as giving results agreeing to within about 1%: 1 grm. of the oil is dissolved in 40 c.c. of ether in a weighed flask, 5 c.c. of glacial acetic acid are added, and the flask and its contents cooled in water to about 11°. Bromine is then added drop by drop until the solution is red, and the flask is closed and allowed to stand for 12 hours in water. The contents are filtered through a disc of paper in a Gooch crucible and the precipitate washed 3 times by decantation and twice in the crucible with 10 c.c. of ether chilled to 5°; it is dried for 3 hours in the water oven, and weighed. Its melting point should range from 141° to 144° in the case of linseed oil.

Comparative determinations of the amounts of insoluble bromide and of the iodine value of linseed oils of various origin showed that

under these conditions the relationship between the two values could be expressed by the formula: Per cent. of bromide = (0.63 iodine value) — 78.0. The precipitated bromides must be white and crumble readily when dried. Certain sorts of bromine give products which when dried are dark and horny; these should be rejected.

Gemmell (*Analyst*, 1914, **39**, 297) was unable to obtain concordant results with various methods, mainly owing to the solubility of the bromides in the various solvents and he therefore recommends the following method, applied to the fatty acids, as being preferable to estimating the bromide obtained directly from the oils: The oil (5 grm.) is saponified with alcoholic potassium hydroxide, the soap dried and dissolved in 100 c.c. water, and the fatty acids liberated in the usual way. The flask is cooled in water, and the fatty acids separated by shaking with ether. The united ether extract (100 c.c.) is divided into aliquot portions (20 c.c.), and to each of these is added 2 c.c. of glacial acetic acid. The flasks are chilled in ice-water and the solution brominated and allowed to stand, the liquid decanted, the precipitates washed thrice in the flasks with chilled ether, then transferred (by means of 5 c.c. of ether) to a weighed filter paper, dried and weighed.

The following results were thus obtained: Raw linseed oils (7 ·kinds) 32.60 to 37.65; boiled linseed oils (6 samples), 25.95 to 33.90; soja bean oil, 4.10; rape oil, 2.35; and walnut oil, 3.0%; Chinese wood oil, *nil*. Satisfactory results may also be obtained in the way with marine animal oils, as is shown by the following typical examples: Cod-liver oil, 35.20; whale oil, 21.70; brown whale oil, 25.80; menhaden oil, 51.70; shark-liver oil, 17.70; and sperm oil, 1.70.

The main objection to Gemmell's modification is the risk of loss of linolenic acid by oxidation during the liberation of the fatty acids. Some of his criticisms upon the direct methods have been answered by Sutcliffe (*Analyst*, 1914, **39**, 388).

The loss due to solubility might possibly be overcome, at all events in the case of linseed oil, by previously saturating the solvent with the insoluble bromide purified by extraction with ether.

Gemmell (*loc. cit.*) points out that the solubility of the bromide from marine animal oils is less than that of the bromide from vegetable oils, so much so that a precipitate is formed as soon as bromine is added. He suggests that this affords a rapid means of detecting fish oils in vegetable oils.

In his opinion the insoluble bromide formed by linseed oil is not that of a mixed glyceride, but the reasons given in support of this view are not conclusive.

Stiepel (*Chem. Zeit.*, 1912, **2**, 175) has found that the amount of insoluble bromide from linseed oil is greatly reduced by heating the oil, whilst the analogous bromide obtained from marine animal oil is no longer formed after heating. Hence a negative result of the "octobromide" test cannot of itself be regarded as a proof of the absence of marine animal oil.

Thus the commercial product *neutraline*, which consists of deodorised fish oil, yields no insoluble bromide, and might therefore be taken for an animal hoof oil.

The suggestion given above of saturating the solvent with insoluble bromide has more recently been adopted by Davidson (*J. Ind. Eng. Chem.*, 1921, **13**, 801) in the following method of estimating the insoluble bromide: 4 grm. of the oil are dissolved in 35 c.c. of ether in a centrifuge tube, the solution cooled to 0°, and 1 grm. of bromine slowly added, with continual stirring. The top of the tube is rinsed down with 5 c.c. of ether, and the tube then kept for 2 hours at 0°, after which it is centrifuged for 3 minutes at 2000 revolutions per minute. The liquid is decanted and the precipitate washed twice with 10 c.c. of ether at 0°, and once with alcohol, and after each washing again separated by centrifugal action. All ether used should be saturated at 0° with the insoluble bromide from a previous estimation. Under these conditions a yield of 50 to 72% (average 60.9 per cent.) of insoluble bromide (m. p. 140° to 145°) was obtained from genuine linseed oils. The precipitates contained from 57 to 58% of bromine.

Bailey and Johnson (*J. Ind. Eng. Chem.*, 1918, **10**, 999) have suggested the use of the determination of the insoluble bromide and iodine values of salmon oil as a means of identifying the species of canned salmon. They show that the iodine values of the expressed oil range from about 127 to 166, and the insoluble bromide values from about 23 to 59, and have proposed certain limits for these valuable applicable to various species of the fish.

Iodine Value.—Free iodine is so slowly absorbed by oils and fats that it has not been found possible to base a satisfactory method upon its use, and it has long been discarded in favour of the Hübl process (*Dingler's polyt. J.*, 1884, 253, 281) in which the reagent is an

alcoholic solution of iodine in conjunction with mercuric chloride in the proportion of at least 1 molecule (I_2) of the former to at least 1 ($HgCl_2$) of the latter.

Hübl's Method.—The reagent is prepared by dissolving 25 grm. of iodine in 500 c.c. of nearly absolute alcohol (free from fusel oil), and 30 grm. of mercuric chloride in an equal volume of the same solvent. The latter solution is filtered, if necessary, and then added to the tincture of iodine. The mixed solution should be allowed to stand for 12 hours before being used, as, owing to the presence of impurities in the alcohol employed, it is liable to undergo considerable reduction in strength, and must in all cases be re-standardised immediately before or after use. The strength is ascertained by titration with N/10 solution of sodium thiosulphate, which in its turn is standardised with a solution of resublimed iodine in the usual way. The mercurial iodine solution acts readily at ordinary temperatures on either free unsaturated fatty acids or their esters to form chloro-iodo-addition products, the total proportion of halogen assimilated being estimated in terms of iodine.

To estimate the iodine-absorption, from 0.2 to 0.3 grm. of drying oil, 0.3 to 0.4 of non-drying oil, or from 0.8 to 1.0 grm. of fat, is weighed accurately, and dissolved in 10 c.c. of chloroform. The solution is mixed in a stoppered flask with 20 c.c. of the standard solution of iodo-mercuric chloride, and if the liquid is not quite clear after agitation a further addition of chloroform is made. If the mixture becomes decolorised, or nearly so, after standing a short time, a further addition of 5 or 10 c.c. of iodine solution must be made. To ensure accurate results, the excess of iodine must be considerable, and hence the liquid ought still to be quite brown after standing for 2 hours.[1] After that time, from 10 to 15 c.c. of a 10 % aqueous solution of potassium iodide should be added, and the whole diluted with about 150 c.c. of water. The free iodine, part of which is present in the aqueous and part in the chloroform solution, is then estimated by titration with thiosulphate, the contents of the flask being frequently agitated, and starch solution being added just before the end of the reaction. A blank experiment with the

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[1] Hübl found that with free fatty acids the action is complete with only a small excess of iodine, but with fats or oils a larger excess must be employed, or the results will be too low. In presence of a sufficient excess of iodine, variations in the concentration of the fatty solution and in the amount of mercuric chloride present do not affect the results. The reaction should be allowed to continue for at least 2 hours (or, according to Archbutt, 6 hours).

same quantities of chloroform, iodine solution, etc., is made side by side with the actual test, so as to obtain a correction for any impurities in the reagents and to ascertain the true strength of the iodine solution. The difference between the volume of thiosulphate used in the blank experiment and that required in the experiment in which the oil was employed is then calculated into its equivalent of iodine, and this to units per cent. of the oil.

The product formed by the action of iodo-mercuric chloride on pure oleic acid is a greasy substance, which is colourless at first, but gradually turns brown from liberation of iodine. Estimations of the chlorine and iodine, as also of its saponification equivalent, show the compound to be a chloriodostearic acid of the formula $C_{18}H_{34}IClO_2$. The similar products formed by the action of the iodine solution on fats and oils are colourless, viscous, or resinous masses, which in general resemble the original substances. In order to render the whole of the iodine available, the presence of mercuric chloride in a ratio of not less than $HgCl_2:I_2$ is essential.

The theory of the reactions taking place in the Hübl process has been discussed by Ephraim (*Zeit. angew. Chem.*, 1895, 254), who regards iodine chloride as the active agent, by Wijs (*ibid.*, 1898, 251) who considers hypoiodous acid to be the active substance, and by Lewkowitsch (*Analyst*, 1899, 24, 257) who in the main agrees with Ephraim. There is a certain amount of substitution of iodine as well as addition, as has been shown by Schweitzer and Lungwitz (*J. Soc. Chem. Ind.*, 1895, 14, 130, 1030).

Wijs' Method.—A very rapid method of estimating the iodine absorption is based by Wijs (*Ber.*, 1898, 31, 750) upon the conclusions drawn from his experiments (*loc. cit.*). The hypoiodous acid, which he regards as the active agent in the absorption, is obtained by the action of water upon iodine chloride ($ICl + H_2O = HCl + HIO$), a solvent being chosen which contains so much of the former as will decompose nearly the whole of the latter, and at the same time not be oxidised by the hypoiodous acid. Good results are obtained with a solution of iodine chloride in 95% acetic acid. This is prepared by dissolving 13 grm. of iodine in 1000 c.c. of acetic acid, estimating the "halogen content" of the solution and passing in a current of chlorine (free from hydrochloric acid) until the "halogen content" has been doubled. With a little practice this point is readily discernible by the change in colour. Or the reagent may be prepared by dissolving

8.5 grm. of iodine and 7.8 grm. of iodine trichloride in a litre of acetic acid.   The solution is employed as Hübl's solution, except that the time required for absorption is greatly reduced.   With oils of low iodine values, the absorption is complete in 4 minutes, and with those of higher value not more than 10 minutes will be necessary if too much oil is not taken.

In the following table the more common oils and fats are classified in accordance with their iodine values as estimated by various chemists by one or other of the preceding methods:

Oils	Iodine value	Fats and waxes	Iodine value
Vegetable oils		*Vegetable fats*	
Castor..........	84-85	Japan wax.......... ..	4.2-15
Olive...........	77-91	Coconut oil....... ...	8.2-9.5
Arachis...... ..	86-99	Palmnut oil..	10.5-17.5
Olive....... .	77-91	Chinese tallow........	23-38
Almond........ ...	93-100	Cacao butter..... ...	32-42
Rape.....	97-105	Bassia tallow.........	54-68
Sesame...	103-115	Cotton oil "stearin"...	89-93
Cottonseed...	104-116		
Maize........ . .	115-128		
Nigerseed..	126-134	*Animal fats*	
Sunflower.. ....:	123-136		
Poppyseed..........	130-141	Tallow...............	35-40
Walnut...	139-148	Beef fat..........	36-42
Hempseed....	145-166	Mutton fat..........	33-50
Tung..... .	155-162	Lard............... .	47.5-64
Linseed...	175-201	Horse fat.............	76-86
Perilla......	185-204		
Animal oils		*Waxes*	
Tallow oil...........	55-57		
Neatsfoot oil.. ...	67-73	Spermaceti...........	2.6
Lard oil........ ..	69-75	Beeswax..............	8.5-11.5
Sperm......	80-84	Wool fat.............	17-52
Bottlenose.... ..	80-85	Carnauba wax.........	55.2
Whale..... . .	116-128		
Shark.... .	115-139		
Seal....... .	130-152		
Codliver... .	138-167		
Menhaden........ .	148-160		

The results obtained by Wijs' method tend to be higher than the Hübl figures, this being most notable in the case of highly unsaturated oils.   It is probable that many of the older values of, *e. g.*, of

linseed oil, were too low, owing to incomplete absorption of the halogen. The results obtained by Wijs with purified allyl alcohol point to his method giving more correct figures than the Hübl process.

Waller's Method.—One drawback to the use of the Hübl solution is that there is a gradual reduction in the amount of free iodine present. As a remedy against this Waller (*Analyst*, 1895, **20**, 280) saturates the iodine solution with hydrochloric acid. His solution is prepared by dissolving 25 grm. of iodine in 250 c.c. of 95% alcohol, and mixing the solution with 200 c.c. of an alcoholic solution of 25 grm. of mercuric chloride and 25 grm. of hydrochloric acid (sp. gr. 1.19), and the whole diluted with alcohol to 500 c.c.

In a solution thus prepared the iodine shown on titration had only fallen from 49.31 grm. to 46.60 grm. in 64 days, while the free acid had increased to a corresponding extent.

In the opinion of Wijs (*Chem. Rev. Fett. Ind.*, 1899, **6**, 5) the fact that hydrochloric acid is not set free from the addition compound, as in Hübl's method, renders it probable that the iodine value obtained when the blank solution is titrated after the absorption is more correct than the Hübl value, although the difference is slight.

Hanus' Method.[1]—The method of Hanus (*Zeit. Unters. Nahr. Genussm.*, 1901, **4**, 913) is frequently used for determining the iodine value. It differs from the Wijs method in the fact that iodine bromide is used as the active agent instead of iodine chloride.

The reagent is prepared by adding 13 grm. of bromine, drop by drop, to 20 grm. of finely powdered iodine contained in a flask chilled so that the temperature does not exceed 5° to 8° during the reaction.

From 0.1 to 0.7 grm. the oil or fat dissolved in 10 c.c. of chloroform is mixed with 25 c.c. of the iodine bromide solution, and after 15 minutes, 15 c.c. of a 10% solution of potassium iodide are added, and the liberated iodine treated with standard thiosulphate solution. The reagent is also standardised with thiosulphate.

Comparative determinations of the iodine values of erucic, elaidic, oleic, ricinoleic and undecylic acids, made by Weiser and Donath (*Zeit. Untersuch. Nahr. Genussm.*, 1914, **28**, 65) by the methods of Hübl, Waller, Wijs and Winkler, gave practically concordant results. In the case of linolic acid the only method that gave theoretical results was that of Winkler, the other methods giving too high values. The iodine values of crotonic, tiglic and cinnamic

[1] The Hanus method is the official method of A. O. A. C. (U. S. A.).

acids could not be determined by the methods of Hübl, Waller, and Wijs, whereas nearly theoretical results were obtained by Winkler's method.

Winkler's Method (*Pharmacop. Hungarica*, 1900, XI) —From 0.1 to 0.5 grm. of the fat is dissolved in 10 c.c. of carbon tetrachloride, and the solution treated with 50 c.c. of Winkler's solution (N/10 potassium bromate solution containing 1 to 1.5 grm. of potassium bromide and 10 c.c. of 10% hydrochloric acid). After 30 minutes to 2 hours (according to the degree of unsaturation of the fat) 10 c.c. of 10% potassium iodide solution are added and the liberated iodine titrated with thiosulphate solution.

Meigen and Winogradoff (*Zeit. angew. Chem.*, 1913, **27**, 241) show that unsaturated fatty acids (oleic acid) absorb more chlorine than iodine from a mixture of the two halogens, while more or less substitution of the chlorine occurs. This substitution is checked by the presence of acid. It is inadvisable, however, to add a large excess of hydrochloric acid (as in Waller's solution) since combination of oleic acid with the hydrochloric acid will then take place. In examining an unknown compound Meigen and Winogradoff advocate the use of Wijs' method, with the addition that after the titration with thiosulphate the product of the action is extracted with water, and the amount of halogen acid in the aqueous extract is titrated with N/10 alkali.

Thus a sample of pure oleic acid treated for 30 minutes with a Wijs' solution containing 13 grm. of iodine per 1,000 c.c. and an equivalent quantity of chlorine gave an iodine value of 99.95 (theory, 89.95), whilst the acid in the aqueous solution corresponded to 4.62 % of substituted iodine. With a Wijs' solution containing an excess of 2% of iodine over the chlorine the iodine value found was 90.95, whilst the acid in the aqueous extract corresponded to 0.53% of substituted iodine. When there was an excess of 10% of chlorine in the Wijs' solution the iodine value of the oleic acid was 105.40, and the acid in the aqueous solution corresponded to 8.31% of iodine. It was proved that halogen acids were only formed by substitution.

Gowing-Scopes (*Analyst*, 1914, **39**, 19) studied the effect of using different chlorohydrocarbons as solvent in Wijs' method and found that the results obtained with trichlorethylene, tetrachlorethylene, tetrachlorethane and pentachlorethane agreed closely with those

obtained with carbon tetrachloride, but that the figures with dichlorethylene were too low.

Ponzio and Gastaldi (*Gazz. Chim. Ital.*, 1912, 42, 92) have shown that although the iodine value of ordinary oleic acid determined by the methods of Hübl, Wijs or Hanus agrees fairly well with the theoretical value, none of the methods, as ordinarily used, gives a trustworthy result with fatty acids, such as crotonic or 2-3-hypogæic acid, in which the double bond adjoins the carboxyl group. It is only the velocity of the reaction which is affected, however, and by prolonging the action to 70 hours with Wijs' solution a fairly normal value (86.8) was also obtained with 2-3-oleic acid, which with the ordinary time of absorption had only given a value of 8.7. It may therefore be possible to establish the position of the double bond in an unsaturated fatty acid by determining the iodine value.

Acetyl Value.—The estimation of the acetyl value as revised by Benedikt and Ulzer (*Monatsh.*, 1887, 8, 41) is based upon the principle that hydroxy-acids, on being heated with acetic anhydride, exchange the hydrogen atom of their hydroxyl group or groups for the radicle of acetic acid. The operation is carried out by heating the free fatty acids with acetic anhydride.

Lewkowitsch (*Proc. Chem. Soc.*, 1890, 6, 72, 91) drew attention to the causes of error in this process, and subsequently (*J. Soc. Chem. Ind.*, 1897, 16, 503) devised the following method, which is now in general use: 10 grm. of the filtered fat are boiled for 2 hours with an equal volume of acetic anhydride in a round-bottomed flask beneath a reflux condenser, and the mixture then transferred to a large beaker, and boiled with several hundred c.c. of water, bumping being meanwhile prevented by passing a slow current of carbon dioxide through a long tube reaching nearly to the bottom of the beaker.

The mixture is allowed to separate into 2 layers, the water is siphoned off, and the oily layer again boiled out in the same manner until the last trace of acetic acid is removed. This is ascertained by testing with litmus paper. The acetylated product is freed from water and finally filtered through filter paper in a drying oven.

This operation may be carried out quantitatively, and in that case the washing is best done on a weighed filter. An increase of

weight would prove that assimilation of acetyl groups had taken place. This method may be found useful to ascertain preliminarily whether a notable amount of hydroxylated acids is present in the sample under examination.

2 or 4 grm. of the acetylated substance are saponified by means of alcoholic potassium hydroxide solution as in the estimation of the saponification value. If the "filtration process" be used, the alcoholic alkali must be measured exactly, and this is also advisable with the distillation process, so as to obtain the saponification value of the acetylated fat. The alcohol is next evaporated and the soap dissolved in water.

From this stage the determination is carried out either by the (a) "distillation process" or (b) "filtration process."

(a) *Distillation Process.*—Add dilute sulphuric acid (1:10), in more than sufficient quantity to saturate the alkali, and distil as usual in Reichert's distillation process. Since several portions of 100 c.c. each must be distilled off, either a current of steam is blown through the suspended fatty acids or water is run into the distilling flask, from time to time, through a stoppered funnel fixed in the cork, or any other convenient device is adopted. It will be found quite sufficient to distil over 500 to 700 c.c., as the last 100 c.c. contain practically no acid. Filter the distillates to remove any insoluble acids carried over by the steam, and titrate the filtrates with N/10 potassium hydroxide solution, phenolphthalein being used as indicator. Multiply the number of c.c. by 5.61 and divide the product by the weight of substance taken. This gives the acetyl value.

(b) *Filtration Process.*—Add to the soap solution a quantity of standardised sulphuric acid exactly corresponding to the amount of alcoholic potassium hydroxide solution employed and warm gently, when the fatty acids will readily collect on the top as an oily layer. (If the saponification value has been estimated, it is, of course, necessary to take into account the volume of acid used for titrating back the excess of potassium hydroxide.) Filter off the liberated fatty acids, wash them with boiling water until the washings are no longer acid, and titrate the filtrate with N/10 potassium hydroxide solution, using phenolphthalein as indicator. The acetyl value is calculated in the manner shown above.

Both methods give identical results; the latter will be found shorter.

The acetyl value indicates the number of mg. of potassium hydroxide required for the neutralisation of the acetic acid obtained on saponifying 1 grm. of the acetylated fat or wax.

In the case of those oils and fats which have a high Reichert value, the apparent acetyl value will be too high, owing to the presence of the volatile acids. This influence will affect the distillation process to a greater extent than the filtration process. To eliminate this error, the volatile acids of the original oil or fat should be estimated in precisely the same manner, and the value thus obtained should be deducted from the apparent acetyl value.

It should be noted that in the case of a fat containing free alcohols (phytosterol, cholesterol), or, in the case of waxes, the acetyl value will be a measure of both the hydroxy-acids and the free alcohols. If present, acetic acid radicles are also absorbed by them. If the free alcohol is isolated its acetyl value may be determined as well. The difference between the acetyl value of the fat or wax and the acetyl value corresponding to the amount of free alcohol present will be the true measure of the hydroxy-acids.

If a free alcohol is acetylated, no complication through formation of anhydrides can arise, and in that case simply the saponification value of the acetylated product—the acetic ester of the alcohol—is determined. This value is also the acetyl value of the alcohol (the saponification value of the original alcohol being *nil*).

In a further study of the acetyl value, Lewkowitsch (*Analyst*, 1899, 24, 319) has shown that it may indicate: 1. hydroxy-acids; 2. free alcohols; 3. oxidised fatty acids; 4. acids of unknown composition; 5. mono- and diglycerides, and 6. rancidity. Hence, until it is possible to determine to what extent these several factors contribute to the acetyl value, that value cannot be regarded as a constant.

The following table gives some of the more important results obtained by Lewkowitsch (*loc. cit.*) by the above described processes:

Oil or fat	I	II	III
	Total volatile acids = mg. of KOH per grm.	Apparent acetyl value	True acetyl value II−I
Linseed..............	2.9	6.85; 6.92	3.98
Maize...............	2.53	8.21; 8.75	5.81
Curcas..............		7.5	
Castor..............	0.0	149.6–150.5	150.05
Colza...............	2.15	16.6; 17.2	14.75
Olive...............	2.54	12.78; 13.48	10.68
Horsesfoot..........	4.08	12.96; 14.40	9.44
Seal................	1.50	16.47; 16.84	15.18
Codliver (old)........	2.60	7.9; 8.9	5.8
Codliver (fresh)......	3.60	4.75	1.15
Cottonseed..........	6.28	24.76; 25.1	15.65
Cottonseed..........	0.99	15.8	14.8
Palm (23% free acids)..	2.34	17.8; 18.8	15.96
Cacao butter.........		2.71; 2.86	
Japan wax...........	10.05	27.3	17.25
Japan wax...........	5.6	31.2; 33.1	26.55
Lard................	6.6; 6.7	9.3	2.65
Tallow..............	1.3	9.4; 10.4	8.6
Croton..............	21.07–21.09	40.68; 41.09	19.82
Palmnut............	11.4	19.0	7.6
Coconut............	20.9	23.2	2.3
Butter-fat..........	49.3; 49.4	48.48; 49.29	9.45
Butter-fat..........	43.32	45.23	1.91

To obtain results comparable with the other values of fat analysis Holland (*J. Ind. Eng. Chem.*, 1914, **6,** 482) suggests that the acetyl value should indicate the number of mg. of potassium hydroxide required to saponify the acetyl taken up by 1 grm. of the fat on acetylation.

It may be rapidly determined as follows: 5 grm. of the fat are heated with 10 c.c. of acetic anhydride over boiling water beneath a reflux condenser for 1½ hours, sufficient ceresin to form a solid disc, when cold, being then introduced. After the addition of 150 c.c. of boiling water the flask is again heated on the water-bath, occasionally shaking, to expel acetic acid, and then cooled The solid cake is again heated with 150 c.c. of boiling water, and this process repeated about 6 times, until the filtrate is nearly neutral.

The solid disc and particles on the filter are now boiled with 50 c.c. of standard alcoholic potassium hydroxide solution and 50 c.c. of alcohol, beneath a reflux condenser (with glass beads to prevent

bumping) and the excess of alkali titrated with standard hydrochloric acid.

The difference between the saponification values before and after acetylation is the acetyl value.

Grün (*Oel. u. Fett. Ind.*, 1919, 1, 339, 364) has directed attention to the fact that the tendency of hydroxy-acids to form inner anhydrides is a source of error in Lewkowitsch's method, since mixed anhydrides may be formed as in the reaction:

$$C_{17}H_{33}COOH + (CH_3CO)_2O = C_{17}H_{33}CO.O.COCH_3 + CH_3COOH$$
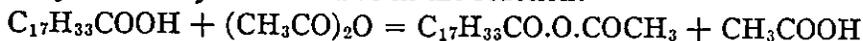
In such cases too much acetic acid will be found by the distillation method. Another source of error is due to the formation of inner esters of hydroxy-fatty acids. For example, ricinoleic acid, when boiled for 8 hours with acetic anhydride, yields acetyldiricinoleic acid instead of acetylricinoleic acid.

$$2C_{17}H_{32}(OH) + 2(CH_3CO)_2O = 3CH_3.COOH + C_{17}H_{32}(OCOCH_3)\text{-}OCO\ C_{17}H_{32}COOH$$
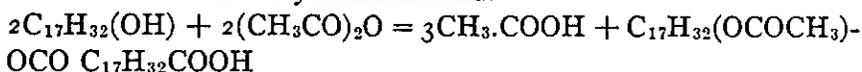
When this by-reaction occurs the acetyl values by Lewkowitsch's method will be too low, whilst by Benedikt and Ulzer's method they will be too high.

These difficulties, and also that due to reciprocal esterification between the triglyceride and acetic anhydride, are avoided by a method in which the fatty acids are converted into esters, which are then acetylated. For this purpose the fat is heated with methyl or ethyl alcohol and 1 to 2% of hydrochloric or sulphuric acid, the alcohol evaporated, and the residue dried. Neither acid anhydrides nor inner esters can be formed on acetylating these esters, which is preferably done by the original method of Benedikt and Ulzer after removal of volatile esters.

The acetyl value of the free acids is found by multiplying the acetyl value of the esters by the theoretical acetyl value of the free acids and dividing by the theoretical acetyl value of the esters. In the case of methyl esters calculation into the triglyceride is unnecessary, since the difference between the groups C_3H_9 and the group C_3H_5 is negligible.

In estimating the amount of mono- and diglycerides the neutralised fat is acetylated and the acetic acid content of the product estimated. The difference between the acetyl value of the neutral fat and that of the mixed methyl esters prepared from it corresponds to the amount of mono- and diglycerides.

OXIDATION OF OILS—DRYING PROPERTIES
(See also under Linseed and other oils.)

Many of the fixed oils thicken on exposure to air, and, under favourable circumstances, gradually dry up into yellowish, transparent varnishes or resin-like substances, to which in the case of linseed oil the name *linoxyn* has been given. The exact nature of the oxidation changes that take place in the drying process is still obscure, though the oils which possess this property in the most marked degree appear (except in the case of tung oil) to be characterised by a high proportion of linolenic and isolinolenic acids.

Strictly speaking, no hard and fast line can be drawn between different classes of oils as regards their drying properties, though for convenience of classification it is usual to group vegetable oils into *drying*, *semi-drying*, and *non-drying* oils.

An experimental investigation of the process of drying of linseed oil has been made by Genthe (*Zeit. angew. Chem.*, 1896, **19**, 2087), who shows that the presence of peroxides plays an important part in the process, and that polymerisation and formation of volatile acids accompany the oxidation. For other investigations of the theory of drying of oils see Livache (*Compt. rend.*, 1895, **120**, 842), Fahrion (*Zeit. angew. Chem.*, 1891, 540; 1892, 171, and *Chem. Zeit.*, 1894, **17**, 1848; 1910, **23**, 722), Fokin (*Zeit. angew. Chem.*, 1909, **22**, 1451, 1492), Morrell, (*J. Soc. Chem. Ind.*, 1915, **34**, 105; *J. Chem. Soc.*, 1918, **113**, 111), Holden and Radcliffe (*J. Soc. Dyers and Col.*, 1918, **34**, 138), and Coffey, (*J. Chem. Soc.*, 1921, **119**).

For testing drying properties, a definite number of drops of the sample may be placed in a watch-glass or flat porcelain capsule, and exposed to a temperature of about 100° for 12 or 24 hours, side by side with samples of oil of known purity. Olive oil will be scarcely affected by such treatment, and rape oil will only become slightly thicker. Cottonseed oil will be considerably affected, whilst good linseed oil will form a hard skin or varnish, which can only with difficulty be ruptured by pressure with the finger. In some respects, a preferable plan is to flood a slip of glass with the oil to be tested, in the manner in which a glass-plate is covered with collodion. The glass with the adhering film of oil is then kept at 100°, and the progress of the drying followed by touching, at intervals, successive

parts of the plate with the finger. Another useful method is to soak a definite measure of thick filter paper in the sample of oil, and then expose it to 100 or 130° for some hours, side by side, with samples of oil of known purity.

Livache's Method.—Livache has shown (*Compt. rend.*, 1886, **102**, 1167) that the absorption of oxygen is accelerated by the addition of finely-divided lead, and on this fact has based the following test, which enables numerical values to be obtained: About 1 grm. of lead[1] is accurately weighed and spread in a thin layer on a watch-glass, and 0.6 to 0.7 grm. of the oil allowed to drop from a pipette upon different parts of the lead, care being taken that they do not run into one another. The watch-glass is then weighed and allowed to stand exposed to the light at the ordinary temperature.

Drying oils will be found to have absorbed the maximum quantity of oxygen after 18 hours, or in some cases after 3 days, whereas non-drying oils do not gain weight until the fourth or fifth day.

The free fatty acids, with the notable exception of cottonseed-oil acids, behave like the oils, *i. e.*, their increase in weight corresponds to the gain in weight of the corresponding neutral oils. Livache's results were as follows:

	Gain in weight of 100 parts		
	Of oil after		Of fatty acids after
	Two days	Seven days	Eight days
Linseed oil............	14.3	..	11.0
Walnut oil............	7.9	..	6.0
Poppyseed oil...... ..	6.8	..	3.7
Cottonseed oil.... .	5.9	..	0.8
Beechnut oil...... ..	4.3	..	2.6
Colza oil....	0.0	2.9	2.6
Rape oil........	0.0	2.9	0.9
Sesame oil....... ..	0.0	2.4	2.0
Arachis oil............	0.0	0.8	1.3
Olive oil.......... ...	0.0	1.7	0.7

To obtain a correct estimate as to the drying properties of an oil, regard must be had not only to the increment in weight, but also

[1] Prepared by precipitating a lead salt with zinc, washing the precipitate rapidly in succession with water, alcohol, and ether, and finally drying in a vacuum.

to the length of time required. Thus, of the two oils in the following table, No. 1 must be considered the better, although both finally reach the same absorption of oxygen:

No of oil	Weight of oil	Weight of lead	Gain in weight of 100 parts after			
			One day	Three days	Six days	Nine days
1	3.246	1.012	14.4	15.7	unchanged	
2	3.154	0.653	2.45	12.0	15.9	unchanged

Bishop's method (*J. Pharm. Chim.*, 1896, [6], **5**, 55) in which the oil is mixed with precipitated silica and manganese resinate (as an oxygen carrier) gives the results more rapidly, but has not yet displaced Livache's method as a practical test.

Oxygen Absorption.—The tendency of fixed oils to absorb oxygen is in direct proportion to their capacity of absorbing bromine or iodine, and to the rise of temperature produced on treating them with sulphuric acid. This is shown by the fact that it is possible to obtain "ozone values" of oils corresponding to the iodine values, as was shown by Fenaroli (*Gazzetta*, 1906, **36**, 292). When dry ozone is allowed to bubble through an oil at a temperature not exceeding 40°, the increase in weight of the oil exactly corresponds to an addition of 1 mol. of ozone for each double-bond in the mol. of the fat. Coffey (*J. Chem. Soc.*, 1921, **119**, 1152) has shown that the real oxygen absorption value of oils is considerably greater than the percentage increment in weight, since there is a simultaneous evolution of volatile products. For the estimation of the true "oxygen value" of drying oils he uses a modification of Genthe's apparatus (*Z. angew, Chem.*, 1906, **19**, 2087): A filter paper (11 cm. in diameter) is saturated with a "standard" solution of the oil in petroleum spirit (b. p. 40° to 60°) and suspended in the apparatus, which is then closed, completely filled with hydrogen, and placed in a thermostat at 100°. When the temperature is constant, the apparatus is rapidly filled with oxygen, and manometer readings taken at intervals. The volume of the apparatus is determined by measurement with water and corrections applied for the volume of absorbents (broken pumice soaked in sulphuric acid, and a stick of sodium hydroxide wrapped in copper

gauze). The oxygen absorption thus determined is a definite quantity for a given oil. In the case of linseed oil it ranged from 28.6 to 29.2, and the fatty acids from the same oil gave a value of 30.05 to 30.20%.

Gravimetric Estimation of Absorption of Oxygen during Drying.—A method devised by Krumbhaar (*Chem. Rev. Fett. Ind.*, 1913, **20**, 290) of measuring the amount of oxygen absorbed by oils during drying may also afford a means of distinguishing between different drying oils. A weighed quantity of the oil is mixed with 0.6% of cobalt resinate and spread over filter paper, which is placed in a U-tube immersed in water at 30°. A steady current of dry air (free from carbon dioxide) is drawn through this tube, and the volatile products formed in the drying process are passed, first through a strongly heated tube of copper oxide (to complete their decomposition into carbon dioxide and water) and then through weighed absorption tubes containing calcium chloride and soda-lime. After every 2 hours the air in the apparatus is replaced by nitrogen, the taps closed, and the tube containing the oil and the absorption tubes weighed, this being continued until the weight becomes constant. The sum of the increase of weight in the oil tube, of the hydrogen absorbed by the calcium chloride tube and of the carbon absorbed by the soda-lime tube gives the amount of oxygen taken up by the oil.

For example, 0.743 grm. of linseed oil showed an increase in weight of 0.128 grm. in 18 hours, whilst the amounts of hydrogen and carbon volatilised were 0.009 and 0.016 grm. respectively, giving a total of 0.153 grm. or 20.6% of oxygen absorbed by the oil. (See also under Linseed Oil, page 485.)

Spontaneous Combustion.—Gellatly has pointed out the close relationship which exists between the drying properties of oils and their tendency to inflame spontaneously when exposed to the air in a finely divided condition. Useful forms of apparatus for testing the liability of oils to spontaneous combustion have been devised by Allbright and Clark (*J. Soc. Chem. Ind.*, 1892, **11**, 547) and by Mackey (*ibid.*, 1895, **14**, 940). In Mackey's apparatus 7 grm. of cotton-waste previously soaked in 14 grm. of the oil, are placed in a roll of wire gauze 5 inches square (24 meshes to the inch), and the whole placed in a water-oven in which the water is boiling. A thermometer is passed through the opening of the oven, so that its bulb reaches to the centre of the wool in the wire roll, and the temperature is taken

at regular intervals.   All oils that take fire or attain a temperature of over 200° in less than 2 hours in this test must be regarded as dangerous.   (See p. 761.)

Oxidised Oil.   Blown Oil.   Base Oil.—The commercial products sold under these names are produced by blowing a stream of air through a fatty oil—rape, cottonseed, or linseed oil being usually chosen for the purpose.   A certain initial temperature is necessary to start the action, but afterwards the heat produced by the oxidation is sufficient to maintain the temperature required.   By proper regulation, products can be obtained which closely resemble castor oil, and equal that body both in sp. gr. and viscosity.   Methods of distinguishing blown oils from castor oil are given in the section treating of the latter products.

CATALYTIC HYDROGENATION OF OILS—HARDENED OILS

Of recent years the analytical problems in the examination of fats have been greatly complicated by the general introduction of hydrogenated oils as commercial product.

Theoretically it should be possible to convert oleic, linolic and other unsaturated fatty acids and glycerides into the corresponding solid acids of the stearic series by the simple addition of hydrogen, the process being analogous to the absorption of halogens or oxygen by the unsaturated compounds

$$C_{18}H_{34}O_2 + H_2 = C_{18}H_{36}O_2$$
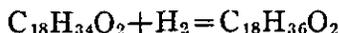
Prior to 1902, however, all attempts to hydrogenate oils by this method proved unsuccessful, but in that year Le Prince and Siveke (Germ. Pat. 141029) claimed a process of solidifying oils by heating them with hydrogen in the presence of a catalytic agent; and an analogous English patent (No. 1515 of 1905) was taken out by Normann.

The development of the new industry and the types of apparatus used in the various processes are described by Ellis (*J Soc. Chem. Ind.*, 1912, **31**, 1155).   See also Crossley (*J. Soc. Chem. Ind.*, 1914, **33**, 1135).

The catalytic agents most commonly used in the commercial processes are nickel and its salts and palladium salts, which are usually precipitated in a fine state of division over a porous material

such as pumice stone, or kieselguhr. Other catalysts include cobalt, iron, platinum, and osmium, and their oxides and other salts. The presence of traces of the catalytic agent, especially nickel, in the hardened fats sometimes affords a proof of the origin of the material, although at the present day most-manufacturers take steps to reduce the proportion of residual metal in the fat to a negligible amount.

Commercial Hardened Oils.—Speaking generally, the solidified products obtained by hydrogenating whale and fish oils are only used for technical purposes such as soap-making. Examples of such fats are *talgol* and *candelite*, which are made at Emmerich.

Edible hardened oils, prepared from cottonseed, sesame and other oils, are being increasingly used in Europe and America in the preparation of margarine and lard substitutes. One of the best known German edible hardened oils is sold under the name of *brebesol*. The physical condition of the products ranges from a semi-solid mass resembling butter to a hard tallow, according to the degree of hydrogenation of the oil.

Analytical Constants of Hardened Oils.—(See also under Margarine, page 428.) Hydrogenation of an oil lowers its refractometer reading and iodine value, and raises its melting point, but has little effect upon the saponification value.

The following results were obtained by Bömer and Leschly-Hansen (*Chem. Rev. Fett. Ind.*, 1912, **19**, 218, 247) in the examination of oils hardened by heating in an autoclave in a current of hydrogen in the presence of nickel reduced on kieselguhr.

Oil	M. p. °	Solid. pt. °	Refractometer reading at 40°	Acid value	Sapon. value	Iodine value
Arachis.................	51.2	36.5	50.1	1.0	188.7	47.4
Sesame.................	47.8	33.4	51.5	0.5	190.6	54.8
Sesame, technical.......	62.1	45.3	{ 38.4 (at 50°) }	4.7	188.9	25.4
Cottonseed.............	38.5	25.4	53.8	0.6	195.7	69.7
Whale.................	45.1	33.9	49.1	1.2	192.3	45.2
Coconut, natural.	25.6	20.4	37.4	0.3	255.6	11.8
Coconut, hardened......	44.5	27.7	35.9	0.4	254.1	1.0

The liquid fatty acids showed the following iodine values: Hardened arachis oil, 82.9 to 91.8; sesame oil, 88.9; cottonseed oil, 115.6; and whale oil, 96.0.

The reduction in the refractive index caused by hydrogenation is shown by the following examples given by Ellis (*J. Ind. Eng. Chem.*, 1914, **6**, 117): Maize oil, 1.4514; whale, 1.4550; soya bean, 1.4538; coconut "olein," 1.4425; linseed, 1.4610; palm, 1.4517; and arachis oil, 1.4547.

Hardened marine animal oils are deodorised in the process, and acquire the appearance of tallow. Two samples analysed by Grimme (*Chem. Rev. Fett. Ind.*, 1913, **20**, 129) gave the following values:

Sp. gr. at 15°	M. p. °	Solid. pt. °	Refractive index at 40°	Acid value	Sapon. value	Iodine value (Wijs)
0.9271	47.2	34.9	1.4529	1.94	189.3	23.24
0.9256	38.5	31.5	1.4575	1.00	188.8	58.34

Hydrogenated fats made from whale oil were found by Sandelin (*J. Soc. Chem. Ind.*, 1914, **33**, 1097) to have the following values:

	M. p. °	Solid. pt. °	Acid value	Sapon. value	Iodine value	Reichert-Meissl value	Mol. equiv. of fatty acids	M. p. of fatty acids °
Original whale oil....	fluid	fluid	9.50	192.2	144.8	0.27	287.7	....
Artificial tallow......	47.5	38.1	9.88	183.7	56.9	0.25	296.4	75.5
Artificial stearine.....	54.3	47.3	7.80	187.7	11.7	0.14	297.0	74.0
Hydrogenated whale oil	41.9	31.9	5.30	190.9	57.8	0.18	282.0	76.0

Colour Tests and Tests for Special Oils.—Hardened marine animal oils often give intense colorations with concentrated mineral acids, but these do not agree with colorations described as characteristic of the untreated oils. The intensity of the coloration varies with the degree of hydrogenation. Sulphuric acid containing a trace of iodine gives a violet-red coloration with hardened whale and fish oils.

Bellier's reagent for seed oils (nitric acid, sp. gr. 1.4 and resorcinol in benzene) gives somewhat different shades of colour with hardened sesame, arachis and cottonseed oils than in the case of the original oils. With hardened marine animal oils both acid and oil give an orange-yellow coloration (Kreis and Roth: *Z. Untersuch. Nahr. Genussm.*, 1913, **25**, 81).

Arachidic acid may be detected in hardened arachis oil (*q. v.*), but a suitable modification is required.

The Baudouin test for sesame oil is intensified, whereas Halphen's cottonseed oil test is inhibited. Hauchehorne's test for cottonseed oil (*q. v.*) is not affected.

According to Leimdörfer (*Chem. Zentralbl.*, 1914, 1, 304) the stearic acid formed in the hydrogenation of oils is chemically identical with natural stearic acid, but the stearin of hydrogenated oils differs in crystalline character and other physical properties from the stearin of ordinary fats.

Hydroxyl groups are more or less split off in the hydrogenating process. Thus the hydroxyl value of a sample of castor oil fell from 156 to 102 (Normann and Hugel: *Chem. Zeit.*, 1913, 37, 815).

The proportion of insoluble bromides given by linseed and marine animal oils is greatly reduced by hydrogenation, so that the insoluble bromide test will not give the same result as before and may even fail to detect the presence of these oils.

As a test for the presence of hydrogenated fish oils Klimont and Mayer (*Zeit. angew. Chem.*, 1914, 27, 645) recommend the following method: From 2 to 3 grm. of the fat are dissolved in 50 c.c. of acetone, and the amount of deposit formed after 12 hours is weighed. Oleomargarine yields 12 to 13% of crystals (m. p. 45° to 47°), whereas mixtures of oleomargarine and hydrogenated fish oil yield up to 16 %.

Unsaponifiable Matter.—Hydrogenation also reduces the amount of cholesterol or phytosterol in the oil, and in proportion to the degree of hardening. The process affects cholesterol more than phytosterol. Thus it has been found by Marcusson and Meyerheim (*Zeit. angew. Chem.*, 1914, 27, 201) that 75 % of cholesterol was resinified during hydrogenation at 200°, whilst phytosterol was not appreciably affected. After treatment at 250° cholesterol no longer gave any crystalline derivatives.

This explains why cholesterol cannot be isolated from *talgol* and similar hardened products of animal oils.

Detection of Nickel in Hardened Oils.—Bömer and Leschly-Hansen (*loc. cit.*) recommend the dimethylglyoxime test From 5 to 10 grm. of the fat are mixed with strong hydrochloric acid in a test-tube which is immersed with frequent shaking for 30 minutes in boiling water. The acid extract (filtered if necessary through

animal charcoal) is then evaporated and the residue tested with a
1 % alcoholic solution of dimethylglyoxime.

Bömer (*Chem. Rev. Fett. Ind.*, 1912, **19**, 221) found 0.01 %
of ash with 0.006 % of nickel oxide in hydrogenated sesame
oil and 0.006 % of ash with 0.0045 % of nickel oxide in hardened
whale oil.

The physiological significance of traces of nickel in hardened
oils is discussed by Ellis (*J. Soc. Chem. Ind.*, 1912, **31**, 1166), Knapp
(*Analyst*, 1913, **38**, 102.) Bömer (*loc. cit.*), and Offerdahl-Larvik
(*Ber. deutsch. Pharm. Ges.*, 1913, **23**, 558).

It has been found by Prall that in some cases pure untreated oils
may give a red coloration; whilst Kerr (*J. Ind. Eng. Chem.*, 1914,
6, 207) has shown that hydrogenated cottonseed oil free from nickel
may yield to hot hydrochloric acid an organic base, which will give
with dimethylglyoxime and ammonia a red coloration closely
resembling that obtained with traces of nickel, except that it
is fugitive. Hence before applying the test for nickel the residue
should be treated with 2 to 3 c.c. of nitric acid to destroy
organic matter. Owing to this uncertainty, Knapp (*Analyst*,
1913, **38**, 103.) prefers the less sensitive ammonium sulphide test:
50 grm. of the fat are heated with 20 c.c. of hydrochloric acid with
vigorous shaking, the acid extract is evaporated to dryness, and the
residue dissolved in 1 drop of water, and tested on a white tile with
1 drop of ammonium sulphide (compare also page 426).

Completely Hydrogenated Oils.—The effect of complete hydro-
genation upon various oil is shown in the following results obtained
by Mannich and Thiele (*Ber. deutsch. Pharm. Ges.*, 1916, **26**, 36):

Hydrogenated oil	M. p.	Iodine value	Saponifi-cation value	M. p. of insol. fatty acids
	deg..			deg.
Olive	70	0.2	190.9	71
Almond	72	0.0	191.8	71
Arachis	64–65	0.0	191.6	67
Sesame	68.5	0.7	190.6	69.5
Cacao butter	63.5–64	0.0	193.9	65.5
Poppy seed	70.5	0.3	191.3	71
Linseed	68	0.2	189.6	70.5
Tallow	62	0.1	197.7	64
Lard	64	1.0	196.8	62
Codliver	65	1.2	186.2	59

ELAIDIN REACTION

When oleic acid is exposed to the action of nitrogen trioxide, it is gradually converted into the isomeric compound elaidic acid, which is solid at ordinary temperatures. Olein undergoes a similar change, being converted into the solid elaidin, as do also oils in which olein predominates. On the other hand, drying oils, in which the chief constituents are linolenic and linolic acids, are not visibly affected by treatment with nitrous acid; and oils largely consisting (probably) of a mixture of olein and linolin give less solid products than those with olein as a main constituent.

The effect can be produced by the gas evolved on heating starch or arsenious oxide with nitric acid; by a mixture of a nitrite with a dilute acid; by dissolving copper or mercury in nitric acid under a layer of the oil; by agitating the oil with a freshly prepared solution of mercurous nitrate; by the direct use of nitric acid of yellow or reddish color, and therefore containing lower oxides of nitrogen; and, lastly, by heating the oil with nitric acid until chemical action sets in and gaseous oxides of nitrogen are evolved.

Poutet's Elaidin Test.—The following method of applying the test devised in 1819 by Poutet is in use in the Paris Municipal Laboratory: 1 grm. of mercury, 5 grm. of nitric acid (sp. gr. 1.35 to 1.41) and 10 grm. of the oil to be tested, are shaken together for 3 minutes in a test-tube, which is then left for 20 minutes, and finally shaken again for 1 minute. The changes that subsequently take place are then noted, including the time required for solidification when that occurs.

Archbutt's Modification (J. Soc. Chem. Ind., 1886, 5, 304) gives more constant results than the above-described method. The reagent is prepared by dissolving 18 grm. of mercury in 15.6 c.c. of nitric acid of sp. gr. 1.42 (22.2 grm.) in a stoppered cylinder, 1 part (8 grm.) of the resulting green solution is shaken with 12 parts (96 grm.) of the oil under examination in a wide-mouthed bottle, which is then closed with a stopper and placed in water maintained at a constant temperature (not lower than 25°), and shaken at intervals of 10 minutes for 2 hours. The time required for solidification is of greater importance than the consistence of the product.

The behaviour of the more important liquid fixed oils, when tested in the foregoing manner, is as follows:

A hard mass is yielded by olive oil, almond oil, arachis oil, lard oil, sperm oil, and sometimes neatsfoot oil.

A product of the consistence of butter is given by neatsfoot, bottle-nose mustard, and sometimes by arachis, sperm, and rape oils.

A pasty or buttery mass which separates from a fluid portion is yielded by rape (mustard), sesame, cottonseed, sunflower, niger-seed, cod-liver, seal, whale, and porpoise oils.

Liquid products are yielded by linseed, hempseed, walnut, and other drying oils.

In practice, the elaidin test receives its most important application in the examination of olive oil, with which it gives a very characteristic result. The subject is further discussed in the sections treating of olive and rape oils.

Investigations of the elaidin reaction and attempts to apply it quantitatively have been made by Farnsteiner (*Zeit. Unters. Nahr. Genussm.*, 1899, 2, 1); by Edmed (*Proc. Chem. Soc.*, 1899, 15, 190); and by Lidow (*Pharm. Zeit. Russland.*, 1895, 34, 105; *Analyst*, 1895, 20, 178).

Interaction of Oils with Sulphur Chloride.—The vegetable drying oils are converted, on treatment with sulphur chloride (S_2Cl_2), into gelatinous or elastic masses, which are employed as substitutes for india-rubber. Bruce Warren investigated the reaction with a view to its employment in the analysis of oils (*Chem. News*, 1888, 57, 113).

COLOUR TESTS OF OILS

Many fatty oils give coloured products when treated with chemical reagents, and in some cases these afford valuable means of detecting even small quantities of special oils in admixture with other oils.

The most characteristic of these tests for special oils are Becchi's and Halphen's tests for cottonseed oil and the Baudouin test for sesame oil; these are described under the special sections dealing with those oils.

Little value can be placed on the results of most of the older colour tests described by Calvert and Chateau, since the particular colorations were often due to accidental impurities in the oils. The tests with sulphuric and nitric acid, however, have some value, especially when applied simultaneously to specimens of oil of known purity.

Sulphuric Acid Colour Test.—The addition of 1 or 2 drops of strong sulphuric acid to 20 drops of the oil produces colorations which, when observed both before and after stirring, are sometimes characteristic. Thus, vegetable non-drying oils often give a light greenish brown coloration, whilst the colours obtained with the more unsaturated drying oils are red-brown to dark brown. Hydrocarbon oils also become dark brown and show a characteristic bule fluorescence. The greater degree of coloration produced by more unsaturated oils is probably to be attributed largely to the effect of the heat produced in the chemical interaction of the oil and acid.

The sulphuric acid test has a greater value in the examination of cod-liver and other marine animal oils, since the presence of certain constituents in considerable proportion in these oils causes the production of characteristic colorations. The colours may be rendered indistinct, however, by the charring action exerted by the reagent. This may be avoided by dissolving 1 drop of the oil in 20 drops of carbon disulphide, and agitating the solution with a drop of strong sulphuric acid. Whale oil, when thus treated, gives a fine violet coloration, quickly changing to brown, whereas with sulphuric acid alone a red or reddish-brown colour changing to brown or black is obtained.

It has been shown by Drummond and Watson (*Analyst*, 1922, 47, 341) that there is some relationship between the colour reaction with sulphuric acid and the vitamin content of oils and fats and that the substance which produces the purple coloration is not confined to liver fats, although they usually give the most intense reactions.

The chromogenic substance is contained in the unsaponifiable matter but is not cholesterol and probably not a lipochrome pigment. It appears to be a normal constituent of the liver, but the body fat of animals may also give the reaction, especially if the animal have been fed on liver oils.

In applying the test quantitatively the oil under examination is diluted with successive quantities of petroleum spirit and the point ascertained at which the colour reaction just appears on the addition of 1 drop of sulphuric acid. Richmond and England (*Analyst*, 1922, **47**, 431) recommend the use of a petroleum fraction of higher b. p. (*e. g.*, liquid praffin B. P.) as the diluting agent, so as to avoid charring of the oil. They apply the test as follows: 1 c.c. of the cod-liver oil to be tested is added to 10 c.c. of liquid paraffin B. P., and 10 drops of the mixture transferred to a white porcelain basin and treated with 1 drop of sulphuric acid (B. P.) and then stirred with a glass rod. If a transient purple coloration develops petroleum oil is added in successive quantities of 5 c.c. until no purple is given and the dilution is recorded at which an only faint transient purple is seen.

If no purple is seen in the first test, quantities of 1 c.c., 1 c.c., 2 c.c. and 5 c.c. of the cod-liver oil are successively added.

Evers and Foster (*Analyst*, 1923, **48**, 58) have found that old oils which have become oxidised or those oxidised in the laboratory do not give the violet coloration, but a brown colouring matter instead, and that the brown chromogenic substance is soluble in the same minimum amount of gasoline petroleum spirit as the violet colouring matter of the original oil.

Hence in order to compare the colour reactions given by two oils it is necessary that another oil should be added to secure the maximum sensitiveness. This condition is attained in the following modification of the test: The oil under examination of its solution in gasoline (petroleum spirit b. p. 40° to 60°; previously purified by shaking with strong sulphuric acid) is measured into a test tube; 2 drops of olive oil or other oil giving no suspicion of colour in the test are added, and then gasoline to 3 c.c. A mixture of 7 c.c. of gasoline and 1 drop of sulphuric acid is then vigorously shaken in a stoppered cylinder until the acid is completely broken up into small drops and this mixture is quickly poured into the test tube. The drops of acid rapidly subside, the violet colour forming in the gasoline as they sink. Under these conditions the colour is uniformly disturbed and the results are more consistent.

The following results were thus obtained:

	Minimum quantity giving colour, c.c.	Colour
Cod-liver oil (cattle).............................	0.01	blue-violet
Cod-liver oil (Newfoundland) (unrefined)......	0.015	blue-violet
Cod-liver oil (North Sea A)........	0.015	blue-violet
Cod-liver oil (North Sea B).	0.015	blue-violet
Whale oil...........................	0.015	red-violet
Ling liver oil.......................................	0.02	blue-violet
Cod-liver oil (Norwegian) (unrefined).......... .	0.035	blue-violet
Cod-liver oil (Norwegian) (refined)..............	0.035	blue-violet
Cod-liver "stearine"....................	0.08	red-violet
Butter (three samples, A, B, C)........	0.2	red-violet
Butter D........................	0.2	brown

In the case of the last sample of butter the brown coloration indicated that oxidation had taken place. The various shades of colour obtained in the test are probably due to the amount of oxidation which the oil has undergone.

Nitric Acid Colour Test.—This is useful as a test for the presence of cottonseed oil in olive and other non-drying oils. 5 c.c. of the oil under examination are shaken with an equal quantity of nitric acid of sp. gr. 1.37, and the mixture left for 24 hours. In the presence of even a small percentage of cottonseed oil there should be a more or less pronounced brown coloration.

PHYSICAL PROPERTIES

The general characteristics of the fixed oils have already been described. Some of their physical properties are of importance for their recognition and estimation, this being especially true of their sp. gr., melting and solidifying points, absorption-spectra, refractive indices, viscosity, and behaviour with solvents. The methods of ascertaining these characteristics are described in detail in the following sections.

Cohesion-figures of Oils.—The surface-tension of oils may in certain cases be capable of useful application, though its value has been much exaggerated. When a drop of oil is allowed to fall gently on to the surface of water it often behaves in a characteristic fashion,

first spreading out and then contracting, forming figures which differ with the nature of the oil. Descriptions and illustrations of typical cohesion-figures are given in Alder Wright and Mitchell's *Oils, Fats and Waxes*, 1921, p. 55.

Absorption-spectra of Oils.—The absorption-spectra of the fixed oils occasionally afford valuable indications of their purity. For observing them a micro-spectroscope may be used, but in many cases the light must be caused to pass through several cm. of the oil to be examined. Although some vegetable oils give exceedingly striking absorption-bands, these are not due to the oils themselves but to the chlorophyll and impurities contained in them. Hence the purification or clarification of an oil tends to reduce the characteristic nature of the absorption-bands, which, indeed, may disappear altogether if the oil be long exposed to sunlight. In one particular, however, the absorption-spectrum furnishes important information. Thus, no oils of animal origin give definite absorption-bands, the spectrum being merely obscured at the more refrangible end, whilst in many vegetable oils the absorption-bands of chlorophyll are exceedingly well marked, especially a band having about the same refrangibility as the line termed B. In this way it is easy to detect the presence of rape, olive, or linseed oil in sperm, cod, or lard oil. Castor and almond oil, on the other hand, give no well-defined bands, and the band at B in the case of sesame oil is faint, though there is strongly marked absorption of the whole of the red portion nearly up to that point.

Patterson (*J. Soc. Chem. Ind.*, 1890, **9**, 36) devised a special absorption-spectrum colorimeter for the spectroscopic examination of oils. (See also Introduction to Vol. 1.) Gardner (*Analyst*, 1921, **46**, 356) has shown that a measurement of the extent of visibility of the spectrum affords a rapid means of identifying certain oils.

The approximate extent of visibility measured under constant conditions, with the use of 3 inches of oil, were as follows: Almond oil, 4.3°, arachis, 2.3°; castor, 2° to 2.3°; coconut, 4.02°; cottonseed (refined), 3.6°; linseed (raw), 2.0°; linseed (refined), 1.30; neatsfoot, 2.34°; olive, 2.3°; and sesame, 2.46°.

Refractive Power.—Valuable indications as to the purity of fats and oils, especially butter-fat, may be gained from the observation of the refractive index. The instrument in general use for this

purpose is the *butyrorefractometer*, which is described in the section dealing with BUTTER. In certain cases, however, such as tung oil and rosin oils, the indices are outside the scale of the butyrore-fractometer, and recourse must be had to the earlier instrument of Abbé.

Abbé's Refractometer.—The following method of using this instrument is prescribed by the A. O. A. C.:

A piece of fine tissue paper, 3 cm. in length by 1.5 cm. in width, is placed on the lower of the two glass prisms of the apparatus. Two or three drops of the sample are placed upon the paper, and the upper prisms carefully fixed in position, so as not to move the paper from its place. In charging the apparatus with the oil in this way it is placed in a horizontal position. After the paper disc holding the fat is secured by replacing the upper prism, the apparatus is placed in its normal position, and the index moved until the light directed through the apparatus by the mirror shows the field of vision divided into dark and light portions. The dispersion apparatus is now turned until the rainbow colours on the part between the dark and light fields have disappeared. Before this s done, however, the telescope, the eye-piece of the apparatus, is so adjusted as to bring the cross-lines of the field of vision distinctly into focus. The index of the apparatus is now moved back and forth until the dark-edges of the field of vision fall exactly in the intersection of the cross-lines. The refractive index of the fat under examination is then read directly upon the scale by means of a small magnifying glass. To check the accuracy of the first reading, the dispersion apparatus should be turned through an angle of 180° until the colours have again disappeared, and the scale of the instrument again read. These two readings should nearly coincide, and their mean is the true reading.

For butter-fats the apparatus should be kept in a warm place, the temperature of which does not fall below 30°. For reducing the results to a standard temperature, say 25°, deduct 0.000176 for every degree above that point, since, as the temperature rises the refractive index falls. The instrument used should be set with distilled water at 25°, the theoretical refractive index of water at that temperature being 1.3330.

Oleorefractometer.—The instrument devised by Amagat and Jean (*Compt. rend.*, 1889, **109**, 616) enables a very rapid comparison to be made between the refractive power of a given oil and that of a genuine oil taken as a standard. The oil to be observed is introduced into a hollow prism, which is immersed in a vessel with parallel sides filled with a standard oil. If the refractive power of the sample is the same as that of the standard, no deviation of the ray of light traversing the apparatus will take place; but otherwise deviation will occur, and can be measured on a micrometer-scale placed on the eye-piece. The angle of the prism, the neutral or standard oil, and the division of the scale are all arbitrary. The standard oil sold with the instrument is sheepsfoot oil.

In the figure, *t t* represent a circular metal vessel with 2 opposite lenses, *l l* in front of the glass sides. From these extend the 2 tubes C and L, the former terminating in a collimator, V, and the latter in a telescope, O*c*. The glass prism-cell is represented by C*y*, whilst E*c* is an arbitrary photographic scale. The instrument is illuminated by means of a gas-jet, and the luminous field may be divided by means of a slide into a light and dark portion.
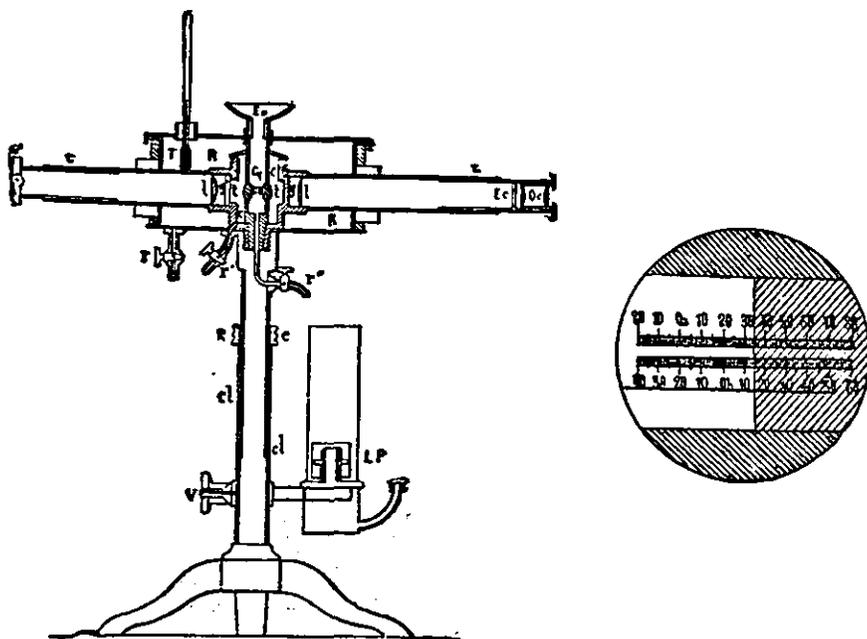
FIG. 2.—Jean's Oleorefractometer. (*Baird and Tatlock.*)

In using the oleorefractometer, the outer vessel is charged with the standard oil (which gives a zero reading), the oil to be tested placed in the inner vessel, and an outer trough (not shown) filled with water. The temperature is then brought to 22° by means of the lamp, L P, and the deviation read upon the scale.

The following results were obtained by Pearmain (*Analyst*, 1895, **20**, 135) with this instrument:

Oil or fat	No. of samples	Deviation	Highest	Lowest	Average
Temperature 22°.					
Almond......................	8	+	10.5	8.0	9.5
Arachis......................	5	+	7.0	5.0	6.0
Bottlenose...................	1	+	50.0	50.0	50.0
Cabbage seed................	1	+	15.0	15.0	15.0
Castor.......................	8	+	42.0	39.0	40.0
Codliver.....................	8	+	46.0	40.0	44.0
Cottonseed (crude)..........	3	+	17.0	16.0	16.5
Cottonseed (refined)........	6	+	23.0	17.0	21.5
Hempseed....................	4	+	37.5	34.0	35.5
Lard oil.....................	6	—	1.0	0.0	0.0
Linseed (crude).............	3	+	52.0	48.0	50.0
Linseed (refined)...........	5	+	54.0	50.0	50.0
Neatsfoot...................	2	—	3.0	1.0	2.0
Nigerseed...................	2	+	30.0	26.0	8.0
Olive.......................	105	+	3.5	1.0	2.0
Peach kernel................	2	+	11.5	7.5	9.5
Pilchard....................	2	+	36.0	32.0	34.0
Poppy seed.................	3	+	35.0	30.0	33.0
Rape.......................	8	+	20.0	16.0	17.5
Ravison....................	2	+	24.0	20.0	22.0
Seal........................	2	+	36.0	30.0	33.0
Sesame.....................	5	+	17.0	13.0	15.5
Shark......................	3	+	35.0	29.0	31.0
Sunflower..................	1	+	35.0	35.0	35.0
Tallow oil..................	2	—	5.0	1.0	3.0
Tea seed...................	1	+	8.0	8.0	8.0
Tung.......................	1	+	75.0	75.0	75.0
Whale......................	2	+	48.0	42.0	45.0
Oleic acid..................	3	—	33.0	29.0	32.0
Temperature 45°.					
Butter-fat..................	15	—	34.0	25.0	30.0
Margarine..................	7	—	18.0	13.0	15.0
Lard.......................	10	—	14.0	8.0	10.5
Tallow.....................	6	—	18.0	15.0	16.0
Paraffin (soft).............	2	+	58.5	54.0	56.0

Optical Dispersion.—A method of using the optical dispersion of oils as a means of identification has been devised by Fryer and Weston (*Analyst*, 1918, 43, 311). For this purpose they use a Zeiss-Pulfrich refractometer and a hydrogen tube with a pressure of about 2 mm., the red and blue rays from which correspond with

the C and F lines of the spectrum. The readings are taken at 40°, and the refractive power calculated by means of the formula—

$$\omega = \frac{n_F - n_C}{n_D - 1}$$

The optical dispersions of most of the oils examined were very similar ranging from 0.0186 to 0.0207, but coconut oil gave 0. 0167, linseed oil 0.0218, and tung oil 0.0371. Relatively low figures were also given by palm kernel oil 0.0180 and butter fat 0.0182. The general results indicated that the dispersion is lowered by the presence of glycerides of low meolecular weight and increased by those of high molecular weight, whilst the presence of free fatty acids has but little influence on the reading. The dispersion is increased by about 0.00002 for each increase of 10 in the temperature.

Action on Polarised Light.—Most of the vegetable oils in common use are either neutral or slightly lævorotatory (−0.1° to − 1.5° in a 200 mm. tube in the polarimeter). Hence, rosin oil, which is strongly dextrorotatory, may often be detected by means of this test in drying oils. Olive oil and sesame oil have a slight dextrorotation, whilst castor oil and croton oil (q. v.) are strongly dextrorotatory. For the values obtained with various oils see Alder Wright and Mitchell's *Oils, Fats and Waxes*, 1921, p. 57, and Peter, *Bull. Soc. Chem.*, 1887, [2], **48**, 483.

Electrical Conductivity.—The measurement of the specific resistance offered by solutions of the potassium soaps obtained under standard conditions from different oils and fats affords a means of distinguishing between them. A method was devised by Herlant (*Bull. de l' Ass. belge Chim.*, 1896, **10**, 48).

Heat of Combustion.—Measurement of the heat of combustion of different oils and fats may be used in their analytical differentiation and in obtaining data as to their food value. A table of the values obtained with the different fatty acids is given by Stohmann, Kleber, Langbein and Offenhaur (*J. pr. Chem.*, 1894, **49**, 99); and results obtained with various oils and fats and their adulterants are given by Schweinitz and Emery (*J. Amer. Chem. Soc.*, 1896, **18**, 174) and Sherman and Snell (*ibid.*, 1901, **23**, 164). For the detection of adulteration the heat of combustion offers no advantage over simpler methods of analysis.

Viscosity.—A useful physical test for oils is based on their relative "body" or viscosity, a property which may be regarded as the converse of fluidity. The viscosity is usually compared with that of rape oil, but it may also be referred to water or glycerol as a standard. The subject is fully discussed in the section on the "Examination of Lubricating Oils."

Specific Gravity.—The sp. gr. of the fixed oils and fats is a property largely dependent on their constitution, and hence is more or less characteristic of each particular oil. As a rule, the sp. gr. of different samples of the same kind of oil varies within very narrow limits, but it is liable to be affected by the treatment to which the oil may have been subjected in the process of refining, the presence of free fatty acids, the age of the oil, and the amount of oxidation it has undergone, and by other circumstances.

The sp. gr. of fixed oils may be ascertained by the usual methods, but great care is necessary. Owing to the high coefficient of expansion of oils, the temperature at which the observation is made should be carefully noted, and in accurate observations the thermometer employed should be an instrument the indications of which have been verified.

When a sufficient quantity of the sample is available, and results of extreme accuracy are not required, the sp. gr. can be ascertained readily and satisfactorily by means of an accurate and delicate hydrometer. In any observations, save those of the roughest kind, the oil should be brought accurately to the standard temperature by immersing the hydrometer-glass in water, cooled, if necessary, to 15.5° by dissolving in it sodium thiosulphate or ammonium nitrate. The hydrometer should be immersed in the oil for 5 or 10 minutes, and the temperature again observed before taking a reading of the sp. gr., as the use of a warm hydrometer may cause an increase of several degrees in the temperature of the oil. Of course, in taking the sp. gr. with a hydrometer, the accuracy of the instrument employed is presupposed, but many of the instruments sold are inaccurate to the extent of several degrees.

The sp. gr. bottle and Sprengel-tube (see Vol. 1) may also be employed for ascertaining the sp. gr. of oils, and allow of more accurate estimations than can be made with a hydrometer. The weight of distilled water which the bottle or tube holds at a tempera-

ture of 15.5° is usually (at least in England) taken as the unit of comparison in stating the sp. gr. of fixed oils.[1]

Solid Fats and Waxes.—As many of the fixed oils are solid or semi-solid at the ordinary temperature, their sp. gr. are not directly comparable with those of the fluid oils. This difficulty may be obviated by taking the sp. gr. of the melted substance at some higher temperature, preferably the b. p. of water. This may be done with a hydrometer or balance, if the cylinder containing the oil be kept for a sufficient time in boiling water before the reading is taken. A sp. gr. bottle is less convenient, but with the Sprengel-tube great accuracy is possible. The weight of the Sprengel-tube and of the volume of water it contains at 15.5° being known, the tube should be completely filled with the oil, by immersing one of the orifices in the liquid and applying suction at the other. The tube is placed in a conical flask containing water which is kept vigorously boiling, a porcelain crucible cover being placed over the mouth of the flask. The oil expands and drops from the orifices. When this ceases, the oil adhering to the outside is removed by the cautious use of filter-paper, the tube removed, wiped dry, cooled, and weighed. The weight of the contents divided by the weight of water contained at 15.5° will give the sp. gr. at 100° compared with water at 15.5°

When the amount of material is sufficient, the observation may be made by means of the plummet (Westphal's balance), the use of which leaves nothing to be desired on the score of rapidity, accuracy, or ease of manipulation   In taking sp. gr. by the plummet at the b. p. of water, it is desirable to employ a cylindrical bath of metal (Fig. 3), the top of which is perforated by two orifices. One of these is fitted with an upright tube, which serves to convey the steam away from the neighbourhood of the balance, while into the other a test-tube, 6 in. in length and 1 in. in diameter, fits tightly, the joint being made perfect by a ring of cork or rubber. The test-tube is filled with the oil, the sp. gr. of which is to be ascertained, and the plummet immersed in it. The water in the outer vessel is then kept in constant ebullition, until a thermometer, with which the oil is repeatedly stirred, indicates a constant temperature, when the plummet is attached to the lever of the balance, and counterpoised in the usual way. (See also Vol. 1 for improved methods of ascertaining sp. gr.)

[1] Oil merchants frequently use a hydrometer on which water is marked 0° and rape oil 28°.

Hager devised an ingenious method of ascertaining the sp. gr. of solid fats at the ordinary temperature. The fat is melted and drawn up into a pipette, from which it is allowed to drop slowly from the height of 2.5 cm. into cold alcohol contained in a flat-bottomed dish, care being taken that each drop of fat falls in a different place. An alternative plan is to melt the fat in a small-lipped capsule and allow drops of it to fall on a plate of glass which has been previously wiped with a wet cloth. On placing the glass in cold water, the drops usually become detached on the slightest touch, but if necessary can be removed with a knife after half an hour. The fat-globules obtained by one of the above methods are removed to a beaker containing dilute alcohol. The sp. gr. of the liquid is then adjusted by addition of alcohol or water, until, after careful stirring, the fatglobules remain in equilibrium in any part of the liquid at a temperature of 15.5°. Ammonia may be substituted for the spirit if preferred. The sp. gr. of the liquid is then taken, and the result obtained recorded as the sp. gr. of the suspended fat. The great objection to this method is that fats and waxes which have undergone sudden cooling have abnormal sp. gr. On this account it

FIG. 3.

is far preferable to employ for the test fragments which have been cut off a mass cooled under normal conditions.
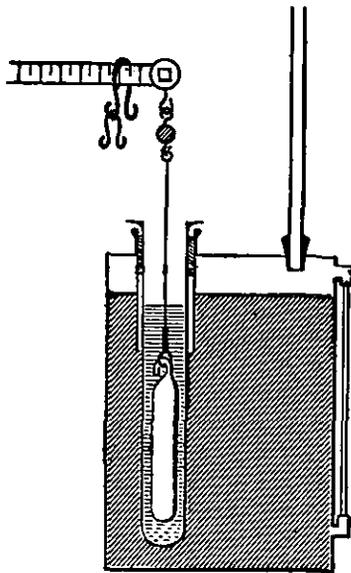
A good method of preparing beeswax and other waxes for this test is to pour the melted substance into a cylinder about 0.5 inch in length cut from narrow glass tubing. The lower end of this is kept pressed against a glass plate until the wax solidifies, after which the outside of the glass is gently warmed, and the core of wax pushed out, and allowed to stand for some hours at the ordinary temperature. It is then brushed over with dilute alcohol, to prevent the subsequent occurrence of air-bubbles, and is immersed in spirit which is diluted or strengthened until of the same sp. gr. as the wax.

The following table shows the sp. gr. (observed by Allen) at different temperatures of various fats and other substances which are solid at the ordinary temperature. In each case the examinations were made on the same sample of substance by the plummet method. A column is added showing the difference in sp. gr. corresponding to a change of $1°$.

The values obtained at the higher temperature were not corrected for the expansion of the glass plummet of the apparatus, and hence many of them are too low by about 0.01 to 0.02.

Nature of fat, etc.	Sp. gr. of melted fats, etc.; water at $15.5°$ ($60°$ F.) = 1,000		Difference for $1°$
Palm oil..................	893.0 at 50°	858.6 at 98°	0.717
Cacao butter..............	892.1 at 50°	857.7 at 98°	0.717
Japan wax................	901.8 at 60°	875.5 at 98°	0.692
Tallow...................	895.0 at 50°	862.6 at 98°	0.673
Lard.....................	898.5 at 40°	860.8 at 98°	0.650
Margarine................	898.2 at 40°	859.2 at 98°	0.672
Butter-fat...............	904.1 at 40°	867.7 at 99°	0.617
Coconut stearine.........	895.9 at 60°	869.6 at 99°	0.674
Coconut oil..............	911.5 at 40°[1]	873.6 at 99°[1]	0.642
Palmnut oil..............	911.9 at 40°[1]	873.1 at 99°[1]	0.657
Spermaceti...............	835.8 at 60°	808.6 at 98°	0.716
Beeswax..................	835.6 at 80°	822.1 at 98°	0.750
Carnauba wax.............	850.0 at 90°	842.2 at 98°	0.975[2]
Stearic acid (commercial)....	859.0 at 60°	830.5 at 98°	0.750
Oleic acid (commercial).....	903.2 at 15.5°	848.4 at 99°	0.656
Paraffin wax.............	780.5 at 60°	753.0 at 98°	0.724

[1] The samples of coconut oil and palmnut oil were old, and had been frequently melted. Some time previously they showed sp. gr. notably less than the figures stated in the table.
[2] For obvious reasons, the rate of expansion of carnauba wax is only a rough estimation.

The figures in the foregoing table represent merely the sp. gr. possessed by *particular samples* of different oils. The limits of variation of sp. gr., and the value of it as a means of recognising and estimating the amount of the various fixed oils in mixtures are discussed in a separate section.

Coefficients of Expansion.—It is always desirable to determine the sp. gr. of oils at the standard temperature, but in many cases in which this cannot be done a suitable correction may be made. The

rate of expansion of an oil may be found by estimating the sp. gr. at two given temperatures as far apart as possible.[1] The rates of expansion of the solid fats, etc., are given in the table on page 68, while from the figures recorded on page 66. Allen calculated the rates of expansion of various oils fluid at ordinary temperatures. The following table shows the values so obtained, together with certain data published by other observers:

Nature of oil	Correc-tion for 1°	Observer	Nature of oil	Correc-tion for 1°	Observer
Sperm oil......	0.648	A. H. Allen	Olive oil........	0.629	C. M. Stillwell
Bottlenose oil...	0.643	A. H. Allen	Arachis oil......	0.655	A. H. Allen
			Rape oil........	0.620	A. H. Allen
Whale oil......	0.697	A. H. Allen	Sesame oil......	0.624	A. H. Allen
Whale oil......	0.722	C. M. Wetherill	Cottonseed oil..	0.629	A. H. Allen
Porpoise oil.....	0.654	A. H. Allen	Coconut olein...	0.665	A. H. Allen
Seal oil.........	0.615	A. H. Allen			
Shark-liver oil..	0.648	A. H. Allen	Nigerseed oil....	0.637	A. H. Allen
Codliver oil.....	0.646	A. H. Allen	Linseed oil......	0.649	A. H. Allen
Menhaden oil...	0.654	A. H. Allen			
			Castor oil......	0.653	A. H. Allen
Neatsfoot oil..	0.625	A. H. Allen			
Lard oil........	0.658	C. M. Wetherill			

It is evident that the *coefficient of expansion* of an oil may be deduced by dividing the temperature-correction by the sp. gr. Thus the coefficient of expansion of olive oil will be $\dfrac{0.646}{916} = 0.000715$

for each degree centigrade.

From the foregoing data Wright (*J. Soc. Chem. Ind.*, 1907, **26**, 513) has calculated the numerical value of the approximate *modulus of expansion, m.* If S_o, S_t, and S_T represent the sp. gr. of the same fat at the respective temperatures $0°$, $t°$ and $T°$ (water at $15.5° = 1$) then

$$S_t = S_0(1 - mt),$$
$$\text{and } S_T = S_0(1 - mT),$$

The mean value of the *m* in the case of the 30 oils, etc., examined by Allen is approximately 0.0007; whence is obtained the equation

$$\frac{S_t}{S_T} = \frac{1 - 0.007t}{1 - 0.0007T};$$

[1] Thus a sample of rape oil was found to have a sp. gr. of 915.0 at 15.5°, and 863.2 at 98°, the difference being 51.8. Dividing this by 82.5, the difference between the temperatures at which the observations were made (98.0 − 15.5 = 82.5) the figure 0.268 is obtained as the correction to be made for a variation of 1° from the standard temperature.

or if $t = 15.5°.$,

$$S_{15.5} = S_T \times \frac{0.98915}{1 - 0.0007T}$$

The following table gives the value of this factor for each degree from 10° to 25.°, so that the sp. gr. of any oil, fat or wax estimated at a temperature other than 15.5° may be rapidly corrected to the latter temperature.

At °	Factor	At °	Factor
10	$\frac{1}{1.00389}$	18	1.00177
11	$\frac{1}{1.00318}$	19	1.00248
12	$\frac{1}{1.00248}$	20	1.00319
13	$\frac{1}{1.00177}$	21	1.00391
14	$\frac{1}{1.00106}$	22	1.00462
15	$\frac{1}{1.00035}$	23	1.00534
16	1.00035	24	1.00605
17	1.00106	25	1.00677

Melting and Solidifying Points.—The observation of the solidifying point of an oil is often of considerable importance, especially in the case of lubricating oils, in which too high a m. p. is a decided disadvantage. Similarly, the suitability of the solid fats for many of the purposes to which they are applied is greatly dependent on their m. p.

Entire uniformity of solidifying or melting-point in the case of particular oils and fats is not to be expected, as the natural fats consist of a mixture of liquid and solid substances, the proportions of which may vary considerably in different samples of what is nominally the same substance. Moreover, the melting-points, like the sp. gr. of the natural oils and fats, are liable to obscure alterations on keeping, and are further modified by the presence of varying amounts of free acid.

It has also been observed that many of the fats solid at the ordinary temperature have at least two distinct m. p. Thus the ordinary

clarified tallow of commerce, if previously melted at a temperature considerably above its m. p., shows a m. p. of 35° to 36°. If it be carefully remelted at that temperature, cooled, and the m. p. again taken, the reading will sometimes be found nearly 12° above the former estimation.

This phenomenon of *double m. p.*, which is a striking characteristic of the mixed glycerides isolated from various fats, has been shown by Grün and Schacht (*Ber.*, 1907, 40, 1778) to be due to the existence of two isomeric modifications of such glycerides, the one of lower m. p. being the more unstable, and undergoing gradual transformation into the modification of higher m. p.

Melting Point.—The substance is melted at a temperature slightly above its melting point, and drawn up into a very narrow glass tube (made by drawing out one end of a piece of ordinary quill tubing), where it is allowed to solidify spontaneously. After an interval of *not less than 1 hour and preferably 12 hours* the tube, open at both ends, is attached by a cork or india-rubber ring to the stem of a thermometer in such a manner that the part of the tube containing the substance is at the same level as, and in close proximity to, the bulb. The thermometer, with its tube, is then
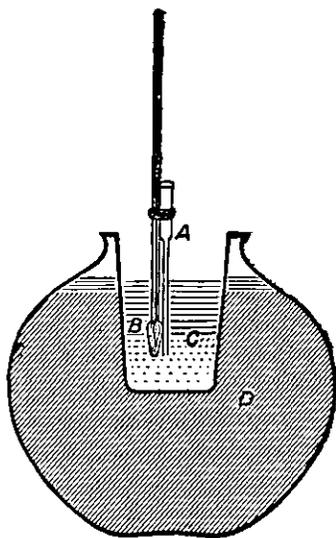
FIG. 4.

immersed in water, which is gradually heated at a rate not exceeding 0.5° per minute until fusion of the contents of the capillary tube takes place, when the temperature is recorded. The flame is then removed, and the temperature at which the fat resolidifies also observed. In cases in which the melting and solidifying points are not notably different, it is usual to record the mean of the two as the true m. p. of the substance. It is desirable to immerse the beaker of water containing the thermometer in an outer vessel also filled with water, and to apply the source of heat to the latter. A 500 c.c. flask, from which the neck has been cut off, filled to the brim (Fig. 4), furnishes a very convenient water-bath, and allows of a very regular and gradual heating of the water contained in the beaker placed in its mouth.

The foregoing method is applicable only to substances melting above the freezing point of water, but by substituting strong brine for the water much lower temperatures may be observed.

By using a tube with its capillary end sealed up, and placing the fat in the upper part of the tube, the *softening point*, which is frequently appreciably lower than the m. p. (the temperature at which the fat falls to the bottom of the tube), may be ascertained, while the point of resolidification is also more accurately observed than is possible in an open tube.

The method of ascertaining the softening point devised by Bevan and Cross (*J. Chem. Soc.*, 1882, **41**, 111) gives very accurate results and is specially suitable for cases in which the fat does not melt readily (see Fig. 6).

A very thin piece of sheet-iron (ferrotype plate) is cut into an elliptical form, about 1 in. long by ½ in. wide. At one of the foci (A) a small depression is made, and at the other a hole (B) is cut, of such size as to allow the plate to be fixed on to the elongated bulb of a thermometer (C), so as to project therefrom at right angles. A glass float (D) is made by blowing a small bulb at the end of a capillary glass tube about 3 in. long, a small looped or hoe-shaped piece of platinum wire (E) being sealed into the bulb at the end opposite the stem of the float. To make an observation, a very small quantity of the sample is melted in the indentation of the iron-plate; and, while still liquid, the loop of the platinum wire of

FIG. 5.

the float is immersed in it and allowed to become fixed by the spontaneous solidification of the substance, the stem of the float being supported in a vertical position. A thermometer is then cautiously introduced into the hole in the plate, and with it supported in a small beaker, which is then filled with mercury or other liquid. This is gradually heated till the substance under

observation melts, when the float is released and instantly rises to the surface of the liquid. The results are very concordant, and are free from certain sources of error to which observations made by the capillary-tube method are liable.

A very rapid method of ascertaining both the temperature of incipient fusion and that of complete liquefaction is to place fragments of the material upon the surface of clean mercury (previously chilled if necessary) in a small basin, which is placed on a water-bath. The temperature is very gradually raised, and the point at which the substance changes its form is ascertained by means of a sensitive thermometer.

Modifications of this method, in which the substance, on fusing, completes an electric circuit and rings a bell, have been devised by Loewe (*Dingler's polyt. J.*, 1871, **201**, 250) and Christomanos (*Ber.*, 1890, **23**, 1098), and an arrangement of the kind is in use in the Paris Municipal Laboratory

A. O. A. C. Method.— The melted and filtered fat is allowed to fall from a dropping-tube from a height of from 15 to 20 cm. on a smooth piece of ice floating in distilled water that has been recently boiled. The discs thus formed are from 1 to 1.5 cm. in diameter, and weigh about 200 mg. By pressing the ice under the water the discs are made to float on the surface, whence they are
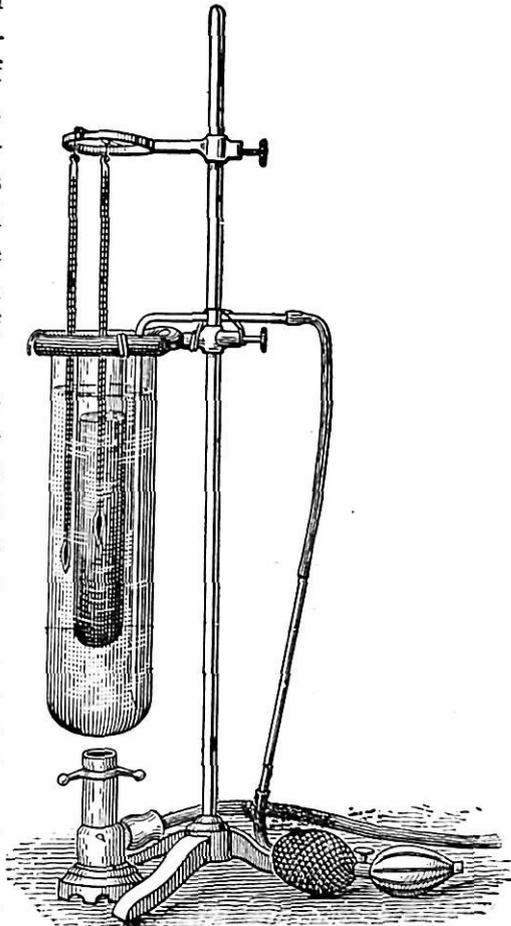
FIG. 6.

easily removed with steel spatula, which should be cooled in the ice-water before using.

The apparatus (see Fig. 71) consists of a test-tube 30 cm. long and 3.5 cm. in diameter, supported in a boiling tube 35 cm. long and 10 cm. in diameter. The test-tube contains a mixture of alcohol and water prepared by separately boiling distilled water and 95 % alcohol for 10 minutes to remove the gases which they may hold in solution. Whilst still hot, the water is poured into the test-tube until it is nearly half full. The test-tube is nearly filled with the hot alcohol, which is carefully poured down the side of the inclined tube to avoid too much mixing. If the alcohol is not added until the water has cooled, the mixture will contain so many air-bubbles as to be unfit for use. These bubbles will gather on the disc of fat as the temperature rises and finally force it to the top. The test-tube containing the alcohol and water is placed in the boiling tube containing water and ice, until cold. The disc of fat is then dropped into the tube from the spatula and at once sinks to the part of the tube in which the sp. gr. of the diluted alcohol is exactly equivalent to its own.

A sensitive thermometer graduated in tenths of a degree is now lowered into the test-tube until the bulb is just above the disc, and is subsequently used as a stirrer to secure uniformity of temperature in that vicinity.

The water in the boiling tube is now slowly heated and kept constantly stirred by means of air introduced by a rubber blowing-bulb attached to a glass tube extending nearly to the bottom of the vessel. When the temperature of the alcohol-water mixture rises to about 6° below the m. p., the disc of fat begins to shrivel and gradually rolls up into an irregular mass. The thermometer is now lowered until the fat particle is even with the centre of the bulb, which should be small, so as to indicate only the temperature of the mixture near the fat. A gentle rotatory motion is given to the bulb, the temperature being meanwhile so regulated that the rise of the last 2° takes about 10 minutes. As soon as the mass of fat is seen to become practically spherical, the reading is taken, with the aid of a cathetometer or reading-glass.

The test-tube is now removed and replaced by a second one containing alcohol and water, and a new observation made with another disc of the fat, the temperature of the bath being now so regulated as

to reach a maximum of about 1.5° above the m. p. of the substance. The new reading should be checked by a third observation, which should be in close agreement with the second result.

Solidification Point.

Dalican's Method.—The useful technical method, devised by Dalican in 1868 for the examination of fatty acids, is largely employed in commercial work in England and France under the name of the *"titer test."* A test-tube, about 5 in. in length by ⅔ in. in diameter, is fitted with a ring or collar of cork or rubber, by which it is fixed in the mouth of an empty bottle or flask. The melted substance is then poured into the (warmed) tube till it is about ⅔ filled, and a delicate thermometer, previously warmed, is suspended freely in the liquid, so that the bulb may be wholly immersed. When the fat commences to solidify at the bottom of the tube, it is slowly stirred by giving the thermometer a circular movement first 3 times to the right and then 3 times to the left. At first the mercury falls, but subsequently rises to a point at which it remains stationary for about 2 minutes. This temperature is taken as the solidification point of the substance, and the results are very constant provided the same apparatus and method of working be employed.

Modification of Dalican's Method (Official in United States).—The following is the A. O. A. C. method: 25 grm. of the fat are saponified in a metal dish with 60 c.c. of 30% sodium hydroxide (36° Be.) and 75 c.c. of 95% alcohol or 120 c.c. of water, and the mass evaporated to dryness. The dry soap is dissolved in 1,000 c.c. of boiling water, and the solution boiled for 40 minutes to expel all alcohol, and then treated with 100 c.c. of 30% sulphuric acid (25° Be.) and heated until the fatty acids are clear. The fatty acids are then thoroughly washed, separated from the water, filtered through a dry filter and dried for 20 minutes at 100°.

The dried fatty acids are allowed to cool to 15° to 20° above the expected m. p., and poured into a test-tube 100 mm. in length by 25 mm. in diameter, which is fitted by means of a cork into a flask 150 mm. in height by 70 mm. in diameter. The thermometer graduated from 10° to 60° in tenths of a degree is passed through an opening in the cork of the tube, so that its bulb reaches to about the middle of the material. The 10° mark on the scale should be 3 to 4 cm. above the bulb and the entire length of the thermometer

should be about 36 cm. The estimation should be made with the outside temperature about 10° lower than the solidification temperature. The readings should be made at short, preferably equal, intervals, and the maximum point reached in the short rise after the mercury ceases to fall is the solidification point or "titer." Duplicate observations should agree within 0.1.

Finkener's Method (Official for Customs Examination in Germany). This method is used in Germany for the technical differentiation of lard, tallow, and candle-fats. If the solidification point is below 30° it belongs to the first class; between 30°and 45°, to the second (tallows); and above 45°, to the third. Pressed tallow, however, may still pass as tallow even with a solidification point above 50°, provided it is declared as such and does not contain more than 50% of free fatty acids. In Finkener's method (*Chem. Zeit.*, 1896, **20**, 132) the fatty acids are dried as in Dalican's method and a larger quantity (150 grm.) introduced into a flask of prescribed dimensions up to a definite mark, the flask being then closed by means of a delicate thermometer on which is an expansion ground to fit the neck of the flask. The flask is then placed in a wooden box, in the top of which is an opening for the stem of the thermometer. The whole is allowed to stand and the readings taken at intervals of 2 minutes after the temperature has fallen to about 50°. The solidification point thus determined is slightly higher than that given by the original Dalican method. This method offers no advantages over the ordinary method.

Wolfbauer's Method (used in Austria).—A test-tube 15 cm. long and 3.5 cm. in diameter is nearly filled with the melted fatty acids, and closed by means of a cork through which passes the thermometer. The tube is then fitted through an opening in the cork of a wide-mouthed bottle. The mass is stirred with the thermometer until it becomes turbid, and the readings then taken without further stirring (*Mitt. d. k. k. techn. Gew. Mus. in Wien.*, 1894, 57).

Shukoff's Method (used in Russia).—The melted fatty acids are introduced into a tube which is fitted into a bottle, as in Wolfbauer's method, though the dimensions are different. As soon as the temperature has fallen to within 5° above the expected solidification point, the apparatus is vigorously shaken from the top to the bottom, until the contents of the tube become turbid, the readings being then taken. Results thus obtained agree closely with those given by

Wolfbauer's method. A vacuum-jacketed tube closed by means of a rubber cork was also employed by Shukoff, but his later apparatus mentioned above is more commonly used (*Chem. Rev. Fett, Ind.*, 1899, **6**, 11; *Chem. Zeit.*, 1901, **25**, 1111).

In comparing results obtained by the foregoing methods it has been found that the method and duration of saponification have no material influence, provided that the alcohol used is subsequently completely expelled and that the fatty acids are thoroughly dried. Thus the solidification point of properly dried acids may be 0.6° above that of the same acids in which a trace of moisture has been left. The form of the apparatus has an influence when the quantity of fatty acids used is small, and cooling from outside proceeds too rapidly. Until an international method has been fixed, it is advisable in giving results to state the method by which they were obtained.

In order to eliminate the factors which have caused such wide divergencies in the recorded m. p. of fats and fatty acids Blichfeldt and Thornley (*Analyst*, 1921, **46**, 180), have devised a method in which the "melting point" is understood to be the temperature at which a column of fat of specified dimensions begins to move in an open tube of specified dimensions under a definite hydrostatic pressure.

A glass tube 6.5 cm. long, 1 mm. bore, and 3 mm. diameter is dipped into the melted fat, and the lower end brought into contact with filter paper so as receive sufficient fat to leave a column 1 cm. long. This column of fat is then solidified by placing the tube for 2 hours between two blocks of ice.

The tube is next fixed vertically in a water bath so that the upper surface of the fat is 1 c.m. below the level of the water, the bath is heated at the rate of 1° per minute and stirred continuously and the temperature at which the fat begins to slide up the tube is noted as the m. p.

Temperature Tests.—The rise of temperature which ensues on treating a fixed oil with concentrated sulphuric or nitric acid, or bromine, is a measure of the extent and intensity of the chemical action which ensues. The use of sulphuric acid was originally proposed by Maumené (*Compt. rend.*, 1852, **35**, 572).

Maumené Test.—The following method of applying this test is recommended by Archbutt, and is still in use: 50 grm. of the oil

are weighed into a 200 c.c. beaker, and the latter immersed in a capacious vessel of water, together with the bottle of strong sulphuric acid, until they are both at the same temperature, which should not be far from 20°. The beaker containing the oil is then wiped, and placed in a cotton-wool nest previously made for it in a cardboard drum, or a wider beaker. The immersed thermometer is then observed, and the temperature recorded. 10 c.c. of the concentrated sulphuric acid should then be withdrawn from the bottle with a pipette, and allowed to run into the oil. During the addition of the acid, which should occupy about 1 minute, the mixture must be constantly stirred with the thermometer, and the agitation continued until no further rise of temperature ensues. This point is readily observed, as the indication remains constant for a minute or two, and the temperature then begins to fall.

The results obtained from a particular oil are remarkably constant, when the acid is of a uniform strength and a defined method of manipulation is rigidly adhered to, but apparently insignificant differences in the mode of operation result in serious discrepancies in the results. Thus Archbutt observed a rise of 78.5°, when the oil was stirred until all the acid was added and the thermometer then held stationary in the middle of the oil, but when the stirring was continued until no further rise of temperature was observed, the increase was only 73.5°.

When the temperature exceeds 60° it is impossible to obtain concordant results. Maumené, therefore, advocated diluting highly unsaturated oils, such as linseed or marine animal oil, with olive oil, so as to prevent charring of the mixture, whilst Ellis (*J. Soc. Chem. Ind.*, 1886, 5, 161) recommended the use of mineral oil for the purpose.

Carbon tetrachloride, however, is preferable to either of these substances as a diluting agent, and Mitchell (*Analyst*, 1901, 26, 169) has shown that, when the oil is diluted with that substance, the rise of temperature with unoxidised oils is, in most cases, proportional to the rise of temperature with bromine. This indicates that, under such conditions, the rise in temperature is probably due solely to absorption of the sulphuric acid by the unsaturated bonds.

Owing to the notable difference in the rise of temperature caused by comparatively slight variations in the mode of operating, many

	Rise of temperature with sulphuric acid; °				
	Maumené	Baynes	Dobb	Archbutt	Allen
Olive oil...............	42	40	39–43	41–45	41–43
Almond oil.............	52–54	35	....	....	....
Rape and Colza oils.....	57–58	60–92	54–60	55–64	51–60
Arachis oil.............	67	....	....	47–60	....
Beechnut oil...........	65	....	....	....	....
Sesame oil.............	68	....	....	65	....
Cottonseed oil; crude....	....	84	61	70	67–69
Cottonseed oil; refined...	....	77	....	75–76	74–75
Poppy seed oil..........	74	....	....	86–88	....
Nigerseed oil...........	....	82	....	....	81
Hempseed oil...........	98	....	....	....	....
Walnut oil.............	101	....	....	....	....
Linseed oil.............	103	104–124	....	....	104–111
Perilla oil[1]............	124	....	....	....	....
Coconut olein..........	....	....	....	....	26–27
Castor oil.............	47	....	....	46	65
Lard oil...............	....	....	....	....	41
Tallow oil.............	41–44	....	....	....	....
Neatsfoot oil...........	....	....	....	43	....
Horsefoot oil..........	51	....	....	....	....
Whale oil; northern......	....	....	....	....	91
Whale oil; southern......	....	....	85–86	92	....
Porpoise oil............	....	....	....	....	50
Seal oil...............	....	....	....	....	92
African fish oil.........	....	....	156	....	....
Shark-liver oil..........	....	....	....	....	90
Codliver oil............	102–103	116	....	....	113
Skate-liver oil..........	102	....	....	....	....
Menhaden oil..........	....	....	....	123–128	126
Sperm oil..............	....	....	....	51	45–47
Bottlenose oil..........	....	....	....	42	41–47
Oleic acid.............	....	....	....	37.5	38.5

[1] Rosenthal.

of the recorded figures obtained by Maumené's test have little value. Hence it is desirable to compare a sample with one or more oils of known purity under exactly similar conditions. The figures in the table show the kind of result to be *expected* from various oils, but they must not be relied on too rigidly.

From these figures it will be seen that with some mixtures, for instance olive with cottonseed oil and rape with linseed oil, the rise of temperature with sulphuric acid may afford a means of forming an approximate estimate of the proportion of ingredients.

In order to obviate the effects of the use of different strengths of acid, Thomson and Ballantyne (*J. Soc. Chem. Ind.*, 1891, **10**, 233) ascertain the rise of temperature obtained on mixing 50 grm. of water with 10 c.c. of strong sulphuric acid and under precisely the same conditions as those used for testing the oil.   The *specific temperature-reaction* of the oil is obtained by multiplying the rise of temperature of the oil-acid mixture by 100, and dividing by the rise of temperature of the water-acid mixture.

Marden and Dover (*J. Ind. Eng. Chem.* 1917, **9**, 858) express the Maumené value in calories per grm. of oil.   They use an apparatus similar to that used by Mitchell and standardized the vacuum tube by measuring the heat evolved on diluting sulphuric acid of definite strength with water.   The final value is obtained by multiplying the observed rise of temperature by the heat capacity of the system and dividing the result by the weight of oil.

It is probable that the Maumené test will, ere long, be entirely displaced by more accurate methods, though it is still frequently employed as a rapid means of obtaining preliminary information.

The bromine thermal method devised by Hehner and Mitchell (*Analyst*, 1895, **20**, 146) is based upon the fact that the heat evolved on the addition of bromine to unsaturated fatty acids or glycerides is, as a rule, proportional to the degree of unsaturation.   Thus, when once a relationship has been established between the iodine value of an ordinary unoxidised fat and its bromine thermal v a l u e obtained under standard conditions, the degree of unsaturation (*i.e.*, the iodine value) of similar fats may be rapidly ascertained.

1 grm. of *e.g.*, lard, the iodine value of which has been accurately determined by Hübl or Wijs' method, is dissolved in 10 c.c. of chloroform or carbon tetrachloride in a small Dewar vacuum-jacketed tube, and the temperature of the solution taken by means of a standard thermometer graduated in tenths of a degree.   1 c.c. of bromine is then introduced by means of Hehner and Mitchell's

bromine pipette,[1] the mixture rapidly stirred with the thermometer, and the rise in temperature recorded.

The ratio between the values gives a factor (*e.g.*, 5.5), which, when multiplied by the rise of temperature observed under identical conditions with a similar fat or oil, gives a result in close agreement with the iodine value of the latter.

An apparatus thus standardised for lard gives good results with other animal body fats, with butter, and with most unoxidised vegetable oils and fats. It does not give concordant values, however, with Japanese wood (tung) oil, blown rapeseed oil, blown cottonseed oil and boiled linseed oil, evidently owing to substitution of the bromine taking place in these cases.

The value and limitations of the bromine thermal process are discussed by Jenkins (*J. Soc. Chem. Ind.*, 1897, **16,** 194) and by Archbutt (*ibid.*, 309), and modifications have been proposed by Wiley (*J. Amer. Chem. Soc.*, 1896, **18,** 378) and by Gill and Hatch (*ibid.*, 1899, **21,** 27). These modifications offer no advantage over the original methods.

Solubilities of Fats and Fixed Oils.

Fats and oils are, without exception, insoluble in *water* and *aqueous liquids* generally.

In cold *alcohol* the fixed oils are, as a rule, but little soluble, and the solid fats and waxes still less so. In boiling alcohol, however, some of the fluid oils dissolve to a considerable extent, especially if the solvent is anhydrous. In many cases, statements as to the solubility can only be regarded as giving a rough indication of the amount of free fatty acids in the sample examined. Speaking generally, it may be stated: (1). That oils containing the esters of lower fatty acids (*e.g.*, porpoise oil, coconut oil, butter-fat) are exceptionally soluble in alcohol. (2). That oils containing the glycerides of linolenic and isolinolenic acids are fairly soluble. (3). That castor and croton oil are readily soluble in alcohol, and are sharply differentiated from most other oils by this characteristic.

Ether, chloroform, carbon tetrachloride, benzene, and oil of turpentine dissolve fixed oils readily, and are in many cases miscible with them in all proportions.

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[1] This consists of a 1 c.c. pipette, connected at the top with a tube bent twice at right angles and containing caustic lime kept in position by means of asbestos plugs. On applying suction to the end of this tube, all bromine vapour is retained by the lime.

Petroleum spirit is also an excellent solvent for most oils and fats, though castor oil (*q. v.*) forms a striking exception, being practically insoluble in that liquid.

Valenta Test.—A method of distinguishing between different fats and oils was based by Valenta (*Dingler's polyt. J.*, 1884, **252**, 296) on the differences in their solubility in glacial acetic acid. A hot solution of the oil is gradually chilled and the temperature at which turbidity occurs recorded.

The incomplete solubility of rape oil and other oils from the *Cruciferæ*, even at the b. p. of acetic acid, is noteworthy, as are the low figures found for linseed oil, nigerseed oil, and menhaden oil, as compared with those for the non-drying oils.

The test is open to the objection that the slightest variations in the strength of acetic acid, and in the method of stirring and observing the turbidity point have the greatest influence upon the results.

To obtain comparable results, it is essential to follow invariably the same details of working, to use acids of exactly the same strength, and to see that the fat is free from water. The most accurate method of ascertaining the strength of glacial acetic acid is to ascertain its solidifying point, and to compare the results with the figures given by Rüdorff (*Pharm. J.*, 1871–2, [3], **2**, 241):

Glacial acetic acid containing water; %	Solidifying point; °
0.0	16.7
0.497	16.65
0.99	14.8
1.477	14.0
1.961	13.25

The modification of the method introduced by Chattaway, Pearmain and Moor (*Analyst*, 1894, **19**, 147) embodies the various precautions necessary for obtaining concordant results; but, at best, the method should only be regarded as a rapid preliminary sorting test, or as a confirmation of results obtained by other methods:

The mixture of 2.75 grm. of the fat and 3 c.c. of glacial acetic acid (99.5% strength) is heated in a stoppered tube about 10 cm. long by 1.25 cm. in diameter, which is immersed in hot water and shaken until a clear solution is obtained. It is then left in warm

water with a thermometer attached to it until the contents become turbid. In the case of oils that have been excessively heated, no reliance can be placed upon the test. The following results were thus obtained:

Oil or fat	Degrees	Oil or fat	Degrees
Butter-fat (24)		Seal oil (2)................	65.0–70.0
Highest.................	39.0	Japan fish oil (2)..........	47.5 and 19.0
Lowest.	29.0	Herring oil...............	90.0
Mean...................	36.0	Nigerseed oil.............	68.5
Margarine (5)		Sunflower oil (2)..........	59.0–62.5
Highest.................	97.9	Bottlenose oil (2)..........	80.0–96.0
Lowest.................	94.0	Lard oil (3)...............	75.0–76.0
Mean..................	95.0	Lard (4).................	97.9–98.0
Olive oil (10).............	83.0–91.0	Neatsfoot oil.............	72.0
Almond oil (5)............	72.0–87.0	Rosin....................	56.0
Cottonseed oil (7)..........	71.0–89.0	Jamba oil (3).............	Above 100
Cod oil (3)...............	26.5–31.0	Cabbage oil..............	Above 100
Codliver oil (3)...........	72.0–76.0	Beef stearin.............	Above 100
Colza (German)............	83.0	Lard stearin	Above 100
Rape oil (4)..............	63.0–78.0	Castor oil	Not above 18
Peach-kernel oil..........	82.0	Wool-grease olein...	Not above 18
Earthnut oil (3)...........	72.0–73.5		
Linseed oil...........	46.0–52.0		

Criticisms and modifications of the Valenta test have been made by Hurst (*J. Soc. Chem. Ind.*, 1887, 6, 22), Thomson and Ballantyne (*ibid.*, 1891, 10, 233), and Jones (*Analyst*, 1894, 19, 151). Its use in butter analysis is discussed in another section.

Fryer and Weston (*Analyst*, 1918, 43, 4) have shown that allowance must always be made for the presence of free fatty acids and moisture in the fats under examination, and, to eliminate error due to alteration in the concentration of the solvent they correct their results by comparison with those obtained under the same conditions with a standard almond oil.

The correction is found by means of the formula

$$V = t + (80 - t'),$$

where V represents the "true Valenta" figure, t the temperature observed with the oil under examination after correction for acidity, and t' the temperature with standard oil (corrected for acidity if necessary) and the same acid.

The correction for 1% acidity is found by reference to a table and adding the calculated result to the observed temperature. This correction has been found to vary with the class of oil or fat, and the following are typical examples: Marine animal oils, 1.90°; drying oils, 1.85°, semi-drying oils 1.77°; non-drying (except rape and castor,

2.27°; vegetable fats (except coconut group) 2.10°; rape oil group, 2.23°; coconut oil and palm kernel oil, 1.73°; animal fats (except butter fat) 2.15°; and milk fats, 1.41°.

Fryer and Weston (*loc. cit*) have found that a mixture of about 92% of ethyl alcohol and an equal volume of ethyl alcohol is an excellent solvent to use as a sorting test. This is standardised by the addition of water until it gives a turbidity temperature of 70.0° with the standard almond oil.

The following "true Valenta values (*i.e.*, corrected for acidity as described above) were thus obtained with the mixed alcohol solvent: Perilla oil, 60.3°; linseed oil, 62.4°; tung oil, 75.8°; soya bean, 67.0°; nigerseed, 60.0°, sunflower, 64.0°; maize, 68.2°; cottonseed, 65.2°; sesame, 68.1°; rape, 83.3°; almond, 70.0°; arachis, 74.3°; olive 69.2°. *Fats:* cacao butter, 76.0°; palm oil, 68.2°; Japan wax, 76.1°; lard, 72.7°; tallow, 72.7°; butter fat, 46.0°; coconut, 34.0°; palm-kernel, 40.0°. *Waxes:* Carnaüba, 82°; candelilla, 63°; beeswax, 76°; spermaceti, 44°; Chinese insect wax, insoluble; montan (refined) 70°; ozokerite, insol.; paraffin, insol; candelilla + 10% paraffin wax, 72°.

Critical Temperature of Solution.—A useful test for distinguishing between different fats and oils was devised by Crismer (*Bull. de l'Ass. belge. Chim.*, 1895–1896, **9,** 71, 143, 359). It is based upon the fact that when a substance is dissolved in, *e.g.*, alcohol under pressure, and the solution slowly cooled, the temperature at which the solid just begins to separate is fairly constant for one and the same kind of substance.

This point, the *critical temperature of solution*, stands in a certain sort of relationship to the amount of insoluble fatty acids in a fat, and in the case of mixture is approximately the arithmetical mean of the values of its constituents.

It is ascertained as follows: A few drops of the melted and filtered substance are mixed with alcohol of known sp. gr. in a tube of a few mm. in diameter. This tube is then sealed up and attached by platinum wire to the bulb of a thermometer, which is immersed in a bath of sulphuric acid. The bath is slowly heated until the meniscus separating the layers of liquid appears a horizontal plane. The tube is then removed, turned sharply once or twice, to render its contents homogeneous, and replaced in the bath, which is now allowed to cool slowly, the thermometer and attached tube being meanwhile continually shaken, until a perceptible turbidity appears.

This temperature is the critical temperature of solution. In this way the following results were obtained:

Substance	Critical temperature of solution	Substance	Critical temperature of solution
With 90 % alcohol	°	*With alcohol of sp. gr. 0.8195*	°
Butter-fat..................	99–106		
Margarine.................	122–125	Mineral oils (various).......	135.5–140
Arachis oil................	123.0	Valve oil..................	197
Cottonseed oil.............	115.5	Animal oil.................	120
Sesame oil................	120.0	Sheepsfoot oil.............	102
Olive oil..................	123.0	Lard oil...................	104
Almond oil................	120.0	Neatsfoot oil..............	95
Rape oil (crude)...........	136.0	Colza oil..................	131–135
Rape oil (refined).........	132.5	Japan fish oil.............	108
Hempseed oil..............	97.0	Butter-fat (10 samples).....	95–100
Nut oil...................	100.5		
Castor oil.................	0.0		
Linseed oil (oxidised)......	70.0		

Old and rancid butter-fat shows a lower value than fresh butter-fat, but after removal of the free fatty acids by treatment with sodium carbonate and washing the fat with hot water, normal values are obtained.

Crismer's figures for butter and magarine were in the main confirmed by Asboth (*Chem. Zeit.*, 1896, **20**, 685). See also "Cacao Butter" p. 250.

Relationship between the Constants of Fats.—It has been pointed out by several chemists that there is a relationship between some of the chemical and physical constants of a fat.

Thus it has been shown by Pickering and Cowlishaw (*J. Soc. Chem. Ind.*, 1922, **41**, 741) that the relationship between the refractive index and iodine value can be expressed by means of the formula

$$n\frac{40}{D} = 1.4643 - 0.000046\,(\text{S.V.}) - 0.0096\left(\frac{\text{A.V.}}{\text{S.V.}}\right) + 0.0001171\,(\text{I.V.}),$$

where S.V. represents the saponification value, A.V. the acid value, and I.V. the iodine value. If a refractive index higher than that calculated from this equation is observed, it is an indication that the oil is oxidised or has been prepared from damaged material.

Backer (*Chem. Weekblad*, 1916, **35**, 954) has shown that this relationship holds good for the principal constants—*viz.* refractive index, *n*, sp. gr., *d*, saponification value, V, and iodine value, I

of ordinary fats, and that it may be expressed by the equation—

$$\frac{n^2t - 1}{n^2t + 2} \times \frac{100}{d\frac{t}{4}} = 33.07 + 0.00075\,I - 0.01375\,V + 0.002\,(t - 15).$$

When hydroxyl acids are present the first figure of the equation is lower.

Ludborough, Watson and Athawale (*J. Soc. Chem. Ind.*, 1923, **42**, 103) have shown that in the case of hydrogenated cottonseed, linseed, arachis, bassia tallow, sesame and sardine oils the relationship between the iodine value and refractive index can be expressed by the following equation with an accuracy of about 0.0005.

$$n\frac{60}{D} = 1.4468 + 1.03 \times 10^{-4}(\text{I.V.}) + 7.3 \times 10^{-3}(\text{I.V.}^2).$$

In the case of castor oil the nature of the catalyst causes a variable reduction of the hydroxyl groups, and the refractive indices of hydrogenated coconut oil are much lower than those of other oils with similar iodine values (see also " Cacao Butter).

CLASSIFICATION OF FATS, OILS, AND WAXES

In studying the characters of fixed oils and identifying oils of unknown nature valuable assistance is obtained from a suitable arrangement of the oils in classes or groups. The classification here adopted is based on a joint consideration of the origin, physical characters, and chemical constitution of the oils. An attempt is likewise made to classify the oils so that each group contains some important commercial oil which is typical of the other members of the group. Thus, the oils included respectively in the rape oil, olive oil, and coconut-oil groups present a more or less close resemblance to rape oil, olive oil and coconut oil, respectively.

I. **Olive-oil Group.**—*Vegetable Oleins.*—The oils of this group have a sp. gr. ranging from 0.911 to 0.923, and hence are, as a rule, lighter than the oils of Groups III, IV, and V. Their viscosity is notably greater than that of the drying oils, but inferior to that of rape oil, and they do not lose their power of producing a greasy stain on paper, however long they may be exposed to the air. They yield very solid products in the elaidin test, and are also characterised by their relatively low iodine values and medium saponification values. They contain olein as a main constituent, with smaller quantities of the glycerides of saturated fatty acids (palmitin, stearin,

arachidin, etc.) and in some cases, at all events, of glycerides of more unsaturated fatty acids such as linolic acid. They yield no insoluble bromides on treatment with bromine, and their fatty acids yield, at most, only traces of linolic tetrabromide. The composition of chaulmoogra and hydnocarpus oils differs materially from that of the typical oils in this group.

II. **Rape-oil Group.**—The oils in this group are derived from the *Cruciferæ*. They are classed as non-drying oils, though this characteristic is less pronounced than in the case of the oils in Group I, from which they may be distinguished by their low saponification values, and by forming a paste-like product in the elaidin reaction. Some of these oils resemble linseed oil in yielding an insoluble product on treatment with bromine, possibly the bromide of a mixed glyceride containing linolenic acid. Their low saponification values are probably due to the presence of glycerides of erucic acid, $C_{22}H_{42}O_2$, whilst rapic acid (isomeric with oleic acid) is present in rape oil.

III. **Cottonseed-oil Group.**—The sp. gr. of these oils range from 0.917 to 0.929, the values of the crude oils being somewhat higher than those of the refined products. They are usually classified as *semi-drying oils* from the fact that they come between the non-drying oils and the drying oils, both in this respect and in their chemical composition. They have fairly high iodine values, and their fatty acids yield considerable amounts of linolic tetrabromide on treatment with bromine. In the elaidin test they yield soft solid masses, intermediate between the hard products given by the oils of Group I and the fluid products from the drying oils. They consist largely of linolin and olein, with smaller quantities of glycerides of solid fatty acids and traces of linolenin.

IV. **Linseed-oil Group.**—*Drying Oils.*—They range in sp. gr. from 0.9215 to 0.9430, and are thus distinctly heavier than the oils of the preceding groups. They are not solidified by treatment with nitrous acid, evolve great heat in the Maumené test, and have high iodine values. Linseed oil (and to a less extent some of the other oils) yields a large amount of an insoluble bromide on treatment with bromine. On exposure to the air in thin layers they absorb oxygen and form varnishes which are at first sticky, but subsequently become plastic or brittle. The viscosity of the drying oils is less than that of the preceding groups. In composition they differ from the

semi-drying oils in containing a greater proportion of the glycerides of the highly unsaturated acids (linolenic and isolinolenic acids). The composition and properties of tung oil differ greatly from those of other members of this group.

V. **Castor-oil Group.**—The oils in this group have little in common, though some are characterised by their great viscosity and high sp. gr. Castor, curcas and croton oils have also the characteristic of ready solubility in alcohol and glacial acetic acid, and of marked purgative properties, but curcas oil is less soluble in alcohol than the others. In castor oil and grapeseed oil glycerides of a hydroxy-acid such as ricinoleic acid predominate, and are indicated by the high acetyl value of the oil. Croton oil has a high Reichert-Meissl value, due to the presence of glycerides of volatile fatty acids.

VI. **Cacao-butter Group.**—*Vegetable Fats.*—This group includes solid fats, consisting mainly of glycerides of higher fatty acids such as myristic, palmitic, stearic and oleic acids. They contain only small amounts of glycerides of volatile acids as is shown by the low Reichert-Meissl values. The fairly high iodine values point to the presence of a considerable proportion of glycerides of oleic and, probably, linolic acids.

VII. **Coconut-oil Group.**—*Vegetable Fats.*—The members of this group are fats of high sp. gr. and with low saponification values. They also include the two commercial vegetable "stearines" obtained from coconut and palmnut oils. The typical fats of the group (coconut and palmnut oils) contain a considerable amount of the glycerides of the lower fatty acids, whence their high Reichert-Meissl values. They are also distinguished from the fats of the preceding group by their high saponification values (indicating glycerides of lower fatty acids) and low iodine value (indicating the small proportion of unsaturated glycerides).

VIII. **Lard-oil Group.**—*Animal Oleins.*—In this group are included the oils, fluid at ordinary temperatures, which are obtained from terrestrial animals. They have lower iodine values than the corresponding vegetable non-drying oils (Group I), though they also yield more or less solid products in the elaidin test. They consist mainly of olein, with smaller quantities of palmitin, stearin, and probably linolin.

IX. **Tallow Group.**—*Animal Fats.*—The tallow group comprises the fats from terrestrial animals, which are solid or semi-solid at the

ordinary temperature. The body fats consist of glycerides of stearic, palmitic, and oleic acids with smaller amounts of linolin and other glycerides; whilst butter-fat is distinguished from the other members of the group by its high sp. gr., low saponification value, and high Reichert-Meissl value, due to the presence of a considerable amount of the glycerides of butyric and other lower fatty acids. Animal fats may be distinguished from vegetable fats by the phytosteryl acetate test (*q. v.*).

X. **Whale-oil Group.**—*Marine Animal Oils.*—This group comprises the majority of the fluid oils obtained from fish and marine mammals. They are distinguished as a class by their offensive "fishy" odour, which becomes more perceptible on warming; by the reddish-brown colour they assume when subjected to the action of chlorine; and by the reddish or reddish-brown colour produced on boiling them with a solution of caustic alkali. With concentrated sulphuric acid they give considerable rise of temperature and colorations, varying from light red to purple and brown. Most members of the group dry more or less on exposure to the air, and yield but little solid elaidin on treatment with nitrous acid. In these respects they resemble the vegetable oils of the cottonseed group, and have similar sp. gr. The oils from the sperm and bottlenose whales are peculiar, as regards physical characters and chemical constitution, and form a separate class (Group XI). "Train oil" includes the oil from the blubber of any marine mammal.

On treatment with bromine, many of the oils of this group yield an insoluble bromide, which may be distinguished from the similar product given by linseed and other drying oils by turning black when heated.

Porpoise oil is characterised by its high saponification value and high Reichert-Meissl value due to the presence of glycerides of valeric acid. The other oils in the group consist largely of glycerides of very unsaturated acids, some of which are isomeric with linolenic acid, and others still more unsaturated. Some of them, such as codliver and other liver oils, also contain a considerable amount of cholesterol and allied biliary products.

XI. **Sperm-oil Group.**—*Liquid Waxes.*—The members of this group differ from all the fatty oils of previous classes in consisting essentially of esters of the ethyl series. In this respect they resemble the true waxes, but are fluid at the ordinary temperature. They are

of less sp. gr. than the true oils at the ordinary temperature and at the b p. of water; and on saponification yield considerable proportions of solid higher homologues of ethyl alcohol. They do not dry or thicken notably on exposure to air and yield solid elaidins on treatment with nitrous acid.

XII. **Spermaceti Group.**—*Waxes.*—The members of this group are solid at ordinary temperatures, and more or less resemble beeswax, the prototype of the class. They consist essentially of esters of the higher radicles of the ethyl series, with in some cases an admixture of higher monatomic alcohols and higher fatty acids in the free state. Carnaüba wax seems also to contain diatomic alcohol radicles. Sperm and bottlenose oils (Table XI) resemble the waxes in constitution, but are liquid at ordinary temperatures. The substances known as Japan wax and myrtle wax (Table VII) are fats, not true waxes. Paraffin wax and mineral wax are hydrocarbons, and hence quite different in chemical constitution from the true waxes of animal and vegetable origin. In this group also belong the bituminous wax, Montan wax and the vegetable candelilla wax product.

The following tables give the values likely to be obtained in the examination of the chief oils, fats, and waxes of commercial importance:

DETECTION OF RANCIDITY IN FATS

The causes leading to the development of rancidity in fats have already been mentioned (see p. 10).

As the development of acidity does not run parallel with the production of rancidity, the determination of the acid value may not always indicate the fact that a fat is not perfectly sound.

Issoglio (*Annali Chim. Appl.*, 1916, **6**, 1) has therefore devised a method in which the degree of rancidity is estimated by means of the "*oxidisability value*" *i.e.* the amount of oxygen consumed under standard conditions by the aldehydes and other products of rancidity after distillation in a current of steam. From 20 to 25 grm. of the fat are distilled with 100 c.c. of water by means of a current of steam, in such a way that 100 c.c. of the distillate are collected in 10 minutes. 10 c.c. of the distillate are diluted wth 50 c.c. of water, 10 c.c. of 20% sulphuric acid, and 50 c.c. of N/100 potassium permanganate solutions added, and the mixture boiled for 5 minutes in

a flask connected with a ground-in condenser. After cooling, the liquid is treated with 50 c.c. of N/100 oxalic acid solution, and titrated with N/100 permanganate solution.

If N represents the amount of permanganate required for the oxidation, n that required in a blank test, and P the weight of fat taken, the *oxidizability value* of the fat is calculated from the equation

$$x = \frac{(N - n)\ 80}{P}$$

that is to say, the oxidisability value represents the mg. of oxygen required to oxidise the organic compounds separated under constant conditions.

In the case of sound fats the oxidisability value ranges from above 3 to 10, whilst rancid fats show much higher values. The oxidisability value does not stand in any relationship to the acid value. For example, 15 samples of sound olive oil had acid values of 1.88 to 8.59 and oxidisability values of 3.20 to 10.45, whilst in the case of 6 samples of rancid olive oil the acid values ranged from 6.51 to 18.56, and the oxidisability values from 14.62 to 59.10

The Meat Inspection Laboratory of the Bureau of Animal Industry, Washington, use a modification of Issoglio's test, in which the distillation is eliminated (Kerr, *J. Ind. Eng. Chem.*, 1918, 10, 471): 25 grm. of the fat are digested with 100 c.c of water on a steam bath, and the liquid then filtered and made up to 100 c.c. 10 c.c. of this filtrate are boiled for 5 minutes, beneath a reflux condenser, with 50 c.c. of water, 10 c.c. of 20% sulphuric acid and 50 c.c. of N/100 permanganate solution, then cooled, treated with 50 c.c. of N/100 oxalic acid solution and titrated with N/100 permanganate. If more than 5 c.c. are required the fat is probably rancid. The test is useful for confirmation, although less trustworthy than the Kreis phloroglucinol test. Kerr (*J. Ind. Eng. Chem.*, 1918, 10, 471) recommends the following modification of the phloroglucinol test of Kreis: 10 c.c. of the oil or melted fat are shaken in a tube with 10 c.c. of hydrochloric acid (sp. gr. 1.19), and 10 c.c. of a 0.1% solution of phloroglucinol in ether are added. If no red or pink coloration is obtained the fat may be regarded as sound. Otherwise the original sample is diluted with 9 and 19 parts, respectively, of purified kerosene oil, and the test repeated with each mixture. A fat which gives a pink tint in the 1 in 20 dilution will be found to be distinctly rancid, whilst one giving a coloration with a dilution of

1 in 10 but not with 1 in 20 may show less outward indications of rancidity. A fat which gives a coloration in the original test but not after dilution will be on the road to rancidity and should be used at once.

Biochemical Test for Rancidity.—It has been found by Vintilesco and Popesco (*J. Pharm. Chem.*, 1915, **12**, 318) that fats absorb oxygen when becoming rancid, and that they can then replace hydrogen peroxide or oxidised oil of turpentine in the test for blood: About 10 grm. of the oil or melted fat are mixed with 4 to 5 drops of an aqueous solution of blood or of 3 % hæmoglobin solution, about 10 c.c. of water and 10 drops of freshly-prepared guaiacum tincture added, and the tube closed and vigorously shaken for 1 minute.

Sound fats produce no coloration, but in the case of rancid fats there will be a blue coloration the intensity of which will be proportional to the degree of oxidation. The oxidation product is soluble in 95% alcohol, and when a fat is only slightly rancid the blue coloration may be rendered more distinct by shaking the mixture with an equal volume of that solvent.

Rancid fats which have been heated for a few minutes at 120° still give the reaction, but not after heating at 200°.

UNSAPONIFIABLE MATTER

The general method of separating unsaponifiable matter is described in the section on saponification p. 15.

In addition to this, the following rapid method of Wilkie (*Analyst* 1917, **42**, 200) may be described: 5 grm. of the fat or wax are boiled beneath a reflux condenser for 1½ hours with 12.5 c.c. of 2N alcoholic potassium hydroxide solution, and the resulting soap solution transferred to a separator with the aid of 50 c.c. of water, and extracted with successive portions of 40, 30, 30 and 30 c.c. of ether. The ethereal extracts are united and transferred to a separator containing 20 c.c. of water. This washing water is run off, without shaking, and the ethereal solution then washed by shaking it vigorously with 2, 5 and 30 c.c. of water, after which it is evaporated and the residue weighed.

This method avoids the difficulties caused by emulsification and enables the final estimation to be completed in about 30 minutes.

Detection of Phytosterol and Cholesterol.—Marcusson and Schilling devised a method of separating phytosterol or cholesterol

by precipitation with digitonin. A simple modification of the method is recommended by Fritzsche. 50 grm. of the melted fat are mechanically stirred for 5 minutes at 60° to 70° with 20 c.c. of a 1% alchoholic solution of digitonin. In the case of fluid and semi-solid fats the mass is at once filtered, with the aid of suction, in a Buchner's funnel, and the residue washed 6 times with ether (5 c.c. each time); in the case of solid fats 20 c.c. of chloroform are added to the hot liquid and the residue washed with two portions (4 c.c.) of hot chloroform and then with six portions of ether to remove all fat. The residue (digitonide) is dried for about 5 minutes at 30° to 40° dissolved in 2 c.c. of hot acetic acid, and the solution boiled for about 5 minutes in a test-tube with a vertical tube to act as condenser and then filtered through cotton wool. The tube and filter are twice washed with 0.5 c.c. of hot absolute alcohol, and the combined filtrate and washings evaporated on the water-bath in a current of air. The residual phytosteryl or cholesteryl acetate is dissolved in 0.5 to 1 c.c. of absolute alcohol, and the crystals drained on porous porcelain and examined in the usual way (see also section on *Butter* and *Cholesterol*).

EXAMINATION OF FATS AND CRUDE OILS FOR FOREIGN MATTERS

The term "foreign matters" used in this connection indicates substances added to the oils, such as rosin, soaps, hydrocarbons, water and mineral matter as well as excess of free fatty acids, but does not apply to substances which are natural constituents of an oil such as colouring matters, cholesterol, albuminous substances or chlorophyll.

The estimation of water, curd, and salt in fats such as butter and margarine is described in the special section dealing with butter. An oil, if clear, may be regarded as free from such extraneous matters, and their presence in a fat may usually be detected by melting the sample. If an opaque or opalescent oil result, or one containing visible particles of suspended matter or globules of water, it should be purified from these by filtration through dry paper before proceeding to search for rosin, fatty acids, soap or hydrocarbons.

Soap is sometimes added, as such, to an oil, but its presence is more frequently due to the use of alkali employed to increase sp. gr. and viscosity. Soap is readily detected by dissolving the oil in about 3

times its volume of ether or carbon tetrachloride, adding a little water, and agitating the whole thoroughly in a separating funnel. The soap will dissolve in the water, whilst the other foreign matters will dissolve with the oil, in the ether or carbon tetrachloride, and may be recovered therefrom by distillation. The soap may be estimated by evaporating the aqueous liquid and weighing the residue after drying at 100° The proportion of soap may also be inferred from the amount of carbonate left after igniting the oil.

Insoluble soaps are not infrequently present in oils, waste greases, and pharmaceutical preparations ("oleates"). Though insoluble in water, many of them are soluble in ether or petroleum spirit. They may be decomposed by agitating the mixture with dilute sulphuric acid, when the acid liquid will contain the metal of the soap, and a corresponding quantity of fatty acid will dissolve in the oily layer. When it is desired to ascertain the proportion of free fatty acids originally present in the oil, a titration with alkali should be made both before and after shaking with dilute acid. The difference between the two estimations represents the fatty acid liberated by the treatment.

Free Acid in Oils.—Commercial oils and fats very frequently contain notable proportions of free acid, which may either be mineral acid, as a result of incomplete separation after refining, or free fatty acid resulting from unskilful refining or from the natural decomposition of the oil.

Mineral acids are only accidentally present in fixed oils, and usually in very small proportions. Even minute quantities are highly objectionable in oil intended for lubricating. but are harmless when the article is to be used for soap-making. Mineral acids may be readily recognized by agitating the oil with warm water, separating the aqueous liquid, and testing it with a solution of methyl-orange, which will give an orange or red coloration if any mineral acid be present. The nature of the mineral acid, which is most commonly sulphuric, can then be ascertained by testing the aqueous liquid with barium chloride, silver nitrate, and other appropriate reagents. Oils which, from over-treatment with acid during refining, contain a sulphonated fatty acid, must be boiled with water for some time, in order to decompose the compound.

Free fatty acids are often normally present, and in some oils (*e.g.*, olive and palm) may occur in very large proportion. Free

oleic acid is largely used as a lubricant in wool-spinning, and free palmitic and stearic acids are employed for making candles and night-lights. All are used for soap-making. Their proportion is estimated as described in the section (page 10) dealing with the *Acid Value*.

Rosin acids present in the sample will be estimated by the above process as fatty acids. Their separation from the latter is described below. *Mineral acids* will affect the accuracy of the results unless an allowance is made for them, or they are previously separated by repeatedly agitating the oil with water. *Soap* and *hydrocarbons* do not interfere with the estimation.

The estimation of the acid value may be supplemented by a gravimetric estimation. The resultant alcoholic liquid is separated from the oil, the alcohol evaporated, and water added. This solution is agitated with a little petroleum spirit (not ether) to dissolve suspended oil, the aqueous liquid separated, and the fatty acid liberated from the soap solution by adding dilute sulphuric acid. On agitating with ether, separating the ethereal solution, and evaporating it to dryness, the fatty acids can be weighed. This method should be used when rosin acids may be present. In their absence, the estimation should be fairly concordant with the result of the titration. *Soap* should be previously separated. *Mineral acids* and *hydrocarbons* do not interfere with the results.

Rosin.—Common *rosin* or *colophony*, which is described in a special section, is added to oils to impart certain properties, but its employment often renders them wholly unsuitable for their intended purposes.

One of the methods of detecting rosin is by the brown colour it imparts to sodium hydroxide. The original sample is saponified, the alcohol boiled off, and the liquid treated with sufficient sodium hydroxide solution to cause precipitation of the soap. The solution, separated from the soap by decantation or filtration through glass-wool, will be dark brown if rosin is present. The same method serves for the recognition of rosin in soap, previous saponification being unnecessary. The method may also be applied to the mixture of fatty and resin acids separated in the manner described in the table on page 23. The dissolved rosin may be recovered by acidifying the alkaline liquid with hydrochloric acid, when a precipitate of resinous odour will be formed. The rosin may be isolated by agitating the liquid with ether and evaporating the ethereal layer

to dryness, and may be identified by its physical and other characteristics.

In the absence of free fatty acids, rosin may be isolated from fixed oils by agitating the sample with moderately strong alcohol, separating the solution and evaporating it to dryness. It may also be isolated, and approximately estimated, by titrating the alcoholic solution of the sample with alkali and phenolphthalein as described elsewhere. As the several acids which ordinary colophony contains are not present in constant proportion, the neutralising power of rosin is variable, ranging from 0.310 to 0.430 grm. of colophony for 1 c.c. of N/1 alkali. The rosin subsequently extracted from the acidified aqueous liquid, and left on evaporating the ethereal solution to dryness, is readily recognisable by the taste and smell on heating, and often shows the physical characteristics of rosin.

In the last method of operating, the rosin is obtained in admixture with any free fatty acids the sample may have contained. These modify the physical properties of the extracted rosin very materially, and render the method useless for quantitative purposes. In such cases, if there is sufficient material for the purpose, a good indication of the relative proportions of fatty and rosin acids iǹ the mixture may be obtained by observing the sp. gr. at the temperature of boiling water, as described on page 64. As, however, rosin varies considerably in sp. gr. and the fatty acids from various oils exhibit similar variations, the method furnishes but very rough results unless the source of the fatty acids be definitely known.

Estimation of Rosin Acids.—The most widely-employed method of separating rosin acids from fatty acids is that of Twitchell (*J. Soc. Chem. Ind.*, 1891, **10**, 804) which yields much more accurate results than many other methods. It is based upon the fact that aliphatic acids are converted into ethyl esters when acted upon by hydrochloric acid gas in their alcoholic solution; whereas colophony undergoes little or no change under the treatment, abietic acid separating from the solution.

The rosin gives an acid indication in alcoholic solution with phenolphthalein, and interacts readily with potassium hydroxide to form a soluble soap. All that is necessary, therefore, is to make the fatty acids interact with alcohol and to titrate the rosin acids with standard alkali; or they may be treated with potassium hydroxide, and

the resulting rosin soap separated from the saponified fatty esters by means of petroleum spirit.

(a). *Gravimetric Method.*—From 2 to 3 grm. of the mixture of fatty acids and rosin are dissolved in 10 times their volume of absolute alcohol in a flask, and dry hydrochloric acid gas introduced in a moderate stream. The flask is set in a vessel with water to keep it cool. The acid is rapidly absorbed, and, after about 45 minutes, the esters separate, floating in the solution, and no more hydrochloric acid is absorbed. The current of gas is now stopped, and the flask allowed to stand for half an hour to complete the reaction. The liquid is diluted with about 5 times its volume of water and boiled until the acid solution is clear, the esters, with rosin in solution, floating on the top. To this is added some petroleum spirit, and the whole transferred to a separating funnel, the flask being washed out with petroleum spirit. The acid solution is then run off, and the petroleum-spirit solution (which ought to measure about 50 c.c.) washed once with water and then shaken in the funnel with a solution of 0.5 grm. of potassium hydroxide and 5 c.c. of alcohol in 50 c.c. of water. The rosin is immediately saponified and the two layers completely separated. The solution of rosin soap can be run off, treated with acid, the rosin collected in any manner desired, dried, and weighed. A second washing of the soap with petroleum spirit is hardly necessary, as very little remains after the first extraction.

(b). *Volumetric Method.*—The first stages of the volumetric method are similar to the gravimetric, with the exception that the contents of the flask are washed into the separating funnel with ether instead of petroleum spirit, and the ethereal solution in the funnel is then thoroughly washed with water until the wash-water is no longer acid; 50 c.c. of alcohol, previously neutralised, are then added and the solution titrated with standard sodium hydroxide solution with phenolphthalein as indicator. If the combining equivalent of rosin is known its percentage may be calculated, or some of the original mixture may be also titrated, when the difference in sodium hydroxide required will correspond to the fatty acids converted into esters.

The average combining equivalent of the samples of rosin examined by Twitchell was 346, and a closely similar value was found by Lewkowitsch (*J. Soc. Chem. Ind.*, 1893, **12**, 504). Hence an approxi-

mately correct result for the amount of rosin may be obtained by multiplying the number of c.c. of N/1 alkali used in the titration by 0.346. Certain varieties of commercial rosin, however, have combining equivalents differing very considerably from this average value. The results of test experiments have shown that in practice the volumetric figures though usually too high, are more accurate than the gravimetric figures which are usually too low. A critical examination of this method was made by Lewkowitsch (*loc. cit.*)

Fortini's Method.—It has been found by several chemists that Twitchell's method may indicate the presence of a small amount of rosin when none is present.

This drawback is overcome in a method devised by Fortini (*Anonali. Chim. Appl.*, 1918, 9, 102) which is also applicable to rosins other than colophony. It is based upon the fact that rosin acids form nitro derivatives which are insoluble in petroleum spirit. The separated acids are dried at 100° (if necessary in a current of carbon dioxide), 2 grm. dissolved in 50 c.c. of petroleum spirit (b. p. 40°–50°) in a separating funnel, and the solution shaken with successive small portions (10 c.c. each) of nitric acid prepared by mixing 25 c.c. of fuming nitric acid (sp. gr. 1.52) with 75 c.c. of ordinary nitric acid (sp. gr. 1.48) and treating the mixture with a few crystals of urea to destroy nitrous acid.

The liquid is shaken for 2 to 3 minutes and left for the two layers to separate. The acid layer is drawn off and the treatment repeated with 5 c.c. of the nitric acid, which is drawn off in turn, and the residual ethereal solution is washed first with ordinary nitric acid, then with water, and filtered, the filtrate is evaporated at a low temperature, and the residue of fatty acids dried and weighed.

The resin acids, which have been converted into nitro-derivatives insoluble in petroleum spirit, are separated with the acid layer.

In the presence of oleic acid the results for the fatty acids will be a little too high, but even then will be within 1 % of the theoretical amount in the case of mixtures containing from 5 to 20% of resin.

Hydrocarbons.

The hydrocarbons most commonly added to fatty oils are:

1. Those produced from *petroleum* and by the distillation of *bituminous shale.*

2. Those produced by the distillation of common *rosin*, having the nature and properties detailed in the section on "Rosin Oil."

3. Neutral *coal oil;* being the portion of the products of the distillation of coal-tar boiling above 170°, and freed from phenolic bodies by treatment with soda.

4. Solid *paraffin wax,* employed for the adulteration of beeswax and spermaceti, and used in admixture with stearic acid for making candles.

Detection of Hydrocarbons.—The presence of hydrocarbons in fats and fatty oils is *detected* by the altered sp. gr. of the sample, which is decreased by members of the first class, and increased by rosin and coal-tar products; by the lowering of the flashpoint and b. p.; by the fluorescence of members of the first two classes; and by the incomplete saponification with alkalis. The taste and odour on heating are also valuable indications.

Sp. gr. is a character of some little value for detecting and approximately estimating hydrocarbons, but in practice the indications obtained are apt to be rendered valueless by the employment of a *mixture* which has the same sp. gr. as the oil to be adulterated.

The tendency of a hydrocarbon is to reduce the flashpoint and boiling point of the fixed oil, and in some cases a distinct separation may be effected by fractional distillation.

Fluorescence is a character of considerable value for detecting the presence of hydrocarbons. If undoubtedly fluorescent, the sample certainly contains some hydrocarbon, but the converse is not strictly true, as the fluorescence of some varieties can be destroyed by treatment, and some hydrocarbons have no fluorescence.

The best method of observing fluorescence is to make a thick streak of the oil on a piece of black marble, or glass smoked at the back, and to place the streaked surface in a horizontal position in front of, and at right angles to, a well-lighted window.

Most of the hydrocarbons employed for lubricating purposes are strongly fluorescent, and many others become so on treatment with an equal volume of strong sulphuric acid. A hydrocarbon possessing strong fluorescence may be evident in presence of a very large proportion of fixed oil; but if any doubt exists, the hydrocarbon should be isolated in the manner described below.

Estimation of Hydrocarbons.—The following method is based on saponification of the oil or fat and extraction of the hydrocarbons from the aqueous solution of the soap by means of a suitable solvent such as ether: 5 grm. of the sample are saponified by alcoholic

alkali, the solution freed from alcohol, and transferred to a separator
of about 200 c.c. capacity, furnished with a tap below and a stopper
at the top.   The tube below the tap should be ground or filed off
obliquely, so as to prevent any liquid from remaining in it.   The
liquid is diluted with water till it measures from 70 to 100 c.c.
From 50 to 60 c.c. of ether should next be added, the stopper
inserted, and the liquids thoroughly shaken and allowed to rest for a
few minutes.   As a rule, two well-defined layers will form, the lower
one brownish, consisting of the aqueous solution of soap, the upper
of ether, containing any hydrocarbon in solution.   The addition of
a few c.c. of alcohol will facilitate the separation when it does not
readily occur.

The aqueous liquid is drawn off through the tap into a beaker.
About 10 c.c. of water and a few drops of caustic alkali solution are
added to the ether which remains in the separator, and the whole
shaken.   The washings are then run off in their turn, and after
repeating the treatment with water, which is removed by the tap as
before, the ethereal solution is poured off through the mouth into a
weighed flask.   The aqueous liquid and washings are then returned
to the separator, and agitated with a fresh quantity of ether, which
is washed and poured into the flask as before.

The agitation of the soap solution is repeated once more, to com-
plete the extraction of the hydrocarbon oil.   The ethereal solution
will usually be strongly fluorescent.   The flask containing it is
attached to a condensing arrangement, and the greater part of the
ether distilled off by immersing the flask in boiling water.   When
distillation has ceased, the condenser is detached and the flask
placed on the top of the water-oven to eliminate the rest of the
ether.   Sometimes the hydrocarbon will contain globules of water;·
in this case the flask should be held horizontally, and rotated rapidly,
so as to spread the oil over the sides in a very thin layer, and facili-
tate the evaporation of the water.   When no more water is visible,
and the smell of ether is scarcely perceptible, the flask is placed on its
side in the water-oven for 10 or 15 minutes and weighed,[1] when the
increase of weight over the original tare gives the amount of hydro-
carbon oil extracted.   Prolonged heating should be avoided, as

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[1] Sometimes it is very difficult to obtain a constant weight by the means indicated in
the text.   In such cases, instead of heating the flask on the water-oven, it should be kept
on the bath of boiling water and a moderate current of air, filtered by passing it through
a tube containing cotton-wool, should be blown through it by a second tube passing through
the cork.   The fittings are then detached, and the flask heated for a short time in the water-
oven.

many hydrocarbons are appreciably volatile at 100°. This is notably the case with coal-tar oil, and hence, in analysing mixtures containing it, the heating in the water-oven should be wholly dispensed with. With rosin oil, paraffin wax, and the denser mineral oils there is but little danger of loss by volatilisation at 100°.

The results obtained are correct to within about 1 % in all ordinary cases.[1] Where extreme accuracy is desired, it is necessary to remember that most, if not all, animal and vegetable oils contain traces of matter wholly unacted on by alkalis. In certain cases, e. g., butterfat and cod-liver oil, this consists largely of cholesterol, $C_{26}H_{44}O$, which may be obtained in characteristic crystalline tablets by warming the ethereal extract with alcohol, and allowing the solution to cool. The proportion of unsaponifiable matter soluble in ether which is naturally present in fixed oils and fats, rarely exceeds 1.5 and is usually much less. Sperm and bottle-nose whale oils, however, constitute an exception, yielding about 38 to 40% of matter soluble in ether and certain shark-liver oils (q. v.) contain a high proportion of the hydrocarbon spinacene.

Spermaceti and the other waxes yield to ether after saponification large percentages of matter, and hence the process is not available for the estimation of paraffin wax in admixture with these substances, though it gives accurate results with the mixtures of paraffin and stearic acid so largely employed for making candles.

The following table indicates the behaviour of the constituents of complex mixtures of fats, oils, and waxes, when the aqueous solution of the saponified substance is shaken with ether:

[1] Traces of fatty oils which had escaped saponification and traces of soap are apt to pass into the ethereal solution, and hence the proportion of unsaponifiable matter found is often slightly reduced on treating the ether-residue with alcoholic potassium hydroxide solution, and again extracting the solution of the soap with ether.

Dissolved by the ether	Remaining in the aqueous liquid	

Hydrocarbon oils; including
  Shale and petroleum oils,
  Rosin oil hydrocarbons,
  Coal-tar oil,
  Paraffin wax and ozokerite,
  Vaseline.
Neutral resins.
Unsaponified fat or oil.
Unsaponifiable matter, as cholesterol from
  liver oils, hydrocarbons from shark-liver
  oils, etc.
Dodecyl alcohol, from sperm and bottle-
  nose oils.
Cetyl alcohol, from spermaceti.
Myricyl alcohol, from beeswax.
Alcohols from montan wax.
Colouring matters, as from palm oil.
	Fatty acids.
	
	Rosin acids
	
	Phenol,
	Cresols,
	  and other phenols
	
	Glycerol (glycerin).
	
	Excess of potassium hydroxide.
		In the form
		of
		potassium
		salts.

The hydrocarbon having been isolated by saponifying the sample and extracting with ether, its nature may be ascertained by observing its sp. gr., taste, and smell, and its behaviour with acids and bromine. If the proportion be small, it may be necessary to operate on a larger quantity than 5 grm. of the sample. A good approximation of the sp. gr. of the extracted hydrocarbons may be made on Hager's principle, by adding a drop of the oil to very dilute alcohol, or ammonia, and adjusting the strength of the liquid so that it may be identical with that of the drop of oil (see p. 65). The sp. gr. of the dilute alcohol is then ascertained in the usual way. The fluorescence of hydrocarbons is best observed in the manner described in Vol. 1, page 41. It often becomes intensified by treating the extracted hydrocarbon with an equal volume of strong sulphuric acid.

The odour and taste of the hydrocarbons are often highly characteristic of their origin. The smell of coal-tar oil is readily observed. and the taste, especially the after-taste, of rosin oil is not to be mistaken. The smell produced on strongly heating a drop of the oil in a platinum capsule is also highly characteristic. Further details respecting the tests for hydrocarbons are given in the section on "Mineral Lubricating Oils."

The *higher alcohols* from sperm and bottlenose oil may be separated from hydrocarbons by treating the ether-residue with rectified

spirit, which dissolves the alcohols without materially affecting the hydrocarbons.

If the aqueous liquid separated from the ethereal layer be treated with dilute sulphuric acid, the fatty acids are liberated, and may be weighed, titrated with standard alkali, or otherwise examined.

When it is merely desired to ascertain approximately the proportion of hydrocarbon oil in a mixture, and not to isolate it and examine it further, there is no occasion to extract the solution of the saponified oil with ether. Instead, the aqueous liquid may be at once acidified with dilute sulphuric acid, a little ether added to promote the separation of the mixed hydrocarbon oils and fatty acids, the aqueous liquid drawn off, and the oily layer repeatedly shaken with water till the washings are no longer acid to litmus. Rectified spirit and a few drops of phenolphthalein solution are then added, and the liquid titrated with N/10 alkali.

The amount of acid, calculated as oleic acid, multiplied by 1.053 gives the amount of saponifiable substances, and the difference may be regarded as unsaponifiable matter.

The latter represents the hydrocarbons, and the former the fat or fixed oil of the mixture, provided that waxes, including sperm and bottlenose oils and shark liver oils containing squalene or spinacene are absent.

When the nature of the fat or oil is known, and it is merely desired to estimate the proportion of hydrocarbon present, and not to ascertain its exact character, a very fair approximation to the truth can be obtained by ascertaining the saponification-equivalent of the sample.

The table on page 102 gives an outline of the processes described in the foregoing section.

IDENTIFICATION OF FATS AND FIXED OILS

The recognition of an unmixed fat or fixed oil may usually be effected by a careful application of the methods of examination already described. Systematic schemes for the purpose have been devised, but cannot be implicitly relied on, owing to the variable nature of the substances themselves. Most of the colour tests are of little value, unless confirmed by other indications.

In examining fats and oils for the detection of adulteration, the relative commercial value of the different kinds should be kept in view. In addition to the adulteration of the more valuable substances

From 5 to 10 grm. of the sample (previously melted by warming if necessary) are passed through a dry filter, unless already perfectly clear.

Residue may contain *curd, salt, water, sand,* and *insoluble matters* generally. It may be washed with ether, dried, and weighed; then ignited gently and weighed again, the loss being the *volatile matter*, mostly organic.	The Clear oil. (N. B.—If an aliquot portion of the clarified oil is not blackened when shaken with alcohol and ammonium sulphide, and leaves no notable ash on ignition, thus proving the absence of metallic compounds, the following treatments with water and dilute H_2SO_4 may be advantageously omitted. The clear oil is shaken in a separating funnel with water and ether. The aqueous solution is separated, and the oil solution again shaken with ether if the previous treatment was found to remove anything.			
	Aqueous liquid contains *soaps of the alkali metals.* It is evaporated to dryness at 100°, and the residue weighed and further examined if desired. The *alkali* may be titrated with H_2SO_4 and Methyl Orange, and the characteristics of the liberated fatty acids determined.	Oil solution. Agitate with dilute H_2SO_4 and separate. Wash residual oil repeatedly by agitation with water till the aqueous liquid no longer reddens litmus.		
		Acid liquid may contain sulphates of metals previously existent as soaps. Also *boric acid* from linseed oil driers, and *phosphoric acid from bone fat.	Solution of oil in ether. Add a few drops of phenolphthalein solution. Then add gradually, with repeated shaking, a solution of 2 grm. of NaOH in 10 c.c. methyl alcohol and 90 c.c. of water, in quantity somewhat greater than is sufficient to produce a permanent red colour. Then separate the undissolved oil without delay. Shake the oil and aqueous liquid respectively with slightly alkaline water and with ether, and add the washings to the main quantities.	
			Aqueous liquid. Add Methyl Orange and then dilute H_2SO_4 till acid reaction is obtained. Then add as much more dilute H_2SO_4, so as to convert alkali into $KHSO_4$. Shake or wash separated fatty acids with boiling water.	**Oil.** Evaporate off ether and saponify residual oil by alcoholic KOH. Boil off alcohol, dissolve soap in warm water, and shake cooled solution with ether. Separate and shake aqueous liquid a second and third time with ether. (In analysis of waxes, treatment of the dry soap with boiling toluene should be substituted for agitation of the solution with ether.)
			Oily layer consists of *insoluble fatty and rosin acids,* free in original sample or as soaps of Al or heavy metals. Collect by help of ether, evaporate, weigh, and further examine.	Aqueous liquid. Distil to small bulk, titrating distillate with barium hydroxide; then evaporate and weigh barium salts of *volatile fatty acids. Non-volatile soluble acids* in retort leave Na_2CO_3 when neutralised by NaOH and evaporated and ignited.

| Aqueous liquid contains *glycerol* and *soap,* formed by saponification of fixed oil of sample. Treated with dilute HCl, the weight of fatty acids obtained, multiplied by 1.055, gives approximately *neutral fixed oil* of sample. Glycerol may be determined in half of aqueous liquid. | Ethereal liquid evaporated at 100° leaves a residue which is weighed, and may contain *hydrocarbons, cholesterol, phytosterol, higher alcohols,* and *colouring matters.* |

with the cheaper, the use of hydrocarbons derived from the distillation of petroleum, shale, coal, and rosin, is also extensively practised.

In practice it is often of less importance to know the origin of a sample than whether it may be used as a substitute for the genuine oil. This may be ascertained with tolerable certainty, and, in some cases, the nature of the adulterants may be definitely detected.

By the following systematic method identification may generally be effected, and much information gained that will suggest the special tests, for the substances suspected to be present:

· 1. Place a drop of the oil on the back of the tongue by means of a glass rod and taste it carefully, avoiding too hasty a decision. In this manner marine animal oils, linseed, croton, mineral, rosin, and some other oils may often be detected. Rosin oil is remarkable for the nauseous after-taste produced by it. Rancidity may also be recognised by taste.

2. Heat a portion of the sample in a porcelain or platinum capsule to about 140 or 150°, and observe the odour carefully. When sufficiently cool, pour a little into one hand, rub with the other, and smell again. A little practice will allow of vegetable oils being readily distinguished from animal oils, and the products of fish and marine mammals from those of terrestrial animals. The odour on heating will also frequently permit the recognition of mineral and rosin oils, and, if the remainder of the sample be strongly heated till it ignites and the flame then blown out, the vapours will often have a characteristic odour.

3. Ascertain the sp. gr. of the sample at 15.5°, if fluid at that temperature but at the b. p. of water (page 65), if solid at the ordinary temperature. This test is valuable, but if the sample be very old, or a mixture of several substances, or if much free acid be present, the indications are less reliable. An unmixed substance may, as a rule, be placed in one of the groups on pages 105–106, though this classification must only be regarded as giving a rough preliminary indication. Many of the fats and oils might be classified in more than one of the groups. More definite figures are given in the tables on pages 109–113.

Sperm and bottlenose oils are readily distinguished from shale and petroleum products of similar density by the elaidin test, their saponification values and the quantitative results of their saponifi-

cation.   Their estimation, when mixed with hydrocarbon oils, may be effected as described under "Sperm Oil."   Oleic acid is distinguished from hydrocarbons by its solubility in an aqueous solution of sodium hydroxide.   Mixtures of oleic acid and hydrocarbons may be analysed by titration with standard alkali.   If fixed oils are present, the methods given on page 10 should be used.

Differentiation of Animal and Non-drying Vegetable Oils.—The non-drying vegetable oils may be distinguished from the similar oils of animal origin by their taste and odour on heating.   Their iodine values and the m. p. of their fatty acids are higher.   Many of the vegetable oils show absorption spectra, which is never the case with the animal oils.   The phytosteryl acetate test (*q. v.*) and the oleorefractometer reading are also valuable means of differentiation.

The vegetable non-drying oils may be distinguished from each other by various tests.   Rape and mustard oils are distinguished from others by relative insolubility in glacial acetic acid, by low saponification values, and by yielding small amounts of an insoluble bromide on treatment with bromine.   Bone oil usually gives an orange or reddish-yellow elaidin of a pasty consistence, whilst lard oil and tallow oil yield a firm product of a pale or lemon-yellow colour. The product from neatsfoot oil is variable.

Coconut olein is distinguished from other vegetable oils by its high saponification value, low iodine value, and the very moderate heating produced by sulphuric acid.

Differentiation of Semi-drying and Non-drying Oils.—The semi-drying oils, of which cottonseed and maize oils are typical, have higher iodine values and sp. gr. than the non-drying oils.   They may also be distinguished by the large amount of linolic tetra-bromide (m. p. 113 to 114°) which they yield on adding bromine to a solution of their insoluble fatty acids in petroleum spirit or carbon tetrachloride.   The nature of the product formed in the elaidin test is also instructive.

OILS

Sub-stance	Sp. gr. at 15° to 16°				
	0.875 to 0.884	0.884 to 0.912	0.912 to 0.920	0.920 to 0.937	0.937 to 0.970
Vegetable oils,	None.	None.	Jamba Apricot kernel Plum kernel Peach kernel Olive Almond Arachis Rape and Colza Mustard Ravison Hazelnut Eruca sativa seed. *Non-drying oils.*	Beechnut Brazil nut Camelene Candle nut Madia Maize Nigerseed Pine nut Safflower Cedar nut Soja bean Pumpkin seed Wheat Cotton-seed Kapok Sesame Sunflower Tomato seed Poppyseed Hempseed Linseed (raw) Perilla Walnut Coconut olein. Curcas. *More or less drying oils.*	Grapeseed. Tung. Croton. Castor. Boiled linseed. Blown oils. Chaulmoogra. oil.
Terrestrial animal oils,	None.	None.	Neatsfoot. Bone. Lard oil. Tallow Oil.	None.	None.
Marine animal oils,	Sperm. Bottle-nose.	None.	Dolphin.	Whale Porpoise. Seal. Menhaden. Codliver. Shark-liver. Sardine.	
Free fatty acids,	None.	Oleic acid.	Linolic acid.	. . . .	Ricinoleic acid.
Hydrocarbons,	Shale products. Petroleum products.	Shale products. Petroleum products.	Heavy petroleum products.	Heavy mineral oil.	None.

FATS

Substance	Sp. gr. at 98° to 100°			
	0.750 to 0.800	0.800 to 0.855	0.855 to 0.863	0.863 to 0.890
Vegetable fats,	None.	None.	Palm oil. Cacao butter. Shea butter.	Palmnut oil. Coconut oil. Japan "wax." Myrtle "wax." Cottonseed "stearin." Palmnut. "stearin." Bassia tallow. Borneo tallow. Chinese tallow. Goa butter. Laurel oil. Mafura tallow. Nutmeg butter. Piney tallow.
Animal fats,	None.	None.	Tallow. Lard. Suet. Dripping. Bone fat. Margarine.	Butter-fat. Compound lard.

WAXES, ETC.

Substance	Sp. gr. at 98° to 100°			
	0.750 to 0.800	0.800 to 0.855	0.855 to 0.863	0.863 to 0.877
Vegetable and animal waxes,	None.	Spermaceti. Beeswax. Chinese wax. Carnaüba wax. Wool fat.	None.	None.
Free fatty acids,	None.	Stearic acid. Palmitic acid. Oleic acid.	None.	None.
Hydro-carbons,	Paraffin wax. Ozokerite.	S h a l e a n d petroleum products.	Vaseline.	. . . .

The hydrocarbon oil produced by the distillation of rosin is not included in these tables, as its high sp. gr. (0.970 to 1.000) places it outside any of the classes. The same remark applies to rosin itself, which is of slightly higher sp. gr. than water, and to coal-tar products of high b. p. which might be mistaken for, or found mixed with, the fixed oils.

Differentiation of Drying and Semi-drying Oils.—The drying, oils differ from the semi-drying oils in having a higher iodine value, and in yielding a solid film in a short time, when exposed to the air in a thin layer. Some of them give bromides insoluble in ether on treatment with bromine, and an insoluble deposit of linolenic hexa-bromide (m. p. 180 to 181°) on brominating a solution of their fatty acids.

Differentiation of Drying and Marine Animal Oils.—These oils, which often have similarly high iodine values, are best distinguished by the behaviour of the deposit formed in the *insoluble bromide test* (*q. v.*) when heated, and the nature of the unsaponifiable matter. The sulphuric acid colour test and Livache's drying test will also afford valuable information in the case of mixtures. On saponifi-cation, marine animal oils give a much darker soap solution than lin-seed or other drying oils.

They may be distinguished from one another by their analytical values (see tables). Porpoise oil and some varieties of whale oil con-tain a notable proportion of esters of lower acids, and give charac-teristic Reichert-Meissl values.

Differentiation of Various Oils.—Oils of sp. gr. above 0.937 are few and easily distinguished. Croton and castor oil are purgative and readily soluble in alcohol, but have little further resemblance. Boiled linseed oil and Japanese wood (tung) oil have sp. gr. between 0.937 and 0.950, dry rapidly on exposure, and give a firm brown or black clot with sulphuric acid. Blown oils closely resemble castor oil, but may be distinguished as described in the section treating of that oil. Rosin oil has a sp. gr. exceeding 0.970, and is not saponi-fied to any considerable extent by alkalis. It is readily identified by its strong after-taste, and the odour of turpentine developed when the sample is heated till it catches fire and the flame then blown out. Mixtures of rosin oil with fatty oils may be analysed as described on page 90.

Hydrocarbons and Waxes.—The solid hydrocarbons having a density below 0.800 at the b. p. of water are described under "Paraf-fin Wax."

The distinctions between the various waxes are fully indicated in the table on page 88 and in the special sections on "Spermaceti," "Beeswax," and "Carnaüba Wax." Free acids are at once distin-guished from the waxes by their solubility in alcohol, behaviour with

alkalis, and their saponification values; from each other by their m. p. and combining weights. Vaseline and similar hydrocarbons are sharply distinguished from the waxes and fatty acids by being incapable of saponification.

Differentiation of Animal and Vegetable Fats.—These are best differentiated by the phytosteryl acetate test (*q. v.*), and distinguished from one another by a comparison of the various analytical values.

Coconut and palmnut oils are soft, melt readily, and have high saponification values, fairly high Reichert-Meissl values and low iodine values. Japan and myrtle wax are hard, wax-like substances of comparatively high m. p. (See " Japan Wax.") Palmnut oil is distinguished from coconut oil and coconut "stearin" by its taste and smell. Butter-fat is the only common fat of animal origin that has a high Reichert-Meissl value.

The nature of the sample having been indicated, further confirmation may be obtained by means of the tables beginning on page 109. The principal fats, oils, and waxes are described at greater length in the following sections.

In the case of a sample consisting of a *mixture of wholly unknown substances*, identification of the constituents is often a difficult problem, but when the leading component is known or can be recognised, the detection of the others' become more feasible. In most cases oils cannot be recognized by distinct and specific tests, such as exist for the different elements; and, in arriving at a conclusion as to the composition of any sample of mixed oils, the analyst must be content to be guided in a great measure by circumstantial evid^nce and a careful c nsideration of probabilities. The foregoing methods of examination are of course employed, and, in addition, such special tests as will be found described under the various heads. The sub-articles descriptive of the more important substances contain a list of the admixtures most commonly found in each together with special tests suitable for their detection.

PROBABLE VALUES OF FRESH OILS BASED ON RECORDED FIGURES

I. OLIVE OIL GROUP

Oil	Sp. gr. at 15.5°	Solidification point °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value	Acetyl value
Almond.................	0.914–0.920	−10 to −20	13–14	188–192	0.5	96	93–100	....
Arachis (earthnut).....	0.911–0.926	+ 3 to +10	27–30	186–194	0.5	95–96	83–101	....
Apricot-kernel.........	0.915–0.921	−14 to −20	3–5	188–193	....	....	100–109	....
Chaulmoogra oil.......	0.9471–0.9535	....	....	189–210	....	....	98–110	....
Hazelnut..............	0.916–0.917	−10 to −20	20–25	191–197	0.9–1.0	95.5	83–90	....
Olive.................	0.914–0.920	Turbid at +2	21–30	185–196	1–0.3	....	77–95	10–11
Olive-kernel...........	0.918–0.920	....	....	182–184	....	....	87–88	....
Peach-kernel..........	0.918–0.923	below −20	10	191–193	....	....	92–101	....
Plum-kernel...........	0.912–0.920	− 5 to − 8	13–15	191–192	....	....	100	....
Tea seed..............	0.917–0.927	− 5 to −12	....	190–194	0.1	96	88–90	....

II. RAPE OIL GROUP

Oil	Sp. gr. at 15.5°	Solidification point °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value	Acetyl value
Black mustard seed....	0.9155–0.9185	−17	16–17	173–175	....	96	104–120	....
Eruca sativa seed	0.915–0.918	....	....	169–174	0.1–0.8	95.5	97.5–99.5	....
Indian mustard seed...	0.916–0 921	....	....	172–180	0.3–0.9	95.5	102–108	....
Jamba................	0.915–0.916	−10 to −12	19–21	173–175	....	96.5	96–102	....
Radish seed...........	0.9163–0.9175	−10 to −17	20	174–178	0.3	96	93–96	....
Rape seed (colza)......	0.914–0.916	−10	16–21	170–175	0.0–0.7	94.5–96.5	97–105	14.5
Ravison..............	0 917–0.922	− 8	....	177–181	....	....	109–122	....
White mustard seed...	0.914–0.916	− 8 to −16	15–16	170–174	....	96–96.5	....	....

III. COTTONSEED OIL GROUP

Oil	Sp. gr. at 15.5°	Solidification point °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value	Acetyl value
Beechnut	0.9220–0.9275	−17	23	191–196		95–96	104–111	
Brazil-nut	0.9170–0.9180	0 to +3	28–30	193–194			95–106	
Cameline	0.920–0.9270	−18	13–14	188			135–152	
Cottonseed	0.9130–0.930	0 to −1	34–40	191–196	0.7–0.9	95–96	104–116	21–25
Cress seed	0.920–0.9240	−15	16–18	180–183	0.2–0.4	95.5	102–118	
Kapok	0.9208–0.9326		38	189–194			78–93	
Madia	0.923–0.9286	−10 to −20	23–26	193			121	
Maize	0.9213–0.9268	−10 to −12	17–22	186–193	4–4.5	93	115–128	11–11.5
Pumpkin seed	0.9200–0.9250	−15	26–28	188–193		96	121–130	
Sesame	0.9210–0.9240	− 4 to − 6	24–32	188–193	1–2	95–96	103–117	
Soya bean	0.9240–0.9270	+ 8 to 15	27–29	191–193		95.5	121–124	
Tomato seed	0.9220			187–192	0.1–0.3	95–96	107–125	11.4–20.5
Wheat	0.9240–0.9290	semi-solid at 0	39–40	183–190	2–3		115	

IV. LINSEED OIL GROUP

Oil	Sp. gr. at 15.5°	Solidification point °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value	Acetyl value
Candlenut	0.920–0.9260	below −18	20–21	189–195	1–2	95–96	140–164	10
Cedarnut	0.930–0.9320	−20	11–12	192	2.0	92–93	150–159	
Hempseed	0.928–0.9330	−15 to −28	17–28	190–195			145–166	
Lallemantia	0.9336	−35	22	185	1.5	93.5	162	
Linseed	0.9315–0.9410	−16 to −27	17–24	190–201	0	95–95.5	175–201	
Nigerseed	0.9248–0.9280	−8	25	186–192	0.11–0.63	95.5	126–134	
Perilla	0.9280–0.9310			187–191			185–204	
Pinenut	0.9215–0.9250	−18 to −20	16–19	191–193			166–120	
Poppy	0.9240–0.9260	−15 to −20	20	193–195	0.0	95.5	153–158 (?)	
Safflower	0.9251–0.9280			187–194	0	95.5	130–149	16.1
Sunflower	0.9240–0.9260	below −17	22–24	188–193			123–136	
Tung	0.9360–0.9430	+2 to +3 after keeping, below −17	30–49	191–196			96–96.5	155–166	
Walnut (nut)	0.9240–0.9268	−12 to − 24	15–20	190–197	0.0	94–94.5	139–148	

V. CASTOR OIL GROUP

Oil	Sp. gr. at 15°	Solidification point °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value	Acetyl value
Castor...............	0.960 ~0.967	−17 to −18	13	175–183	2.5	....	84–85	150
Croton..............	0.9426–0.9437	−8 to −18	17–19	205–215	12–13.5	88–90	102–109	20–39
Curcas..............	0.9190–0.924	+30	24–30	192–210	0.2–0.6	95.2	98–110	14–25
Grape seed..........	0.9350	−10 to −24	23–25	178–179	0.45	92.0	94–96	144.5

VI. CACAO BUTTER GROUP

Fat	Sp. gr.	M. p. °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value
Bassia tallow...................... (Mixture of Mohwah and Mahua butters)	0.9175 at 15° 0.8943 to 0.8981 at 100°	25–42	39.5–45	187–194	0.5–0.8	94.5–95	54–68
Borneo tallow......................	0.892 at 100°	37.5	53.5	192.4–196	....		30–31
Cacao butter......................	0.964–0.974 at 15° 0.8577 at 98°	30–34	48–53	192–195	0.2–0.9	....	32–42
Chinese tallow.....................	0.9180 to 0.9217 at 15°	36–46	39–57	179–203	0.2	....	23–38
Cotton oil stearin.................	0.867 at 100°	30–40	27–45	194.5	....	96.5	89–93
Goa butter........................ (Kokum butter)...................	0.911 at 50° 0.8889 at 100°	41–43	61.0	187–191.5	0.1–1.5	93.5–95.5	25–34
Laurel oil.........................	0.8806 at 98.5/11.5	32–36	....	198–199	1.6	....	68–80
Mafura tallow......................	0.902 at 40°/15°	29–40	51–55	201–221	1.5	....	43.5–56
Nutmeg butter.....................	0.945–0.996 at 15°	43–51	42.5	154–161	1–4.2	....	48–85
Palm oil...........................	0.9210–0.9245 at 15°	27–43	48–50	200–205	0.8–1.9	94.5–97	53–58
Phulwara butter (Karité fat)........	0.8970 at 100°/100	39	....	191	0.4	95	42
Piney tallow....................... (Malabar tallow)...	0.915 at 15° 0.8900 at 100°	36–42	56	189–191	0.2–0.4	....	38–39
Shea butter........................ (Galam butter)...................	0.9175 at 15° 0.859 at 99.5°/15.5°	23–28	39.5–56	179–192	....	94.8	56–67

VII. COCONUT OIL GROUP

Fat	Sp. gr.	M. p.	M. p. of fatty acids	Saponification value	Reichert-Meissl value	Hehner value	Iodine value
Coconut oil	0.9259 at 15° ⎫	20–28	24–25	246–262	6.6–8.4	82.5–90.5	8.2–9.5
(Coconut oil)	0.8736 at 100° ⎬						
Coconut "stearine"	0.8700 at 100°	29.3–29.5	28.1	252	3.4	....	4.0–4.5
Japan wax	0.984 to 0.993 at 15.5°	50.4–56	56 to 62	214–237.5		90–90.5	4.2–15
Macassar oil	0.924 to 0 942 at 15°	22–28	52.55	213–230	9	91–91.5	48–55
Myrtle wax	0.875 at 98–99/15.5°	40–88	47.5	206–217	0.5	....	1.9–3.9
Palm-nut (Palm kernel) oil	0.8731 at 99°/15.5	23–30	21–28.5	243–255	5 to 6.8	91–91.5	10.5 to 17.5
Palm-nut "stearine"	0.8700 at 100°	31.5–32	28 5–29.5	242	2.2	....	8

VIII. LARD OIL GROUP

Oil	Sp. gr. at 15.5°	Solidification point	M. p. of fatty acids	Sapon. value	Hehner value	Iodine value
Lard oil	0.913–0.919	−4 to +10	29–38.5	193–198	97	67–82
Neatsfoot	0.914–0.916	−2 to +10	29–41	191–200	93.5–91.5	66–74
Tallow oil	0.916	0 to + 6	....	193–200	....	60–78

Horsefoot and sheepsfoot oil not included since usually sold as neatsfoot oil. Reichert-Meissl value for neatsfoot oil, 0.9–1.2.

IX. TALLOW GROUP

	Sp. gr. at 15.5°	Sp. gr. at 98–100°	M. p.	Solidification point	M. p. of fatty acids	Sap. value	Reichert-Meissl value	Hehner value	Iodine value
Beef fat	0.8950	0.8626	42–50	31–38	41–47.5	196	0.3–0.5	96–96.5	36–42
Bone fat			44–45		42.5–44	190–196.3	0 2–1.7	94–95	52.0
Butter fat	0.909–0.913 at 38.5°		28–36		38–42	215.8–241.1	21.0–33.4	85–89.5	28–42
Horse fat	0.916–0.922		35–43		31–54	195–199.5	0.3	94.5–97.5	76–86
Lard		0.8600	30–44	27–30	37–47	195–203	0.2	93–95	47.5–64
Mutton fat	0.937–0.953		47–49		34–36	196	0.3	95	33–50
Tallow	0.925–0.940		38–50	34–46	41–49	193–198	0.2	95–96	33–48

X. WHALE OIL GROUP

Oil	Sp. gr. at 15.5°	Solidification point °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value
Codliver	0.922 to 0.930	−3	21–25	179–190	0.2	95.5	154–170
Menhaden	0.925 to 0.931	−4	....	189–193	1.0	....	139–174
Porpoise	0.926	....	....	203–253	46–56	68–72	30–125
Sardine	0.928–0.933	....	....	189–193	....	94.5	192–193
						(Japanese sardine oil,	181–188
Seal	0.924–0.9270	deposit at +3	22–23	190–193	0.2	93–96	130–152
Shark	0.916–0.9190	....	21–22	157–164	....	87–97	115–139
Whale	0.917–0.9237	....	14–18	184–194	0.7–2.0	93.5–96.5	116–128

XI. SPERM OIL GROUP

Oil	Sp. gr. at 15.5°	Solidification point °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value	Acetyl value
Bottlenose (Doegling)	0.876 to 0.881	....	10.5	123–130	1.4	....	80–85	....
Dolphin	0.918–0.922	deposit at −5	....	198	5–6	93	99.5	....
Sperm	0.878 to 0.884	....	13–14	120–137	1.3	....	80–84	4.4–6.4

XII. BEESWAX GROUP. WAXES

Wax	Sp. gr. at 15.5°	Sp. gr. at 98°–99°	M. p. °	Acid value	Sap. value	Iodine value	Acetyl value
Beeswax	0.959–0.970 }	0.818 to 0.827	62–66	17–22	88–98	8.5–11.5	15.2
usually	0.962–0.966 }						
Candelilla wax	....	....	68–70	17.0	51	....	....
Carnauba wax	0.995–1.000	0.842 to 0.850	83–86	4–8	79–84	13.5	55.2
Chinese insect wax	....	0.809 to 0.811	81–83	....	80–93	....	....
Montan wax	....	....	....	73	74.0	16.0	....
Spermaceti	0.942 to 0.946	0.808 to 0.816	42–49	0.0–1.8	126–134	3–4	2.6
Wool fat	0.970–0.973	....	39–42	....	82–130	17–52	....
(Lanoline)	0.973	....	36–43	0.6–2.8	81–102	10–31	108–122

SPECIAL CHARACTERS AND MODES OF EXAMINING FATS, OILS AND WAXES

By C. AINSWORTH MITCHELL, M.A., F. I. C.

I. OLIVE OIL GROUP

Arachis (Earthnut) Oil.	Olive Oil.
Almond Oil.	Olive-kernel Oil.
Apricot-kernel Oil.	Peach-kernel Oil.
Chaulmoogra Oil.	Plum-kernel Oil.
Hazelnut Oil.	Tea-seed Oil.

ARACHIS OIL. EARTHNUT OIL. GROUND NUT OIL. PEANUT OIL

(See also p. 109) Arachis oil is obtained from the nuts of *Arachis hypogæa*, a leguminous creeping plant indigenous to India and the coasts of South Africa and South America, and now cultivated in many countries, the oil being expressed chiefly in France. The seeds contain about 45% of oil, which in India is called *katchung oil*, and is largely used as a substitute for olive oil. Arachis oil is extracted by cold pressure and hot pressure, the cold pressed oil being extensively used as a salad oil and for burning, and the hot-pressed oil for soap-making.

The Indian or Mozambique nuts are usually decorticated before shipment to Europe. As they undergo "heating" on the voyage they cannot be used to produce the best edible oil and are mainly worked up for soap oils. The Bombay nuts yield a somewhat better quality and the largest nuts are those cultivated in Fiji. The greatest quantity of arachis nuts comes from Senegal.

Arachis oil is usually pale greenish-yellow, and of a peculiar nutty flavour and smell, but may be prepared nearly colourless and almost tasteless. It becomes turbid at about 3°, and solidifies at −3° to −4° (Schaedler). The sp. gr. at 15 to 15.5° usually ranges from 0.916 to 0.920, but values ranging from 0.911 (Sadtler) to 0.9256 (Crossley and Le Sueur) have been recorded.

Arachis[1] oil contains olein, hypogæin, linolin, palmitin, stearin, arachidin and lignocerin, probably as mixed glycerides.

Two specimens of arachis oil expressed from nuts of the Spanish and Virginian types respectively were found by Jamieson, Baughman and Brauns (*J. Amer. Chem. Soc.*, 1921, **43**, 1372) to have the following percentage composition:

Oil from	Oleic acid	Linolic acid	Palmitic acid	Stearic acid	Arachidic acid	Lignoceric acid	Unsaponifiable matter
Spanish nuts..	52.9	24.7	8.2	6.2	4.0	3.1	0.2
Virginia nuts..	60.6	21.6	6.3	4.9	3.3	2.6	0.3

The mixed fatty acids yielded a linolic tetrabromide.   No hypogæic or behenic acid was present.

Sadtler (*Amer. J. Pharm.*, 1897, **69**, 490) obtained the following results with arachis oil from various sources.

	Oil from Virginia nuts	Oil from Spanish nuts	Oil from African nuts	Oil from puducheri	Commercial oil
Sp. gr. at 15°..........	0.917	0.9175	0.911	0.920	0.9209
Saponification value.....	192.53	190.68	194.0	193.1	192.1
Iodine value...........	91.75	94.17	85.6	95.	98.4
Hehner value..........	94.87	95.31	....	....	95.86
Reichert-Meissl value....	0.48	1.60	....	....	....
Free acid as oleic, %.....	0.55	0.79	0.62	....	6.20
Cold test...............	+3°	+3°	+2°	....	+10°
Maumené test..........	56.75°	....	....	49°	45.5°
M. p. of fatty acids......	29°	34°	30	29°	28°
Solidifying point of fatty acids.................	27.5°	32.5°	29°	25°	25°

Crossley and Le Sueur (*J. Soc. Chem. Ind.* 1898, **17**, 989) recorded the following values given by 4 samples of genuine arachis oil from Madras.

[1] H. Meyer and R. Beer state that stearic acid and hypogæic acid are not present and that they have found the fatty acid of high melting-point isolated by Hehner and Mitchell to be a mixture of arachidic and lignoceric acids. (*Monatsh.*, 1913, 34, 1195–1208.)

	1	2	3	4
Sp. gr. at 15.5°......................	0.9223	0.9223	0.9256	0.9195
Saponification value.................	190.1	185.6	194.8	192.1
Iodine value.........................	98.47	98.42	92.43	100.82
Hehner value........................	95.63	......	......	......
Reichert-Meissl value...............	nil	nil	nil	nil
Free acid as oleic, %...............	1.45	2.42	8.28	6.80
Butyro-refractometer, 40°...........	......	57.5	......	......
Optical rotation, 200 mm., 15°.......	$-0°,7'$	$+0°,24'$	$\pm0°$	$-0°,7'$
Efflux time, Redwood, 70° F., (secs.) of 50 c.c..............	350.1	347.0	429.3	306.9

It will be seen from the foregoing that arachis oil exhibits a wide range of values. Schnell (*Zeit. Nahr. Genussm.*, 1902, **5**, 961) found several earthnut oils from West Africa with iodine values from 84.4 to 85.7; others, from the East Indies, had values ranging from 89.7; to 95.0. Values as high as 105 (Oliveri) and as low as 83.3 (Tortelli and Ruggeri) have been recorded.

Some oleo-refractometer values of this oil are given on p. 61. The following are some results of examination of the mixed fatty acids:

		Observer
Sp. gr. at 100°/15.5°.....................	0.846-0.8475	Allen.
Sp. gr. at 100°/100°.....................	0.879	Archbutt.
Titer test................................	28.1-29.2	Lewkowitsch.
Refractive index at 60°..................	1.4461	Thoerner.
Iodine value of mixed fatty acids..........	99.5-103.4	
Iodine value of liquid fatty acids..........	105-129	Various.

Arachis oil contains from 4.3 to 5.4% of arachidic and lignoceric acids, which, owing to their sparing solubility in cold alcohol, can be isolated without much difficulty. Olive and most other oils, except those of rape and mustard seed, contain not more than traces of these acids. Upon this difference in composition, Renard (*Compt. rend.*, 1871, **73**, 1330) based the following process for the detection and estimation of arachis oil, which is described with some modifications in detail introduced by Archbutt: (*J. Soc. Chem. Ind.*, 1898, **17**, 1124).

Renard's Process.—10 grm. of the oil are saponified in a deep porcelain basin with 8 c.c. of sodium hydroxide solution (containing approximately 50 grm. sodium hydroxide in 100 c.c.) and 70 c.c. of alcohol, boiled down gently to about 20 c.c., rinsed with hot water into a separating funnel, decomposed with hydrochloric acid in excess, and shaken with ether to extract the fatty acids. After distilling off the ether in an 8-oz. wide-necked flask, the fatty acids are dried by heating the flask on a steambath and sucking out the vapour, and are then dissolved by pouring 50 c.c. of rectified alcohol (sp. gr. 0.834) into the hot flask.

To the solution, which should not be hotter than 43°, and must not be allowed to cool below 38°, lest crystals of fatty acids should separate, 5 c.c. of a 20% aqueous solution of lead acetate are added, which will precipitate the whole of the arachidic and lignoceric acids as lead salts, together with some lead stearate and oleate.[1] After cooling to about 15° and allowing the flask to stand for half an hour, the alcoholic liquid is decanted through a filter, and the lead soaps are washed on the filter once with ether.   They are then rinsed back into the flask and digested with ether, again filtered and again rinsed back and digested with ether.   After this has been done about 4 times, the same filter being used each time, all the soluble lead salts will have been dissolved out.   The extraction with ether should be continued until the washings give no colour, or only a pale brown colour, when shaken with aqueous hydrogen sulphide.

The filter paper containing the lead arachidate, etc., is opened in a large plain funnel placed in the neck of a separating funnel, and, before the soaps have had time to dry, they are rinsed into the separator with a jet of ether from a washing bottle.   The soaps which adhere to the paper and flask may be decomposed and transferred by rinsing with warm dilute hydrochloric acid, followed by ether.   About 20 c.c. more hydrochloric acid (1.10 sp. gr.) are poured into the separator, which is stoppered and shaken until all the lead salts are decomposed.   The aqueous liquid is then run off, and the ethereal solution of the fatty acids washed with small quantities of water until the lead chloride is removed.   The ether is distilled off in an 8-oz. flask, and the residual fatty acids are heated in the water-oven until dry.   They are then dissolved by warming

[1] This quantity of lead is sufficient for 10 grm. of arachis oil.   If more is added, a larger precipitate is produced, containing more lead oleate, which takes more washing out with ether, but no more arachidic and lignoceric acids are obtained.

with 50 c.c. of 90% ethyl alcohol (sp. gr. 0.8340), and the solution is cooled to 15°, when arachidic and lignoceric acids, if present, will crystallise out, either at once or after standing a short time. The flask should be closed by a cork carrying a thermometer.

According to Tortelli and Ruggeri, (*Chem Zeit.*, 1898, 22, 600) a rough estimate of the amount of arachis oil present may be made at this stage by observing the temperature at which the crystals begin to form. For this purpose the liquid in the flask must be heated until the crystals have redissolved, and then allowed to cool slowly.

Temperature at which the crystals commence to form; °	Arachis oil; %
35–38	100
31–33	60
28–30	50
25–26	40
22–24	30
20.5–21.5	20
18–20	10
16–17	5

In order to estimate the proportion of arachis oil more accurately, the liquid is allowed to stand from 1 to 3 hours, with occasional agitation, at 15° or 20°, or at some intermediate temperature which is nearest to that of the laboratory, the crystals are then collected on a small filter placed over a 100 c.c. cylinder, the filtrate alone being used to rinse out the flask, and are washed several times with small quantities of 90% alcohol until the filtrate and washings measure 70 to 80 c.c., unless the quantity of crystals obtained is very small, in which case less may be used.[1] The filtrate and washings with 90% alcohol must be measured. The crystals are then washed thoroughly with 70% alcohol (sp. gr. 0.8898), in which arachidic and lignoceric acids are quite insoluble. These washings are not measured, but the washing is continued until a few c.c. of the filtrate remain clear when diluted with water in a test-tube, showing that all soluble fatty acids have been washed out. The washed crystals are then dissolved off the filter with boiling ether, distilled

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[1] It is a good plan to do this washing with 3 separate quantities of alcohol, either 10 c.c. or 5 c.c. each, according to the size of the precipitate, and, after collecting the washings each time in a small beaker, to pour them back through the filter 2 or 3 times, so as to saturate them thoroughly before adding them to the main filtrate. Obviously, this must be done at the same constant temperature as that at which the crystallisation took place. A paper filter may be used, but a Gooch filter used with moderate suction is better, because the crystals can be more completely separated from the mother liquor.

down in a tared flask, and dried in the water-oven until constant in weight, for which one hour or less usually suffices. Finally the m. p. is determined in a capillary tube, or preferably by Bensemann's method, and the point of incipient fusion should not be lower than 71°.

Instead of weighing the crystals at this stage, Tortelli and Ruggeri recommend redissolving them in 50 c. c. of 90% alcohol, recrystallising for 1 hour at the same temperature as before, again filtering and washing, first with 90% and then with 70% alcohol, and then weighing. The crystals from pure oil, when thus purified, melt, by Bensemann's method, at 72.3 to 73.3°.[1] This recrystallisation is essential in the case of some Tunisian olive oils (Archbutt *J. Soc. Chem. Ind.*, 1907, **26**, 454 and 1185) mixtures containing cottonseed oil (Tortelli and Ruggeri), and solid fats such as lard (Smith), (*J. Amer. Chem. Soc.* 1907, **29**, 1756), which contain large percentages of saturated fatty acids, and must always be resorted to if the m. p. of the first of crystals falls below 70°.

As the mixed acids are slightly soluble in the 90% alcohol used for recrystallisation and washing, a correction must be made, which was given by Renard as 0.0025 grm. for each 10 c.c. of 90% alcohol used in the crystallisation and washing of the acids, if the manipulation was conducted at 15°; or a correction of 0.0045 grm. per 10 c.c., if at a temperature of 20°. But Tortelli and Ruggeri have shown that the correction varies according to the weight of mixed acids obtained. The following table contains their experimental results:

Weight of fatty acids (grm.)	M. p. °	Solubility in 100 c.c. of 90% alcohol at			Obtained from
		15°	17.5°	20°	
2.7000	74.3–74.5	0.0729	0.0820	0.0910	More than 20 grm. arachis oil.
1.5600	75.1–75.5	0.0715	0.0801	0.0922	
1.2506	74.8–75.5	0.0730	0.0811	0.0902	
1.0000	74.3–74.5	0.0688	0.0866	0.0914	About 20 grm. of arachis oil.
0.9604	74.0–74.6	0.0680	0.0869	0.0918	
					20 grm. of a mixture containing.
0.5503	74.0–74.6	0.0650	0.0806	0.0879	50% arachis oil.
0.5008	74.0–74.6	0.0643	0.0799	0.0844	
0.3899	74.4–75.5	0.0602	0.0673	0.0740	40%
0.2615	74.0–75.0	0.0539	0.0610	0.0680	27%
0.1690	74.0–75.0	0.0447	0.0544	0.0662	18%
0.1064	74.0–75.0	0.0343	0.0402	0.0472	11%
0.0504	74.4–75.5	0.0301	0.0398	......	5%
0.0505	74.2–74.6	0.0314	0.0410	......	

[1] Tortelli and Ruggeri found the m. p. of the recrystallised acids, determined by the capillary method, to lie between 74° and 75.5°.

By plotting these results the following table of corrections has been constructed:

Weight of mixed acids obtained (grm.)	Correction (grm.) to be added per 100 c.c. of 90% alcohol used for crystallisation and washing at		
	15°	17.5°	20°
0.05	+0.031	+0.040	+0.046
0.10	0.036	0.045	0.052
0.20	0.048	0.056	0.062
0.30	0.055	0.064	0.071
0.40	0.061	0.071	0.078
0.50	0.064	0.076	0.084
0.60	0.066	0.080	0.088
0.70	0.067	0.082	0.090
0.80	0.069	0.083	0.092
0.90	0.700	0.084	0.092
1.00	0.071	0.084	0.091
2.70	0.073	0.082	0.091

The percentage of crude arachidic acid isolated from pure arachis oil by Renard, De Negri and Fabris, Allen, Tortelli and Ruggeri, and Archbutt has varied from 4.28 to 5.50%, averaging about 4.8%. Therefore, the weight of mixed acids obtained, multiplied by 21, is approximately equal to the weight of arachis oil in the quantity of oil taken for experiment.

The degree of accuracy obtainable by this method has been tested by experiments with known mixtures of olive oil and arachis oil. Thus, De Negri and Fabris, (Lewkowitsch, Oils, Fats and Waxes, 2, 253), working on 10 grm. of oil, obtained the following results:

Arachis oil taken, %.......... 30   20   15   10   10   10   10
Arachis oil found, %.......... 29.1 20.2 14.0 10.3   ?   9.5   ?

Tortelli and Ruggeri, working on 20 grm. of a mixture of olive, sesame, rape, cotton, maize, and arachis oils, and recrystallising the crude arachidic acid, obtained the results set out in the following table:

Compn. of oil tested		Volume of alcohol / Temperature / Solubility Coefficient	Arachidic and lignoceric acids				M. p. °	% of arachis oil found
Arachis oil	Olive oil		Dissolved in 90% alcohol	Weighed	Total in 20 grm. oil	%		
100	..	260 c.c. / 15° / 0.068	0.1768	0.8894	1.0662	5.3300	{ 74.1 — 74.3 }	100.0
60	40	150 c.c. / 17.5° / 0.08	0.1200	0.5231	0.6431	3.2155	{ 74.0 — 74.6 }	60.0
50	50	250 c.c. / 15° / 0.06	0.1500	0.3931	0.5431	2.7155	{ 74.0 — 74.6 }	5 .0
40	60	280 c.c. / 15° / 0.06	0.1509	0.2770	0.4279	2.1395	{ 74.5 — 75.1 }	40.0
30	70	260 c.c. / 15° / 0.05	0.1300	0.2056	0.3356	1.6780	{ 74.1 — 74.6 }	31.0
20	80	250 c.c. / 15° / 0.046	0.1150	0.1260	0.2410	1.2050	{ 73.9 — 74.4 }	22.0
10	90	220 c.c. / 15° / 0.031	0.0682	0.0514	0.1196	0.5980	{ 72.2 — 74.6 }	11.0
5	95	150 c.c. / 15° / 0.03	0.0434	0.0241	0.0675	0.3375	{ 73.0 — 73.5 }	6.7

Archbutt, using 10 grm. of oil and following the method already described, obtained the results given below:

Composition of oil taken		Volume of 90% alcohol	Mixed arachidic and lignoceric acids					Arachis oil found, %
Olive oil	Arachis oil	Temperature / Solubility Coefficient	Dissolved in the alcohol	Weighed	Total	%	M. p. by capillary tube	
	100	80 c.c. / 15° / 0.063	0.0504	0.4480	0.4984	4.98	71°	
90	10	73 c.c. / 15° / 0.031	0.0226	0.0265	0.0491	0.491	71°	9.9
80	20	73 c.c. / 15° / 0.033	0.0241	0.0715	0.0956	0.956	71°	19.2

Instead of isolating the arachidic acid by fractional precipitation of the free fatty acids with lead acetate, as described above, Lewkowitsch (Oils, Fats and Waxes, Vol. 2, 252) prefers to neutralise the soap solution with acetic acid, with the use of phenolphthalein as indicator, and to precipitate the whole of the soaps with lead acetate in excess. The lead salts are filtered off and extracted with ether in a Soxhlet.apparatus, thus separating the lead salts of the unsaturated fatty acids from the insoluble lead salts of the saturated fatty acids. The latter are then decomposed with hydrochloric acid in the presence of ether, and the ethereal solution having been separated and the ether distilled off, the residual fatty acids are dissolved in alcohol and crystallised as already described.

Tortelli and Ruggeri proceed in a somewhat similar manner. They take 20 grm. of the sample, saponify with alcoholic potassium hydroxide and neutralise with acetic acid. The neutral soap solution is poured gradually into a wide-necked flask containing a boiling-hot solution of 20 grm. of lead acetate in 300 c.c. of water, and the whole is well shaken for 10 minutes in boiling water. The lead salts are thus caused to adhere to the walls of the flask, and the clear liquor having been poured off, the soaps are washed three times with hot water, then cooled, dried with filter-paper, and boiled with

220 c.c. of ether for 20 minutes under a reflux condenser.   After the flask has been cooled in running water for half an hour, the ethereal solution is passed through a filter-paper into a separating funnel, and the residue again boiled with 100 c.c. of ether.   This is poured through the filter, and the insoluble soaps are then brought on to the filter and thoroughly washed with ether.   The ethereal solution of the lead salts of the unsaturated acids is decomposed with hydrochloric acid, and the fatty acids obtained are used for the silver nitrate test for cottonseed oil and the furfural test for sesame oil, which are said to be absolutely characteristic under these conditions, since neither test is given by the unsaturated fatty acids of any other edible oil.   The lead salts of the saturated acids are decomposed with hydrochloric acid in presence of ether, and the crude arachidic acid is isolated in the manner already described.

F. Jean (*Rev. de Chim. Ind.*, 1898, 9, 162) has proposed a process based upon qualitative tests by Girard and Blarez.   10 grm. of the oil are saponified by being heated at 110° with a mixture consisting of 3 grm. of potassium hydroxide dissolved in 3 or 4 c.c. of water and 5 c.c. of alcohol at 36°.   The mass is well stirred with a spatula, the heating continued till the soap becomes dry, when it is transferred to a flask and mixed with 100 c.c. of alcohol at 36° previously saturated with potassium arachidate at 11° to 12°. The flask is warmed under a reflux condenser until the soap dissolves, and is then left for 12 hours at a temperature of 15°.   The precipitate is filtered off and re-crystallised in the same way from the saturated alcohol.   It is then collected, transferred to a flask, and boiled with 50 c.c. of water containing some hydrochloric acid, in order to liberate the arachidic acid.   The latter is subsequently extracted with petroleum spirit in a separating funnel, and after evaporation of the solvent, dried at 100° and weighed.   Its m. p. should not be lower than 72°.

Bellier's Test.—J. Bellier (*Ann. Chim. Anal.*, 1899, 4, 4) has proposed the following simple qualitative test for arachis oil in olive oil, which Archbutt also recommends from personal experience.   Solutions required are:

Alcoholic potassium hydroxide, made by dissolving 8.5 grm. pure potassium hydroxide in 70% alcohol and making up to 100 c.c.

Acetic acid of such strength that 1.5 c.c. will exactly neutralise 5 c.c. of the alkali solution [120 c.c. of British Pharmacopœia

(36%) acetic acid diluted with water to 150 c.c. is, approximately, of the right strength].

Weigh 1 grm. of the sample into a dry boiling tube, add 5 c.c. of the alkali solution and boil gently over a small flame, holding the tube in the hand, until saponification is complete, which will take rather more than 2 minutes, avoiding evaporation as far as possible. Add 1.5 c.c. of the acetic acid, or just sufficient to neutralise the 5 c.c. of alkali solution, mix well, rapidly cool by placing in water at 17° to 19° and leave in the water for about 30 minutes (not less), shaking occasionally. Then add 50 c.c. 70% alcohol containing 1% by volume of hydrochloric acid (1.16), shake well, and again place in the water for 1 hour. If no arachis oil is present, a clear or opalescent liquid is formed; if more than 10% of arachis oil is present, a flocculent, crystalline precipitate remains; even with 5% of arachis oil a distinct precipitate remains and separates on standing.

Industrial neutral olive oils, known in commerce as "Saponified Oils" and prepared from the olive residuum oils and oils of the third pressing, which frequently contain as much as 3% or even more of unsaponifiable matter, apparently derived from the shell of the olive kernel, may give a flocculent precipitate in Bellier's test, though free from arachis oil.

For the *quantitative* estimation of arachis oil, Bellier takes 5 grm., saponifies with 25 c.c. of the alcoholic alkali solution, exactly neutralises with acetic acid, and places in running water for 1 hour. The precipitate is collected on a filter, and washed with 70% alcohol containing 1% of hydrochloric acid (1.16) at 15°-20°, until the filtrate does not become perceptibly turbid on the addition of water. The residue is dissolved off the filter with 25 to 50 c.c. of boiling rectified alcohol, which is then mixed with sufficient water to reduce the strength to 70%, and kept at 20° for 1 hour. The crude arachidic acid is filtered, washed with 70% alcohol free from hydrochloric acid, and weighed. The m. p. should be about 72°. By this process, Bellier obtained 4.2% of crude arachidic acid from Bordeaux earthnut oil and 4.17% from a sample of Marseilles oil. A large number of European and African olive oils which were examined yielded from nil to 0.060% of fatty acid, the latter amount, corresponding to 1.44% of earthnut oil, being obtained from an oil from Tunis. Known mixtures of olive oil and arachis oil gave correct results when analysed by this process. Samples of cotton-

seed oil and sesame oil also gave small quantities of insoluble acids corresponding to 0.72 and 0.48%, respectively, of earthnut oil. This process is much shorter than Renard's, but needs further investigation. Archbutt has obtained good results by the qualitative, but low results by the quantitative method.

Bellier's test has been very carefully investigated by Evers (*Analyst*, 1912, **37**, 487) who has confirmed the statement that low results are obtained by this process as usually carried out.

He has compared the method with Renard's process and obtained the following results:

TABLE I

Oil	Renard			Bellier		
	Arachidic acid, %	M.p., °C.	Arachis oil, %	Arachidic acid, %	M.p., °C.	Arachis oil, %
Arachis (A)...............	4.59	73.5	....	3.56	71	78
Arachis (B)...............	5.15	72.0	....	3.76	71	83
Olive oil, Nice superfine....	0	....	....	0	....	....
Olive oil, "seconds"........	0 .	....	....	Trace	....	....
Olive oil, Malaga....	0	....	....	Trace	....	....
Olive oil, 50% Arachis (A), 50% }........	2.28	73.5	50	1.36	72	30

Evers suggests that the low results obtained may be due either to the solubility of arachidic and lignoceric acids in 70% alcohol or to the incomplete precipitation of the fatty acids on account of their solubility in the strong solution of oleic and other fatty acids. Renard (*Compt. rend.*, **73**, 1330) states that arachidic and lignoceric acids are quite insoluble in 70% alcohol, but Evers contests this statement and having prepared these acids from arachis oil by Renard's process, obtained the following mean values for their solubility in 70% alcohol under the stated conditions.

About 0.2 grm. fatty acid was dissolved in 93% alcohol and sufficient water added to reduce the strength of alcohol to 70%. After standing for several hours the liquid was filtered and a measured volume evaporated to dryness, the solubilities given below being calculated from the weight of residue.

TABLE II

Melting point	Solubility, grams per 100 c.c.	
	At 13°	At 18°
71° C.	0.016	0.023
72° C.	0.012	0.017
73° C.	0.009	0.012

The solubility was also determined when the fatty acids were washed on a filter paper, about 0.2 grm. being used. Thus:

M. p., °	Grams dissolved per 100 c.c.
71	0.008
72	0.006
73	0.005

From the foregoing and other figures, Evers has drawn up Table III giving the corrections for practical working, and as a result of his experiments he has modified the process as given below.

TABLE III

Weight of acids (corrected for 90% alcohol)	Correction per 100 c.c., 70% alcohol		
	M. p., 71°	M. p., 72°	M. p., 73°
Above 0.10 grm.	0.013 grm.	0.008 grm.	0.006 grm.
0.08–0.10 grm.	0.011 grm.	0.007 grm.	0.005 grm.
0.05–0.08 grm.	0.009 grm.	0.007 grm.	0.005 grm.
0.02–0.05 grm	0.007 grm.	0.006 grm.	0.005 grm.
Less than 0.02 grm.	0.006 grm.	0.005 grm.	0.004 grm.
Factor for conversion of percentage of fatty acids to arachis oil.	17	20	22

Modified Renard's Process.—Weigh out 5 grm. of the oil into a flask, add 25 c.c. of alcoholic potassium hydroxide (80 grm. potassium hydroxide dissolved in 80 c.c. water and diluted to a litre with 90% (by vol.) alcohol), and saponify for about 5 minutes under a reflux condenser. To the hot soap solution add 7.5 c.c. of acetic acid (1 vol. of glacial acetic acid to 2 vol. of water) and 100 c.c. of 70% alcohol containing 1% (by vol.) of hydrochloric acid, and cool to 12° to 14° for an hour. Filter and wash with 70% alcohol containing 1% of hydrochloric acid at 17° to 19°, the precipitate being broken up occasionally by means of a platinum wire bent into a loop. Continue the washing until the filtrates give no turbidity with water, the washings being measured. Dissolve the precipitate, according to its bulk, in 25 to 70 c.c. of hot 90% alcohol, and cool to a fixed temperature between 15° and 20°. If crystals appear in any quantity, allow the vessel to stand at this temperature for 1 to

3 hours, filter, wash with a measured volume of 90% alcohol (about half the volume used for crystallisation), and finally with 50 c.c. of 70% alcohol.   Wash the crystals with warm ether into a weighed flask, distil off the ether, dry at 100°, and weigh.   If the melting point is lower than 71°, recrystallise from 90% alcohol.   Add the correction for the solubility in 90% alcohol as in Renard's process, from the table given by Archbutt (see p. 123), and also for the total volume of 70% alcohol used in the precipitation and washing (including the 100 c.c. added in the first instance) from Table III.

TABLE IV

Oil	Alcohol used for crystalli- sation, %	Weight of crystals, grm.	Correction for 90% alcohol. grm.	Correction for 70% alcohol. grm.	Total	%	M. p., °	% of arachis oil by factor
Arachis (A)	90	0.160	0.040	0.027	0.227	4.54	73	100
	70	0.218	....	0.065	0.283	5.66	71	96
Arachis (B)	90	0.163	0.045	0.032	0.240	4.80	72	96
	70	0.233	....	0.068	0.301	6.02	71	102
Arachis (C)	90	0.152	0.054	0.034	0.240	4.80	72	96
Arachis (D)	90	0.194	0.033	0.028	0.255	5.10	72	102
Arachis (A), 50%...... Olive "Nice," 50%....	90	0.056	0.032	0.022	0.110	2 20	73	48
	70	0.090	....	0.055	0.145	2.90	71	49
Arachis (A), 35%..... Olive "Nice," 65%....	90	0.045	0.020	0.029	0.094	1.88	71	32
	90	0.029	0.040	0 020	0.089	1.78	72.5	37
	70	0.059	....	0 040	0 099	1.98	71	34
Arachis (A), 20%....... Olive "Nice," 80%..	90	0.024	0.012	0.019	0.055	1.10	71	19
	70	0.030	....	0.024	0.054	1.08	71	18
Arachis (C), 20%....... Olive "Malaga," 80%..	90	0.012	0.020	0.015	0.047	0.94	72	19
	70	0.021	....	0.027	0.048	0.96	71	16
Arachis (A), 10%...... Olive "Nice," 90%.. ..	90	0.009[2]	0.008	0.008	0.025	0.50	73	11
	70	0.008	....	0.015[1]	0.023	0.46	70	8
Arachis (B), 10%.... . Olive "Nice," 90%.. ..	90	0	....	....	....	0	......	......
	70	0.012	....	0.018	0.030	0.60	71	10
Arachis (C), 10%.... . Olive "Malaga," 90%...	90	0	....	....	....	0	......	......
	70	0.011	....	0.016	0.027	0.54	71	9
Arachis (A), 5%....... Olive "Nice," 95%....	70	0.007	....	0.012[1]	0.019	0.38	......	6.5
Sesame	90	0	....	....	....	0	......	......
	70	0.012	....	....	....	0.24	64	......
Cottonseed	90	0	....	....	....	0	......	......
	70	0.006	....	....	....	0 12	50–55	......
Olive "saponified"....	90	0.014	....	....	....	0.28	64–67	......
	70	0.021	.....	....	....	0.42	64–68	......

[1] In these cases the correction has been added for melting point 71°.
[2] This result was obtained by recrystallising the fatty acids obtained from 70% alcohol from 10 c.c. of 90% alcohol.

If there are no crystals from 90% alcohol, or only a very small amount, add a sufficient quantity of water to reduce the strength of the alcohol to 70% (31. c.c. of water to 100 c.c. of 90% alcohol). Crystallise at 17° to 19° for an hour, filter, wash with 70% alcohol and weigh as before, adding the correction for 70% alcohol from Table III. If the melting point is below 71° recrystallise from a small quantity of 90% alcohol, or again from 70% alcohol.

The results obtained by this method are given in Table IV.

The following oils gave no crystals: Olive oils, including "Nice superfine," "Nice seconds," "Malaga," and eight of unknown origin, almond, poppy and rape oils. "Saponified" olive oil on the other hand usually gives crystals (see Olive Oil, page 156).

The qualitative method of Bellier has been shown by Franz and Adler (Abst. *J. Soc. Chem. Ind.*, 1912, 30, 691) to be capable of yielding approximately quantitative results by determining the temperature at which turbidity is first produced. For this purpose they give the following table of "temperatures of crystallisation."

Oil	Temperature of crystallisation	Oil	Temperature of crystallisation
	°C.		°C.
Olive oil..............	11.8–14.3	Arachis oil, 50%.......	33.8
Arachis oil, 5%........	15.9–17.0	Arachis oil, 60%.......	35.3
Arachis oil, 10%........	19.8	Arachis oil, 70%.......	36.6
Arachis oil, 20%........	25.7	Arachis oil, 80%..... .	38.0
Arachis oil, 30%........	29.2	Arachis oil, 90%.....	39.3
Arachis oil, 40%........	31.5	Arachis oils..........	40.0–40.8

Revis and Bolton have had the opportunity of noting these "temperatures of crystallisation" for a considerable number of mixtures and find them to give most useful indications, which are approximately correct in the majority of cases. In connection with this application of the test, H. Lüers (*Zeit. Unters. Nahr. Genussm.*, 1912, 24, 683) draws attention to a turbidity given by certain olive oils which were proved to be free from arachis oil, and he states that the addition of 3 drops of glacial acetic acid, in addition to the dilute acetic acid, prevents the formation of this turbidity.

In the examination of samples of arachis oil for adulterants, an estimation of the crude arachidic acid should be made, as it is the

most characteristic test for this oil.   Tortelli and Ruggeri found the following percentages in arachis oil from different sources:

Description of arachis oil	Crude arachidic acid; %	M. p.; °
Buenos Ayres, expressed at 45° to 50°......	5.24	74.4–74.7
Buenos Ayres, extracted with ether...	4.92	74.2–74.8
Ruffisque, extra, 1st pressing..............	4.31	74.2–74.6
Ruffisque, fine, 2d pressing.................	4.55	74.4–75.2
Gambia, extra, 1st pressing.......	4.59	74.5–75.1
French (commercial oil)................. .	5.33	74.1–74.4
Spanish (commercial oil)...........	5.40	74.3–75.4

Separation of Magnesium Arachidate.—Thomas and Yu (*J. Amer. Chem. Soc.*, 1923, **45**, 115) have based a method of estimating arachidic and lignoceric acids upon the relative insolubility of their magnesium soaps in 90% alcohol, 100 grm. of which at 25° dissolves only 0.006 grm. of magnesium lignocerate, but 8.60 grm. of magnesium oleate.

For the estimation 10 grm. of the oil are saponified for 30 minutes with a mixture of 50 c.c. of 5% alcoholic potassium hydroxide and 50 c.c. of 95% alcohol.   The soap solution is neutralised, while still warm, with 20% alcoholic acetic acid, then made just alkaline to phenolphthalein, and treated with 25 c.c. of a solution of 50 grm. of magnesium acetate, prepared by boiling a 50% aqueous solution of the salt, filtering, and diluting the filtrate with 3 times its volume of 95% alcohol.   After standing overnight the insoluble magnesium soaps are filtered off and washed with 30 c.c. of 90% alcohol, and then boiled for 5 minutes with 100 c.c. of 5 N-hydrochloric acid.   The liberated fatty acids are precipitated with cold water, thoroughly washed, and extracted with 3 portions (20 c.c. each) of warm 90% alcohol, and the solution left for 12 hours at 20° to 25°.   The resulting crystals are separated and washed twice with 10 c.c. of 90% alcohol and then with 70% alcohol until the washings give no turbidity with water.

The volume of the filtrate and washings is measured, the solid acids washed into a weighed beaker with alcohol, the solvent evaporated, the residue dried at 80° and weighed, and a correction applied for the lignoceric and arachidic acids dissolved by the filtrate and washings.

Assuming arachis oil to contain 5% of the mixed acids, an estimate, accurate to within about 5%, can be made of the amount of arachis oil in cottonseed or olive oils, but as magnesium erucate and elæomargarate are also insoluble in 90% alcohol, the method cannot be used for estimating arachis oil in the presence of rape or tung oil. It should be noted that hydrogenation of arachis oil does not interfere with the tests for arachidic acid.

Sesame oil should always be looked for, as it is frequently present in large quantity. Soltsien (*Chem. Rev. Fett. Ind.*, 1901, **8**, 202) found it by the Baudouin test in all samples of commercial arachis oil examined by him, and states that it is customary to add sesame oil to the finest grades of arachis oil with the object of lowering the cold test and improving the miscibility of the oil for salads. As arachis oil is frequently offered as a lubricating oil in place of olive oil, the absence of sesame oil is important, as even genuine arachis oil has more strongly marked drying properties than olive oil, and any addition of sesame oil increases the tendency to oxidise. Sesame oil may be detected by the furfural test. It will raise the sp. gr., also the iodine, and oleo-refractometer values. Sesame oil contains more linolic acid than arachis oil.

Poppy oil would also raise the sp. gr., iodine value and oleo-refractometer value of arachis oil, and would lower the solidifying point of the oil and of its mixed fatty acids, as well as increasing in a marked degree the tendency to oxidise.

Cottonseed oil would be indicated by Halphen's colour test and the reaction with nitric acid, and by the much higher iodine value of its liquid fatty acids and much larger yield of tetrabromides.

A rapid method of detecting arachis oil in cottonseed oil has been devised by Biazzo and Vigdorcik (see p. 153).

Rape oil would lower the saponification value and increase the viscosity in a marked degree.

ALMOND OIL

(See also p. 109.) Almond oil is a fixed oil expressed from either sweet or bitter almonds, the kernels of *Prunus amygdalus*. The oil of commerce is mostly obtained from bitter almonds (*P. amygdalus amara*), the marc of which is then distilled with water to obtain the essential oil. Fixed oil of almonds must not be confounded with

the essential oil of bitter almonds.   It is largely employed in the preparation of ointments and emulsions, for which it is better adapted than olive oil.

Rosenthaler (*Ber. Deut. Pharm. Ges.*, 1922, **32**, 237) found sweet almonds to contain 45.3 to 67.1% of oil, with an average of 58.9%. The average oil content in almonds not exceeding 1 grm. in weight, was   60.5%   and   in   those   exceeding   1.5   grm.   in   weight 55.3%.

The amount of oil in bitter almonds ranged from 35.5 to 62.5%, the average being 51.3%.   Pronounced variations in the oil content according to the weight of the kernel were not observed in the case of bitter almonds.

Almond oil is nearly odourless, of a straw-yellow colour and bland taste.   It does not solidify till cooled to about $-20°$, some samples only becoming turbid at that temperature.   According to the German Pharmacopœia, almond oil should remain clear when exposed to a temperature of $-10°$.   The sp. gr. ranges from 0.914 to 0.920.[1] It is soluble in 24 parts of cold alcohol or in 6 parts at the b.p.   It consists chiefly of olein and a small quantity of linolin (Farnsteiner, *Zeit. Nahr. Genussm.*, 1899, **2**, 1).   Only small quantities of solid glycerides are present, and no stearin (Hehner and Mitchell.   *Analyst*, 1896, **21**, 316).   It is not a drying oil and, according to Lewkowitsch, does not easily turn rancid.

The chief physical and chemical constants of this oil are given on p. 109 and the oleo-refractometer value on p. 61.   7 samples of oil from sweet and bitter almonds tested by Lewkowitsch (*Analyst*, 1904, **29**, 105) in the butyro-refractometer at 40° gave numbers ranging from 56.5 to 57.5.   The refractive indices of 35 samples determined by Harvey (*J. Soc. Chem. Ind.*, 1905, **24**, 717) in the Abbe refractometer ranged from 1.4702 to 1.4709 at 20°.

The mixed fatty acids have an exceptionally low m. p. (see p. 133). According to the German Pharmacopœia, they should remain permanently fluid at 15°, should give a clear solution with an equal volume of alcohol at 15°, and this solution should remain clear on adding twice the volume of alcohol.

The following are some further results of the examination of the mixed fatty acids of almond oil:

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[1] Most observers give a smaller range (0.9175 to 0.920 at 15.5°).

	Sweet almonds	Bitter almonds	Observer
Solidifying-point ("titer" test).....	9.5–10.1	11.3–11.8	Lewkowitsch
Refractive index...................	1.4461	1.4461	Thoerner
Iodine value of mixed fatty acids...	93.5–95.5	94.1–96.5	De Negris and Fabris
Iodine value of liquid fatty acids...	101.7	....	T o r t e l l i and Ruggeri

Commercial Almond Oil.—Almond oil is frequently adulterated with, and sometimes entirely substituted by peach-kernel or apricot-kernel oil, which is sold in England as "foreign almond oil," or "oil of sweet almonds, French" (*oleum amygdalarum gallicum*). Genuine almond oil is sold under the name of "Almond oil, English." Olive, lard, arachis, rape, sesame, cottonseed, and poppy oils are also liable to be employed as adulterants.

Many of these additions may be detected by observing the absorption spectrum of the sample, almond oil differing from most vegetable oils in not giving either a banded spectrum or producing strong absorption in the red or violet.

Lard oil and olive oil are indicated by the formation of a white granular deposit when the sample is exposed to a temperature of −5° for 20 minutes, by the high m.p. of the mixed fatty acids and by their incomplete solubility in alcohol at 15°. Lard oil will be further indicated by the odour developed on warming the sample, and especially by the phytosteryl acetate test (see under "Cholesterol").

Arachis oil may be detected by Renard's test (see "Arachis Oil"); *rape oil* by the reduced sp. gr. and saponification value of the sample; *cottonseed oil* by Halphen's colour test, as well as by the high m. p. of its mixed fatty acids and its marked drying properties; *sesame oil* by the Baudouin colour test; and *poppyseed oil* by the increased iodine value and refractive power of the sample.

The detection of the last-mentioned oils presents no great difficulty. It is otherwise with *apricot-kernel* and *peach-kernel* oils, which so closely resemble almond oil that the ordinary tests are not available. Apricot-kernel oil has a somewhat higher average iodine value than almond oil, but the difference is not great enough, and the results given by almond oils from different sources are too variable, for any definite conclusion to be based upon this test in the case of mixtures. Further investigation of the liquid fatty acids might lead to a test

based upon a difference in the yield of tetrabromides, as Lewkowitsch has suggested, and an observation by Dieterich that the critical temperature of solution determined by Crismer's method (p. 84) of almond oil is much lower than that of apricot-kernel oil or peach-kernel oil is also worth following up.

Ross and Race (*Analyst*, 1911, **36**, 263) have compared certain analytical figures for almond and apricot oils, and for the fatty acids obtained from them by fractional distillation; from their results they conclude that the composition of the two oils is so similar thay they may, for practical purposes, be considered identical.

This statement is most unfortunate and misleading, for it is obvious that the purchaser of almond oil would be greatly defrauded if he were to be sold apricot-kernel oil, which is usually less than half the price. C. A. Hill (*ibid.*) records his disagreement with the statement that the oils may be considered as identical. The same authors have shown that notwithstanding the similarity in general composition, apricot-kernel oil is distinguished by means of the Bieber reaction (*infra*) and that the chromogenic substance, which is not volatile, is not destroyed by subjecting the oil to steam distillation for some hours. Moreover, they found that even in the case of a sample a year old, through which air was blown while warm for 3 days, the Bieber reaction was still so strong that as little as 5% could be detected when mixed with almond oil.

The following table gives the limits of the figures obtained from the analysis of 4 samples of almond and 3 samples of apricot-kernel oil bought commercially and for 1 sample sold as peach-kernel oil.

	Limits of four samples of almond oil	Limits of three samples of apricot-kernel oil	Peach kernel
Iodine value	97 to 102	100 to 106	101.6
Saponification value	183.3 to 207.6	184 to 192.4	191.7
Sp. gr., $\frac{15°}{15°}$	0.9178 to 0.9199	0.9198 to 0.9200	0.9167
Ref. index at 40° (Zeiss)	57.5° to 58°	57° to 58.5°	55.5°
Bieber reaction	nil.	strong	strong

FATTY ACIDS

Saponification value	200.4 to 207	197 to 202	201.6
Ref. index at 40° (Zeiss)	56° to 58°	57° to 59°	53°

Acidity.—The acidity of 23 samples of almond oil has been esti-
mated by J. C. Umney (*Perf. and Essent. Oil Record*, 1914, 5, 101)
who found it to range from 0.6 to 9.2% for acid calculated as oleic,
and that an oil of high acidity was satisfactory in odour and lustre
after keeping 6 months. Apricot oil, on the other hand, was not
satisfactory in these respects after 12 months. 34 samples of peach
and apricot-kernel oils were found to have acidities ranging from
0.6 to 5.97% (as oleic acid). Lewkowitsch (*Analyst*, 1904, 29, 106)
gives the following table of figures.

Description of oil	Sp. gr.	Saponification value	Iodine value	Butyrorefrac-tometer at 40° C., deg.	Free fatty acids[1]	Fatty acids		Bieber's test
						Neutral-isation value	Saponi-fication value	
Almond oils expressed from:								
1. Valencia sweets....	0.91995	207.6	99.4	57.5	2.61	207 8	207.6	Colourless.
2. Blanched valencia sweets.............	0.9182	191.7	103.6	57.5	1.46	196.4	201.7	Colourless.
3. Sicily sweets........	0.9178	183.3	100.3	57.0	0.39	198.8	202.2	Colourless.
4. Mazagan bitters....	0.9180	188.6	102.5	56.5	1.56	196.8	203.1	Colourless.
5. Small Indian al-monds............	0.91907	189.2	96.65	57.0	1.46	195.8	200.7	Colourless.
6. Mogador bitters....	0.9183	194.98	104.2	57.0	0.65	197.1	203.2	Colourless.
7. Peach-kernel oil....	0.9198	191.4	95.24	57.5	1.51	196.8	205.0	Colourless at first, then pink.
8. Apricot-kernel oil...	0.9200	192.4	107.4	58.0	1.16	198.0	202.0	Pink colora-tion.
9. Apricot-kernel oil from Mogador ker-nels..............	0.9172	198.2	107.9	57.0	1.41	194.0	200.7	Slightly pink.
10. Californian apricot-kernel oil.	0.92026	190.3	108.7	58.0	0.61	197.8	202 8	Very slightly pink.

[1] Calculated from acid values.

In the light of our present knowledge reliance has mainly to be
placed upon the following colour reactions for detecting the adultera-
tion of almond oil:

Bieber's Test.—5 volumes of the sample are shaken with 1
volume of a cold mixture of strong sulphuric acid, water, and fum-
ing nitric acid in equal parts by weight. Pure almond oil gives a
white or yellowish-white liniment, apricot-kernel oil a deep salmon-
red or peach-blossom colour, changing to dark orange. Lewkowitsch
recommends this test in preference to others. The reagent should
be freshly prepared. Mixtures of almond oil and apricot-kernel

oil containing ⅓ of the latter are distinctly coloured, but with 25% the colour is slight.   Peach-kernel oil gives the same test much more faintly and only after standing for some time; this oil will, therefore, be still more difficult to detect in mixtures.

Kreis' Phloroglucinol Test (*Chem. Zeit.*, 1902, **26**, 897).—A few c.c. of the sample of oil are poured upon an equal volume at nitric acid of 1.4 sp. gr.; a similar quantity of a 0.1% solution of phloro-glucinol in ether is then added and the whole well shaken together. Peach-kernel and apricot-kernel oils give an intense raspberry-red colour, inclining to violet.   Chwolles, who recommended this test, found that genuine almond oil gave no colour or only a faint rose-red colouration and that 10% of peach-kernel oil could be detected in admixture, but Lewkowitsch found that several genuine almond oils gave the coloration more or less strongly and recommends great caution in the use of this test.   It should be noted that the raspberry-red colour is also obtained with arachis, sesame, cotton-seed, walnut, and castor oils, but not with olive or lard oils (Kreis).

Nitric Acid Test.—Almond oil, if shaken with nitric acid of 1.4 sp. gr. becomes pale yellow; apricot-kernel and peach-kernel oils become orange-coloured (Micko).   According to the British Phar-macopœia, if 2 c.c. of almond oil "be well shaken with 1 c.c. of fuming nitric acid and 1 c.c. of water, a whitish, not brownish-red, mixture should be formed, which, after standing for 6 hours at about 10°, should separate into a solid white mass and a nearly colourless liquid (absence of peach-kernel and other fixed oils)."   The United States Pharmacopœia and the Swiss Pharmacopœia also give this test for the detection of peach-kernel oil, but Umney (*Pharm. Jour.*, July, 1899, p. 106, and Jan., 1900, p. 8) found the test incapable of detect-ing peach-kernel oil, though useful for detecting apricot-kernel oil. F. B. Power, in a paper read before the British Pharmaceutical Conference in July, 1900, suggests as an explanation of this ap-parent discrepancy the statement of Hirsch that "Pfirschkernël," for which the Swiss Pharmacopœia gives the test with fuming nitric acid as specific is not the oil from the kernels of the common peach, but is derived from a small sort of the bitter almond, *Amydgalus communis*.   This oil, Power states, shows the behaviour described in the Pharmacopœia.

APRICOT-KERNEL OIL.[1] PEACH-KERNEL OIL.[1]

PLUM-KERNEL OIL

(See also p. 109.) These three oils, obtained, respectively, from the kernels of the apricot, *Prunus armeniaca*, the peach, *Amygdalus persica*, and the plum, *Prunus domestica*, closely resemble almond oil, for which they are largely used as adulterants and substitutes (see "Almond Oil"). Apricot and peach-kernel oils are known commercially as *Ol-Amygdalæ Persic.* (Squire).

CHAULMOOGRA OIL

(See also p. 109.) Chaulmoogra oil is derived from the seeds of the plant *Taraktogenos Kurzii (Gynocardia odorata)*, which grows in various parts of India. Seeds from Madras were found by Brill and Williams (*Philippine J. Sci.*, 1917, **12**, 207) to contain 61.4% of kernels, which when extracted with petroleum spirit (gasoline) yielded 53.0% of oil.

The oil has been found of value in the treatment of leprosy, its physiological action being attributed to the presence of an active principle, *gynocardin*, $C_{13}H_{19}O_9 + 1.5 \ H_2O$; the amount of this principle ranged from 0.11 to 0.56% in eight samples of the oil examined by Brill and Williams.

The oil extracted from the seeds of *Hydnocarpus anthelmintica* resembles chaulmoogra oil in many respects and is not infrequently substituted for it, but it does not possess its medicinal properties.

Ten samples of genuine chaulmoogra oil examined by Brill and Williams (*loc. cit.*) gave the following results.

	Sp. gr. at 30°	Rotation in chloroform solution, sodium light	Acid value	Saponification value	Iodine value
Maximum....	0.9535	+58.20	21.48	210.5	110.4
Minimum....	0.9429	+45.69	1.55	189.1	97.6
Mean........	0.9471	+50.81	10.79	200.4	102.4

A sample of hydnocarpus oil (Madras) gave the following figures:

Sp. gr. at 30°	Specific Rotation	Acid Value	Saponification Value	Iodine Value
0.9487	+49.50	0.6	206.2	90.8

[1] See Lewkowitsch, *Analyst*, 1904, **29**, 105.

According to Chattopadhay (*Amer. J. Pharm.*, 1915, **87**, 473) chaulmoogra oil is composed of glycerides of lauric, linolic and chaulmoogric acid.

Chaulmoogric acid, the chemical nature of which has been studied by Power and Barrowcliffe (*J. Chem. Soc.*, 1905, **87**, 349, 1910, **97**, 1285), is a representative of a new type of fatty acids with a cyclic structure, and having the general formula, $C_nH_{2n-4}O_2$.

Chaulmoogric and hydnocarpic acids isolated by Brill and Williams from the mixed fatty acids of the respective oils gave the following results:

	Neutralisation value	Specific rotation	Iodine value
Chaulmoogric acid............	200.5; 202.4	+59.05; 58.10	89.5; 90.7
Hydnocarpic acid............	222.7; 218.2	+67.70; 67.60	100.2; 99.9

Cofman (*Pharm. J.*, 1919, **103**, 269) has found that the acidity of chaulmoogra oil varies with the mode of preparation and time of keeping. Two samples freshly extracted had acid values of 8.3 and 7.7 respectively, whilst five commercial samples had values ranging from 18.5 to 76.7.

The values of freshly expressed or extracted oil rose steadily on keeping, and from these results it would seem that the limits for the acidity of chaulmoogra oil prescribed by the B. P. are of no value as an identification test and require modification.

Lifschutz (*Chem. Zeit.*, 1921, **45**, 1264) describes a colour reaction for gynocardia (chaulmoogra) oil. When strong sulphuric acid (4 to 5 drops) is added to a solution of 1 drop of the oil in 0.5 c.c. of chloroform and 1.5 c.c. of glacial acetic acid an intense grass-green coloration is produced, and the solution shows a red-violet colour by transmitted light, and has a characteristc complex absorption spectrum.

Freshly expressed oil does not give this reaction, but does so after oxidation *e.g.* with a crystal of benzoyl peroxide. It is still obtained with the fatty acids after separation of the unsaponifiable matter.

Dean and Wrenshall (*J. Amer. Chem. Soc.*, 1920, **42**, 2626) have shown that the only satisfactory way of separating the chaulmoogric and hydnocarpic acids in chaulmoogra oil is by direct distillation

in vacuo, followed by recrystallisation of the chaulmoogric acid from 80% alcohol and of the hydnocarpic acid from petroleum spirit (gasoline).

Even in the case of chaulmoogra oil of low grade at least 100 grm. of pure chaulmoogric acid (m. p., 68°; iodine value, 90.1; specific rotation, + 56°), and at least 50 grm. of pure hydnocarpic acid (m. p. 590; iodine value 100.2; specific rotation, + 68.1) should be obtained under the conditions specified.

The B. P. defines chaulmoogra oil as a brownish-yellow oil or soft fat, with a characteristic odour and somewhat acrid taste. m. p., about 20° to 30°; sp. gr. at 45° about 0.940; acid value, 21 to 27; saponification value, 198 to 213; iodine value, 96 to 104. Soluble in ether, in chloroform and in carbon disulphide; partly soluble in cold alcohol (90%); almost entirely soluble in hot alcohol (90%).

HAZELNUT OIL

(See also p. 109.) This is a golden-yellow coloured, non-drying oil, obtained from the seeds or nuts of *Corylus avellana*, the common hazel. The nuts contain from 50 to 60% of the oil. It is used in perfumery, in pharmacy, and also as a lubricant for clocks.

Hanus (*Zeit Nahr. Genussm.*, 1899, 2, 617) states the composition of the fatty acids of this oil to be, oleic acid 85%, palmitic and stearic acids 10%. About 1% of stearic acid was found, but no arachidic acid, and no linolic or linolenic acid. The oil forms a green-coloured, solid elaidin. It contains about 0.5% of phytosterol. Hanus obtained the following values:

	Oil	Mixed fatty acids	Liquid fatty acids
Sp. gr. at 15°........	0.9169		
Maumené test...	36.2°		
Saponification value..	193.7	200.6	198.5
Iodine value........ .... , ..	90.2	90.6	91.3
Hehner value................. ..	95.6		
Reichert-Meissl value..... ... .·	0.99		
Acetyl value........	3.2		

Tortelli and Ruggeri found the iodine value of the cold-pressed oil to be 83.9, and that of the liquid fatty acids to be 97.6, which points to the presence of fatty acid more unsaturated than oleic.

Pritzker and Jungkunz (*Zeit. Nahr. Genussm.*, 1921, **42**, 232) recommend the estimation of arachidic acid for the detection of arachis oil in hazelnut oil. The various colour reactions recommended for hazelnut oil are untrustworthy.

OLIVE OIL

(See also p. 109.)   Olive oil is expressed from the fruit of the olive, *Olea europæa*, and oil of inferior quality is extracted from the residual marc by carbon disulphide ("sulphocarbon oil") or petroleum spirit. Peano (*J. Soc. Chem. Ind.*, 1903, **22**, 35) states that in estimating the oil in olives, carbon disulphide should be used and not ordinary ether, as the latter dissolves another substance.

Of the commercial varieties, Provence and Tuscan oils are among the most esteemed. The finest grade in the market is "finest cream sublime oil," which is imported from Leghorn. Oils of other origin are Gallipoli, Sicilian, Spanish, Portuguese, Levant, and Mogador. That sold in the so-called "Florence flasks," is usually of inferior quality. Lucca and Gallipoli oils are well-known brands, and much excellent oil is expressed in Spain, and exported from Malaga and Seville. Olive oil is now largely prepared in California, Tunis, Algeria, and Morocco. Much African oil goes to Nice and is there blended with the oil of the district and sold as pure Nice olive oil (*Chemist and Druggist*, Aug. 19, 1905).

The oil which exudes from the ripe olives under moderate pressure in the cold is sold as "virgin," "sublime," or "first expressed " oil; it is the best edible oil. Ordinary oil, from a second pressing with the aid of hot water, has a less agreeable flavour than the first and is more liable to become acid, but the two sorts are often mixed, forming several varieties. "Pyrene" oil, "bagasses" oil, "huile tournante," "huile d'enfer," etc., are very impure acid oils, recovered from residues which have fermented. Industrial neutral olive oils, known as "saponified" oils, are prepared from these residuum oils and oils of the third pressing by washing with alkali to remove the free fatty acids.

The variations in the quality are largely dependent on the manner in which the olives are treated, as, *e. g.*, the care with which the fruit is plucked, the length of time it is stored before being crushed, etc. The flavour of the oil, which largely governs its commercial value for edible uses, apart altogether from its purity or genuineness, depends

upon the variety of olive from which the oil is expressed, the degree of ripeness of the fruit when picked, and the process of extraction.

In some countries olive oil is an important article of diet. It is employed in the manufacture of woolen cloth, and in dyeing fabrics Turkey-red, though its application for these purposes is decreasing. The inferior varieties are employed in soap making. It is highly esteemed as a lubricant, and is largely employed when price permits. The quantity used in this way depends much on the price of rape oil, which is usually much cheaper, and, though more liable to "gum" than olive oil, is less apt than the latter to become acid.

Olive oil differs in physical characters according to its quality. The finest kinds have a pale yellow colour, with a tinge of green, are almost wholly free from odour, and possess a mild and agreeable taste. Inferior qualities have a greenish-yellow or brownish-yellow colour, an unpleasant odour, and a decidedly acrid after-taste.

The absorption spectrum of the fresh oil shows well-defined chlorophyll bands, which become changed or altogether destroyed on exposure to sunlight or heating with alkali hydroxide.

When cooled to about $2°$, olive oil begins to deposit a white granular fat. At $0°$ to $-6°$ it solidifies to a product which can be separated by pressure into a solid tallow-like fat and a fluid "oleine."

Chemically, olive oil is chiefly composed of the glyceryl esters of oleic and palmitic acids, with a small proportion of linolic acid. The proportion of esters of solid fatty acids in very variable in the oils from different sources, and exceptionally large in the Tunisian oils from Sfax and Sousse which, in consequence of their depositing solid fat at temperatures as high as $10°$, are "demargarinated" before being placed on the market. The fatty acids exist partly as mixed glycerides. Holde and Stange have isolated about 1.5% of oleo-dimargarin, and Holde has' obtained evidence that the remainder of the solid acids are present as mixed esters containing 1 molecule of saturated fatty acid and 2 molecules of oleic acid (*Ber.*, 1901, **34**, 2402; 1902, **35**, 4036; 1905, **38**, 1247). Hehner and Mitchell found no stearic acid in olive oil. Minute traces of arachidic acid have been isolated, but not sufficient even in Tunisian oils to lead to erroneous conclusions being drawn from the results of Renard's and Bellier's tests for arachis oil (Archbutt, *J. Soc. Chem. Ind.*, 1907, **26**, 453 and 1185).

Olive oil is the type of a non-drying vegetable oil. It does not thicken materially, even on prolonged exposure to air, but gradually becomes rancid, a change which appears to be mainly due to oxidation (Ryan and Marshall, *Amer. Jour. Pharm.*, 1907, **79**, 308). In very thin films it dries slowly. The following results obtained by Archbutt (*J. Soc. Chem. Ind.*, 1899, **18**, 346) show how it compares with some other well-known oils in this respect:

Kind of oil	Time required for a thin film to dry in air at 50° (0.1 grm. oil on a glass surface 7 cm. square)
Olive oil.........................	More than 13 days.
Rape oil.........................	About 48 hours.
Curcas oil.......................	About 24–30 hours.
Cottonseed oil...................	About 21 hours.
Maize oil........................	About 18 hours.
Linseed oil......................	About 12 hours.

If free from acid, it is only slightly soluble in alcohol, but dissolves in about 1.5 times its weight of ether, and is miscible in all proportions with carbon disulphide, chloroform, and hydrocarbons.

When heated to about 120°, olive oil becomes lighter in colour, and at 220° nearly colourless and at the same time rancid. At 315° it suffers decomposition, emitting a disagreeable odour of acrolein.

The following are some observed analytical data of the mixed fatty acids of olive oil not given on p. 109:

		Authority
Sp. gr. at 99°/15.5°.......................	0.843	Allen.
Sp. gr. at 100°/100°.......................	0.874–0.876	Archbutt.
Solidifying-point (titer test).................	16.9°–26.4°	Lewkowitsch.
Refractive index at 60°......................	1.4410	Thoerner.
Iodine value of mixed fatty acids.............	86–90	Various.
Iodine value of liquid fatty acids........... .	92.8–104.2	

Analysis of Genuine Olive Oil.—Genuine olive oil often contains a notable quantity of free acid, the proportion of which increases by keeping and exposure. In 151 samples from various sources Archbutt found the following percentages of free (oleic) acid:[1]

[1] *J. Soc. Chem. Ind.*, 1889, **8**, 685.

Number of samples	Source	Free (oleic) acid %		
		Highest	Lowest	Average
70	Spain.....................	25.1	1.5	5.5
36	Italy.....................	25.2	0.9	8.5
28	Sicily....................	16.6	0.5	9.1
12	Candia...................	16.8	5.5	9.5
3	Levant...................	13.5	8.5	10.4
2	Zante....................	8.7	4.8	6.7

Thomson and Ballantyne (*J. Soc. Chem. Ind.*, 1891, **10**, 233) and Thomson and Dunlop (*Analyst*, 1906, **31**, 281) found in 20 samples of commercial oils from very varied sources free (oleic) acid ranging from 3.86% in a sample from the Levant to 24.72% in a sample of Mogador oil.

Tolman and Munson found in 18 Italian oils from 0.57 to 2.79% and in 38 Californian oils from 0.20 to 3.51% (*J. Amer. Chem. Soc.*, 1903, **25**, 954).

The following results were observed by N. J. Lane in the United States Customs Laboratory at New York:[1]

Free fatty acid, %	Number of samples		
	French oil	Italian oil	Total
Not exceeding 3.........................	28	35	63
3 to 5..............................	7	8	15
5 to 10.............................	10	5	15
10 to 20............................	3	8	11
29.2................................	1	0	1
	49	56	105

Most of this free acid is caused by allowing the fruit or the pulp to ferment before the oil is expressed from it, or by storing the oil in a crude state.

It has been shown (Milliau, Bertainçhaud and Malet, *Monit. Scient.*, 1900, **56**, 508) that if the oil be filtered immediately after expression, to remove the insoluble impurities, the acidity does not increase by storage, or at any rate only very slowly.

[1] *J. Soc. Chem. Ind.*, 1900, **19**, 223.

Oil intended for table use, for lubricating, and for burning in lamps, should be as free as possible from acid, a maximum of 4% being the desirable limit.   In lubricating oils, the free acid corrodes the bearings, forming metallic soaps which dissolve in and thicken the lubricant (Archbutt and Deeley, Lubrication and Lubricants, p. 213).   In lamp oils excess of acid causes charring of the wick. For soapmaking, free acid is no detriment, and for Turkey-red dyeing a very acid oil ("tournante oil") is preferred, as it readily emulsifies with a solution of sodium carbonate.   Lewkowitsch states that 25% of free fatty acids should be present in Turkey-red oil.   For woolcombers' use free acid is not necessarily objectionable, providing the oil does not form sticky and varnish-like films on the wool.   (See below.)

The proportion of free acid in olive oil can be ascertained with ease and accuracy by titration in presence of alcohol with standard caustic alkali and phenolphthaleïn, in the manner described on p. 10.

Burstyn (*Dingl. polyt. J.*, 1875, **217**, 314; *J. Chem. Soc.*, 1876, **29**, 769) has described the following method for estimating the free acid in olive oil.   The process appears well suited for rapid technical investigations, though the volumetric method described elsewhere will be preferred by chemists.   The oil is shaken with an equal measure of rectified spirit of 0. 830 to 0.840 sp. gr., the exact figure being accurately determined.   After the liquids have separated, the sp. gr. of the spirit is determined.   Burstyn finds that an oil, 100 c.c. of which contains free acid in quantity sufficient to neutralise 1 c.c. of normal alkali (=0.282% of oleic acid), will raise the gravity of the alcohol from 0.830 to 0.8325, and that each additional 1 c.c. of alkali neutralised corresponds to an increase of 0.0003 in the sp. gr. of the spirit.   Hence, the increase due to the solution of a trace of neutral fat is 0.0022, and each increase of 0.0001 in sp. gr. beyond this number represents $\frac{0.282}{3} = 0.094$ grm. of free acid per 100 c.c.   Burstyn states that the action of olive oil on brass is regularly and directly proportional to the percentage of free acid present.

In examining oil intended for cooking or table use, the flavour and odour should be carefully observed, as many apparently genuine specimens which are fairly free from acid are unsatisfactory in this respect.

Richardson and Jaffé (*J. Soc. Chem. Ind.*, 1905, 24, 534) find that some olive oils thicken and gum by oxidation much more readily than others, and are, therefore, less suitable for oiling wool. This property has no necessary relation to the percentage of free oleic acid present, but the source of the oil is of far greater importance (See also Milliau, Bertainchaud and Malet, *Monit. Scient.*, 1900, 56, 508). In order to test the oxidisability of an oil, they place 10 grm. in a tin tray measuring 4 in. by 6.5 in. by 0.5 in. deep, contained in a special oven,[1] pass over the oil a current of air at 100° for 6 hours or 204° (400° F.) for 4 hours, and determine the time of efflux at 100° of 5 c.c., before and after oxidation, from a jacketted 5 c.c. pipette The following results were obtained:

Description of oil	Free (oleic) acid, %	Percentage increase of viscosity after heating for	
		6 hrs. at 100°	4 hrs. at 204°
Gallipoli	21.3	10.5	
Seville	3.82	32.6	73
Gallipoli	4.23		644
Seville	4.23		315
Levant	12.69		

These results ·explain the preference given to Gallipoli oil by wool-combers, but the excessive acidity would be objectionable for lubricating.

EXAMINATION OF OLIVE OIL FOR ADULTERANTS

Olive oil is very liable to adulteration, the sample being sometimes coloured to give it the appearance of green olive oil. A coloration due to copper can be detected by adding ether and shaking with dilute sulphuric acid, which removes the green colour. On drawing off the acid liquid, copper will be found in it by the usual tests and may be quantitatively determined.

Cottonseed oil is probably the most frequent adulterant of olive oil, especially in America; but arachis, sesame, poppy, lard, and rape

[1] Obtainable from Messrs. Reynolds and Branson, Leeds, England.

oil are also used.   Poppy oil, on account of its sweet taste and slight odour, is said to be a frequent adulterant in Europe, but it is doubtful if it is ever used in America (Tolman and Munson).   The acrid taste of even refined rape oil would be against its use in edible olive oil, but it might be added to lubricating oil.   Maize oil, which is largely produced in America, is a not unlikely adulterant, and has been sold as a substitute for olive oil (see below).   Lard oil, expressed at a low temperature and specially refined, is largely used when the price permits, "Superfine Lucca oil" being stated to contain sometimes as much as 60 to 70% of it.   Fish oils are occasionally employed, menhaden oil being said to be used frequently.   Hydrocarbon oils are also used.   During the war a paraffin oil coloured with a yellow dye was frequently palmed off as olive oil.

In the United States, cottonseed oil was once sold under the name of olive oil.   In fact, until the adoption of the recent food laws, especially the Federal Act, the label "Huile d'Olive vierge, E. Loubon, Nice," was generally understood in the grocery trade to indicate cottonseed oil.   Bulletin No. 77 (1905) of the United States Department of Agriculture contains illustrations of several spurious labels. A bottle labelled "Frères & du Peaux, Bordeaux, France.   Huile D Olive" contained cottonseed oil.   Another containing mixed olive and cottonseed oil bore the label "Tisserand & Fils. Huile d' Olive extra surfine, Bordeaux, France.   Falcon brand."   A mixture of olive and peanut oil was described as "Huile D'Olive, extra surfine, Jules Chambon & Cie., Bordeaux, France."   This label also bore the signature of the alleged importer.   On enquiry at Bordeaux, no trace could be found of the above-named firms, and most likely the labels as well as the oil were of American manufacture.   A label of another kind was found on a bottle of maize oil. This, at first glance, appears to read "Superior Olive Oil.   Dove Pure Oil Co.," but, on closer inspection, it is seen to bear the words "Superior in quality, purity and flavour to any olive oil in the market."

In examining olive oil, the most important indications are sp. gr., iodine value, saponification value, rise of temperature on treatment bromine, amount and nature of the unsaponifiable matter, some form of oxidation test, and some colour indications.   Some require the application of special methods for their detection.

The *sp. gr.* of olive oil usually ranges from 0.915 (rarely 0.914) to 0.917 at 15.5°, but genuine Tunisian and Californian, and even

some Italian oils, may have as high a sp. gr. as 0.918. Even 0.919 has been recorded for Tunisian oil and 0.9203 for an olive oil from the Punjab (Crossley and Le Sueur, *J. Soc. Chem. Ind.*, 1898, **17,** 998). On the other hahd, a sp. gr. as low as 0.9122 has been observed in an oil containing 31% of free (oleic) acid (*Bull. No.* 77 (1905) U. S. Dept. of Agriculture, p. 15). High gravity oils are usually dark in colour, and may contain oil from the kernel and endocarp. All samples over 0.917 in sp. gr. should be submitted to a very critical examination for adulterants. An admixture of rape, lard, or arachis oil would not be indicated by the sp. gr. Cottonseed, poppyseed, or sesame oil would tend to raise it, but the sp. gr. could be adjusted by a judicious mixture of these with sperm or mineral oil, which would, however, be readily detected by other tests.

The *iodine value* is a most useful test, but for its correct interpretation a knowledge of the source of the oil is needed. Genuine samples usually absorb from 82.0 to 86.0% of iodine, but lower and higher values may be met with and the oil still be genuine. The results of numerous observers for oils from various countries tabulated by Lewkowitsch (*Chem. Tech.*, **2,** 275) range from 77.28 to 94.7. Italian and Spanish oils rarely absorb more than 86% of iodine; the highest values are to be looked for in the oils from California, Tunis, Algiers, Morocco, and Dalmatia. The following values have been recorded for single samples:

Observer	Source of oil	Iodine value
Colby[1]	California	93.5
Crossley and Le Sueur[2]	Punjab	93.67
Ahrens and Hett[3]	Morocco black olives, hand pressed	91.5
Guozdenovic[4]	Dalmatia	92.8
Thomson and Dunlop[5]	Mogador	94.3
Archbutt[6]	Mornag (Tunis). Olive (var.) Chetui.	94.7
	Bizerte (Tunis). Olive (var.) Chetui.	91.1
	Medjez-Amar (Algeria)	90.5

[1] *California Agr. Expt. Sta. Rept.*, 1897–8, 168.
[2] *J. Soc. Chem. Ind.*, 1898, **17,** 989.
[3] *Zeits. Oeffentl. Chem.*, 1903, **9,** 284.
[4] Lewkowitsch, *Chem. Tech.*, **2,** 275 (footnote).
[5] *Analyst*, 1906, **31,** 281.
[6] *J. Soc. Chem. Ind.*, 1907, **26,** 453 and 1185.

A few varieties of olives grown in certain districts appear to give these exceptionally high results, oils from other varieties and districts giving normal or more nearly normal figures.   In ordinary cases, an iodine value of over 87 would indicate adulteration.   Goldberg's observation that the solid and liquid portions of chilled olive oil absorb practically the same amount of iodine shows that the iodine value of demargarinated oil is not likely to be appreciably higher than that of the entire oil from the fruit.

Tolman and Munson (*Bull. No.* 77, U. S. Dept. of Agriculture) give a large number of analyses of genuine Californian olive oils obtained from all parts of the State and representing the different soils and climatic conditions.   The iodine values of 42 samples ranged from 78.5 to 89.8, with an average of 85.1.   11 samples examined by Blasdale ranged from 80.0 to 86.5; average 84.0. Samples of known purity examined by Colby ranged from 77.7 to 93.5. Tolman and Munson have found that the iodine value increases as the percentage of solid fatty acids and the m. p. of the mixed fatty acids decrease, and they recommend that the iodine value should be considered in conjunction with these other factors and with the iodine value of the liquid fatty acids.   They give the following table:

RELATION BETWEEN IODINE VALUE, SOLID FATTY ACIDS AND M. P. OF MIXED FATTY ACIDS (CALIFORNIA OILS)

Iodine value	Solid fatty acids, %	M. p. of mixed fatty acids, °	Iodine value	Solid fatty acids, %	M. p. of mixed fatty acids, °
79.9	10.91	31.0	85.6	4.92	21.3
83.0	7.62	28.0	85.7	6.27	23.4
82.9	5.70	25.0	86.2	3.39	21.1
84.3	7.23	23 4	88.2	4.42	23.5
85.6	5.12	22.6	88.5	2.43	20.2

The same relation was found to hold good in a general way for Italian oils, but Milliau did not find this relation in the oils from Tunis.   He found oils, for example, with an iodine value of 88 and a m. p. of fatty acids of 37°.   The following table shows the relation between the iodine value of certain olive oils and that of their liquid fatty acids:

Kind of olive oil		Iodine values				
		Of oil		Of liquid fatty acids		
		Tolman and Munson	Tortelli and Ruggeri	Tolman and Munson		Tortelli and Ruggeri
				Determined	Calculated[1]	
Italian	Maximum	86 1	85.4	98.4	104.1	101.5
	Minimum	79.2	80.0	89.8	89 1	95.5
	Average	81.6	83.6	94 0	96.5	97 5
Spanish...... ..	Maximum	.... .	87 2	... ...	.	104.2
	Minimum	.... ..	78.5	. . . .	. ... .	95.5
	Average		85 5	. .. ..	. ... .	100.4
Californian......	Maximum	89.8		96 6	98.8	
.	Minimum	78.5	. .	88.9	90.5	
	Average	85.3	..	92 8	95.0	

[1] Calculated from the iodine value of the oil, the percentage of solid fatty acids, and the average Hehner value (95.5).

Tolman and Munson have ascertained the iodine values and the solid fatty acids of a number of oils, and they point out that the relation between these numbers gives a great deal more information in the analyses of mixtures than the simple iodine values of the oils themselves. Their results are summarised in the following table.

AVERAGE IODINE VALUES AND PERCENTAGE OF SOLID FATTY ACIDS OF VARIOUS OILS, OBTAINED BY TOLMAN AND MUNSON

Number of samples	Kind of oil	Iodine value of		Solid fatty acids, %	
		Oil	Liquid fatty acids		
18	Olive (Italian)...........	81.6	96.5	10.50	Maximum 17.7 / Minimum 5.0
39	Olive (Californian).......	85.3	95.0	5.86	Maximum 13.0 / Minimum 2.0
4	Lard................ ..	73.8	99.9	21.58	Maximum 26.7 / Minimum 18.9
6	Cottonseed..............	106.6	138.9	21.17	Maximum 23.6 / Minimum 17.9
4	Rape...................	96.9	102.1	0.64	
3	Mustard................	107.3	113.6	1.13	
2	Sunflower..............	106.2	115.8	3.90	
1	Sesame.................	106.6	115.4	10.70	
3	Maize..................	120.7	136.4	7.04	
1	Poppy.................	134.9	151.7	6.67	

The *saponification value* of genuine olive oil, according to De Negris and Fabris, who examined 203 samples, may range from 18.5 to 19.6%, and is usually 19.0.   106 samples examined by Oliveri had values ranging from 19.05 to 19.5, 38 Californian oils tested by Tolman and Munson ranged from 18.9 to 19.5; 400 samples of commercial oil (mostly Spanish and Italian) tested by the writer had values ranging from 18.80 to 19.29%, and 20 samples of oil from Tunis and Algeria ranged from 18.92 to 19.19%.   A low saponification value might be due to the presence of olive-kernel oil or to adulteration with rape, mustard, sperm, or mineral oil.   No adulterant likely to be added would materially *raise* the saponification value of olive oil.

The *rise of temperature* on treating the sample *with sulphuric acid* (Maumené's test) or *with bromine* (Hehner and Mitchell's test) affords a rapid indication of the purity of olive oil.   Almost all oils, except coconut olein and tallow and lard oils, produce more heat than olive oil, so that a rise of temperature of more than $45°$ with sulphuric acid (10 c.c. of acid containing 97% H_2SO_4 and 50 grm. of oil) may at once be considered as indicating probable adulteration.

Portuguese Oils.—O. Klein (*Chem. Zentr.*, 1912, **1**, 1664) has examined 30 samples of oil prepared from known varieties of olives and 30 commercial samples from which he deduces the following limiting values for Portuguese oils:

	Sp. gr.	Refractive index (25° C.)	Iodine value	Saponification value
Maximum.........	0.918	1.4682	85.0	195.0
Minimum.........	0.915	1.4660	75.0	185.0
Average..........	0.9168	1.4670	80.5	190.0

Archbutt (*J. Soc. Chem. Ind.*, 1897, **16**, 309) has determined the *heat of bromination* of 10 samples of olive oil and obtained results ranging from 13.55 to 14.5, using 1 grm. of oil and 1 c.c. of bromine. The thermal values when multiplied by 5.7 agreed very nearly with the iodine values.

The *elaidin test* is of little use unless carried out under standard conditions (Archbutt, *J. Soc. Chem. Ind.*, 1886, **5**, 303).   The reagent should be prepared by dissolving 6 grm. of mercury in 15.6 c.c. of nitric acid (1.42) in a 50 c.c. stoppered cylinder immersed in cold water, it should be mixed with the oil in the proportion of 1 part

of reagent to 12 of oil by weight, and the mixture kept at a fixed temperature and shaken every 10 minutes. Under these conditions, at 10°, genuine olive oil is converted into a solid pale yellow mass of elaidin in about 1 hour, arachis oil rather more slowly, but rape, cottonseed, sesame, and other more strongly drying oils remain partly or wholly liquid and are coloured orange or red. To increase the delicacy of the test, it should be made at 25°. At that temperature olive oil will take from 200 to 400 minutes to solidify, and 10% of more strongly drying oils, if present, will delay the solidification, darken the colour, and soften the consistence of the elaidin formed. It is said that as little as 5% of poppy oil can be detected by this test at 10°, which requires confirmation, but most adulterants are more readily detected by other tests. Olive oil which has become bleached by exposure to sunlight no longer forms a solid elaidin.

Useful information as regards the *oxidising properties* of an olive oil may be obtained by exposing 0.5 grm. on a watch-glass to the air in a water-oven at 100° for about 16 hours side by side with an equal weight of a standard sample on a watch-glass of the same curvature. Livache's or Bishop's tests (pp. 45 and 46) may also be used.

Reference to the table on p. 61 will show that the *oleo-refractometer* of Amagat and Jean is a valuable instrument for the rapid testing of olive oil, the recorded deviation of genuine samples ranging from 0° to + 3.5°. 106 samples examined by Oliveri (*J. Soc. Chem. Ind.*, 1894, 13, 45) ranged in their readings from 0° + 2°. All fixed oils likely to be added as adulterants would increase the refraction, except neat's-foot, arachis, lard, and tallow oils.

The *unsaponifiable matter* of genuine olive oil contains phytosterol, but no cholesterol. It does not exceed 1.5% in normal olive oils of the first and second pressing. In olive residuum oils (*les huiles de grignon d'olives*), however, and also in certain olive oils of the third pressing, larger quantities, even as much as 3.3%, of unsaponifiable matter have been found, derived, according to Milliau, from the shell of the olive nut. Any excess would probably include hydrocarbons from mineral or rosin oil, or wax alcohols from sperm or some other marine animal oil.

Cottonseed oil, unless it has been rendered insensitive by heating, would be detected by Halphen's colour test (page 177), the result of which must, however, be interpreted in conjunction with the quantitative values, especially the sp. gr., refractive power, iodine value,

thermal tests, and the "titer" test of the mixed fatty acids, all of which would be raised by the addition of cottonseed oil. Some of these might be adjusted by the addition of a third oil, but the fraud would be detected by an abnormality somewhere if a complete examination were made. The addition of mineral oil or sperm oil, for instance, would increase the percentage of unsaponifiable matter. Other colour tests which may be applied are those with silver nitrate (*Bechi*, *Milliau*) and nitric acid (see under "Cottonseed oil"). As some genuine olive oils have been found to give a brown colour in Bechi's test and a yellowish-brown colour with nitric acid, the results of these colour tests must be used with caution. A mixture of cottonseed and lard oils could be made having the normal sp. gr. and iodine value of olive oil, but the oleo-refractometer, the "titer" test of the mixed fatty acids, and the iodine value of the liquid fatty acids, would detect adulteration with such a mixture.

To detect small quantities of cottonseed oil, Bolton and Revis recommend that the Halphen test be carried out in sealed tubes as suggested by Steinmann, while for still smaller quantities (down to 1%) R. Marcille (*Ann. Falsific.*, 1910, 3, 235) proposes that the sealed tubes be heated in an oil bath at a temperature of 120°, when 5 to 10% of cottonseed oil give a bright red colour within 12 minutes, and 1% a distinct red after 1 hour.[1] Attention is drawn to the fact that certain olive oils give a red colour when heated to 130°, and for this reason care must be taken not to exceed 120°, which temperature is stated not to produce any red colour with pure olive oil after 6 hours' heating, though a slight yellow tint is usually observed.

Sesame oil would be detected by the very delicate furfuraldehyde test (p. 188). Some genuine olive oils have been found to give a pale violet or rose-red coloration in this test, but it is unlikely for error to occur if proper consideration be given to the quantitative values. Sesame oil, if present, would affect the quantitative values very much in the same way as cottonseed oil.

Arachis oil can be detected in olive oil by Bellier's test (p. 124) and estimated by Renard's process (p. 118). The ordinary quantitative values of this oil are little different from those of olive oil. Some indications of its presence might be obtained by an abnormally high iodine value, but this would be very uncertain (recorded values for

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[1] Other improvements suggested for this test are described under Cottonoil, p. 178.

arachis oil, 83.3 to 105; for olive oil, 76.2 to 94.7). It may be noted that sesame oil is frequently mixed with arachis oil, and the two may, therefore, occur together. Arachidic acid occurs in *rape* and *mustard* oils, but these would betray their presence by lowering the saponification value and raising the iodine value and thermal values of olive oil.

A rapid test for the detection of small amounts of arachis oil in olive oil has been devised by Biazzo and Vigdorcik (*Annali Chim. Applic.*, 1916, **6**, 179) the principle of the method being that suggested by Kreis and Roth (*Zeit. Nahr. Genussm.*, 1913, **25**, 81). The fatty acids are first separated and the liquid acids separated by the lead-ether method. The solid fatty acids are then dissolved in 90% alcohol containing 10 drops of N/1 hydrochloric acid per 1000 c.c. and the flask immersed for 10 minutes in water at 15°. The resulting crystals are separated and dissolved in 25 c.c. of the alcohol, and the solution again cooled. Any further crop of crystals is then dissolved in 12.5 c.c. of alcohol and if they still separate they are dissolved in 5 c.c. of the alcohol, and the solution allowed to stand at the ordinary temperature. By thismeans an olive oil containing only 5% of arachis oil will yield a sufficient quantity of crystals for the determination of the m. p.

Poppy oil or maize oil added to olive oil would affect the sp. gr., iodine value, and thermal values much in the same way as cottonseed oil, but they would not alter the "titer" test of the mixed fatty acids, nor increase the percentage of solid fatty acids as cottonseed oil would do. Poppy oil has a high iodine value and dries strongly. Maize oil is said to give a peculiar red colour when shaken with nitric acid (1.37), which is quite different from the colour obtained with cottonseed oil.

Lard oil in most of its quantitative values closely resembles olive oil, and would not be detected by the ordinary tests. The odour of the sample when warmed might reveal its presence, but the detection of cholesterol in the unsaponifiable matter by Bömer's test (see under "Cholesterol") would be the best evidence of the presence of lard oil. It might also be worth while to look for stearic acid in the mixed fatty acids by Hehner and Mitchell's process, since olive oil contains no stearin. Lard oil would increase the percentage of solid fatty acids.

Fish and other marine animal oils would probably show themselves by the taste, the smell on warming the sample, and the red colour produced on heating the oil with caustic soda solution.   Most fish oils would raise the sp. gr. and iodine value, but they would be especially identified by the insoluble bromoglyceride formed by adding bromine to the solution of the oil in chloroform and acetic acid in Eisenchiml and Copthome's process (p. 466).   *Linseed Oil* would, of course, give a similar precipitate.

The characters of commercial olive oil must depend to some extent upon whether, in the process of expression or extraction, the olive kernels have been crushed and the *olive-kernel oil* included.

Rape oil may be detected by Tortelli and Fortini's method, the details of which must be followed *exactly*.   20 grm. of the oil are saponified with 6 grm. of potassium hydroxide dissolved in 50 c.c. of 90% alcohol by heating under a reflux condenser.   The liquid is neutralised to phenolphthalein with 10% acetic acid, and the solution then slowly poured into a boiling mixture of 200 c.c. of 10% lead acetate and 100 c.c. of water, with vigorous shaking during the addition.   The mixture is cooled under the tap, a rotatory motion being maintained until the soaps begin to stick to the sides (if they do not stick at first, they will do so during the first washing).   The water is poured off and the soaps washed 3 times with 200 c.c. of warm (60 to 70°) water, the water being then drained off and, as far as possible, removed with filter paper.   To the dried soaps 80 c.c. of ether are added, and the whole is well shaken for several minutes until the mass is broken up, after which it is heated under a reflux condenser for 30 minutes, being shaken at intervals. The flask is then closed and placed in water at *exactly* 15° *for 1 hour*, after which the contents of the flask are poured on to a filter, the funnel being placed in the mouth of a separator and the filter closely covered until as much ether as possible has filtered out.   The filter and contents are dropped back into the flask and the ether treatment (boiling and cooling) is repeated in exactly the same way, 40 c.c. of ether being used, and the mass filtered as before, the filter again being tightly covered and the liquid allowed to drain as completely as possible.   The flask is washed out with a further 40 c.c. of ether on to the filter, the contents of which are well stirred up with the ether, which is then allowed to drain off.   The combined ethereal solutions of the lead salts so obtained are decomposed in

the separator by shaking twice with 150 c.c. of 10% hydrochloric acid, after which the ether is washed with two quantities of 100 c.c. of water, the ethereal solution being then run out into a dry flask and allowed to evaporate spontaneously or with the aid of the use of gentle warmth in a current of hydrogen. The liquid fatty acids so obtained are dissolved in 40 c.c. of strong alcohol (97%) and a saturated solution of sodium carbonate added until the liquid is saturated (sodium carbonate separates). The alcohol is distilled off and the residue dried, first in the water oven, after being distributed as completely as possible over the sides of the flask, and finally in a vacuum desiccator for at least 48 hours. The dry sodium soaps are then boiled with 50 c.c. of *absolute* alcohol and filtered in a hot funnel, the insoluble residue being boiled with a further quantity of alcohol and the treatment repeated till nearly the whole has been dissolved. The mixed alcoholic filtrates are freed from alcohol by distillation and the sodium soaps dried as completely as possible in a vacuum desiccator over sulphuric acid.

According to Tortelli and Fortini the test is concluded as follows: 0.5 grm. of the dry soaps is placed in a large test-tube and dissolved by heating in 20 c.c. of absolute alcohol. A thermometer is then placed in the mixture, which is allowed to cool and the turbidity temperature noted.

The following table gives some results obtained by them:

Oil	Turbidity temperature
Olive	20–24°
Rape	45–50°
1 pt. olive } 1 pt. rape	35–40°
8 pt. olive } 2 pt. rape	30–35°
9 pt. olive } 1 pt. rape	30–34°
Cotton	14–16°
Sesame	18–20°
Arachis	18–22°

Bolton and Revis find it more satisfactory to dissolve 0.75 grm. of the soaps in strong alcohol (97 to 98%) and to leave the solution to stand at a temperature of 20°. Under these circumstances rape oil begins to precipitate in a granular form in 15 to 30 minutes,

and 5 to 10% of rape oil in admixture with other fats produces a spongy gelatinous precipitate within 2 hours, whilst in the absence of rape oil no precipitate usually forms under 15 to 18 hours.   As the results are dependent on the degree of dryness of the soaps and the strength of the alcohol employed it is more satisfactory to carry through the test with some oil, such as cottonseed oil, as a control. The test under these conditions is quite reliable.

Biazzo and Vigdorcik (*Annali Chim. Applic.*, 1916, **6**, 185) have based a method of detecting rape oil on the hydrogenation of the erucic acid into behenic acid.   The fatty acids from 20 grm. of the olive oil are dissolved in 180 c.c. of anhydrous acetone, and the solution heated nearly to boiling, treated with 20 c.c. of N/1 potassium hydroxide solution and cooled at 15°.   The precipitated potassium soaps are washed with 4 portions (10 c.c. each) of cold acetone and dissolved in water, and the fatty acids liberated by acidifying the solution and shaking it with 100 c.c. of ether.   The ethereal solution is washed twice with 100 c.c. of water and shaken for 5 minutes with 15 c.c. of a 30% solution of lead acetate, and the insoluble lead soaps tested for arachidic and lignoceric acids.   The ethereal solution, which will contain the lead salts of the liquid fatty acids and also, if rape oil was present, erucic acid, is washed free from mineral acid, and hydrogenated in the presence of finely divided platinum, after which the ether is distilled off and the hydrogenated fatty acids fractionally crystallised as when testing for arachis oil (*supra*).   If the last fraction melts above 71° the presence of behenic acid is indicated.   As a rule in the case of oils containing rape oil, the m. p. of the crystals finally obtained is above 76°. In test experiments hydrogenation of erucic acid by this method yielded a behenic acid with m. p. 78.5°, and after three recrystallisations from alcohol, 82°.   Behenic acid is also characterised by being only sparingly soluble in 90% alcohol.

"Saponified" olive oils are liable to be taken as adulterated with foreign oils on account of the different analytical figures which they give, and more particularly on account of the large precipitate which they yield when subjected to Bellier's test (see Arachis Oil).   Archbutt (*J. Soc. Chem. Ind.*, 1911, **30**, 5) has investigated this point and has shown that one particular sample of oil of this type, which contained 3.2% of unsaponifiable matter and gave a precipitate by Bellier's test, yielded no trace of arachidic acid by Renard's process, and

another sample which gave an unusually marked indication by Bellier's test, was found by Renard's method to contain less than 5% of arachis oil. Archbutt points out the necessity for a careful interpretation of this test and due confirmation by Renard's method before the presence of arachis oil be certified. Attention is drawn to the turbidity of these oils, which is usually due to the presence of moisture, and to the increased viscosity, together with various other analytical differences exemplified in the following table of analyses of nine samples examined by him.

Sp. gr. at 15.5°.........	0.9167	0.9165	0.9175	0.9186	0.9169	0.9175	0.9169	0.9161	0.9179
Efflux time of 50 c.c. from Redwood's viscometer at 15.5° (seconds)...........	516.0	450.0	437.0	478.0	480.0	561.0	524.0	428.0	465.0
Saponification value...	186.1	186.9	189.3	186.9	186.0	185.5	185.9	185.4	185.8
Free (oleic) acid.......	2.9	3.3	1.0	1.1	0.9	2.3	1.8	0.4	1.6
Iodine value..........	86.4	85.1	85.8	84.4	85.5	85.6	85.0	86.5	86.2
Unsaponifiable matter.	2.49	2.34	2.08	2.70	3.30	3.32	3.23	2.98	2.67
Arachidic acid, by Renard's process........	......	......	......	......	......	....	......	......	......

"Extracted" olive oil, obtained by means of carbon disulphide, is liable to contain traces both of this solvent and of free sulphur. The latter may be detected by warming a silver coin or strip of copper in the oil. Carbon disulphide may be detected by the method suggested by E. Millau (*Ann. Chim. Anal.*, 1912, **17**, 1) who distils 50 grm. of the oil with 10 c.c. of pure amyl alcohol, collecting the first 5 c.c. of the distillate, and to 4 c.c. of the distillate adds 1 c.c. of kapok or cottonseed oil together with a few mg. of sulphur, and heats the mixture in a sealed tube for 1 hour.

Bolton and Revis found that as little as 0.05% of carbon disulphide can be easily detected in this way. Olive oils which have been extracted by carbon disulphide have been examined by F. Canzoneri and G. Bianchini (*Annali Chim. Applic.*, 1914, **2**, 1), who found them to differ from the ordinary expressed oil in the following respects: (1) High specific gravity; (2) Lower solidification of the fatty acids (*e. g.*, 17.5° to 19.7°); (3) Lower iodine value (77.5 to 80.2); (4) High acetyl value; (5) Lower refractive index (59° to 61° Zeiss) except in the case of oils bleached by oxidation, in the case of which the reading exceeds 63°; (6) Saponification value lower than normal.

In some recent methods of refining industrial oils sulphur compounds are removed by heating at 38° to 45°. Colza and ravison rape oils which have been refined do not show a reaction when

heated with a globule of mercury for 15 minutes, at 100° (Canzoneri and Bianchini) (*Annali Chim. Applic. (loc. cit.)*). Such oils, however, may be distinguished from extracted olive oils by their high refractometer reading (70°).

OLIVE-KERNEL OIL

This oil was formerly believed to be quite different in properties from ordinary olive oil (the oil of the mesocarp), having a sharp and bitter taste, a dark green or brown colour, and being readily soluble in alcohol owing to the presence of much free fatty acid; but it has been shown by Klein (*Zeit. angew. Chem.*, 1898, 847) that the characters formerly assigned to olive-kernel oil were really those of *pyrene* or *bagasses* oil, the dark coloured, much decomposed oil expressed from the stones and refuse of the first and second pressings of the olives. Pure olive-kernel oil, prepared both by cold and warm expression from the kernels alone, without any admixture of the pulp, was found to have the following characters, as compared with a sample of *bagasses* oil:

	Olive-kernel oil	"Bagasses" oil
Sp. gr. at 15.5°..........................	0.9186 to 0.9191	0.9277
Saponification value, %..................	18.23 to 18.38	19.05
Iodine value, %.........................	86.99 to 87.78	71.57
Refractive index........................	1.4682 to 1.4688	
Free fatty acids, %.....................	1.00 to 1.78	11.12

From these results it appears that pure olive-kernel oil is higher in sp. gr., somewhat higher in iodine value, and lower in saponification value than most olive oils, but it does not naturally contain an excess of free fatty acid.

In consequence of the belief prevalent among manufacturers and dealers that the presence of kernel oil in olive oil causes rapid decomposition of the latter to take place, Klein made mixtures of pure olive oil and pure olive-kernel oil and kept them in well-stoppered bottles, excluded from light, for 6 to 7 years. Scarcely any change took place either in the colour, taste, or smell of the oil, and the increase of free fatty acid was trifling in amount, proving that there

is no reason why the stones and fruit of the olive should not be crushed together if the oil is properly refined immediately afterward.

Klein detected no arachidic acid in olive-kernel oil.

TEA-SEED OIL[1]

(See also pp. 109.) This oil, obtained from the seed of the tea plant, *Camellia theifera,* has long been used in China as an edible oil, for burning, and for soap-making. It resembles olive oil in general characters and forms a solid elaidin. Two varieties, Chinese and Assam, are recognised. Oil of Assam tea seed, grown in Java, examined by Itallie, was a pale yellow thin oil, having an acrid taste and contained of palmitin, olein, and linolin, with traces of volatile acids, lecithin and phytosterol. A plant, *Camellia oleifera,* closely allied to the tea plant, is largely cultivated in China for the sake of the pale bland oil obtained from its seeds, which is said to be a very good lubricant for delicate machinery. It is dangerous for use as a food, unless refined, owing to the presence of saponin. The seeds of the Japanese *Camellia japonica* also yield an oil which is said to excel as a lubricant.

The following figures have been obtained by Bolton and Revis for a sample of commercial oil obtained from Chinese tea seed.

Sp. gr. at 15.5°....................................	0.9163
Iodine value..	84.35
Refractive index at 40° (Zeiss)......................	53.8
Saponification value................................	190.5
Free fatty acids (as oleic)..........................	1.84

Menon has examined seeds from Upper Assam which on extraction with petroleum spirit yielded 16.1% of an oil having the following characteristics:

Oil:

Sp. gr. 15°/15°....................................	0.9028
Saponification value...............................	189.9
Reichert-Meissl value..............................	0.56
Titration value of insoluble volatile acids..........	0.56
Iodine value......................................	92.7

Fatty acids:

Insoluble fatty acids + unsaponifiable...............	2.6
Insoluble fatty acids..............................	93.04
Melting point.....................................	38.9°
Neutralisation value...............................	199.9
Mean molecular weight.............................	280.5
Iodine value......................................	94.13

[1] Schaedler, Technologie der Fette (1892) p. 579; *J. Soc. Chem. Ind.,* 1894, **13,** 79; *Chemist & Druggist* 1001.

The fatty acids consisted of about 25% of solid acids melting at 57.8° and having a neutralisation value of 209.8, mean molecular weight 267.3, iodine value 13.84, and 74.75% of liquid acids of the neutralisation value 191.1, mean molecular weight 293.5, and iodine value 117.8.

Uchida (*J. Soc. Chem. Ind.* 1916, **35**, 1089) obtained the following results with a specimen of tea seed oil: Sp. gr. 30°/30°, 0.9126; $n_{D}^{27.6}$ = 1.4669; acid value, 4.12; saponification value, 193.8; Reichert-Meissl value, 0.10; Hehner value, 95.76; iodine value, 86.2; solidifying point of fatty acid, 25.5; and neutralisation value of fatty acids, 190.5. When treated with strong sulphuric acid this oil gave an indigo-blue coloration, changing to greenish brown on stirring.

Tea seed oil so closely resembles olive oil in its chemical characters that it is now used as a common adulterant of that oil. A colour reaction, which is not entirely satisfactory, has been devised by Cofman-Nicoresti (*Pharm. J.*, 1920, **104**, 139) for its detection. The oil under examination is shaken with a mixture of sulphuric and nitric acids and water, and the tube then left for 20 minutes in boiling water. Pure tea seed oil or an olive oil containing 20% of that oil gives a pink coloration when thus tested.

Dybowsky and Millia (*Inter. Rev. Sci. Agric.*, 1921, **11**, 1193) describe a test which consists in shaking 4 c.c. of the oil for 30 seconds with a mixture of 5 c.c. of pure sulphuric acid, 3 c.c. of nitric acid and 3 c.c. of water; the whole mixture is then kept at 5° for 5 minutes and the colour noted after 15 minutes. In the case of pure olive oil the oily layer shows a straw coloration and remains clear; with pure tea seed oil the layer becomes deep black and turbid; and with mixtures containing 5% of tea seed oil a dark straw coloured turbid mass is obtained. It is not improbable, however, that the tea seed oil giving these reactions had not been refined.

II. RAPE OIL GROUP

Black Mustard Seed Oil.	Radish Seed Oil.
Eruca Sativa Seed Oil.	Rape Oil (Colza Oil).
Indian Mustard Seed Oil.	Ravison Oil.
Jamba Oil.	White Mustard Seed Oil.

BLACK MUSTARD OIL. WHITE MUSTARD OIL

(See also p. 109.)   These oils, obtained, respectively, from the seeds of *Brassica* (*Sinapis*) *nigra* and *Brassica* (*Sinapis*) *alba*, resemble rape oil in composition and general characters. The resemblance is closest in the case of white mustard oil, that of black mustard being higher than rape oil in sp. gr. and iodine value.

The black seeds contain about 30% of oil, which is usually obtained as a by-product from the manufacture of mustard.

The Indian oil is often adulterated with sesame and similar oils.

The white seeds contain about 25% of oil.   The following figures have been recorded by Grimme for the oil obtained from four different kinds of seeds, (Lewkowitsch, *Oils, Fats and Waxes*, 5th Ed., 2, 271) including *Eruca sativa* (*q.v.*).

	Sinapis arvensis L.	Sinapis chinensis L.	Sinapis dissecta L.	Eruca sativa Lmk.
Oil:				
Sp. gr. at 15°..........	0.9228	0.9230	0.9221	0.9198
Solidifying point........	−13° to −15°	−14°	−13° to −14°	−8° to −10°
Saponification value.....	179.4	177.3	178.2	174.4
Iodine value...........	102.6	103.3	105.6	101.8
Refractive index at 20°..	1.4738	1.4736	1.4725	1.4723
Fatty acids:				
Fatty acids, %..........	94.21	94.28	94.34	94.24
Unsaponifiable matter, %	1.12	0.96	0.96	1.07
Solidifying point........	4–5°	14–15°	5–8°	8–10°
Melting point....... ...	6–8°	17–18°	9–10°	12–13°
Neutralisation value	179.8	182.0	181.7	180.1
Mean molecular weight..	312.4	308.6	309.1	311.8
Iodine value...........	106.6	106.7	109.0	103.6
Refractive index at 20°..	1.4625	1.4648	1.4645	1.4643

The amounts of essential mustard oil obtained from the seeds of the above species are given in the following table:

Name	Essential mustard oil in seed, %	Essential mustard oil in extracted seed meal, %
Sinapis arvensis.................	0.959	1.308
Sinapis chinensis.	1.407	2.022
Sinapis dissecta........	0.833	1.150
Eruca sativa..........	1.075	1.586

A method for the estimation of essential oil of mustard is given in Abs. *J. Chem. Soc.*, 1912, ii, 308.

A sample of crude mustard-husk oil (by-product from the manufacture of mustard from black and white seed mixed) examined by Archbutt gave the following results:

Sp. gr. at 15.5°...................................	0.9203
Viscosity at 15.5°...............................	Practically the same as that of rape oil.
Saponification value.............................	173.1
Iodine value (Wijs).............................	116.9
Unsaponifiable matter, %........................	3.3
Free (oleic) acid, %.............................	3.6
Maumené thermal test (50 grm. oil + 10 c.c. 97% H₂SO₄).	75.0°

Oils extracted in the laboratory and technically expressed were found by Raynes (*Analyst*, 1918, 43, 217) to have the following iodine values: Expressed oil, 119.6 to 121.0; black mustard oil, 114.4; white mustard oil, 104.7 to 108.6.

A sample of mustard-husk oil examined by Hehner and Mitchell gave 1.5% of brominated glyceride insoluble in ether.

Mustard oil is used for soap-making, burning, and lubricating. In drying properties it resembles rape oil, and contains arachidic acid (Arch butt, *J. Soc. Chem. Ind.*, 1898, 17, 1009).

INDIAN MUSTARD OIL

(See also p. 109.) Two samples of this oil, from the seeds of *Brassica juncea*, a plant closely allied to *B. nigra*, were examined by Crossley and Le Sueur (*J. Soc. Chem. Ind.*, 1898, 17, 992) and gave the results stated below. The oil is clear yellow in colour, and is largely used in India as an article of food and also medicinally. The first sample was from Bombay, variety "mustard," the second from Bengal, variety "rai."

Sp. gr. 15.5°	Saponification value	Iodine value	Reichert-Meissl value	Hehner value	Efflux time (seconds) of 50 c.c. at 70° F. Redwood	Butyro-refractom-eter de-grees at 40°	Optical activity in 200 mm. tube	Free (oleic) acid, %
0.9206	180.1	108.29	0.89	.....	382.8	....	−25′	0.94
0.9158	172.1	101.82	0.33	95.49	379.3	60.0	−18′	1.79

ERUCA SATIVA SEED OIL [1]

(See also p. 109.) This oil is obtained from the seeds of a plant closely allied to the mustards, extensively cultivated in India, and is used there for burning and to some extent as a food. It is yellow in colour and has an odour of turnip or mustard. Crossley and Le Sueur describe it as a non-drying oil, but it probably resembles rape oil in this respect, as it does in general physical and chemical characters. The three samples examined gave results as follows:

Sp. gr. 15.5°	Saponi-fication value	Iodine value	Reichert-Meissl value	Hehner value	Efflux time (seconds) of 50 c.c. at 70° F. Redwood	Butyro-refractom-eter de-grees at 40°	Optical activity in 200 mm. tube	Free (oelic) acid, %
0.9152	169.0	97.41	0.11	.....	405.8	59.2	−11′	0.93
0.9165	174.1	99.10	0.77	.....	369.4	....	−18′	0.63
0.9177	170.4	99.72	0.66	95.49	371.0	....	....	0.53

See also mustard oil p. 109.

RADISH SEED OIL

(See also p. 109.) This oil is obtained from the seeds of *Raphanus sativus*, or oil-radish. It resembles rape seed oil, and is used for the same purposes.

RAPE OIL. COLZA OIL

(See also p. 109.) This oil is obtained from the seeds of several varieties of *Brassica campestris*, of the order *Cruciferæ*, cultivated extensively in France, Germany, Austria-Hungary, Roumania, S. Russia, India, China, and Japan. The oils yielded by the different varieties of seed, though their botanical origin is quite distinct, are similar in their chief physical and chemical characters, and are not distinguished commercially, being all sold as rape or colza oil, although at one time the term "colza oil" was restricted to the product expressed from the finest French seed.[2]

Rape oil is obtained from the crushed seed by expression or by extraction with solvents. The crude oil is yellowish-brown or brownish-green in colour, has a peculiar odour and somewhat pungent taste, and contains foreign matters which separate to some

[1] Crossley and Le Sueur. *J. Soc. Chem. Ind.*, 1898, 17, 992.
[2] For further particulars see Archbutt and Deeley. *Lubrication and Lubricants*, 107.

extent on keeping the oil, but cannot be wholly removed by passive treatment. These lessen the combustibility, cause much smoke during the burning, and also tend to promote decomposition of the oil, with liberation of free acid. To remove them, the crude or "brown rape oil" is usually refined by agitating it, while warm, with from 0.5 to 1.5% of strong sulphuric acid; and after the foreign matters and suspended acid have subsided, the oil is washed by agitation with steam and hot water. This process is simple and rapid, but it has the disadvantage that some hydrolysis of the esters takes place, increasing the amount of free fatty acid in the oil, which is detrimental to it as a lubricant; the refined oil is also liable to retain traces of free sulphuric acid. Rape oil intended for use as a lubricant is, therefore, preferably refined with fuller's earth. Refined rape oil is pale yellow in colour and has a characteristic taste and smell.

The following results were obtained with a consignment of Chinese rape seed oil, before and after refining on a large scale.

	Crude	Refined
Sp. gr. at 15.5°..........................	0.9146	0.9147
Saponification value.................	172.1	171.9
Iodine value..........	101.1	101.0
Maumené thermal value.....	58.7°	57.8°
Unsaponifiable matter, %.........	1.65	1.20
Free (oleic) acid, %..........................	0.4	1.4

Rape oil stands between drying and non-drying oils. It does not thicken readily when heated and exposed to the air, and yet gives but an imperfectly solid elaidin with nitrous acid. In non-drying characteristics it is decidedly inferior to olive oil, but owing to its usually lower price, freedom from excess of acidity, and less tendency to decompose and become rancid, it is extensively used in admixture with mineral oils for engine and machinery lubrication, especially on railways. As an illuminant for railway carriages it has been almost superseded by gas and electricity, but it is still used very largely as a burning oil for other railway lamps and miners' safety lamps.

Rape oil has been found to contain esters of rapic and erucic acids,[1] but the presence of rapic acid requires confirmation. The

[1] Reimer and Will (*Ber.*, 1886, 19, 3320) found in some casks of old rape oil, a tallow-like deposit consisting of di-erucin.

high iodine value of the oil points to the presence also of an acid or acids of the linolic or linolenic series (*Vide infra*). Esters of saturated fatty acids occur in very small proportion[1] and include arachidic and, probably, lignoceric acids. Ponzio (*J. pr. Chem.*, 1893, 48, 487) found 0.4% of arachidic acid in one sample. Alén (*Svensk. Kemisk Tidskrift*, 1893, 179) found arachidic acid in the oil from Guzerat seed, but not in that from the European varieties. Archbutt (*Jour. Soc. Chem. Ind.*, 1898, 17, 1009) found 1.43% of arachidic (and lignoceric) acids in rape oil extracted by means of ether from Guzerat seed, and 1.14% in commercial (Stettin) rape oil expressed from rape and rubsen seed. Of 51 samples of commercial rape oil which were specially examined by Renard's process, about two-thirds were found to contain arachidic acid. Indian rape oil from *B. glauca* seems to contain more of this acid than the European oil, and the extracted oil more than the expressed oil; of the latter, the cold-pressed oil probably contains less than the hot-pressed.

Toyama (*J. Chem. Ind.* Japan, 1922, 25, 1044) has found that the amount of saturated acids is less than 2%; they include palmitic, stearic, behenic, arachidic and lignoceric acids. The main constituent is erucic acid (about 65%) and there are also small amounts of linolic and linolenic acids.

Rape oil and other oils from the *Cruciferæ* are commonly stated to contain sulphur compounds and to give rise to silver sulphide on treating their ethereal solutions with a few drops of solution of silver nitrate in alcohol. If the oil is boiled with a 10% solution of pure potassium hydroxide, an immersed silver coin becomes blackened. Sulphur is present sometimes, but is accidental.

According to Schaedler, rape oil solidifies at $-2°$ to $-10°$; but Holde states that all rape oils sooner or later solidify at $0°$. The following experiment was made by Archbutt. Some genuine refined rape oil was placed in a glass tube, immersed in melting ice for 3 hours without stirring, and then for 3 hours longer, with stirring at intervals. It remained clear and fluid. Some of the same oil, previously frozen, having been added, the oil was kept in ice for 3 hours longer, with occasional stirring, but the frozen oil slowly melted. The temperature was then gradually reduced to -10 to $-9°$, and the oil became very turbid, but after remaining

[1] Tolman and Munson found from a trace of 1.43 % of solid fatty acids in 4 samples of rape oil, by Muter's method.

for 2 hours at this temperature, with stirring, it did not lose its fluidity. After still further reducing the temperature to −11.6° and stirring, the oil solidified in about half an hour.

The chief physical and chemical constants of rape oil are given on p. 109, and the oleo-refractometer value on p. 61. Some constants of a number of Indian crude rape oils expressed from different varieties, of pure seeds have been determined by Crossley and Le Sueur (*J. Soc. Chem. Ind.*, 1898, **17**, 989) and are given in the table on p. 168. The following results by Archbutt were obtained with rape oil extracted from the seed by ether in the laboratory:

	Yellow Guzerat seed oil	Brown Calcutta seed oil	Madras seed oil
Sp. gr. at 15.5°........	0.9133	0.9146	0.9140
Saponification value...	175.0	174.2	174.5
Iodine value..........	97.8	102.7	99.6

The following are some observed data from the mixed fatty acids of rape oil:

		Observer
Sp. gr. at 99°/15.5°........................	0.8438	Allen.
Sp. gr. at 100°/100°.......................	0.8758	Archbutt.
Solidifying-point ("titer" test) { colza oil.....	12.7–13.6	Lewkowitsch.
{ rape oil......	11.7–12.2	Lewkowitsch.
Refractive index at 60° F...................	1.4491	Thoerner.
Iodine value of mixed fatty acids...........	96.3–105.6	Various.
Iodine value of liquid fatty acids............ {	124.2–125.5	Tortelli and Ruggeri.
{	120.7	Wallenstein and Finck.

Analysis of Commercial Rape Oil.—Owing to the enormous extent to which rape oil is used for lubricating and burning, the estimation of *free acid* is of great importance (see under "Olive Oil," p. 144). The method is described on p. 10.

According to Archbutt and Deeley,[1] commercial refined rape oil contains on an average about 2.2% of free acid calculated as oleic acid, ranging from 1% to about 6%, but seldom exceeding 4%.

[1] Lubrication and Lubricants, p. 211.

378 samples, all representing large contracts, gave the following results:

Number of samples	Free (oleic) acid, %
122	1.1 to 1.9
223	2.0 to 2.9
30	3.0 to 3.9
3	4.0 to 5.7
378	Average, 2.21%

It is evident from these figures that carefully refined rape oil should not contain more than 3% of total acidity. The traces of free sulphuric acid in 3 samples of rape oil refined with this acid were determined and found to range from 0.0026 to 0.0056%, from which it is concluded that the percentage of free *mineral* acid in refined rape oil should not exceed 0.006% of H_2SO_4, which is equivalent to 0.035% of oleic acid.

Rape oil is subject to numerous adulterations, the more important of which can be detected with tolerable certainty.

The *sp. gr.* of genuine rape oil averages 0.915 at 15.5°. Of 52 samples examined by Archbutt (*J. Soc. Chem. Ind.*, 1886, 5, 310), 7 had sp. gr. below 0.9140, 27 above 0.9139 and below 0.9150, and 18 above 0.9149 and below 0.9160. The lowest was 0.9132 and the highest 0.9159. 30 samples of brown rape oil, known to be genuine, examined by Redwood, ranged in sp. gr. from 0.9145 to 0.9154, the average being 0.9149. The 7 samples of crude oil examined by Crossley and Le Sueur given on page 168 ranged in sp. gr. from 0.9142 to 0.9171, but from the abnormally high viscosity and low iodine value of the latter sample, it would appear to have become oxidised. 358 samples of the commercial oil more recently examined by Archbutt gave the following results:

	Number of samples
0.9136 to 0.9139	13
0.9140 to 0.9149	241
0.9150 to 0.9159	103
0.9160	1
	358

INDIAN RAPE OILS.   CROSSLEY AND LE SUEUR

Botanical name	Variety	Locality	Sp. gr. at 15.5°	Saponification value	Iodine value	Reichert-Meissl value	Hehner value	Efflux time (seconds) of 50 c.c. at 70° F. Redwood	Butyro-refractometer degrees at 40°	Optical activity in 200 mm. tube	Free (oleic) acid, %
Brassica campestris..... ..	red.........	N. W. Provinces...	0 9148	171.6	99.20	0.79	96.30	390.6	....	−7′	0.73
Brassica campestris.......	glauca......	N. W. Provinces...	0.9142	171.4	97.71	0.67	95.04	402.6	59 2	−10′	0.45
Brassica campestris.......	dichotoma..	N. W. Provinces..	0.9154	172.2	104 84	0.22	95.57	371.8	....	...	0.39
Brassica campestris.......	....	Punjab..........	0.9163	173.4	96.25	0.43	94.56	393.2	....	...	0.65
Brassica campestris.......	brown......	Bombay..........	0.9171	172.8	94.10	0.00	....	464.6	....	...	1.00
Brassica campestris.......	yellow......	Bombay..........	0.9141	169.4	96.66	0.00	....	413.8	....	−5′	0.36
Brassica campestris.......	napus......	Bengal..........	0.9146	167.7	97.70	0 00	95.55	398.0	58.8	−15′	0.95

The average sp. gr. was 0.9147. The experience of Allen confirmed the results of Archbutt and Redwood, so that 0.9160 may be regarded as the maximum sp. gr. for genuine rape oil at 15.5°. North German (Baltic) rape oil is usually somewhat heavier and less pure than the French and Belgian products. The seed crushed in England, imported from the East Indies and all parts of Europe, gives an oil varying in sp. gr. from 0.9136 to 0.916. Black Sea rape (ravison) oil is an inferior, more strongly drying oil than that expressed from cultivated rape seed, and its presence in rape oil must, therefore, be regarded as adulteration.

The *sp. gr.* of rape oil is a valuable indication of its purity, as all the ordinary adulterants are heavier than the genuine oil, with the exception of mineral oil and sperm oil, which can be detected and estimated with accuracy by methods described on pp. 20 and 97. Foreign *seed oils* of more or less drying character, as sesame, sunflower, niger-seed, hempseed, cottonseed, or linseed oil, or possibly coconut olein, all range between 0.920 and 0.937. Hence, if the sample has a sp. gr. of 0.918, it may possibly contain even 50% of these oils, while the smell and colour will be little affected. Seed and nut oils deteriorate rape oil by increasing its gumming properties, with the exception of arachis oil and coconut olein, and the addition of either of these is improbable. Arachis oil could be detected as in olive oil (page 152), due allowance being made for the arachidic acid naturally present in rape oil itself (see p. 165), and coconut olein would be indicated by the raised saponification value and reduced iodine value of the sample.

The *viscosity* of rape oil is a valuable indication of its purity, as it is moderately constant and exceeds that of any oil likely to be used as an adulterant. The sample should always be compared with a specimen of rape oil known to be genuine, or with pure glycerol diluted to 1.226 sp. gr., which at 15.5° has the same viscosity as average rape oil. The time of efflux of 50 c.c. from Redwood's viscometer at 70° F. should not be less than 370 seconds, and ranges from this up to about 415 seconds.[1] The number 464.6 recorded by Crossley and Le Sueur for Bombay rape oil is exceptionally high. The lowered viscosity of an adulterated oil could be corrected by the addition of castor or blown oil, but these would raise the sp. gr. and acetyl value. Heavy mineral oil would be found in the unsaponifiable matter.

[1] These numbers refer to an instrument which delivers 50 c.c. of water at 70° F. in 25.74 seconds.

The *saponification value* of genuine rape oil ranges from 170.0 to 175.0. A value in excess of 175.0 would indicate the presence of ravision or other more strongly drying oil. A lower value than 170.0 would indicate the presence of an unsaponifiable oil or sperm oil, or both. Refined rape oil has been frequently adulterated with a specially purified mineral oil. This addition interferes with the burning qualities of the oil, causing it to smoke and form much deposit on the wick.

The *iodine value* of rape oil ranges from 97 to 105%, being slightly less than that of cotton or sesame oil, and considerably below that of the more strongly drying oils. This test is useful for the detection of ravison oil, which has a higher iodine value than rape oil.[1]

The *Maumené thermal value*, or rise of temperature on mixing genuine rape oil (50 grm.) with sulphuric acid (10 c.c.) containing 97% of H_2SO_4, ranges from about 58° to 63°. An abnormally high result indicates ravison or other more strongly drying oil, and a low figure indicates mineral or sperm oil. Hehner and Mitchell's *bromine thermal test* (p. 78) may be used for the same purpose.

The *melting and solidifying-points of the mixed fatty acids* of rape oil are raised by cottonseed and lowered by many other oils, such as ravison, linseed, or fish oils.

Separation of Erucic Acid.—Thomas and Yu (*J. Amer. Chem. Soc.*, 1923, **45**, 129) have based a qualitative test for rape oil on the fact that magnesium erucate is soluble in 90% alcohol. The fatty acids obtained by hydrolysis of the insoluble magnesium soaps, as described under Arachis Oil (p. 130), are dissolved in 60 c.c. of 90% alcohol, and the solution allowed to stand overnight. The m. p. and iodine value of any crystals which separate are then determined. In the case of two samples of genuine rape oil about 25% of the hydrolysed fatty acids were thus separated and showed m. p. 35° (erucic acid = 32°) and iodine value 70 to 72 (erucic acid = 74.9).

The *unsaponifiable matter* should not exceed 2%. In the expressed oil it is usually near 1%, but in the case of rape oil extracted from the seed by petroleum spirit some allowance must be made for residual hydrocarbons. If more than 2% of unsaponifiable matter

[1] Milrath (*Zeitsch. öffentl. Chem.*, 1907, **19**, 371) obtained the following results with 3 samples of Austrian rape oil: Sp. gr., 0.9138 to 0.9155; refraction at 25°, 67.7 to 67.9; at 40°, 59.7 to 59.8; acid value, 3.1 to 7.2; saponification value, 173.1 to 174.3; iodine value, 106.9 to 108.2. These are exceptionally high iodine values.

be found, it should be purified by re-saponification; and if still in excess of 2%, the purified product should be further examined to ascertain whether mineral or rosin oil, cholesterol from animal oils, or wax alcohols from sperm oil are present. In genuine rape oil, the unsaponifiable matter consists mainly of phytosterol.

A simple and useful *oxidation test* may be made by exposing 1 grm. of the sample on a watch-glass to the air in a water-oven at 100° for about 16 hours, side by side with a sample of known purity; both samples being contained in watch-glasses of the same curvature. On examining the condition of the oils when cold, genuine rape oil of the best quality for lubricating will be found to be still quite fluid when caused to flow by inclining the glass, and will not have dried; inferior samples will have dried at the edges or have crept up and formed dry spots on the sides of the glass, and most rape oils will have thickened more or less considerably. Livache's test may also be used.

An abnormally low sp. gr. and viscosity of extracted rape oil is sometimes due to incomplete expulsion of the petroleum spirit used in the extraction process. Such oil will have an abnormally low *flash-point*. When tested in the Pensky-Martens or Gray closed-test apparatus, normal rape oil usually flashes at 410° to 450° F. (210° to 232°). Archbutt has occasionally met with samples of extracted oil flashing at 180° F. and losing about 1% in weight in 1 hour when 1 grm. of the oil was heated in a platinum dish in the water-oven.

Valenta's acetic acid test (p. 80) gives very characteristic indications in the case of rape oil and may be found useful in certain cases.

Halphen's colour test for cottonseed oil (p. 177) and the *furfural test* for sesame oil should not be omitted. They may be relied upon to give negative indications with genuine rape oil. Both tests are very delicate and must only be used as confirmatory evidence. The amount of foreign oil present must be calculated from the quantitative values. Press-bags which have been used for cottonseed and afterward for rape seed may be the cause of traces of colour in Halphen's test.

Ravison and cottonseed oils are two of the commonest adulterants of rape oil. Both raise the sp. gr., saponification value and Maumené thermal value, and lower the viscosity. Ravison oil raises the iodine value, and lowers the m. p. of the fatty acids. Cottonseed

oil does not appreciably affect the iodine value of the oil, but it raises the iodine value of the liquid fatty acids and raises also the m. p. of the oil and of its mixed fatty acids. Cottonseed oil can only be added to refined rape oil; if added to the crude oil, it causes it to become red when refined with sulphuric acid. Both ravison and cottonseed oils are more strongly drying oils than rape.

Linseed oil is a very objectionable adulterant of rape oil. It may be added before refining or by crushing the seeds together. It causes such a marked effect in raising the sp. gr., iodine value, thermal values with sulphuric acid and bromine, in lowering the viscosity of the oil and the m. p. of the mixed fatty acids, and in increasing the tendency of the oil to oxidise, that even a small admixture cannot fail to be detected. Linseed oil and fish oils are especially identified by means of Hehner and Mitchell's bromo-glyceride test.

Fish oils are recognisable by their peculiar taste and odour on warming, also by the colorations developed with caustic soda and sulphuric acid. They lower the viscosity in a marked degree, and affect the quantitative values much in the same way as linseed oil. Liver oils are said to be best detected by agitating 100 drops of the oil with 1 of sulphuric acid, when the depth of the red coloration will follow the proportion of the adulterant present.

Hedge-mustard oil may be used for adulterating rape oil, which it closely resembles. The most characteristic test is said to be the production of a green colour when the oil is treated with a quantity of alcoholic potash insufficient for complete saponification. and the filtered liquor strongly acidified with hydrochloric acid.

JAMBA OIL

The oil mentioned under this name in the table on p. 109 is a kind of rape oil which is occasionally exported from Kurrachi. It closely resembles ordinary rape oil, but according to Lewkowitsch behaves abnormally when an attempt is made to convert it into thickened or "blown oil."

BLACK SEA RAPE OIL. RAVISON OIL

Oil expressed from the wild rape seed of the Black Sea district, largely exported from Odessa, and known as ravison oil, is inferior in

quality to, and cheaper than ordinary rape oil. It has a higher sp. gr., higher saponification and iodine values, lower viscosity, and more strongly marked drying properties than ordinary rape oil. The unacknowledged admixture of this oil with rape must, therefore, be regarded as adulteration. To prevent any possible dispute, it should be definitely excluded in contracts for rape oil. The chief physical and chemical characters of a few samples of this oil are shown in the following table:

Sp. gr. at 15.5°..........................	0.9175 to 0.9217
Saponification value........ ....|	177 to 181.3
Iodine value............... ....|	109 to 122
Maumené thermal value... .. ..|	66° to 76°
Viscosity...........................	About 6 to 13% lower than that of re-fined rape oil.
Sp. gr. of mixed fatty acids at $\frac{100°}{100°}$.....	0.880

III. COTTONSEED OIL GROUP

Beechnut Oil.	Madia Oil.
Brazil-nut Oil.	Maize Oil.
Cameline Oil.	Pumpkin Seed Oil.
Cottonseed Oil.	Sesame Oil.
Cress Seed Oil.	Soya Bean Oil.
Kapok Oil.	Tomato Seed Oil.

Wheat Oil.

BEECH OIL. BEECHNUT OIL

(See also p. 110.) This oil is obtained from the kernels of the fruit of the common or red beech tree, *Fagus sylvatica*. It has a clear yellow colour, a peculiar odour, and faint flavour; when freshly drawn it has an acrid flavour, which disappears in time. It is used in France for cooking and as an illuminant. It does not readily become rancid.

BRAZIL-NUT OIL

(See also p. 110.) This oil is obtained from the Brazil nuts of commerce, the produce of *Bertholletia excelsa*, a tree which flourishes in northern Brazil and Venezuela. It is a pale yellow oil, odourless and of pleasant taste, but easily turning rancid. It is used for culinary purposes when fresh, also for burning and soap-making.

According to De Negri and Fabris oil obtained by extraction has a lower iodine value (93.5 to 95.8) than the expressed oil. Hehner and Mitchel found that the oil does not yield an insoluble bromoglyceride.

CAMELINE OIL. GERMAN SESAME OIL

(See also p. 110.) This oil is obtained from the seeds of *Camelina sativa (Myagrum sativum)*, "Gold of Pleasure," a plant of the order *Cruciferæ*. According to Schaedler, it has a golden yellow colour, a sharp, peculiar taste and smell, and dries slowly. It is used for burning and for making soft soap. The cold-pressed oil is sometimes also used as an edible oil. Cameline oil is said to be used as an adulterant of rape oil, but would be readily detected by its higher sp. gr., and iodine value. It is liable to be present in linseed oil from East Indian seed, and may account for the low iodine value and inferior drying properties of some samples of that oil.

According to De Negri and Fabris it is mainly composed of the glycerides of oleic, linolic and palmitic acids, with a small amount of erucin.

COTTONSEED OIL

(See page 110.) Cottonseed oil is now expressed in enormous quantities in the United States, on the continent of Europe, and in Great Britain, from the seeds of the different varieties of the cotton plant.

Crude cottonseed oil has a sp. gr. ranging from 0.916 to 0.930. It contains in solution, often to the extent of 1%, a characteristic colouring matter, which gives it a ruby-red colour, sometimes so intense as to appear nearly black. The crude oil gives a bright red coloration with strong sulphuric acid (page 55). The soap from crude cottonseed oil rapidly oxidises on exposure to air with production of a fine purple or violet-blue coloration.[1] This test is characteristic.

[1] "Cottonseed blue" is stated by Kuhlmann to have the composition of $C_{17}H_{24}O_4$. It is amorphous; readily destroyed by oxidising agents; insoluble in water, dilute acids and alkalis; sparingly soluble in carbon disulphide and chloroform, but more readily in alcohol and ether; and dissolves in strong sulphuric acid, forming a purple solution. The unoxidised colouring matter of cottonseed oil has been examined by J. Longmore, who, in a communication to Allen, stated that it is a pungent golden-yellow product, insoluble in water, but soluble in alcohol and alkaline solutions, and precipitated from the latter on addition of acids. It dyes well and is perfectly fast on both wool and silk.

The colouring matter causes the oil to produce stains, and it is removed by agitating the crude oil at the ordinary temperature with 10 to 15% of solution of sodium hydroxide of 1.06 sp. gr. when the alkali combines with the colouring matter and the free fatty acids of the oil. The mixture becomes filled with black flocks which deposit on standing,[1] and leave the oil but slightly coloured. The loss from refining is usually from 4 to 7.5%, but occasionally amounts to 12 or 15. Hence it is desirable, before purchasing crude cottonseed oil for refining, to ascertain by a laboratory experiment what the percentage of loss is likely to be. Frequently the treatment with alkali is only carried far enough to remove the greater part of the colouring matter, the oil being then boiled with a solution of bleaching powder and subsequently treated with dilute sulphuric acid. This method of treatment is economical, but the oil acquires an unpleasant taste and smell which cannot be removed. Hence such chemical bleaching cannot be used for the oil which is required for edible purposes.

Refined cottonseed oil is of a straw or golden-yellow colour, or occasionally nearly colourless. The sp. gr. usually ranges from 0.922 to 0.926 and the solidifying point from 1° to 10°. By subjection to cold and pressure a certain proportion of "stearine" is separated, the m. p. of the residual oil being correspondingly lowered. This refined oil is usually almost free from acid, and, when properly prepared, is of pleasant taste. It is extensively employed for edible and culinary purposes. It is now substituted for olive oil in some of the liniments of the *United States Pharmacopœia*, but its principal applications are in soap-making and the manufacture of margarine.

Colour Standards.—A series of colour standards for the classification of cottonseed oils has been developed by Arny, Kish and Newmark (*J. Ind. Eng. Chem.*, 1919, **11**, 950). These standards, termed the Co–Fe–Cu standard, have the following composition: *Red:* N/2 solution of cobalt chloride in 15% hydrochloric acid. *Yellow:* N/2 ferric chloride solution. *Blue:* N/2 copper sulphate solution; all in 15% hydrochloric acid.

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[1] The deposit thus formed, consisting of colouring and albuminous matters, alkali, and partially saponified oil, is technically called "mucilage." It is decomposed with a slight excess of acid, and the resulting dark-coloured grease is heated to a temperature of 120° (250° F.) with concentrated sulphuric acid, which renders insoluble the colouring matters, etc., while the impure fatty acids rise to the surface. On distilling these with superheated steam, a mixture of fatty acids is obtained, which is separated into stearic and oleic acids by pressure. The "cottonseed stearine" thus obtained is employed for making soap and composite candles and for various adulterations.

The following limits are suggested for the specification of commercial grades of cottonseed oil:

Cottonseed oil	From—				To—			
	Fe	Co	Cu	Water to—	Fe	Co	Cu	Water to—
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Prime white.............	6	0.4	......	50	16.0	1.4	......	60
Choice summer yellow....	22	3.4	......	50	33.3	3.3	......	50
Off. summer yellow.......	42	6.2	......	60	39.0	7.2	......	50

Chemical Composition.—The solid esters of cottonseed oil consist mainly of palmitin, with a little stearin; the liquid esters contain olein and linolin.

Cottonseed oil is characterised by the high m. p. of its mixed fatty acids (38°) and by the colour tests described below. In the elaidin test it gives an orange-coloured semi-fluid mass. It is not itself very liable to adulteration, owing to its cheapness, but it is frequently employed to adulterate other oils. Most oils likely to be added to cottonseed oil would lower the m. p. of the fatty acids; linseed oil and whale oil would be found by Hehner and Mitchell's bromo-glyceride test. For the detection of maize oil see under "Maize Oil."

For the detection of cottonseed oil in other oils, Halphen's colour test generally suffices, and a determination of the sp. gr., iodine value, and melting- or solidifying-point of the mixed fatty acids will generally enable the proportion present in a mixture to be determined.

The unsaponifiable matter is usually near to 1% and contains phytosterol. The rise of temperature of 50 grm. of the oil with 10 c.c. of sulphuric acid (97% H_2SO_4) is about 75° to 81°. The viscosity at 15.5° is about ¾ that of refined rape oil at the same temperature.

The following are some observed analytical data from the mixed fatty acids of cottonseed oil:

		Observer
Sp. gr. at 15.5°/99°.................	0.8467	Allen.
Sp. gr. at 100°/100°......................!	0.8816	Archbutt.
Solidifying-point ("titer" test)..	35.6°–37.6° 1	⎫
	32.2°–32.7° 2	⎬ Lewkowitsch.
	33.3°–34.1° 2	⎪
	34.4°–35.2° 2	⎭
	28.1°–28.5° 3	
Refractive index at 15.5..................	1.4460	Thoerner.
Iodine value of mixed fatty acids......	111–116	Various.
Iodine value of liquid fatty acids........ ..	142–152	Various.

1 Natural refined oil.
2 Partly "demargarinated" oils.
3 Winter oil.

Cottonseed stearine (*cotton oil stearine*) is, properly speaking, the solid fat separated from cottonseed oil by cooling and pressing. It is a pale yellow fat, of butter-like consistency, and is used in the manufacture of butter substitutes. The article known in commerce as "cottonseed stearine" is usually impure stearic acid from cottonseed oil, obtained by the method given in the foot-note on page 175. The crude oil expressed from decorticated cottonseed is sometimes very rancid and semi-solid at the ordinary temperature from the separation of solid fatty acids in the free state. By pressure it would yield a product similar to that obtained by distillation.

Colour Tests for Cottonseed Oil.

Halphen's Colour Test.[1]—If cottonseed oil or oil containing it is heated with carbon disulphide, sulphur and amyl alcohol, a characteristic red is produced, the intensity of which is not the same with all samples of cottonseed oil, but with the same sample is proportional to the quantity of cottonseed oil present. In making this test, 3 c.c. of the oil, 3 c.c. of amyl alcohol, and 3 c.c. of a 1% solution of sulphur in carbon disulphide are mixed in a small test-tube and heated in a bath of boiling water. With a little as 5% of cottonseed oil present, a distinct red is developed in from 15 to 30 minutes; the colour is more intense and more rapidly produced the greater the proportion of cottonseed oil. Less than 5% can be detected by longer heating, and especially if the colour is compared with that given by a pure sample of oil. This indication is not quite characteristic of cottonseed oil, but is given also by kapok and baobab oils

1 *J. Pharm. Chim.*, 1897, 6, (9), 390.

(Milliau, *Compt. rend.*, 1904, **139**, 807), to detect which Milliau recommends the following procedure: The oil is saponified and the mixed fatty acids are liberated, washed, and dried.   5 c.c. of the melted acids are mixed with 5 c.c. of a 1% solution of silver nitrate in absolute alcohol, shaken *cold* and allowed to stand.   The presence of even 1% of kapok and baobab oils is said to cause a dark brown coloration after 20 minutes, while cottonseed oil causes no reduction until the mixture is warmed.

The nature of the chromogenetic substance in cottonseed oil is not known, but it is rapidly destroyed by heating the oil to 250°.   Raikow (*Chem. Zeit.*, 1899, **23**, 1025) says that heating with open steam has no effect, but superheated steam or simple heating to between 210° and 220° quickly destroys, and heating to 150° for several hours very gradually destroys, the active agent.   This has been confirmed by others.   The heated oil becomes darkened in colour and acquires a disagreeable flavour, hence would be less likely to be mixed with an edible oil or fat than with a lubricating oil.   Fischer and Payne have also shown that cottonseed oil is rendered insensitive to the test by treatment with chlorine or sulphurous acid (*Zeitsch. Nahr. Genussm.*, 1905, **9**, 81).   Hence a negative reaction in Halphen's test does not prove the absence of cottonseed oil, and a pink colour must not be considered a proof of its presence, unless the quantitative reactions afford corroborative evidence.   It has been shown that the fat of animals which have been fed on cottonseed cake may give the colour indications of cottonseed oil.   Thus lard from the fat of pigs, and butter from the milk of cows fed on cottonseed cake may give the test and yet be quite free from cottonseed oil.

Various improvements have been suggested in order to render the Halphen test still more delicate (some of these are described under olive oil).   One of the most important and one which Bolton and Revis have found to be extremely delicate, is the substitution of pyridine for amyl alcohol, as suggested by E. Gastaldi (Abst. *J. Soc. Chem. Ind.*, 1912, **31**, 934), who carries out the test by mixing in a strong test-tube, 5 c.c. of the oil or fat to be tested, 1 drop of pyridine and 4 c.c. of carbon disulphide containing 1% of sulphur, corking the tube and heating in the water-bath for half an hour. As little as 0.25% of cottonseed oil will be found to produce a distinct red tint if compared with a control tube.

Utz (*Chem. Rev. Fett Ind.*, 1913, **20**, 291) proposes to substitute pentachlorethane (b. p. 159°) for carbon disulphide so as to obtain a higher temperature, and states that he has obtained a reaction with 1% of cottonseed oil and that the colour is produced without the presence of amyl alcohol, if the temperature is sufficiently raised. Gastaldi and others, however (*vide* olive oil), have shown that if the temperature is raised appreciably above 120° a red colour is often produced when no cottonseed oil is present. The statement of Utz must therefore be accepted with due reserve.

Silver Nitrate Test.—This test, originated by Bechi (*Chem. Zeit.*, **11**, 1328), depends upon the presence in cottonseed oil of a substance which gives a brown precipitate with silver nitrate. It may be applied to the oil or to the mixed fatty acids there from. Several modifications are in use. The method recommended by an Italian Government Commission in 1887 (See *Analyst*, 1887, **12**, 170), which is substantially that of Bechi, requires the two following reagents:

A. Silver nitrate, 1 grm.; alcohol (98% by volume) 200 c.c.; ether, 40 c.c.; nitric acid, 0.1 grm.

B. Amyl alcohol, 100 c.c.; rape oil, 15 c.c.

10 c.c. of the oil to be examined are mixed in a test-tube with 1 c.c. of reagent A, and then shaken with 10 c.c. of reagent B. The mixture is next divided into two equal portions, one of which is immersed in boiling water for 15 minutes. The heated sample is then removed from the water-bath, and its colour compared with the unheated half. Presence of cottonseed oil is indicated by the reddish-brown coloration of the heated portion. Only the purest alcohol should be used, and the rape oil used should be "cold drawn," and only slightly coloured; it should be filtered in a hot-water oven before preparing the reagent. To guard against errors from impurity of the materials, a blank test should be instituted side by side with the actual test.

The part played by the rape oil in this test is explained, according to Bechi, by the fact that whereas fresh cottonseed oils give the silver nitrate indication without rape oil, old and rancid samples or their mixed fatty acids do not interact unless this oil is added. Many chemists consider the addition of rape oil unnecessary. Thus, in the official method of the Swiss Society of Analysts (*J. Suisse Chim. Pharm.*, **35**, 448) a single reagent is used, which is

prepared by dissolving 1 grm. of silver nitrate in 5 c.c. of water, adding 200 c.c. of alcohol, 40 c.c. of ether and 0.1 c.c. of nitric acid (1.42).   10 c.c. of the oil are heated for 15 minutes in boiling water with 3 c.c. of this reagent, and it is said that 1% of cottonseed oil, if present, will be detected.   Petkow (*Zeit. öffentl. Chem.*, 1907, **13**, 21), who recommends this method, states that the sensitiveness of Bechi's test depends upon the relative amount of silver nitrate used.

Milliau (*J. Amer. Chem. Soc.*, 1893, **15**, 153) prefers to apply the test to the mixed fatty acids, but in preparing these regard must be had to the fact that prolonged heating of the acids at 100° or washing them by boiling with water must be avoided, as both cause a loss of the reacting substance.[1]

This is probably the reason why some chemists have concluded that Milliau's test is less delicate than Bechi's.   The following is the procedure recommended by Archbutt: Approximately 5 grm. of the oil are saponified, and the fatty acids in a separating funnel and dissolved by shaking with about 70 c.c. of ether.   The ethereal solution left after the aqueous liquid has been drawn off, is well washed with small quantities of cold water and poured through a dry filter into a dry flask.   The ether is distilled off, and the fatty acids are heated on the steam bath for about 5 to 10 minutes to drive off the remaining traces of ether and water, and at once dissolved by pouring 20 c.c. of absolute alcohol into the flask.   The solution is transferred to a 1-in. diameter test-tube and heated to boiling, after which 2 c.c. of a 30% aqueous solution of silver nitrate are added and the test-tube is shaken and held over a white tile. In the presence of 5% of cottonseed oil a characteristic brown turbidity is produced almost immediately.   If there is no immediate coloration, the solution is kept under observation for a minute or two at boiling heat by moving the tube to and fro from the tile to the flame, and if only 2% of cottonseed oil is present a distinct brown coloration will be obtained, though more slowly developed.

This test has been examined by a large number of chemists and is known to be given only by cottonseed, kapok, and baobab oils and to a very slight extent by madia oil.   To distinguish these last two oils from cottonseed oil, see under "Halphen's Colour Test."   Some genuine rape oils appear to reduce the silver nitrate very slightly, but the reaction takes place slowly and the colour produced is black-

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[1] Archbutt and Deeley. Lubrication and Lubricants, 2nd Ed.

ish, whilst with cottonseed oil it is brown. It has also been observed that some olive oils give a brown colour in Bechi's test. Fats which have been exposed to the air or have become rancid may reduce the silver solution owing to the presence of aldehydic compounds. Thus Bevan (*Analyst*, 1894, **19**, 88) found that lard which had been exposed to the air for some days gave a reaction in Bechi's test, whilst some taken from the interior of the mass had no reducing property. It has also been shown that genuine butter and lard from animals fed on cottonseed oil may give this reaction. On the other hand, Bechi's test, like Halphen's, is not given by cottonseed oil which has been heated to 250°, and all cottonseed oils do not respond to the test to the same extent. Therefore, this test is no more certain than Halphen's and can only be used as an auxiliary to the quantitative reactions.

It should be noted that Tortelli and Ruggeri (*Annali Lab. Chem. Gabelle*, 1900, **4**, 249) state that by applying this test to the fatty acids from the lead soaps soluble in ether, cottonseed oil which has been heated to 250° long enough not to respond to the ordinary test may still be detected. 5 grm. of the oil are saponified with 30 c.c. of alcoholic potassium hydroxide (60 grm. of the hydroxide in 1000 c.c. of 90% alcohol), the solution exactly neutralised with 10% acetic acid and poured in a thin stream into a hot solution, about 300 c.c. in volume, containing 5 grm. of lead acetate. The washed and dried lead soaps are warmed for about 20 minutes with anhydrous ether under a reflux condenser, and the ethereal solution, when cold, is filtered into a separating funnel and decomposed by shaking with dilute hydrochloric acid. After the aqueous liquid has been separated and the ethereal solution well washed with cold water, the ether is distilled off and the residual fatty acids are dissolved in 10 c.c. of 90% alcohol and 1 c.c. of a 5% aqueous solution of silver nitrate. The liquid is transferred to a test-tube and placed in water at 70° to 80°. It is stated that 1% of cottonseed oil can be detected in olive oil by heating for 2 minutes, and by heating for several hours 10% of oil which had been heated to 250° for 20 minutes could still be detected.

Nitric Acid Test.—This test is given in the form recommended by Lewkowitsch. A few c.c. of the oil are vigorously shaken in the cold with an equal volume of nitric acid of sp. gr. 1.375 and then allowed to stand. Cottonseed oil gives an immediate coffee-brown

coloration, which becomes very intense on standing, and mixtures of other oils with cottonseed give a similar brown colour. Stronger acid gives less definite results. The only advantage this test has over Halphen's test is that the brown colour is still given by cottonseed oil which has been heated so as to no longer respond to the latter test; on the other hand, Lewkowitsch states that he has met with many American cottonseed oils which have given with nitric acid such a faint coloration that 10% of these in olive oil could not be detected.

In applying this test to a sample of oil, the colour obtained should be compared with that given under the same conditions with a pure sample of the same kind of oil, and this pure sample should, if possible, be an oil of the same commercial variety as the one under test. Mixtures of the oil with different proportions of cottonseed oil should also be tested. The test is most useful in the case of olive oil, most samples of which, when pure, are scarcely altered in colour by the nitric acid, or at the most give a light brownish-green or brownish-yellow colour on standing. But there are some olive oils which give a darker brown and yet give no other indication of the presence of cottonseed oil. It must also be borne in mind that many genuine rape oils give a brown colour with nitric acid, one such sample tested by Archbutt when mixed with olive oil in the proportion of 20% gave a brown colour in forty minutes which could not be distinguished from the colour given by 20% of cottonseed oil. Coste and Shelbourne (*J. Soc. Chem. Ind.*, 1903, 22, 778) have thrown doubt upon this test for cottonseed oil in neat's-foot oil, as some pure samples of the latter also gave a brown colour on standing. Soya bean oil has also been found to give a similar coloration. It is, therefore, evident that great caution and much experience is needed in drawing conclusions from the result of this test, which may nevertheless prove useful in certain cases.

CRESS SEED OIL

(See p. 110.) This oil is obtained from the seed of the garden cress, *Lepidium sativum*. It has a brownish-yellow or orange colour, and peculiar disagreeable smell. It is used for burning and soap-making (Schaedler).

KAPOK OIL

Known also under the name of bastard cotton oil, is chiefly obtained from the seeds of *Eriodendron anfractuosum* which yields a fruit similar to that of the cotton plant, the chief distinction being that the seeds themselves are quite free from the hairs so characteristic of cotton seeds, and are small, round and black in colour—the hard shell constituting about 40% of the whole. The tree abounds in Java, the West Indies, Africa, etc., where it is often termed the "silk cotton tree," the same name being applied to the East Indian tree, *Bombax malabaricum*, which is very similar and from which kapok oil is also obtained, there being no commercial distinction drawn between the oils from these two sources. Sprinkmeyer and Diedrichs (*Zeitsch. Nahr. Genussm.*, 1913, 26, 86, and 450) have examined the oils obtained from the various species in order to differentiate between them if possible, and some of the figures which they have obtained are given in the following table.

Source	Java, E. Africa Ceylon, etc.[2]		Bombax mala- baricum[1]	Mexican Bombax (variety)[1]	Commer- cial[2] oil
Sp. gr. at 15/15°.......	0.9235–	0.9326	0.9600	....	0.9217
Ref. index at 40° (Zeiss).	51.7	– 59.7	57.0	57.4	56.2
Iodine value..........	85.2	– 93.5	73.6	95.7	97.54
Acid value...........	18.5	–21.02	3.0	12.62	15.0
Saponification value....	189.2	–194.5	194.3	192.8	192.5

[1] Sprinkmeyer and Diedrichs (*Zeitsch. Nahr. Genussm*, 1913, 26, 86 and 450).
[2] *Fatty Foods*, p. 222.

A specimen of oil from Indian Kapok (*Bombax malabaricum*) (yield 22.3%) was examined at the Imperial Institute (*Bull. Imp. Inst.*, 1920, 18, 335). It had: Sp. gr. at 15°/15°, 0.9208; $n^{20}D$, 1.461; acid value, 9.3; saponification value, 193.3, iodine value, 78.0; and solidification point of fatty acids, 38.0°.

This oil, therefore, differs from the oil Java kapok (*Eriodendron anfractuosum*) which has an iodine value of 95 to 110.

Kapok oil is very like cottonseed oil in most respects and even gives the Halphen reaction to a slightly greater extent than the latter. Small quantities of kapok oil may, however, be detected in cotton-

seed oil by means of a modification of Bechi's test devised by Milliau when applied in the form recommended by Durand and Band. The test is carried out as follows:

15 c.c. of the oil are saponified with sodium hydroxide and alcohol in the usual manner, 200 c.c. of boiling water are added, and the whole boiled till the alcohol is evaporated. The fatty acids are then thrown out by the addition of N/10 sulphuric acid in slight excess. The fatty acids are skimmed off, and shaken twice with 15 c.c. of *cold* distilled water, the water being then drained off and the fatty acids dried rapidly in an oven at 105°. 5 c.c. of these fatty acids are shaken with 5 c.c. of a 1% solution of silver nitrate in absolute alcohol.

Under these circumstances cottonseed oil only produces a *barely perceptible brown colour*, whilst kapok oil rapidly develops a *deep coffee coloration*. By means of this test it is possible to recognise 1% of kapok oil in other liquid oils.

The imports of kapok seed to Holland and America are steadily increasing. The oil is used for the same purposes as cottonseed oil, with which it is often mixed, and increasing quantities are refined for edible purposes, more particularly in Holland.

The content of the oil in the whole seed ranges from 22% to, in some cases, 30%, while the kernels themselves usually contain about 40%. The seeds of *B. malabaricum* generally contain rather more oil than *Eriodendron* seeds.

MADIA OIL

(See p. 110.) This oil is obtained from the seeds of *Madia sativa*, a native of Chili. It has a deep yellow colour and dries slowly. It is used for burning and soap-making. It yields a fluid mass in the elaidin test, and gives a faint brown coloration in Bechi's test for cottonseed oil (p. 179).

MAIZE OIL. CORN OIL

(See also p. 110.) Maize oil is expressed from the fruit germs or embryos of maize or Indian corn, *Zea mais*, which are separated from the grain in the manufacture of starch or after malting. The

oil has a pale yellow or golden-yellow colour and an odour of maize meal or malt. It is a semi-drying oil, rather more strongly drying than cottonseed oil (Archbutt, *J. Soc. Chem. Ind.*, 1899, 18, 346), but much less so than linseed oil. It is, therefore, unsuitable either for lubricating or for mixing with paint. It is used to some extent as an edible oil and for burning, but its proper use is for soap-making. It makes an excellent soft soap, pale, and as free as can be from objectionable odour.

The sp. gr. of maize oil ranges from 0.921 to 0.928 at 15.5°. It solidifies at −10° (Schaedler[1]); below −20° (Smith[1]); −36° (Hopkins[2]); but deposits solid fat on standing, even at the ordinary temperature (Lewkowitsch) (Oils, Fats and Waxes, II, 131). It dissolves in 50 volumes of absolute alcohol at 16°. The absolute viscosity at 15.6° is 0.789 (Archbutt, *J. Soc. Chem. Ind.*, 1899, 18, 346) (viscosity of cottonseed oil, 0.82 to 0.91). The oil does not form a solid elaidin. In Maumené's test, the rise of temperature ranges from about 81 to 89°.

Maize oil is chiefly composed of olein and linolin, with a small proportion of saturated esters (*J. Amer. Chem. Soc.*, 1898, 20, 948). The high Reichert value, 4.2, found by Vulte and Gibson (*J. Amer. Chem. Soc.*, 1900, 22, 453) proves the presence of volatile acids, and may help in the detection of maize oil in mixtures. The unsaponifiable matter ranges from about 1.4 to 1.7% and contains, according to Gill and Tufts (*J. Amer. Chem. Soc.*, 1903, 25, 251), sitosterol, the acetate of which melts at 127.1°. As the phytosteryl acetate prepared from cottonseed oil phytosteryl was found to melt at 120° to 121°, Gill and Tufts have proposed to make use of this difference for the detection of maize oil in cottonseed oil. From 1.1 to 1.5% of lecithin has been found in maize oil.

Maize oil is more likely to be used as an adulterant of other oils than to be itself adulterated. It gives no coloration with Halphen's reagent or with furfural; the presence of cottonseed oil or sesame oil could, therefore, readily be detected, unless the cottonseed oil had been heated. In the latter case, the raised m. p. and solidifying-point ("titer" test) of the mixed fatty acids would indicate cottonseed oil. Fish oils would be indicated by the bromoglyceride test and the odour on warming the sample.

[1] *J. Soc. Chem. Ind.*, 1892, 11, 504.
[2] *J. Amer. Chem. Soc.*, 1898, 30, 948.

The following are some data obtained by examination of the mixed fatty acids from maize oil:

		Observer
Sp. gr. at 100°...............................	0.8529	Winfield.
Titer test..	19.	Lewkowitsch.
Iodine value.....................................	112–129	
Iodine value of the liquid fatty acids............	136–144	

PUMPKIN-SEED OIL

(See p. 110.)   This oil is largely used for culinary purposes in Austria and Hungary, and ranks there next to olive oil in price.   It is obtained from the seeds of the common gourd or pumpkin, *Cucurbita pepo.*   The cold-expressed oil prepared by Poda (*Zeitsch., Nahr. Genussm.*, 1898, 625) was greenish, with faint red fluorescence; that prepared by roasting and subsequent hot expression, as on a commercial scale, was brownish-green with deep red fluorescence.   It easily becomes rancid, and has considerable drying properties.   As a result of the examination of several commercial samples, as well as of genuine samples expressed by himself, Poda gives the following limits for the genuine oil:

Sp. gr..	0.923–0.925
Iodine value.....................................	122.76–130.68
Saponification value.............................	188.4–190.2
Butyro-refractometer, 25°........................	70.0–72.5
M. p. of fatty acids, commenced.................	26.5–28.5
M. p. of fatty acids, ended......................	28.4–29.8

Linseed, sesame, cottonseed, and rape oils are said to be used as adulterants.

SESAME OIL.   TEEL OIL.   GINGILI OIL

(See p. 110.)   Sesame oil, sometimes called benne oil, but distinct from the oil of *ben* or *behen*, is pale yellow, usually of a deeper hue than almond oil, nearly odourless, and has a bland and agreeable taste.   The oil expressed from the seeds congeals at about $-5°$, but that extracted by solvents at about $+5°$.   It is used as an edible oil, in cookery, and in the manufacture of margarine, it being compulsory in Germany and Austria to add a certain proportion of it to

butter substitutes to facilitate their detection when used to adulterate butter (see p. 385). In Belgium, 5% must be added (Lewkowitsch). Sesame oil is used in pharmacy and perfumery, for soap-making, and for adulterating almond and olive oils. It is also commonly mixed with arachis oil. It dries more strongly than rape oil, but much less than cottonseed oil, and does not readily turn rancid. "German sesame oil" is a name sometimes given to cameline oil.

Sesame oil contains olein, linolin, palmitin, and stearin, but its exact composition is not fully known. The unsaponifiable constituents, amounting to about 1.0 to 1.4% (Lewkowitsch), include phytosterol, 0.2 to 0.5% of a strongly dextrorotatory substance, "sesamin," and a phenolic body, "sesamol," which gives a brilliant red coloration with furfural and hydrochloric acid, by means of which sesame oil can be identified. Sesamol exists in the oil as a complex compound, from which it is liberated by an acid.[1]

Sesame oil is dextrorotatory and, in the absence of castor, croton, and rosin oils, this property may assist in its detection. The following observations have been published:

	Rotation in 200 mm. tube at 13° to 15°
Bishop,[1] 6 samples......................	+3.1 to +9.0
Rakusin,[2] 3 samples...................	+1.9 to +2.4
Utz,[3] 3 samples......................	+0.8 to +1.6
Sprinkmeyer and Wagner,[4] 3 samples...	+1.03 to +1.42

[1] *J. Pharm. Chim.*, 1887, 300.
[2] *Chem. Zeit.*, 1906, 30, 143.
[3] *Pharm. Zeit.*, 45, 490.
[4] *Zeitsch. Nahr. Genussm.*, 1905, 10, 347.

The chief physical and chemical constants of this oil are given on page 110 and the oleo-refractometer value on page 61.

The mixed fatty acids have given the following figures:

		Observer
Solidifying-point ("titer" test).............	$\begin{cases} 21.2°-22.9° \\ 22.9°-23.5° \\ 23.7°-23.8° \end{cases}$	Lewkowitsch. Lewkowitsch. Lewkowitsch.
Refractive index at 15.5°....................	1.4461	Thoerner.
Iodine value of mixed fatty acids...........	$\left. \begin{matrix} 109-112 \\ 126-140 \end{matrix} \right\}$	Various.
Iodine value of liquid fatty acids...........		

[1] Compare Villavecchia and Fabris, *Zeit. angew. Chem.*, 1893, 17, 505; Bomer, *Zeitsch. Nahr. Genussm.*, 1899, 2, 705; Kreis, *Chem. Zeit.*, 1903. 27, 1030 and 1904, 28, 956; Canzoneri and Perciabosco, *Gazzetta*, 1903, 33, 253; and Malagnini and Armanni, *Chem. Zeit.*, 1907, 31, 884.

Comparative examinations of African, Indian, and Levantine sesame oils have been published by Utz (*Pharm. Zeit.*, 45, 490) and by Sprinkmeyer and Wagner (*Zeitsch. Nahr. Genussm.*, 1905, 10, 347), some of whose results are collected in the following table:

	African		Indian		Levantine	
	U.	S. & W.	U.	S. & W.	U.	S. & W.
Sp. gr. 15.5°..........	0.9232	....	0.9218	....	0.922	....
Rotation, 200 mm., 15°	+1.6°	+1.42°	+1.4°	+1.03°	+0.8°	+1.11°
Butyro-refractometer degrees, 25°........	67.5	69.2	66.2	68.2	67.0	68.0
Butyro-refractometer degrees, 40°........	59.5	....	58.2	....	59.1	....
Iodine value..........	106.3	114.11	104.8	108.31	107.7	108.84
M. p. of mixed fatty acids..............	{ 24.6° – / 24.8° }	....	24.2° – / 24.8°	....	24.6° / 24.7°	....
Butyro-refractometer degrees of mixed fatty acids, 25°.....	53.2	....	53.5	....	54.0	....
Butyro-refractometer degrees of mixed fatty acids, 40°.....	45.0	....	47.2	....	45.1	....
Iodine value of liquid fatty acids........	....	132.7	....	127.2	....	126.3

Utz found that African oil gave the strongest furfural and stannous chloride reactions, and Indian oil the weakest.

The iodine values of 37 samples of sesame oil pressed from seeds of various origins were found by Wijs to range from 106.1 to 116.8; the oils from the "second pressings" gave values ranging from 105.2 to 110.3, and the "third pressings" from 103.9 to 109.8.[1]

Colour Tests.

Furfuraldehyde Test.—Sesame oil contains a substance ("sesamol," see above) which produces a rose-red coloration when the oil is shaken with cane-sugar and hydrochloric acid (Camoin, Baudouin). o.1 grm. of cane-sugar is dissolved in 5 c.c. of cold hydrochloric acid (1.16), 10 c.c. of the oil are added, the tube is corked, shaken for 10 minutes, and allowed to stand.   If only 2% of sesame oil be present, the acid which separates will be pink.   If 5% or more be present, the emulsion will become pink while being shaken.   Villavecchia and Fabris concluded that this coloration was caused by *furfural*,

[1] *Zeitsch. Nahr. Genussm.*, 1902, 5, 1150.

produced by the action of the acid on the sugar, and they have modified the test by using a solution of furfural instead of sugar As furfural itself gives a violet coloration with hydrochloric acid, a very small quantity only must be used.

A 2% solution of furfural in alcohol is prepared. 0.1 c.c. of this solution is placed in a test-tube, 10 c.c. of hydrochloric acid (1.16) and 10 c.c. of the oil are added, the tube is then corked, shaken for half a minute and allowed to stand. If only 1% of sesame oil is present, the acid which separates has a pink coloration; with 5%, a strong rose-red colour is obtained. This test is recommended, as it is simpler than that with sugar, and half a minute's shaking is quite sufficient. Wauters suggests pouring the oil on the reagent, and says that less than 1% can be detected by a crimson colour at the point of contact.

Lehnkering (*Zeit. öffentl. Chem.*, 1903, **9**, 436), in examining a series of pure sesame oils, found some which, while of normal iodine value and refractive index, gave only feeble colours in the furfural test, not more than 1/10 as much colour as was given by the oils which reacted most strongly. Oils extracted from the seeds with ether gave colours ranging in intensity from 5 to 8 on the same scale.

Rancid oils may give a brownish tint in the Baudouin test, which will mask the reaction when only small amounts of sesame oil are present. Sprinkmeyer (*Zeitsch. Nahr. Genussm.*, 1908, **15**, 20) found that rancid cottonseed oil containing sesame oil gave no red colour unless at least 17% of sesame oil were present. This shows the importance of using fresh cottonseed oil in testing margarine, which, according to German law, must contain sufficient sesame oil to give a distinct red coloration when 0.5 c.c. of the clear melted fat is mixed with 9.5 c.c. of cottonseed oil and shaken with hydrochloric acid and furfural as directed above. Kreis (*Chem. Zeit.*, 1908, **23**, 87) states that rancid sesame oil gives a less intense coloration than fresh oil. Ambühl obtained an indigo-blue colour in applying the Baudouin test to some old rancid sesame oil. Kreis (*Chem. Zeit.*, 1899, **23**, 802) thinks this must have been a mixture of the red colour due to furfural with the green colour obtained in Bishop's test. Bishop (*J. Pharm. Chim.*, 1889, **20**, 244) found that fresh sesame oil gives no colour when shaken with 1.5 times its volume of hydrochloric acid (1.19), but if exposed to air and light for a few days it colours the acid green. Oil which had been exposed for years

coloured the acid almost blue, and a blue colouring matter separated on standing, the acid becoming green again. This reaction may, therefore, modify the colour obtained in the Baudouin test with old sesame oils, but it is stated that the oil which separates from the green- or blue-coloured hydrochloric acid will give the red colour on being shaken with hydrochloric acid and furfural.

Several observers have found that in applying the furfural test to certain olive oils of undoubted purity the acid liquid assumes a violet coloration after a short time; da Silva (*Bull. Soc. Chim.*, 1898, **19**, 88) found Douro olive oil gave this colour. It has also been observed that some genuine Italian, Tunisian and Algerian olive oils give a rose coloration, similar to that produced by about 5% of sesame oil (Villavecchia and Fabris, *Zeit. angew. Chem.*, 1892, 509). According to Milliau, this is caused by a colouring matter derived from the aqueous part of the pulp of the fruit, and if the test be applied to the mixed fatty acids instead of to the original oil any possibility of error is obviated. Therefore, Milliau's modification should be adopted in cases where doubt exists as to the cause of the coloration.

It has more recently been shown that a hydroxy-furfural, and not furfural, is formed by the action of hydrochloric acid on sugar, and the substitution of furfural for the sugar in Baudouin's test is therefore incorrect. Weehuizen (*Pharm. Weekblad*, 1918, **55**, 77) therefore reverts to the old tests which he applies by shaking a small quantity of lævulose or cane sugar with 3 to 5 c.c. of a saturated alcoholic solution of hydrochloric acid for about one minute, then adds an equal volume of the oil under examination and again shakes the tube for about 1 minute. Olive oil containing 5% of sesame oil gives a purple alcoholic layer after 5 minutes whilst pure olive oils give a light red or greenish colour.

Soltsien's Test.—The oil is mixed with an equal volume of stannous chloride solution, (German Pharmacopœia strength) shaken vigorously (once only), and placed in boiling water. A red coloration is produced in the presence of sesame oil. This reaction is said to be more delicate than Baudouin's, and to be specially applicable to butters and margarines artifically coloured with coal-tar dyes, which are reduced and rendered colourless. As the delicacy of the reaction is impaired if the liquids remain too long in contact without separating, Soltsien recommends diluting

the oil with twice its volume of petroleum spirit, adding half the volume of stannous chloride, shaking well, and standing the tube in water at about 40°.

Tocher's Test.—15 c.c. of the oil are shaken for about 30 seconds with a freshly made, practically colourless solution of 1 grm. of pyrogallol in 15 c.c. of concentrated hydrochloric acid (1.16). The aqueous liquid is drawn off through a wet filter-paper and heated for 15 minutes on a water-bath. In the presence of sesame oil it becomes coloured reddish-purple, appearing red by transmitted, and blue by reflected light. The test is very delicate, and will readily detect 2% of sesame oil in rape or olive oil. Bellier says this reaction is not given by certain genuine olive oils which give a red colour in the furfural test (*Ann. Chim. Anal.*, 1899, 4, 217).

Attention has been drawn by Zimmermann (*Mitt. K. Techn. Versuchsamt*, 1912, 1, 71) to the failure of highly refined sesame oil to give many of the usual colour reactions, and he states that Soltsien's stannous chloride test is the least affected. In the experience of Bolton and Revis it is possible to obtain a strong Baudouin reaction from the refined oil, though some processes of refining do, as stated above, considerably diminish the sensitiveness of this test. At one time the German regulations required 10% of sesame oil to be added to all butter substitutes to facilitate their detection, but owing to the aforesaid reduction in the sensitiveness of the Baudouin reaction, it was necessary subsequently to modify these regulations, and to require such an amount of sesame oil to be added as would suffice to give a distinct red colour under specified standard conditions without laying down any limits as to the quantity of sesame oil which might be required to fulfil these conditions.

Adulteration with *rape oil* would lower the sp. gr. and saponification value of sesame oil and the melting- and solidifying-points of the fatty acids.

Poppyseed oil would raise the iodine value and thermal tests, and also the refractometer numbers. It would lower the melting- and solidifying-points of the mixed fatty acids.

Cottonseed oil, unless it has been altered by heating, would be indicated by Halphen's test. It would raise the melting- and solidifying-points of the mixed fatty acids and would tend to raise the iodine value of the liquid fatty acids, sesame oil acids absorbing

from 126.3 to 139.9 and cottonseed oil acids from 141.9 to 151.7% of iodine.   Cottonseed oil would increase the rise of temperature in the thermal tests.   It would not materially alter the other values. The mixed fatty acids of cottonseed oil were found by Farnsteiner (*Zeitsch. Nahr. Genussm.*, 1899, **2**, 1) to contain rather more linolic acid than those of sesame oil, he having obtained tetrabromides corresponding with 18.5% of linolic acid from the former and 12.6 to 15.8% from the latter.   But a larger number of samples need investigating.

Arachis oil would be detected and estimated by isolating its arachidic acid.

OIL OF CERATOTHECA SESAMOIDES

Attention has been drawn by Bolton (*Analyst*, 1919, **44,** 233) to the oil of *Ceratotheca sesamoides*, a plant closely allied to *Sesamum indicum*, and producing seeds of similar general appearance.   Oil extracted from seeds derived from the Gold Coast gave the following values: Specific gravity (15°/15°), 0.9163; refractometer reading (Zeiss), 59.60; free fatty acids, 0.63%; saponification value, 190.2; and iodine value, 110.6.

The oil does not give the Baudouin reaction for sesame oil, nor Halphen's reaction for cottonseed oil.   It is noteworthy that most of the values fall within the limits of those accepted for sesame oil.

SOYA-BEAN OIL

This oil is obtained from soya or soy. beans, the seeds of *Soja japonica* (*Soja hispida*), a plant native to China, Manchuria, Korea, and Japan, but also grown elsewhere.   It has marked drying properties and, according to De Negri and Fabris, readily solidifies. The values on p. 193 are based upon the results of Morawski and Stingl, De Negri and Fabris, and Shukoff.   Four commercial samples of Chinese bean oil examined by Korentschewski and Zimmermann (*Chem. Zeit.*, 1905, **29,** 777), one obtained direct from the factory in Kharbin, gave the following results, some of which are quite different from those previously recorded by the other observers.   The oil is described as dark brown, having a faint odour suggesting tung oil, and a bland taste.

Sp. gr. at 15°............................	0.9264 to 0.9287
Solidifying-point........................	−14.6° to −15.3°
Saponification value........	207.9–212.6
Hehner value..........	93.6–94.28
Iodine value............................	114.8–137.2
Maumené value......	102°–116°
Acid value..............................	1.86–15.46
Solidifying-point of mixed fatty acids.... ..	16°–17.3°
M. p. of mixed fatty acids................	20°–21°

A sample of the crude commercial oil extracted from the beans in this country, examined by Archbutt, had a yellowish-brown colour, a somewhat pungent odour suggestive of crude mustard or rape oil, and gave the following results

Sp. gr. at 15.5°......................................	0.9254
Solidification-point..................................	−10°
Saponification value...............................	184.0
Iodine value..........	119.9%
Halphen's test.......................................	Negative

Soya beans are imported into Europe in large quantities from Manchuria. The beans contain about 17 to 18% of oil and, being rich in albuminoids and carbohydrates, have a high feeding value. The following further analyses by Archbutt show the character of the oil on the market in 1909.

	Unrefined	Unrefined	Refined
Sp. gr. at 15.5°............	0.9256	0.9250	0.9226
Solidification-point.........	−16°	....	....
Saponification value...	190.5	189.7	188.6
Iodine value......	139.3	138.9	136.1
Unsaponifiable matter, %....	1.54	1.27	1.30
Free (oleic) acid, %.........	0.3	0.5	1.2

According to Newhall (*J. Ind. Eng. Chem.*, 1920, 12, 1174) soya bean oil gives a distinctive yellow emulsion when shaken with 5 c.c. of chloroform, a few drops of gum arabic solution, and 5 c.c. of 2% uranium nitrate or acetate solution.

Arachis, cottonseed, sesame, rape, coconut oil etc. give a white or slightly coloured emulsion, and it is claimed that the test will detect

5% of refined soya bean in those oils. In the case of linseed oil, which gives a brownish emulsion, the test is not so sharp.

As soya bean oil is now being used in increasingly large quantities, especially in the United States it has become a commercial product of great importance.

Many investigations have been carried out with the object of utilising the oil for various purposes other than that of soap-making and the recorded statements of different observers are most contradictory. This divergence of opinion may be explained by the great variety of different species of soya beans, and it is hardly to be expected that they should all yield an oil having identically the same properties.

Maximilian Toch (*J. Soc. Chem. Ind.*, 1912, 31, 572) has examined 33 different varieties of soya beans, and he points out that in the records of the Department of Agriculture at Washington some 280 varieties of soya beans have been described. This investigator explains the contradictory statements of other workers on the ground that the oil from certain varieties of beans is suitable for use in paints (*i.e.*, as a substitute for linseed oil) and goes on to draw a favourable comparison between those types and linseed oil, pointing out that the type of oil adapted for use in paint possesses two characteristics, (*a*) that when heated to 500° F. for a few minutes, it will become bleached and remain bleached, and in this respect resembles linseed oil to a certain extent; (*b*) that when heated to 500° F. and blown with dry air for 5 to 7 hours, it thickens in a similar manner to linseed oil and attains a sp. gr. of 0.960 or over. The following figures were obtained by this author for a standard sample of cold-pressed Manchurian bean oil, which was heated to 500° F. and, after cooling to 300° F., blown vigorously for 7 hours.

	Sp. gr.	Acid value	Iodine value
Original oil.....................	0.929	2.6	133.6
Blown oil......................	0.963	1.9	105.6

Blown soya oil is used in linoleum manufacture. The figures given in the following table were obtained in Messrs. Toch Bros.' research laboratory.

Name	Colour of seed	Colour of oil	Sp. gr., 15°	Acid value	Iodine value
Meyer...............	Brown	....	0.9264	0.44	127.0
Peking..............	Black		0.9279	0.14	135.4
Haberlandt..........	Straw-yellow	} Extremely pale. {	0.9244	0.00	129.8
Farnham............	Straw-yellow		0.9234	0.65	131.8
Taha...............	{ Black, Olive, Saddle	{ Pale amber somewhat deeper than than above. {	0.9248	0.16	127.0
Mammoth...........	Straw-yellow		0.9222	0.47	118.2
Edward.............	Straw-yellow	Med. amber.	0.9257	1.14	124.6
Shanghai............	Black	{ Same depth as previous olive tone.	0.9241	0.63	127.8
Refined linseed.......	....	....	0.933	1.0	180.1

The mixed fatty acids from a specimen of soya bean oil with an iodine value of 134 were found by W. B. Smith (*J. Ind. Eng. Chem.*, 1922, 14, 530) to contain from 9 to 10% of saturated acids, 26 to 27% of oleic acid, 55 to 57% of linolic acid, and 2 to 3% of linolenic acid. Soya oil is used to a certain extent as an edible oil, but has not fulfilled anticipations; while there is no difficulty in preparing a tasteless and odourless oil, it has been the experience of Bolton and Revis that this does not keep very well, and has a tendency to develop an unpleasant "oxidised" taste.

TOMATO SEED OIL

Tomato seed oil is obtained from the seeds of the tomato plant which according to Jamieson and Bailey (*J. Soc. Chem. Ind.*, 1919, 38, 781A) yield about 18% of oil on expression.

Battaglia (*Ann. Chem. Anal.*, 1901, 6, 437) found an oil extracted from the seeds to consist of olein, linolin, stearin and nugristin whilst Janueson and Bailey (*loc. cit.*) separated about 0.4% of arachidic acid. The following values were recorded by these chemists:

	Sp. Gr.	Saponification Value	Iodine Value	Reichert Miessl Value
Battaglia............	0.922 (15°)	190.4	106.9	
Jamieson and Bailey...	0.9184 to 0.9196 (at 25°)	187.0 to 192.0	117.5 to 125.0	0.1 to 0.3

		Hehner Value	Refractive Index	Acetyl Value
Battaglia............		95.1	1.473	
Jamieson and Bailey...		95.0 to 96.6	1.4715 to 1.4725 (25°)	11.4 to 20.5

WHEAT OIL

(See p. 110.) Wheat oil is obtained from the germs of wheat, *Triticum*, by extraction with petroleum spirit. A yellowish-brown

oil is thus obtained, having an odour of wheat.   It easily becomes rancid.   Frankforter and Harding (*J. Amer. Chem. Soc.*, 1899, **21,** 758) found in this oil from 2.4 to 2.6% of unsaponifiable matter which, as in the case of maize oil, contains sitosterol.   About 2% of lecithin was also found.   The viscosity of the oil at 20° was 2.57 times that of rape oil at the same temperature.   The refractive index at 20° was 1.4832.   De Negri, *Chem. Zeit.*, 1898, **22,** 976, obtained the following results from the mixed fatty acids:

Solidifying-point......... .... 29.7
Iodine value.. 123.3

IV.   LINSEED OIL GROUP

Candle Nut Oil.	Pine Nut Oil.
Cedar Nut Oil.	Poppyseed Oil.
Hempseed Oil.	Safflower Oil.
Lallemantia Oil.	Sunflower Oil.
Linseed Oil.	Tung Oil.
Niger Seed Oil.	Walnut Oil. Nut Oil.
Perilla Oil.	

CANDLE NUT OIL

(See also p. 110.)   This oil is obtained from the seed-kernels of *Aleurites moluccana (A. triloba),* a tree which flourishes over the whole of the South Sea Islands.

In addition to the seeds obtained from the South Sea Islands large quantities are exported from Hongkong and Fiji, as well as Australia and New Zealand.

The oil is also known as "Kekune" or "Country Walnut oil," etc.

The seeds of *Aleurities triloba* are said to produce an edible oil, but that obtained from *Aleurities moluccana* has, as has been pointed out by Lewkowitsch, purging properties.   The seeds from both varieties are sold indiscriminately under the names of "Candle nuts," "Baio nuts," "Lumbang nuts," etc.

The oil dries less rapidly than linseed oil and is used for mixing paints and making oil-varnishes.   It is obtainable in enormous quantities, and may be employed as an adulterant of linseed oil (Lewkowitsch).   The published iodine and saponification values of this oil vary considerably, as is shown in the following table.

	De Negri[1]	Lew-kowitsch[2]	Kassler[3]	Fendler[4]	Imp. Inst.[5]
Sp. gr. at 15°............	0.920a, 0.926b	....	......	0.9254	0.9274
Sp. gr. at 15.5°.........	....	0.9256	0.9248	....	....
Butyro-refractometer, 25°..	....	76	....	....	....
Saponification value.......	184a, 187.4b	192.6	189.5	194.8	204.2
Iodine value..............	136.3a, 139.3b	163.7	152.8	114.2	139.7
Reichert-Meissl value.....	....	... .	....	1.2	....
Acetyl value.............	....	9.8	....	....	....
Unsaponifiable matter, %	....	....	0.53	....	....
Mixed Fatty Acids					
Solidifying-point........	13°	....	12.5°	15.5°	.. .
Solidifying-point (t i t e r test)................	....	....	....	.. ..	17.8
Iodine value.............	142.7a, 144 1b	....	157.5	....	.....
Iodine value of liquid fatty acids.................	....	185.7	....	....	.....
	Extracted from the seeds by (a) petroleum spirit, (b) ether.	Extracted from kernels of nuts of *A. moluccana* (South Sea Islands).	Oil from Fiji.	Extracted by ether from seeds of *A. moluccana* from the Cameroons.	Extracted from the kernels of Chinese *A. triloba*.

[1] *Oesterr. Chem. Zeit.*, 1898, **1**, 202.
[2] Technology of Oils, II, 67.
[3] *Seifensieder Zeit.; Farben-Zeit.*, 1903, **8**, 359.
[4] *Zeitsch. Nahr. Genussm.*, 1903, 1025.
[5] *Bull. Imp. Inst.*, 1907, **5**, 135.

Walker and Warburton (*Analyst*, 1902, **27**, 237) obtained from 7.28 to 8.21% of brominated glycerides by Hehner and Mitchell's process from the sample examined by Lewkowitsch.

A sample of the commercial oil, described as lumbang oil, examined by Archbutt, was light brown in colour, had an unpleasant and somewhat pungent odour, and gave the following results:

> Sp. gr. at 15.5°........... .... 0.9252
> Saponification value....... .... 193.6
> Iodine value........................ .... 154.6

The oil dried nearly as rapidly as linseed oil, and had about half the viscosity of rape oil at 15.5°. It contained 23.6% of free (oleic) acid. The saponification and iodine values agree with those observed by Lewkowitsch and Kassler. A specimen of oil expressed from *Aleurites triloba* by Lespinasse (*Ann. Falsific.*, 1919, **12**, 152) had the following characters. Sp. gr., (15°), 0.927; acidity (as oleic acid), 0.7%; saponification value, 175 and iodine value 137.

It was found that the purgative principle remained almost entirely in the press cake.

An expressed sample (from *A. Moluccana*) examined by West and Montes (*Philippine J. Sci.*, 1921, **18**, 619) gave the following values:

Sp. gr. at 31°/4°..................................... 0.9206
Saponification value................................. 214
Iodine value (Hübl).................................. 140

It also gave results corresponding with a composition of 6.5% of linolenin, 33.4% of linolin, 56.9 of olein and 2.8% of glycerides of solid fatty acids.

Although the tabulated results indicate that, as a rule, the oil from *A. triloba*, has a higher saponification value and a lower iodine value than that from *A. moluccana*, the results obtained by West and Montes show that this is not invariably the case.

Bolton and Revis (*Fatty Foods*, p. 251) extracted samples of the oil from authentic specimens of the seed of both varieties and obtained the following figures:

	Aleurities moluccana	Aleurities triloba
Saponification value...........................	190.3	202.5
Iodine value..:...............................	164.0	143.8
Ref. index at 40° C. (Zeiss scale)..............	65.7	61.8
Free fatty acids (as oleic)....................	20.1%	1.0%

A sharp distinction must be drawn between candle nut oil and tung oil. The former does not polymerise like the latter when heated to 200°. All the tung oils are poisonous.

CEDAR NUT OIL

(See p. 110.) The commercial oil is expressed from the seeds of the Siberian cedar, *Pinus cembra;* it is golden-yellow, and of agreeable, though somewhat rancid taste. It contains the glycerides of linolic and oleic acids, the former predominating; a very little linolenic acid is also present; among the solid fatty acids palmitic acid has been identified and there is also present a considerable proportion of volatile fatty acids.

A specimen of this oil examined by von Schmoelling (*Chem. Zeit.*, 1900, **24**, 815) gave the following results:

	Oil	Mixed fatty acids
Sp. gr. at 15°..........	0.930	....
Solidifying-point...........................	....	11.3°
Saponification value.........................	191.8	....
Iodine value (Waller).......................	159.2	161.3
Hehner value................................	91.97	....
Volatile fatty acids.........................	3.77	....
Free fatty acids............................	1.60	....
Neutralisation value........................	....	193.0
Unsaponifiable matter, %....................	1.3	....
Maumené test (Archbutt's method)......	98°	....
Liquid fatty acids, % (Muter's method)........	....	87.0
Iodine value of liquid fatty acids..............	....	184.0

Cedar nut oil is used in Siberia as an edible oil, and is said to be technically of value as a fairly rapid drying oil of pale colour. Von Schmoelling states, however, that the "varnish" produced by heating the oil with 5% of manganese borate for 4 hours to 140° or 150° took twice as long to dry on glass as linseed oil varnish similarly prepared, and the product was very viscid and resembled a blown oil. The last-mentioned characteristic, together with the high price of the oil would, he thinks, prevent it from being used in the manufacture of varnish.

HEMPSEED OIL

(See also p. 110.) This oil is obtained from the seeds of the hemp plant, *Cannabis sativa* the yield being from 33 to 35%. The expressed oil is at first greenish- or brownish-yellow, deepening in colour on exposure to the air. It consists of the glycerides of liquid and solid fatty acids, the former composed approximately, according to Hazura and Grüssner, of 70% of linolic, 15% of linolenic and isolinolenic and 15% of oleic acids; the solid fatty acids are said to be palmitic and stearic acids.

Hempseed oil has a high iodine value and is a strongly drying oil, though it dries less rapidly than linseed oil. It is used for making paints and varnishes, and as an adulterant of linseed oil; also for making soft soaps.

The following figures were obtained by Bolton and Revis from one genuine sample:

Sp. gr. 15/15°....... .... 0.9283
Saponification value................... .... 191.0
Iodine value........,............................. .... 161.7
Ref. index at 40° (Zeiss)....................... .... 73.5
Free fatty acids, per cent.......................... 2.3

LALLEMANTIA OIL

(For constants see p. 110.)   This oil, used in Russia as a lamp oil, is expressed from the seeds of *Lallemantia iberica*.   It has excellent drying properties, and is not improbably used as a substitute for linseed oil.

LINSEED OIL

(See special article, p. 447)

NIGER SEED OIL.   NIGER OIL

(For constants see p. 110.)   The seeds of *Guizotia oleifera*, which grows wild on the Gold Coast of Africa and is cultivated in Abyssinia and many parts of India, yield this oil, some being expressed in England.   It is a good drying oil, of yellow colour, sometimes used as a substitute for linseed oil.   It is said to have been used as a substitute for sesame oil and castor oil, though it would be easily distinguished from these oils.   It has been employed as an adulterant of rape oil.   Niger seed oil is said to contain but little stearic or palmitic acid, and hence soap made from it, though very white, is soft.   A sample tested by Archbutt gave a temperature-rise of 100° in Maumené's test.   The viscosity of the oil is about two-thirds that of rape oil at 60° to 70°F.

The present reviser has found that niger seed oil gives only a slight turbidity in the insoluble bromide test, which can therefore be used for distinguishing between it and linseed oil.

PERILLA OIL

(For constants see p. 110.)   Perilla oil is the commercial name for the oil expressed from the seeds of the tree *Perilla ocimoides*, which is indigenous to China, Japan and certain districts of India.   It yields about 45% of a pale yellow oil (*J. Ind. Eng. Chem.*, 1912, 4, 229), which is used for edible purposes in China, whilst in Japan it is valued as a drying oil and used for various technical purposes such as the manufacture of varnishes and printing inks.

It is characterised by its very high iodine value (up to 260 has been recorded), and, in accordance with this characteristic, the fatty acids yield a high proportion of linolenic hexabromide (45 to 51%, Fox). The oil also contains the glycerides of oleic, linolic, palmitic and stearic acids.

Bauer (*Chem. Zeit.*, 1922, **46**, 538) separated the mixed fatty acids by the lead-ether method into 12% of saturated acids (mainly palmitic acid) and 88% of unsaturated acids, which when oxidised with permanganate yielded a tetrahydroxystearic acid (m.pt. 135°–140°), a mixture of hexahydroxystearic acids, and an acid of m. p. 165°. The sativic acid obtainable from linseed oil was not given by this perilla oil.

The analytical values of this oil were as follows: Sp. gr. 20°, 0.9280; $n\frac{20}{D}$, 1.4830; saponification value, 187.4; iodine value (Hanus), 204.3; and insoluble bromide value 50.8.

Perilla oil from seed grown experimentally in Cyprus from seed of Japanese origin has given the following values (*Bull. Imp. Inst.*, 1920, **18**, 479). Sp. gr. at 15°/15°, 0.9298; $n\frac{40}{D}$, 1.472; saponification value 190.5; and iodine value, 185. This value for the sp. gr. is lower than any previously recorded for perilla oil.

Standard Specifications D 125–23, for Perilla Oil, Raw or Refined, Adopted by the American Society for Testing Materials in 1923.

(American Society for Testing Materials, Standards 1923) are as follows:

PROPERTIES AND TESTS

1. Perilla Oil, raw or refined, shall conform to the following requirements:

	Maximum	Minimum
Foots, %	2.5	....
Loss on heating at 105 to 110°, %	0.2	....
Sp. g. at 15.5°/15.5°	...	0.932
Acid number	5.0	....
Saponification number	...	190
Iodine number (Hanus)	...	191
Unsaponifiable matter, %	1.5	....
Colour	Not darker than a freshly prepared solution of 1.0 grm. potassium dichromate in 100 c.c. pure H_2SO_4 (sp. gr. 1.84)	

For *Methods of Testing* see reference made in original. Note by American Editors.

PINE NUT OIL.　FIRSEED OIL

(For constants see p. 110.)　Under this name are included the products of the nuts or seeds of different kinds of pine trees, such as *Pinus sylvestris*, *P. abies*, *P. picea*, etc.　All have more or less pronounced drying characteristics and are used in the manufacture of paint and varnish.　They probably differ a good deal from one another in chemical composition and properties.

The data in the following table have been collected by Lewkowitsch.[1]

Oil from	Yield oil, %	Sp. gr. at 15°	Solidifying point	Saponification value	Iodine value (Wijs)	Ref. index	Observer
Pinus sylvestris, L...........	32.1	0.9326	−28 to −29	189.8	147.1	1.4704 at 35°	Grimme.
Pinus montana, Mill.......	29.6	0.9318	−25 to −26	189.6	145.7	1.4698 at 35°	Grimme.
Pinus cembra, L.............	....	0.930	−20	191.8	159.2	....	v. Schmoelling.
Pinus cembra, L.............	35.7	0.9316	−20 to −21	188.0	156.3	1.4710 at 40°	Grimme.
Pinus picea, L.............	32.8	0.9268	−25 to −26	190.5	120.9	1.4879 at 35°	Grimme.
Pinus abies, L.............	31.6	0.9312	−26	192.0	120.5	1.4742 at 35°	Grimme.
Pinus Gerardiana, Wall......	30.7	0.9307	−17	191.3	120.9	1.4685 at 40°	Grimme.
Pinus pinea, L.............	21.8	0.9326	−22	192.6	118.3	1.4679 at 35°	Grimme.
Cupressus sempervirens v.horizontalis, Mill.	10.8	0.9320	− 4	188.6	135.1	1.4857 at 35°	Grimme.
Thuja occidentalis, L........	15.0	0.9298	− 8	186.7	154.8	1.4795 at 35°	Grimme.
Pinus monophylla......... *Pinus Fremontiana*........	....	0.933	....	192.8	101.3	1.4769 (?)	Blasdale.
Pinus monophylla......... *Pinus Fremontiana*.........	....	....	....	189.0	108.0	1.4543 at 40°	Adams and Holmes.

POPPYSEED OIL.　POPPY OIL

(For constants see p. 110.)　This oil is expressed from the seeds of the opium poppy, *Papaver somniferum*, the yield ranging from about 41 to about 50%, according to the variety.　The seed is black, brown, yellow, or white, the latter being considered the richest.　The plant is extensively cultivated in Egypt, Asia Minor, Persia, India, and China; it is also grown in France and Germany.

The cold-drawn oil extracted by the first pressing (*huile blanche*) is straw yellow in colour, limpid, and almost odourless; it has a

[1] *Oils, Fats and Waxes*, 5th Ed., Vol. 2, p. 141.

pleasant almond-like flavour, and being slow to become rancid is largely used on the continent of Europe as a salad oil and also as an adulterant of olive oil. Owing to its drying properties and pale colour, which it retains, it is in demand for the manufacture of artists' pigments, the sun-bleached oil being used for white pigments and the unbleached but pale coloured oil for coloured pigments (Lotter, *Chem. Zeit.*, 1894, 18, 1696). The inferior varieties of poppy oil, obtained by a second pressing (*huile rouge*) and from inferior seed, are used for soap-making and burning.

The oils obtained from different varieties of poppy seed are divided commercially under two headings:

(1) "*Huile d' œillette*," obtained from the grey or blue European seed.

(2) "*Huile de pavot*," from the brown or mottled seeds of foreign origin.

"Huile d'œillette" is the better oil and commands a higher price.

The following simple test serves to distinguish the two types of oil.

The oil is violently shaken in a bottle when it will be found that (1) gives a fine emulsion of air bubbles, rendering the oil turbid, (2) behaves quite differently and does not give a fine emulsion nor is the froth so persistent.

"Huile d'œillette" possesses a much more golden-yellow colour than "huile de pavot," and so much so, that it is often necessary to colour the latter in order to render it saleable (Vuaflart, *Ann. Falsific*, 1909, 2, 276).

In a sample of oil from genuine poppy-seed, Tolman and Munson found 6.67% of solid fatty acids. The liquid fatty acids were found by Hazura and Grüssner (*Monatsh. Chem.*, 1888, 9, 180) to consist, approximately, of oleic acid 30%, linolic acid 65%, linolenic and isolinolenic acid 5%. The calculated iodine value of such a mixture is 158, which approximates to the actual iodine value of the liquid fatty acids, found by Tortelli and Ruggeri to be 149.6 and by Tolman and Munson, 151.7. Hehner and Mitchell obtained no insoluble brominated glyceride from 4 samples of poppyseed oil.

Utz (*Chem. Zeit.*, 1903, 27, 1176) has stated that practically all the commercial poppy oils examined by him contained more or less (up to 40%) of sesame oil, not added as an adulterant, sesame seed and oil being dearer than those of the poppy, but due to careless methods

of manufacture, the two kinds of oil being expressed in the same works.   The sesame oil is detected by its lower iodine value, and by the colour tests of Soltsien and Baudouin.   Owing to this admixture, Utz believes that the iodine value of genuine poppyseed oil, usually stated as 130 to 141, has been generally understated.   The oil which he extracted with petroleum spirit from three varieties of seed gave the following results:

Oil from	Iodine value	Butyro-refrac-tometer at 15°
Indian poppyseed......................	153.48	78.1
Levantine poppyseed.......	157.52	78.4
German poppyseed..........	156.94	78.4

A specimen of commercial poppy oil which probably contained less than 5% of sesame oil had an iodine value of 151.65, and another, which gave only faint indications of sesame oil by the colour tests, absorbed 150.63% of iodine.   It may be mentioned, however, that Tolman and Munson obtained iodine values of 133.2 and 134.9 from cold-drawn poppy oil expressed from seed which they state was identified as that of *P. somnifera.*

Utz confirms Bishop's statement that pure poppy oil is optically inactive, and suggests that the sample examined by Crossley and Le Sueur which had a rotation of +4' may have contained sesame oil.

The viscosity of poppyseed oil at 70° F. is about two-thirds that of refined rape oil at the same temperature.   4 samples tested by Crossley and Le Sueur required from 254 to 259 seconds for the outflow of 50 c.c. from Redwood's viscometer, water at 70° F. requiring 25.4 seconds from the same instrument.

Other results for poppy oil are:

		Observer
Maumené test................................	86°–88°	Archbutt.
Sp. gr. of mixed fatty acids at 100°/100°........	0.8886	Archbutt.
"Titer test" of mixed fatty acids..............	15.4°–16.2°	Lewkowitsch.

SAFFLOWER OIL

(For constants see p. 110.)   Safflower or saffron oil is the product of the seeds of the safflower (saffron) plant, *Carthamus tinctorius,* which

is being increasingly cultivated in the Caucasus and in Turkestan (Tylaikow, *J. Soc. Chem. Ind.*, 1902, **21**, 864); it was at one time extensively cultivated all over India, and is still grown to some extent in that country.

The oil is obtained from 2 distinct varieties, *Carthamus tinctorius* and *Carthamus oxyacantha* the latter being "wild" safflower. The seeds are commonly known as "Kurdee" or "Kardai" seeds, and the quantities expressed are largely on the increase. The oil-cake produced, from the decorticated seed, contains nearly 50% of protein. The figures in the following table have been obtained by Leather (*Mem. Depart. Agric.*, India, March, 1907).

District	No. of samples	Oil, %	Wt. of 100 seeds in grm.
Central Provinces.	6	23.54–31.82	3.405–6.774
Bombay Presidency	9	28.79–32.23	4.210–5.516
Madras Presidency	8	23.88–33.55	2.973–4.622
United Presidency	6	27.94–29.78	3.348–4.936
Bengal	1	22.47	3.209

The oil has a pleasant taste, especially when obtained from the husked seeds, when it is of better quality than that obtained from the unhusked seeds. It has a bright yellow colour, and a taste very similar to that of sunflower oil. It is a good drying oil and is used by the natives in parts of India for the manufacture of linoleum. The viscosity of the samples examined by Crossley and Le Sueur (*J. Soc. Chem. Ind.*, 1898, **17**, 932) was about two-thirds that of refined rape oil, 50 c.c. requiring from 243 to 294 seconds to flow from Redwood's viscometer at 70° F. The same observers obtained butyro-refractometer readings at 40° from 65.2 to 68.2.

According to Le Sueur (*J. Soc. Chem. Ind.*, 1900, **19**, 104), the insoluble fatty acids of safflower oil consist of about 10% of solid acids (palmitic and stearic) and 90% of liquid fatty acids (oleic and linolic). No linolenic acid was present, although the oil has been stated to yield an insoluble bromide. This point requires further investigation.

SUNFLOWER OIL

(For constants see p. 110.) This oil is expressed from the seeds of the sunflower, *Helianthus annuus*, which is widely grown in southern Russia.

It is usually obtained, however, from the fruits of the *common* sunflower, and seldom from the seeds alone as is generally supposed. It should be noted that the portion usually termed "the seed" is really the whole fruit. The plant is indigenous to Mexico, but is extensively cultivated in Russia, China and Hungary and is so abundant in South Africa that it is used to mark out the boundaries of fields. Notwithstanding the fact that it is a very easy plant to grow and produces an enormous yield of fruits, the attempts to introduce it into India and the United States have not proved very satisfactory, and the crop in Great Britain is too small to be of any commercial importance, though the climatic conditions lend themselves to its production. It appears that the value of the crop is not realised by the conservative British farmer.

The fruits vary in colour from white to a dark brownish black, and contain about 22–25% of oil (45–50% calculated on the true seed). The oil from the white fruits has been found by Bolton and Revis to have a much lower iodine value (106) and a lower refractive index than that yielded by the black seeds.

The cold-pressed oil is pale yellow and of pleasant, mild taste and odour. It is used for culinary purposes, also as the vegetable oil in margarine, and has been detected as an adulterant of olive oil. Oil of the second pressing, which is more coloured, is used as a lamp oil, and in the manufacture of varnishes as a substitute for linseed oil, but it dries much more slowly than that oil. It is also used for soap-making. It is somewhat difficult to refine owing to its tendency to form emulsions.

Sunflower oil contains the glycerides of palmitic, oleic, and linolic acids, and probably also of linolenic and isolinolenic acids in small proportion. Tolman and Munson obtained 3.67 and 4.10%, respectively, of solid fatty acids from 2 samples, which also gave the following results: iodine values, 108.3 and 104.1; iodine values of the liquid fatty acids, 117.8 and 113.8. Tortelli and Ruggeri found the iodine value of the liquid fatty acids 154.3, from a sample of oil which absorbed 137% of iodine. A sample examined by Jean (*Ann. Chim. Anal.*, 1901, 6, 166) contained 0.72% of unsaponifiable matter.

TUNG OIL. CHINESE WOOD OIL. JAPANESE WOOD OIL. WOOD OIL[1]

(For constants see p. 110.) Tung oil is derived from the seeds of *Aleurites cordata* (*Elæococca vernicia*) a plant which is grown extensively in both China and Japan, also of *A. fordii* (*Bull. Imp. Inst.*, 1907, 5, 134) and perhaps other species of *Aleurites*. The seeds contain 53% of oil, of which about 40% is obtained by expression.

Tung oil is either golden-yellow or dark brown in colour, according to whether it has been expressed in the cold or with the aid of heat, and it has, or develops on keeping, a somewhat pungent, peculiar odour, suggestive of bacon fat. It is the most powerful drying oil known, and is used extensively in China, the darker kind for caulking and varnishing junks, shop fronts, etc., and making putty, and the better sort for varnishing furniture. The light coloured oil of late years has been imported into Europe and America, chiefly from China, and used in the manufacture of lacquers and varnishes, though owing to the peculiar manner in which the oil dries, forming a film which is not transparent and elastic like that formed by linseed oil, but opaque and waxy looking, crumbling when rubbed, and to its property of gelatinising when heated to 250°, special treatment is necessary in using it.

Tung oil is composed of the esters of fatty acids, 25% of which were found by Cloëz to consist of ordinary oleic acid and 75% of an acid to which he attributed the formula $C_{17}H_{30}O_2$ and named *eloemargaric acid*, but which has been shown by Kametaka (*J. Chem. Soc. Trans.*, 1903, 83, 1042) to be a stereoisomeride of linolic acid, having the formula $C_{18}H_{32}O_2$. Walker and Warburton obtained little or no (0.39% to nil) insoluble brominated glyceride by adding bromine to a solution of tung oil in ether and acetic acid. From 2 samples, Jenkins obtained 10.4 and 10.6%, respectively, of glycerol.

Tung oil possesses the remarkable property of becoming *polymerised by heating*, a fact first observed by Cloëz. Jenkins (*Analyst*, 1898, 23, 113) found that by heating the oil to 250° for 2 hours in a closed flask, out of contact with the air, it became converted into a sticky elastic jelly. Another sample formed a hard, dry, elastic solid when similarly treated. In an investigation of polymerised

[1] The term "wood oil" is also applied to Gurjun balsam, an oleoresin obtained from the East Indies.

tung oil, Normann (*Chem. Zeit.*, 1907, **31,** 188) found the saponification value of the polymerised oil only slightly lower than that of the original oil (190.5 compared with 195.5), whilst the neutralisation value of the liberated fatty acids was even less changed. The iodine value of the fatty acids, however, was found to be 101.3 as compared with 162.4, and the molecular weight in benzene solution, ascertained by the freezing-point method, showed that while the fatty acids of the original oil have a molecular weight of 399.6 to 432.8, those of the polymerised oil gave values ranging from 554.4 to 699.6. In a further experiment, in which the oil was heated for several hours in a sealed tube at 300 to 320°, the iodine value of the fatty acids was reduced to 68.5 and the molecular weight increased to 852.0, showing that in this case polymerisation had proceeded still further. Polymerised tung oil is insoluble in the usual solvents, and hence the molecular weight of the polymerised oil itself could not be determined.

Both the glyceride and the α-acid which it contains are converted into isomeric forms (B) when exposed to light or the action of catalysts (Bauer and Herberts *Chem. Zeit.*, 1922, **29,** 220).

Iodine also has a remarkable action on this oil. Jenkins found that if a saturated solution of iodine in chloroform or carbon disulphide is dropped upon the oil it immediately solidifies it. Bromine has no such action. If 1 grm. of tung oil is dissolved in 5 c.c. of chloroform, mixed with 5 c.c. of a saturated solution of iodine in chloroform and stirred, the whole may become suddenly converted into a jelly in a few seconds. Some samples take much longer, and may need gentle warming; some refuse to gelatinise unless a larger quantity (2 to 4 grm.) of the oil be taken.

Tung oil *dries very rapidly.* 0.5 grm. was exposed to the air in a water-oven at about 100° on a watch glass. In about 3 minutes a dry ring formed round the spot of oil, and in 3 hours the oil was dry throughout and had gained 1.56% in weight. Raw linseed oil similarly treated had just begun to dry at the edges in 3 hours, and had gained 0.92% in weight (Archbutt).

5 grm. of tung oil stirred in the cold with 2 c.c. of carbon disulphide and 2 c.c. of sulphur chloride for 90 seconds suddenly stiffened to a thick and sticky jelly, not nearly so hard as the product obtained in a similar manner from either castor or linseed oil (Jenkins, *J. Soc. Chem. Ind.*, 1897, **16,** 195).

In the *elaidin test*, Jenkins obtained a brownish-red product, consisting of an oily layer resting on a nearly solid portion. When stirred up, the whole would scarcely flow.

In the *Valenta test*, using glacial acetic acid, Jenkins found the turbidity temperatures of two samples to be 44° and 47°, respectively.

Strong sulphuric acid immediately solidifies tung oil, forming a black clot, but by mixing 10 grm. of the oil with 40 grm. of olive oil, Jenkins found it possible to measure the rise of temperature, and after making a correction for the heat developed by the olive oil obtained *specific temperature reactions* of 298 and 330 with two different samples.

Nitric acid (1.4) rapidly converts tung oil into a tough mass, which darkens and becomes more brittle on standing.

The *viscosity* seems to be very variable, possibly due to a partial polymerisation of some samples. Two samples tested by Jenkins required, respectively, 1433 and 858 seconds for the outflow of 50 c.c. from Redwood's viscometer at 60° F.

Gardner and Reilly (Circ. 138, *U. S. Paint Manufacturers' Assoc.*, Nov., 1921) found the viscosity of Japanese tung oil to be intermediate between that of the Chinese oil and raw linseed oil.

Halphen's reaction for cottonseed oil gives no coloration with genuine samples of tung oil.

Commercial samples of tung oil have been found to contain from 0.44 to 0.74% of *unsaponifiable matter* and from 0.39 to 5.30% of *free (oleic) acid*.

The *mixed fatty acids* have been found to solidify at 31.2 to 37.2° and to have an iodine value of 150 to 159.

Tung oil is said to cause severe ulcers when brought into contact with the skin (Hertkorn, *Chem. Zeit.*, 1903, 27, 635), and its use in cosmetic and similar preparations (for which patents have been taken out) should be prohibited.

Blakeman (U. S. Patent, 767682, 1904) has patented as a drying oil a mixture of 85 parts of a "non-drying oil such as cottonseed oil" and 15 parts of tung oil mixed with a drier.

Test for Eloeomargaric Acid.—The qualitative test devised by Thomas and Yu (*J. Amer. Chem. Soc.*, 1923, 45, 120) for rape oil (see p. 170) is also applicable to tung oil. The insoluble magnesium

soaps are filtered off while still hot, washed with 90% alcohol, and the fatty acid liberated by treatment with dilute hydrochloric acid in the absence of air. This fatty acid, which has an odour of tung oil, melts at about 44° and rapidly oxidises, eventually changing into a brown mass. A yield of about 20% of this acid is obtained.

Chinese Wood Oil.—The enormous increase in the use of this oil of late years has caused it to be the subject of many investigations, one of the chief objects in view being to arrive at some satisfactory method of estimating its purity, and to set up a standard specification for purpose of sale, to which all pure samples should conform. As might be expected, a number of quite useless tests have been put forward.

A general survey of the more important methods has been made by Chapman (*Analyst*, 1912, **37**, 543) whose paper should be consulted. He points out that the analytical determinations of the greatest importance are the sp. gr., the iodine value, the refractive index, the viscosity and the polymerisation test.

The Wijs method of determining the iodine value is recommended, if carried out in the following manner:

About 0.1 grm. of the oil is dissolved in 20 c.c. of purified carbon tetrachloride, 30 c.c. of the Wijs solution added and the absorption allowed to proceed for 3 hours in the dark.

In connection with the viscosity (time of efflux) the same author draws attention to the fact that the viscosity of tung oil is greater than that of any other fatty oil likely to be used as an adulterant, but the warning is added that the viscosity may be considerably increased by heating the oil to a temperature short of that required for solidification.

Polymerisation Tests.—A great number of the tests put forward are based on the property which this oil possesses of setting to a firm mass when heated (*vide supra*). It has been suggested to solidify the oil by heating it under standard conditions and to grind and extract the mass with ether, but Bolton and Revis have found this to be most misleading and unsatisfactory except in the case of gross adulteration which could be more easily detected by other methods.

In a circular issued by the New York Produce Exchange a method devised by C. V. Bacon is tentatively put forward.

"In a test-tube ¾ in. diameter and 4 in. in length there are trans-ferred about 10 c.c. of pure China wood oil; into another test-tube there is transferred a similar volume of pure China wood oil adulter-ated to the extent of 10%. A sample of the oil to be tested is treated in a like manner, and these are placed in a proper support and immersed in an oil bath which has a temperature of about 288°; so that when the tubes are in it a temperature of 280° or 285° (maxi-mum) can be maintained. The oil bath containing the tubes is maintained at this temperature for exactly 9 minutes, the tubes are then withdrawn and the test sample is compared with the pure oil, and with the same oil adulterated with 5 and 10% of foreign oil. After the tubes are withdrawn from the oil bath, each tube should be stabbed from the top to bottom with a small bright spatula. Pure oil will give a hard, clean cut, and when the knife is withdrawn the incision will look like a straight line, but an oil having an adulteration as low as 5% will invariably be softer, and the incision will have a peculiar feathered effect; whilst an adulteration of 10% will be soft and "pushy," an adulteration exceeding 12% in many instances will remain entirely liquid."

A further test which is used by the New York importers and var-nish makers is described as follows:

"Hankow and Shanghai wood oil, 100 grm., should be heated in an open basin (6 in. in diameter) as soon as possible to a temperature between 540° and 560° F. and if it solidifies in about 6 to 6½ min-utes, cuts dry, and is firm in body, without discoloration and without being sticky, it should be passed as a good delivery. For Canton and Hongkong wood oil deliveries, the time should be from 4½ to 5½ minutes in an open basin as above. Should a longer time be taken by what is presumably pure wood oil, other tests confirming purity shall be positive.

Chapman (*ibid.*) criticises these tests and as a result of considerable experience states that he attaches more importance to the hardness of the jelly obtained under standard conditions than the time required for bringing about polymerisation. He has devised the following method of carrying out the test, which he finds to be capable of yielding definite and concordant results:

In the following table he gives the results of the examination of 17 samples of Chinese wood oil from Hankow:

Sample	Iodine value	Sp. gr. 15°/15°	Saponi-fication value	Ref. index at 20°	Time of efflux at 15.5°. seconds	Polymerisa-tion 1 hour at 250°
No. 1.	169.9	0.9419	196.6	1.5207	2,178	Very hard.
No. 2	168.4	0.9406	193.8	1.5181	1,636	Hard.
No. 3............	166.5	0.9426	194.3	1.5190	1,946	Fairly hard.
No. 4.	166.4	0.9417	193.0	1.5170	1,880	Fairly hard.
No. 5....	168.8	0.9430	195.6	1.5195	2,017	Very hard.
No. 6.......	170.0	0.9440	191.5	1.5180	1,849	Hard.
No. 7............	168.6	0.9416	193.0	1.5150	....	Fairly hard.
No. 8............	171.0	0.9414	192.0	1.5170	....	Hard.
No. 9............	169.7	0.9437	194.1	1.5176	1,997	Hard.
No. 10...........	173.0	0.9420	192.5	1.5165	1,722	Hard.
No. 11...........	176.2	0.9417	192.0	1.5168	1,605	Hard.
No. 12...........	172.6	0.9429	196.0	1.5180	1,740	Hard.
No. 13...........	174.2	0.9427	194.6	1.5182	1,690	Hard.
No. 14...........	173.7	0.9430	195.0	1.5194	1,820	Hard.
No. 15...........	172.8	0.9440	194.6	1.5193	2,047	Hard.
No. 16...........	169.5	0.9420	195.2	1.5160	1,804	Hard.
No. 17...........	169.6	0.9433	195.2	1.5187	1,820	Very hard.
Average........	170.6	0.9425	194.2	1.5179	1,850	

The following extract has been taken from his paper:

"About 5 c.c. of the oil to be examined are introduced into each of 2 test-tubes 6 in. long by ⅝ in. diameter. These are then immersed in a bath containing melted paraffin wax at a temperature of approximately 100°. The temperature of the bath is then raised to 250°, taking about 15 minutes for the operation. As soon as that temperature is reached the time is noted, and the source of heat adjusted so that the temperature of the bath is maintained constant at 250°. At the end of half an hour one of the tubes is withdrawn, allowed to cool, and, when cold, is broken, and the jelly examined. The other tube is kept in the bath at 250° for a further period of half an hour, at the end of which time it also is withdrawn and allowed to cool; it is then broken, and the hardness of the jelly observed. Chinese wood oil of good quality should give at the end of half an hour a fairly firm jelly, which, at the end of 1 hour, should become quite hard. It is advisable in all cases to carry out comparison tests alongside of the oil under examination, using for the purpose a sample of oil known to be of good quality.

"I have not found it possible to express the hardness of the solidified cylinders by means of numbers, but with a little experience it is very easy to distinguish between a sample of genuine oil and the same oil containing a small percentage of some fatty oil, such as soya bean or sesame. In referring to the polymerisation experiments, I have used the words "very hard," "hard," and "fairly hard," to denote the consistency of the polymerised oil, since such expressions are quite sufficient for the purpose. In addition to the degree of hardness of the solid cylinders of oil, some attention should be given to their physical characters. When cut with a knife or broken across, the cut or fractured surface should be smooth and free from stickiness, and small portions when rubbed in the hand should break down completely into a soft crumbly mass, which should not adhere to the fingers."

Insoluble Bromide Test.—This test becomes of considerable importance for the detection of other oils which yield insoluble bromides, such as fish or marine animal oils as well as linseed, rubberseed oil,

etc., for it has been shown by Hehner and Mitchell and independently by Jenkins and by Chapman (the latter having worked on the 17 samples above referred to as well as on 4 samples of Japanese wood oil) that no insoluble bromides are obtained by the methods proposed by Hehner and Mitchell (*Analyst*, 1898, **23**, 310). Bolton and Revis have applied this test, as modified by Halphen (*Fatty Foods*, p. 42), to a large number of samples without obtaining a precipitate in any one case.

Candle nut oil (p. 196) obtained from another species of *Aleurites*, as well as perilla and hemp seed oils, yield notable quantities of insoluble hexabromides.

Ware and Schumann (*Proc. Amer. Soc. Test. Mat.*, 1914), give the following method of detecting adulterating oils, which is based on the insolubility of the potassium soaps of Chinese wood oil in absolute alcohol. 3 grm. are saponified for 30 minutes under a reflux condenser with 100 c.c. of N/4 absolute alcoholic potassium hydroxide and the soap solution is cooled for 10 minutes at 0° and filtered through a Gooch crucible surrounded by ice. The precipitate is washed with ice-cold absolute alcohol previously saturated with the potassium soap of elœomargaric acid and the residue dried *in vacuo* at 75° to 80°, in a current of hydrogen or carbon dioxide and weighed. The weight of the dry insoluble soap may be taken as measuring the wood oil in the sample.

Experiments on test samples containing from 5 to 40% of linseed and soya bean oils gave results within 1 to 2% of the theoretical.

	1	2	3
Sp. gr. 15.5°/15.5°... . .	0.9406	0.9396	0.9276 to 0.9416
Ref. index at 25°.....	1.5143	1.5186	1.4790 to 1.5200
Moisture and volatile matter.	0.012 %	0.02 %	....
Ash	0.0068 %	0 0026 %	....
Acid value..	3.45	0 90	0.2 to 0.8
Saponification value.	192.27	193.02	188.2 to 192 4
Unsaponifiable matter.....	0.73 %	0 47 %	....
Iodine value (Hubl, 18 hours) . .	169.3	169.6	151.6 to 171.7
Iodine-jelly test[1].............	3 min. 37 sec.	4 min. 43 sec.	3 min. to 8 min.
Heating test[2]......	9 min. 54 sec.	9 min. 23 sec.	10 min. to 11.5 min.

[1] *Iodine-jelly Test.*—This test is carried out by mixing 1 grm. of the oil with 5 c.c. of chloroform at 25°, adding 5 c.c. of a saturated solution of iodine in the same solvent and stirring the mixture until a jelly is formed. The time is noted from the addition of the iodine to the formation of a jelly.

[2] *Heating Test.*—5 c.c. of the oil are placed in a test-tube containing a glass rod and heated in an oil-bath at 282°, the rod is raised after 9 minutes and afterwards at intervals of 50 seconds, the time being noted when a jelly is formed.

In a report of the same Society (1914, **17,** 38) the figures in the foregoing table are given for two samples of Chinese wood oil, No. 1, being commercially obtained from the exporter and No. 2 expressed in the laboratory from Chinese wood oil nuts.

In column 3 is a summary of the average results of 11 investigators upon 3 samples of tung oil pressed from American grown nuts.

Japanese Wood Oil.—There is considerable divergence of opinion as to the exact botanical species from which Japanese wood oil is obtained.   Whilst Lewkowitsch,[1] states that the oil is derived from the fruits of *Elæococca vernicia*, quoting Kametaka (*J. Coll. Sci. Imp. Univ. Tokyo*, 1908) and distinctly states that this tree differs from *Paulownia imperialis*, Chapman (*supra*) examined oil extracted by himself from the fruits of the latter plant and obtained values closely agreeing with samples of Japanese wood oil obtained from Japan.   Later, however, Wilson (*Bull. Imp. Inst.*, 1913, **13,** 441) states that the seeds actually examined by Chapman were those of *Aleurites cordata* and not those of *Paulownia imperialis*. In view, however, of the fact that Chapman himself examined oil extracted in his own laboratory from the seeds of *A. cordata*, it seems difficult to make these statements harmonise.

In a private communication to Bolton and Revis, Chapman stated that the oil examined by him was prepared from seeds forwarded to him from an authentic source in Japan and from a district in which the oil was being commercially manufactured, and he was informed that the seeds in question were obtained from *Paulownia imperialis*, and he further stated that the seeds in question were quite different from those of *Aleurites cordata* in his possession, one specimen of which had been received from the Imperial Institute. In view of these facts, there is little reason to doubt that Chapman's statement as to the botanical source of these seeds must be taken as correct, though whether *Paulownia imperialis* is to be considered a botanical synonym for *Aleurites cordata* must be left an open question.

Whatever may be the source of the oil, it undoubtedly differs from Chinese wood oil, more particularly with regard to its powers of polymerisation, and the iodine value is distinctly lower.

[1] *Oils, Fats and Waxes*, 5th Ed., 2, 82.

The following figures have been obtained by Chapman:

Source	Wakasa	Idzumo	?	Paulownia imperialis
Iodine value...................	158.0	149.0	151.8	153.5
Sp. gr. 15/15°.................	0.9377	0.9400	0.9349	0.9351
Saponification value...........	195.2	193.4	196.3	193.5
Refractive index at 20°........	1.5083	1.5052	1.5034	1.5050
Time of efflux at 15°, seconds..	1230.0	1620.0	....	....
Polymerisation, 2 hours at 250°	Soft.	Soft.	Very soft.	....
Bromine thermal value (rise in degrees).	....	....	....	24.5

Lewkowitsch[1] has contrasted the polymerising powers of Chinese and Japanese wood oils in the following table:

	Japanese tung oil	Chinese tung oil	
		No. 1	No. 2
Original oil.......	0.93386	0.9412	0.9419
Heated rapidly in wide-mouthed flask to 213° (420° F.).........	0.9649	0.9428	0.9432
Heated rapidly in wide-mouthed flask to 232° (450° F.).....................	0.9355	0.9445	0.9411
Heated rapidly in wide-mouthed flask to 250° (482° F.).....................	0.9477	0.9448	0 9504
Heated rapidly in wide-mouthed flask to 300° 572° F.).	....	0.9592	Solidified to hard jelly.
Heated rapidly in wide-mouthed flask to 310° (590° F.).....................	0.9553	0.9638	....
Heated rapidly in wide-mouthed flask to 320° (608° F.).........	0.9650	0 0700	... .
Heated rapidly in wide-mouthed flask to 330° (626° F.).	0.9694	Solidified to a jelly.	....
Heated rapidly in wide-mouthed flask to 340° (644° F.)......	0.9760	....	....
Heated to 150° and kept there for 2 hours.....	Solidified to a soft jelly.	0.9365	.. ..
	0.9477	0.9363	0.9463

Standard Specifications D 12–16, for Purity of Raw Tung Oil Adopted by American Society for Testing Materials in 1916 (American Society for Testing Materials, Standards 1921) are as follows:

[1] *Oils, Fats and Waxes.* 6th Ed., 2, 85.

PROPERTIES AND TESTS

1. Raw tung oil shall conform to the following requirements:

	Maximum	Minimum
Sp. Gr. at 15.5°/15.5°.....................	0.943	0.939
Acid number...............................	6	.....
Saponification Number.....................	195	190
Unsaponifiable Matter, %...................	0.75	.....
Refractive Index at 25°C...................	1.520	1.515
Iodine Number (Hubl, 18 hours).............	.....	165
Heating Test (Browne's Method), minutes.....	12	.....
Iodine Jelly Test, minutes.................	4	.....

For *Methods of Testing*, see reference made in original.   Note by American Editor.

WALNUT OIL.   NUT OIL

(For constants see p. 110.)   This oil is obtained by expression mainly from the kernels of the walnut, *Juglans regia* which, if the nuts have been kept for 2 to 3 months after they have been gathered, yield from 63 to 66%; if kept too long, the oil expressed from the kernels may be rancid.

·The first-expressed, "virgin," oil is almost colourless, with faint odour and not unpleasant flavour; it is largely used in some parts of Europe as a substitute for olive oil for edible purposes.   The second-pressed or "fire-drawn" oil is greenish-coloured, with an acrid flavour.   Being an excellent drying oil, forming a varnish which is pale in colour and less liable to crack than linseed oil varnish, walnut oil is much used for preparing artists' colours.   It is also a good lamp oil, and can be used for making soft soap.

Walnut oil contains the glycerides of myristic, lauric, oleic, linolic, linolenic and isolinolenic acids.   According to Hazura and Grüssner, 80% of the liquid fatty acids consist of linolic acid, 13% of linolenic and isolinolenic acids, and 7% of oleic acid.   The calculated iodine value of this mixture of liquid acids is 187 (Hehner and Mitchell); the iodine value of the liquid fatty acids determined by Tortelli and Ruggeriw as found to be 166.8, the oil from which they were obtained having an iodine value of 148.9.

Bulgarian Walnut Oil.—5 samples of cold-pressed Bulgarian walnut oil examined by Petkow (*Zeit. Nahr. Genussm.*, 1901, **4**, 828) gave results as follows:

```
Sp. gr. at 15°.................................  0.9255-0.9260
Refractometer reading, 40°....................      67-68
Iodine value..................................  147.92-148.43
```

Indian Walnut Oil.—A sample from the Punjab examined by Crossley and Le Sueur gave a butyro-refractometer reading of 64.8 at 40°, and 50 c.c. required 232 seconds to flow from Redwood's viscometer at 70° F.

Oil from Juglans nigra.—A sample of black-walnut oil from *J. nigra* examined by Kebler (*J. Frank. Inst.*, 1901, **151**, 394) was a straw yellow coloured oil, having an agreeable walnut-like odour and taste, and gave the following results:

```
Sp. gr. at 15°............................         0.9215
The oil became turbid at......................      −12°
Acid value....................................      8.6-9.0
Saponification value..........................   190.1-191.5
Iodine value..................................   141.4-142.7
Hehner value..................................      93.77
Reichert-Meissl value.........................      15 c.c.
M. p. of fatty acids..........................       0°
```

Confirmation of the high Reichert-Meissl value of this sample is required, seeing that ordinary walnut oil has no Reichert-Meissl value. *Juglans nigra* is largely cultivated in North America, where the oil it yields is known as *pecan oil*.

The following figures were obtained by Deiler and Traps (*Amer. Chem. J.*, 1910, **43**, 90) with oil extracted from the seeds (kernels) with ether.

```
Sp. gr. at 15/15° C...........................      0.9184
Saponification value..........................     198.0
Iodine value (Hubl's method)..................     106.0
Reichert-Meissl value.........................       2.2
Insoluble fatty acids + unsaponifiable........      93.4
```

The iodine value of this oil is abnormally low and requires confirmation.

Fouchet (*Bull. Sci. Pharmacol*, 1910, **43**, 90) has extracted by means of cold petroleum spirit a yellow oil from seeds of a cross

between *Juglans nigra* and *Juglans cinerea*, the yield being 50%. The oil so obtained gave the following figures:

Sp. gr. at 12/4°......................................	0.925
Ref. index (n)ᴅ at 22°................................	1.4765
Critical temperature of solution in absolute alcohol.....	78.5°
[α]ᴅ	±0
Saponification value.................................	191.0
Acid value...	0.37
Iodine value...	151.0
Acetyl value...	11.0

The oil consisted mainly of the glycerides of stearic oleic, linolic and linolenic acids, there being 70% of linolic acid.

Japanese Walnut Oil.—Matsumoto (Abst. *J. Soc. Chem. Ind.*, 1923, 42, 276A) describes the oil expressed from the Japanese walnut, *Juglans Sieboldiana.* The kernels yielded 59.6% of a pale yellow, odourless oil, with the following characters: Sp. gr. (15°), 0.9332; n_D, 1.4800; acid value, 0.68; Hehner value 92.3; saponification value, 191.1; Reichert-Meissl value 0.62: and iodine value (Hübl), 150.8. It had good drying properties.

Adulteration of Walnut Oil.—Walnut oil is liable to adulteration with other oils, most of which would lower the iodine value. Poppy oil would not appreciably alter the ordinary constants, and Bellier (*Ann. Chim. Anal.*, 1905, 10, 52) has proposed a test for this oil based upon the difference in solubility of the solid fatty acids in 70% alcohol at 17° to 19° in presence of a definite amount of potassium acetate. 1 c.c. of the oil is warmed in a test-tube with 5 c.c. of a solution of 16 grm. potassium hydroxide in 100 c.c. of 91 to 93% alcohol, until a clear solution is obtained, a similar test being simultaneously made with a walnut oil of known purity. The tubes are then closed and kept at about 70° for 30 minutes. A quantity of dilute acetic acid (1 volume of glacial acetic acid and 3 volumes of water) exactly equivalent to the potassium hydroxide is added, and the tubes and contents are cooled, first to 25°, and then to 17° to 19° with frequent shaking. Under these conditions, pure walnut oil requires a much longer time to give even a small precipitate of fatty acids than an impure sample, whilst poppy oil gives an abundant precipitate, and other oils also give a precipitate more quickly and in larger quantity than walnut oil. The test is said to be capable of detecting 10% of poppy oil, and has been confirmed by Balavoine (*J. Soc. Chem. Ind.*, 1906, 25, 499).

The difference in the yields of brominated glycerides insoluble in ether and acetic acid affords a means of detecting adulteration of walnut oil with oils which are not readily detected by other tests. From genuine walnut oil, Hehner and Mitchell obtained a yield of 1.5 to 1.9%; from poppy oil, none; and from linseed oil, 24 to 26%.

V. CASTOR OIL GROUP

Castor Oil.	Curcas Oil.
Croton Oil.	Grape-seed Oil.

CASTOR OIL

(See also p. 111.) Castor oil is expressed from the seeds of *Ricinus communis*, of which it constitutes nearly half the weight. It is also prepared by extraction. Cold-pressed ("cold-drawn") oil of the first quality is used as a medicinal purgative, but the lower grades are largely employed for lubrication by the Indian and Cape railways, for the manufacture of Turkey-red oils, for soap-making and leather dressing. It does not readily dry on exposure to the air, nor does it easily turn rancid (Lewkowitsch).

Castor oil is a transparent, colourless, or pale greenish-yellow liquid, having a faint odour and disagreeable taste. At a low temperature it thickens and deposits white granules, and at or about $-18°$ it solidifies to a yellowish mass.

Castor oil is distinguished in its physical characteristics from most other fixed oils by its high sp. gr. and viscosity, ready solubility in alcohol and insolubility in petroleum spirit. These characteristics are of value for the examination of commercial samples, and are described below. Castor oil is dextrorotatory. 23 samples of Indian castor oil examined by Deering and Redwood (*J. Soc. Chem. Ind.*, 1894, 13, 959) in a Hofmann-Laurent polarimeter with 200 mm. tube caused a rotation ranging from $+7.6°$ to $+9.7°$. Dowzard[1] gives $+8°$ to $+9°$; Rakusin[2] $+8°$ to $+8.65°$. Lythgoe[3] found the optical rotation of 44 samples of genuine castor oil to range from $+23.4°$ to $+26.1°$ (Ventzke, 200 mm., 20°); these numbers fall within the limits given by Deering and Redwood, whose values correspond with 21.9° to 28° Ventzke.

[1] *Chemist and Druggist,* 1901, 58, 325.
[2] *Chem. Zeit.,* 1906, 30, 143.
[3] *J. Amer. Chem. Soc.,* 1905, 27, 888.

Castor oil consists mainly of triricinolein, the glyceride of two isomeric hydroxylated acids, ricinoleic and isoricinoleic acid. Small quantities of tristearin and of the glyceride of dihydroxystearic acid are also present. Palmitin and olein are absent. Lewkowitsch (Oils, Fats and Waxes, II, 326) points out that less saturated fatty acids than ricinoleic must also be present, otherwise the iodine value of castor oil would not exceed about 67.

Crude Ricinoleic Acid, $HC_{18}H_{33}O_3$, may be prepared from castor oil by the method employed for the preparation of oleic acid from oils; or castor oil may be saponified, and the soap fractionally precipitated with calcium chloride. The first third should be rejected. The later fractions are purified by crystallisation from alcohol, and decomposed with dilute hydrochloric acid.

Ricinoleic acid is a thick oily liquid, which solidifies below $0°$. It is insoluble in water, but is miscible in all proportions with alcohol and ether. The alcoholic solution has an acid reaction, an unpleasant, persistent, acrid taste, and does not oxidise in the air. Like oleic acid, it combines with two atoms of bromine, and by treatment with nitrous acid is gradually converted into a stereo-isomer, ricinelaidic acid, a body crystallising from alcohol in white needles, melting at $50°$, and forming an additive compound with Br_2. When heated with phosphorus, iodine, and water, ricinoleic acid yields an iodo-acid, which by the action of nascent hydrogen (hydrochloric acid and zinc) is converted into stearic acid.

When distilled in a partial vacuum, ricinoleic acid yields œnathol or normal heptoic aldehyde, $C_6H_{13}.CHO$, and an acid of the acrylic series. This behaviour may be used for the detection of castor oil. For this purpose the sample should be saponified, and the fatty acids liberated and rapidly distilled in a small retort. The distillate is shaken with a saturated solution of acid sodium sulphite, the resultant crystals pressed, dissolved in a solution of sodium carbonate, and the liquid distilled in a current of steam. The œnanthol will collect on the surface of the distillate as a highly refractive liquid, of peculiar aromatic odour, boiling at $154°$. Œnanthol is also produced by subjecting the alkali-metal salts of ricinoleic acid to dry distillation, but if sodium hydroxide be present in addition, sodium sebacate is formed, and methyl-hexyl carbinol and methyl-hexyl ketone are found in the distillate.

Ricinoleic acid forms a series of salts, many of which are soluble in, and may be crystallised from, alcohol or ether.

The oleo-refractometer value of castor oil is given in the table on p. 61. The butyro-refractometer readings of the 44 samples examined by Lythgoe averaged 81.2 at 20°, and 78.1 at 25°, the variations from these numbers being slight and not exceeding ±0.5. Lythgoe gives the values for each 0.5° from 15° to 35°.

The following are some results of examination of the mixed fatty acids of castor oil (see also p. 111):

		Observer
Sp. gr. at 15.5°............	0.9509	Allen.
Sp. gr. at 98°–99°......	0.8960	Allen.
Solidifying-point.................................	. 3°	Hübl.
Refractive index at 60°...........................	1.4546	Thoerner.
Iodine value of mixed fatty acids....	87–88	
Iodine value of liquid fatty acids................	106.9	Tortelli and Ruggeri.

COMMERCIAL CASTOR OIL

The peculiar physical characteristics of pure castor oil distinguish it sharply from most other oils, but it is liable to adulteration with oils, such as arachis, cottonseed or rape oils, blown oils, rosin oil, etc., which may be lower in price, and for the detection of which the following tests may be used.

The *sp. gr.* of genuine castor oil is exceptionally high, and should lie between 0.959 and 0.968 at 15.5°. Adulteration with any other natural fixed oil or mixture of oils would lower the sp. gr., and although this might be adjusted by the addition of rosin oil, which often has a sp. gr. as high as 0.998, the presence of the latter would be easily detected by an estimation of the *unsaponifiable matter*, which in genuine castor oil is usually less than 0.7%. Blown rape or cotton-seed oil might be added without altering the sp. gr., and without causing any large increase of the unsaponifiable matter, but these oils would be detected by some of the following tests.

The *viscosity* of castor oil at the ordinary temperature exceeds that of all other natural fixed oils, but is approached by that of rosin oil and may be exceeded by that of blown oil. Twenty-three samples of Indian castor oil tested by Deering and Redwood in the Redwood

viscometer required from 1160 to 1190 seconds for the outflow of 50 c.c. at 100° F. The absolute viscosity, determined by Archbutt and Deeley, was found to be 2.729 at 100° F., 0.605 at 150° F., and 0.169 at 212°F. (*Lubrication* and *Lubricants*, p. 167.)

The *solubility in alcohol* of castor oil is greater than that of any oil likely to be used as an adulterant. Absolute alcohol dissolves castor oil in every proportion; 90% alcohol (sp. gr. 0.834) dissolves less, 1 volume of castor oil requiring from 2.4 to 2.94 volumes of 90% alcohol at 20° according to experiments by Itallie (Lewkowitsch, Oils, Fats and Waxes, II, 330), or from 3 to 4 volumes according to Dowzard (*J. Soc. Chem. Ind.*, 1901, **20,** 370). A genuine sample tested by Archbutt dissolved perfectly in 2 volumes of 90% alcohol at 15°. 23 samples of Indian castor oils examined by Deering and Redwood were completely soluble in 3 volumes of alcohol of sp. gr. 0.830 at 15.5°. From these results it appears that castor oil, if genuine, should dissolve completely in 3 volumes of 90% alcohol at 20°. It is usual, however, to employ 5 volumes of alcohol, as recommended in the British Pharmacopœia. Archbutt and Deeley (*Lubrication* and *Lubricants*, p. 319) found that when only 5% of either rape, blown rape, cottonseed, poppy, maize, or curcas oils were mixed with castor oil, 5 volumes of 90% alcohol gave a strongly turbid mixture at 15°, which deposited a small quantity of oil on standing. The following test, originally recommended by Finkener (*J. Soc. Chem. Ind.*, 1887, **6,** 148) (who used a slightly stronger alcohol), may therefore be employed with confidence as a rapid method of assay: Measure exactly 10 c.c. of castor oil in a graduated, stoppered test cylinder, add 50 c.c. of alcohol (sp. gr. 0.834) and well mix. If genuine, a clear and bright solution will be obtained at 15°. If as little as 5% of foreign oil be present, the liquid will remain strongly turbid, even on warming to 20°. *Oleic acid* would not be detected by the alcohol test, but it can be estimated with accuracy by titrating the sample with standard alkali, the acidity of genuine commercial castor oil being usually under 3%.

The *critical temperature of solution* in alcohol under specified conditions is also a useful test of the purity of castor oil (Chercheffsky, *Ann. Chim. Anal.*, 1918, **23,** 75).

Castor oil is readily soluble in *glacial acetic acid*. It is easily miscible with an equal measure of that solvent at the ordinary temperature, whereas most other fixed oils, except croton oil, are only

dissolved on heating, and yield solutions which become turbid before they have again cooled to the ordinary temperature.

The behaviour of castor oil with ether is highly characteristic. As far as has been recorded, all other fixed oils dissolve with facility in petroleum spirit, and are probably miscible in all proportions therewith, and with mineral lubricating oil. On the other hand, castor oil is not soluble in ether, though it is itself capable of dissolving its own volume of that liquid. The following information is given on the authority of Archbutt and Deeley: (*Lubrication* and *Lubricants*, p. 114) At 15° castor oil is practically insoluble in petroleum spirit and in burning oil. In "865" Scotch shale oil, at the same temperature, it dissolves to the extent of about 1 to 1.5%; "890" shale oil dissolves about 2 to 2.5% of it; and "907/12" American mineral oil dissolves rather more. Therefore, at the ordinary temperature, castor oil is very sparingly soluble in mineral oils; the solubility is greater the more dense and viscous the mineral oil; it increases with rise of temperature and diminishes as the temperature falls.

On the other hand, castor oil is able to dissolve mineral spirit and mineral oils in proportions which decrease as the sp. gr. of the mineral oil increases. The following table shows the maximum volumes which were found to give a clear solution at 15° with 10 c.c. of pure castor oil.

Mineral oil used	Sp. gr. at 15.5°	Maximum volume miscible with 10 c.c. of pure castor oil at 15°
Mineral (petroleum) spirit	0.692	9.2 c.c.
"White Rose" petroleum	0.788	5.5 c.c.
Scotch shale oil	0.865	3.7 c.c.
Scotch shale oil	0.890	2.45 c.c.
American pale mineral oil	0.907–0.912	1.7 c.c.

Although pure castor oil almost refuses to mix with mineral lubricating oil, the difficulty entirely disappears if a third oil, such as rape, tallow, or lard oil, is present, a clear mixture of the three being readily obtained. Pure castor oil mixes with refined rosin oil in all proportions.

Frabot (*Ann. Chim. Anal.*, 1917, **22**, 217) has based a test for detecting small amounts of arachis oil in castor oil on the turbidity

temperature of a solution of 1 volume of the oil in 5 volumes of 95% alcohol. In the case of pure castor oil the solution remains clear at −20°, whereas with 1% of arachis oil it becomes opalescent at −4 to −5° and turbid at −9°.

Another test is to shake 20 c.c. of the oil with 80 c.c. of (petroleum spirit, gasoline, b. p. 35° to 70°) in a stoppered cylinder and to allow the liquids to separate. In the case of pure castor oil the increase in volume of the oily layer due to solution in the gasoline, will be about 11 or 12 c.c., whereas in the presence of foreign oils the oily layer will be greater, and the amount of increase affords a rapid criterion of the purity of the oil. After complete separation 50 c.c. of the gasoline layer are evaporated and the residue weighed. The average amount yielded by pure castor oils was 8.52%, whilst oil containing 4% of arachis oil yielded 12.73%, and oil containing 1% of arachis oil gave 10.04%.

The *acetyl value* (see p. 111) of castor oil (146.7 to 150.5) exceeds that of any other known oil, and is one of the most valuable indications of its purity. Although blown oils also have high acetyl values (about 45 to 65) they do not nearly approach castor oil in this respect, and the detection of 10% of blown oil in castor oil is possible. Grape seed oil, if added to castor oil, would lower the sp. gr.

The *Hehner value* (95.3. to 95.5%) and the *iodine value* would be lowered by adulteration with blown oil; the *Reichert-Meissl value*, *Maumené thermal value*, and *saponification value* would, on the other hand, be raised. Refined *rosin oil*, which has been extensively employed for the adulteration of castor oil, neutralises no alkali, or only a trifling quantity, and would, therefore, lower the saponification value.

The high *optical rotation* caused by castor oil has already been referred to and would be lowered by most other natural fixed oils, except croton oil and laurel oil (Rakusin). It would not be available in the presence of *rosin oil*, which is strongly dextrorotatory. Some samples of sesame oil have a marked rotatory power (see p. 61). The *refractometer* would also be useful. Lythgoe mentions an instance in which 50% of *cottonseed oil* was found in a sample of "castor oil" from Massachusetts. This was detected at first by the low optical activity of the sample, and was confirmed by the low refractive power and sp. gr. and the high iodine value, also by Halphen's colour reaction.

Among other possible adulterants, *poppyseed oil* would lower the sp. gr., acetyl value, and viscosity, and would raise the iodine value; *lard oil* would lower the oleo-refractometer value, sp. gr., viscosity, acetyl, and iodine values; *coconut oil* would raise the saponification value and would lower the sp. gr., Hehner value and iodine value; and *seal oil* would lower the sp. gr., viscosity and acetyl value, and would raise the iodine value. *Sesame oil* would be detected by the characteristic colour tests for this oil.

The formation of sebacic acid, when the sample is distilled alone or with a quantity of alkali insufficient for its complete saponification, may be employed as a test for foreign fixed oils in castor oil.

On passing a current of phosgene gas through castor oil a trichlorocarbonic product is obtained which, when washed with hot water, was found by Piutti and Curzio (*Giorn. Chim. Ind. Appl.*, 1921, 3, 2421) to contain 8.96 to 9.15% of chlorine, whereas the products given by olive, arachis, almond and other oils free from hydroxyl groups contained only 0.08 to 0.18% of chlorine. Hence, the method may be used as a means of detecting the presence of adulterants in castor oil.

When castor oil is distilled at 300° until it has lost from 5 to 10% of its weight, a yellowish-brown oil with green fluorescence remains, which is miscible in all proportions with mineral oils, ceresin or vaseline, and is not soluble in alcohol or acetic acid. The name "floricin" has been given to this product. According to Fendler (*Deutsch. pharm. Ges. Ber.*, 1904, 14, 135), it contains the ester of undecylenic acid. A similar product is obtained by heating the oil in an autoclave to 260°–300° under a pressure of 4 to 6 atmospheres for about 10 hours.[1]

Estimation of Castor Oil.—Lane (*J. Soc. Chem. Ind.*, 1907, 26, 597), having found that lead ricinoleate is insoluble in petroleum spirit, has devised the following method of estimating castor oil in mixtures, soaps, and alizarin oils. The liquid acids in these cannot be estimated by the lead-soap and ether method, because lead stearate and palmitate are soluble in a solution of lead ricinoleate in ether.

From 3 to 3.5 grm. of the oil or fatty acids are taken. If the sample is sulphonated (Turkey-red oil), a quantity sufficient to yield this amount of fatty acid must be first boiled for about 2 hours

[1] *Eng. Pat.* 24935, 1905.

with dilute hydrochloric acid (1:5), with frequent shaking, until desulphonation is complete, the acid liquid being then poured into a separating funnel, shaken with ether, and the ethereal solution washed with water until free from acid.   The ether having been distilled off, the fatty matter is weighed and saponified with alcoholic potassium hydroxide, a drop of phenolphthalein added, the solution rendered slightly acid with acetic acid and then very faintly pink with N/10 sodium hydroxide.   The liquid is then slowly poured into a boiling mixture of 200 c.c. of water and 30 c.c. of a 10% solution of lead acetate contained in a 500 c.c. Erlenmeyer flask, the boiling is kept up for 5 or 6 minutes, and the liquid is then cooled by rotating the flask under a stream of running water, the movement being continued until the lead soaps adhere to the sides of the flask and the aqueous solution is clear.   If it remains milky, desulphonation was not complete, and the test must be repeated. The aqueous solution is poured off, or filtered if necessary, the flask is then heated on the steam-bath until the contents are melted, again cooled, and any remaining water shaken out.

The flask containing the dry lead salts is heated, and about 10 c.c. of petroleum spirit are added, which usually mixes with the soaps and renders them more fluid.   75 to 80 c.c. more petroleum spirit are added, and the solution is boiled under a reflux condenser. It is then poured into a stoppered, graduated, 500 c.c. cylinder of thin glass, having a stop-cock just below the 250 c.c. mark, or into a 500 c.c. graduated flask.   The flask containing the salts is repeatedly rinsed with petroleum spirit, which is boiled each time, and as much as possible of the lead soaps transferred to the cylinder or flask, about 200 to 225 c.c. of petroleum spirit in all being used. The ethereal solution is then diluted nearly to the 500 c.c. mark with petroleum spirit boiling at 28° to 30°, the whole is boiled for 1 minute (neglect of this detail will cause an inaccurate result) and allowed to stand in a cool place for at least 3 hours, and preferably all night, in order that the lead ricinoleate, etc., may completely separate.

If the sample contains 80% or more of castor oil, petroleum spirit of 38° to 40° b. p. is used for rinsing and washing the flask; if under 80%, that of 28° to 30° b. p. is used, the percentage of castor oil present being judged, approximately, by the fact that when under 80% the soaps will dissolve in the hot spirit of 30° b. p., whilst if

over 80% a semi-fluid mass remains which is more perfectly extracted by the solvent of higher b. p. It is essential, however, that the greater part of the solvent used for the dilution should be of the lower b. p. The lead ricinoleate is precipitated from this, on cooling, as a characteristic, flocculent mass resembling aluminum hydroxide, whilst lead stearate and palmitate form white, slowly subsiding powders.

After the complete separation of the insoluble lead salts, the liquid is diluted to exactly 500 c.c., shaken and allowed to settle. 250 c.c. are then drawn off, filtered if necessary, distilled down to 75 or 80 c.c., shaken in a separating funnel with 10 c.c. of 10% acetic acid, and washed with water until the washings are perfectly neutral to phenolphthalein and made alkaline by one drop of N/10 sodium hydroxide. The solution is then distilled from a 200 c.c. Erlenmeyer flask until most of the petroleum spirit has been expelled, mixed with 50 c.c. of neutral alcohol, and titrated with N/10 sodium hydroxide. The volume of N/10 used × 0.0282 gives the equivalent weight of oleic acid, and if we assume that the other oils in the mixture are vegetable oils, such as olive, maize, etc., which contain approximately 80% of liquid acids, the result $\times \frac{100}{80}$ represents *oil other than castor oil.* If the admixed oil can be identified, however, its percentage of liquid acids should, of course, be substituted for 80. The weight thus obtained, multiplied by 2, subtracted from the weight of oil or mixed fatty acids taken, multiplied by 100 and divided by the weight taken, gives the percentage of castor oil in the sample. If the mixed fatty acids are used for the estimation, the result must of course be divided by 0.95 to give the equivalent of neutral oil.

Lane obtained the following results by this method:

Mixture prepared		Castor oil found, %
Castor oil	Olive oil	
50	50	45.83
70	30	69.96
85	15	84.57
85	15	84.45

A commercial sample composed of castor oil, olive oil, and oleic acid, said to contain 75% of castor oil, was found to contain 76%.

ALIZARIN OIL. TURKEY-RED OIL

In dyeing cotton goods red with alizarin, the use of a fatty acid at one stage of the process is essential. Experience has shown that the best results are obtained by employing the ammonium salt of ricinoleosulphuric acid, $C_{18}H_{33}(HSO_3)O_3$, a substance which is obtained, mixed with unaltered esters and with the products of its decomposition (see "Sulpholeic Acid"), by the action of sulphuric acid on castor oil. The details of the method of preparation vary considerably; a common plan is to treat castor oil with strong sulphuric acid, added slowly with stirring, so that the temperature does not rise above 35°. The excess of sulphuric acid is then removed by agitating the product with water and then with a solution of common salt or, preferably, sodium sulphate, and the oily layer of crude ricinoleosulphuric acid is partly neutralised with ammonia, or with a mixture of ammonia with potash or soda, and diluted to the required strength. The product, which is a complex mixture of ricinoleosulphuric, ricinoleic, and polyricinoleic acids, existing partially in the free state, partly combined with ammonia or soda, and partly as mixed glycerides, together with unaltered esters and water, constitutes "alizarin or Turkey-red oil," also called "sulphated oil," "soluble oil," "red oil" or "olein."[1] True Turkey-red oil is made from castor oil exclusively (Wilson), but similar products are prepared from olive oil and cottonseed oil;[2] these may be distinguished as olive Turkey-red oil and cottonseed Turkey-red oil, respectively.

When castor Turkey-red oil is shaken with water and ether, the sulphonated fatty acids are dissolved by the water, and the non-sulphonated acids and unaltered glycerides by the ether; the former may be caused to separate from the aqueous portion by saturating it with common salt or sodium sulphate, and the latter can be recovered

[1] The composition and mode of action of Turkey-red oils have been the subject of numerous researches. See Lewkowitsch, Oils, Fats and Waxes, III, 154; Alder Wright and Mitchell, Oils, Fats and Waxes, p. 206, 433; Knecht and Rawson, A Manual of Dyeing, p. 160.

[2] Maize oil, neatsfoot oil and other oils are sulphonated in the United States. The American Editors in their laboratory have examined samples consisting of mixtures of sulphonated oils, containing some castor. In one case sodium silicate had been used instead of ammonia to neutralize the acidity. Mineral oil is a frequent constituent. The analytical constants of such mixed sulphonated fats or oils are generally not published and the analyst must bear in mind the possibility of encountering difficulties in interpreting analytical results. AMERICAN EDITORS.

by evaporating off the ether. The solubility of Turkey-red oil in water is due to the presence of the sulphonated acid.

The proportion of fatty matter present in alizarin oil varies considerably. It may be as low as 40, and occasionally reaches 65%, the usual proportion being about 50%. The amount required should be specified by purchasers and controlled by analysis.

Turkey-red oil, if properly prepared from pure castor oil, when *largely* diluted, even with hard water, will bear the addition of ammonium hydroxide to alkaline reaction without showing any turbidity on standing for several hours. A turbidity or precipitate denotes the presence of solid fats, and indicates the employment of either impure castor oil (*e.g.*, castor oil foots) or of rape, cottonseed, olive, or other oil containing stearin or palmitin.

The sp. gr. of Turkey-red oil is very variable. According to Wilson (*J. Soc. Chem. Ind.*, 1891, **10,** 26), the sp. gr. of a 45% oil ranges from 1.017 to 1.035.

The analysis of Turkey-red oil may have as its object the estimation of (1) the amount and nature of the fatty matter, alkali, etc., contained in the sample, and (2) the source of the fatty matter and the presence or absence of adulterants.

In the estimation of the *total fatty matter* it is customary to decompose the sulphonated oils by boiling with dilute hydrochloric acid. Lewkowitsch (Oils, Fats and Waxes, III, 158) recommends *Benedikt's* method. About 4 grm. of the sample are accurately weighed into a porcelain basin, and 20 c.c. of hot water are added gradually. Should the liquid be turbid, ammonia is run in until it is faintly alkaline to phenolphthaleïn. A clear solution will thus be obtained. 15 c.c. of dilute sulphuric acid (equal volumes of strong acid and water) are next added and an accurately weighed quantity, about 10 grm., of paraffin wax. The mixture is heated until a clear oily layer floats upon the surface. It is then made quite cold, and the solidified cake is removed, carefully dried and weighed. From the weight, that of the added paraffin wax is deducted, and the remainder represents the total fatty matter in the quantity taken.

According to Herbig (*J. Soc. Chem. Ind.*, 1902, **21,** 367; from *Chem. Rev. Fett Ind.*, 1902, **9,** 5), the simplest method is that of *Finsler-Breinl.* 30 grm. of the oil are weighed into a flask of 210 c.c. to 250 c.c. capacity, having a long narrow neck graduated

in tenths of a c.c.   100 c.c. of water and 25 c.c. of sulphuric acid
(62° B = 1.753 sp. gr.) are added and the mixture is heated until
the oily layer which forms is perfectly transparent.   A hot solu-
tion of sodium chloride or sulphate is then poured into the flask to
bring the oily layer into the neck, and after standing half an
hour the volume is read off.   Each 1 c.c. = 3% of fatty matter,
but as the average sp. gr. of the oil is 0.945 the result should be mul-
tiplied by this factor.

In a later paper[1] Herbig recommends the following method:
10 grm. of the oil are heated in a flask with 50 c.c. of water, until
dissolved, and the solution is then mixed with 25 c.c. of dilute
(1 : 5) hydrochloric acid and boiled for 3 to 5 minutes.   When cold,
the contents of the flask are transferred to a separating funnel with
water and well shaken with about 200 c.c. of ether.   The aqueous
layer is drawn off, and the ethereal solution washed with three
successive quantities of cold water.   The greater part of the ether
is distilled off, the residue transferred to a beaker, and the rest of
the ether allowed to evaporate spontaneously.   The residual oil
is heated for 1 or 2 minutes over a free flame until bubbles cease
to appear, then dried for 30 minutes at 105° and weighed.   The
aqueous extract and washings, if mixed and heated to expel the
dissolved ether, may be used for estimation of the fatty sulphuric
acid and glycerol.

To estimate the *total free acid*, Wilson dissolves 5 to 7 grm. of
the oil in alcohol or alcohol-ether and titrates with N/2 alcoholic
potassium hydroxide, keeping the temperature low and stirring
rapidly so as to avoid local excess of alkali, owing to the great ten-
dency of the esters in all Turkey-red oils to undergo hydrolysis.   The
amount of free acid, calculated as ricinoleosulphuric acid, in a 45%
oil may range from 22 to 30%.   This method is intended for Turkey-
red oils prepared with sodium hydroxide or potassium hydroxide,
but good results may be obtained even in the case of ammonia
Turkey-red oils.   Obviously, the figure obtained gives no idea as
to the percentage of total fatty acids actually present, owing to the
great difference in the molecular equivalents of the different acids.
If this information be desired, the percentage of neutral oil should
be estimated and the fatty acids found by difference.

[1] *Chem. Rev. Fett Ind.*, 1906, 13, 187, 211 and 241; abs. in *J. Soc. Chem. Ind.*, 1906, 25, 1009.

For the estimation of the *neutral oil*, Lewkowitsch[1] dissolves 30 grm. of the sample in 50 c.c. of water, adds 20 c.c. of ammonia and 30 c.c. of glycerin, and shakes twice with ether, using 100 c.c. each time. The ethereal solution is washed with water to remove traces of soap, run through a dry filter into a tared flask, the ether distilled off, and the residual oil dried at 100° and weighed.

Herbig (*Färber Zeit.*, 1914, 25, 169, 194) takes advantage of the fact that the potassium salts of ricinoleic and sulphoricinoleic acids are largely soluble in cold acetone and the sodium salts only sparingly soluble, to effect a practically quantitative separation from the neutral oil. He proceeds as follows: From 2 to 5 grm. of the oil, according to the water content determined by Fahrion's method (*J. Soc. Chem. Ind.*, 1913, 32, 1118), are neutralised with N/1 or N/10 alkali, evaporated to dryness on the water-bath and the residue dried by Fahrion's method (*loc. cit.*). The dried mass (which must not be overheated) is boiled with 4 successive portions (75 c.c. each) of anhydrous acetone, each extract being cooled with ice and decanted through a filter. The solution is evaporated, the residue of oil weighed and its acid and saponification values determined. The separated salts are readily soluble in hot water, yielding a solution ranging from faint yellow to deep yellow ("monopol soap"). This solution is treated with boiling hydrochloric acid to liberate the combined sulphuric acid and fatty acids, the latter being subsequently extracted with ether and examined. From 66% ("monopol soap") to 77% (Turkey-red oil) of the total sulphuric acid was found in the salts insoluble in acetone.

The ratios between the percentages of acetone extract and fatty acids were: "monopol soap" 1.13; Turkey-red oils 1.45 and 1.78. The sum of water and total fat constituted about 90% of the samples of oil (84% in the case of "monopol" soap). This affords a practical sorting test.

Scheurer-Kestner (*Compt. rend.*, 112, 158 and 395), after pointing out the different shades produced in dyeing and printing by the *sulphonated* and *non-sulphonated fatty acids*, respectively, proposed a method of roughly estimating these volumetrically by titration with standard ammonia solution, dependent upon the fact that litmus becomes blue when the sulphonated acids are neutralised, whilst phenolphthalein does not become reddened until the neu-

[1] Oils, Fats and Waxes, III, 159.

tralisation of the whole of the fatty acids present is completed. In a particular sample he found the molecular weight of the mixed non-sulphonated acids 472, and that of the sulphonated acids 402. The following are the molecular weights of some of the pure acids which may be present:

                    Ricinoleic.. 298
                    Di-ricinoleic.. 578
                    Ricinoleosulphuric....................................... 378
                    Di-ricinoleosulphuric.................................... 658

Jouillard (*Bull. Soc. Chim.*, 1891, **6**, 638), says this method gives inaccurate results, especially as diricinoleosulphuric acid is almost invariably present. He advises an estimation of the *molecular weight* of the fatty acids soluble and insoluble in water, by *Raoult's method*, taking care, in separating these by shaking with water and ether as already described, that the whole of the water-soluble acids are extracted. Jouillard also recommends an estimation of the glycerol and sulphuric acid in the sulphonated oil.

For the estimation of *fatty-sulphuric acid*, Herbig (*loc. cit.*) boils 4 grm. of the oil with 30 c.c. of dilute hydrochloric acid (1 : 5) for 40 minutes, removes the oil by shaking with ether, and estimates the SO_3 in the aqueous liquid by precipitation with barium chloride. From the weight obtained should be deducted the amount of SO_3 existing as sodium or ammonium sulphate, which Lewkowitsch estimates by dissolving a weighed quantity of the sample in ether, shaking repeatedly with small quantities of saturated brine free from sulphate, and estimating the SO_3 in the brine washings.

The *total alkali* may be estimated by titration. Wilson takes 5 to 7 grm., dilutes with water to about 50 c.c., and titrates with semi-normal acid, using Methyl Orange as indicator. The result is calculated to ammonia or sodium hydroxide. If both are present, the oil should be dissolved in ether and well shaken with dilute sulphuric acid. The ammonia, sodium hydroxide (and potassium hydroxide) can then be estimated in the aqueous washings by the usual methods.

Traces of *iron* seriously affect the brilliancy of alizarin colours. If 10 c.c. of the oil are shaken in a stoppered cylinder with 20 c.c. of dilute sulphuric acid (1 : 1) and a few drops of potassium ferrocyanide solution, and after adding 50 c.c. of ether if the mixture be again well shaken, even a trace of iron gives a blue ring at the junction

of the ethereal and aqueous liquids (*Leipziger Färber u. Zeugdr., Zeit.*, 1901, 14, 153).

For the purpose of ascertaining the source of the oil with which the sample of Turkey-red oil has been prepared and the *detection of adulterants*, Wilson (*J. Soc. Chem. Ind.*, 1892, 11, 495) saponifies 100 grm. by boiling with alcoholic potassium hydroxide and obtains the mixed fatty acids in the usual way. He then ascertains the *acetyl value, sp. gr., m. p.*, and *saponification value*. The acetyl value should be determined by Lewkowitsch's method (see p. 39) and should be 125 or over if pure castor oil has been used in the preparation of the sample. A lower value would show that other oils have been used. The following average results were obtained by Wilson with mixed fatty acids from Turkey-red oils made from castor, olive, and cottonseed oils, respectively:

	Castor oil acids	Olive oil acids	Cottonseed oil acids
Westphal gravity at 98°.........	0.892	0.851	0.872
M. p. by capillary tube.........	....	40°	44°
Neutralisation value...........	180–184	173–176	171–175

The fatty acids from castor Turkey-red oil deposit no more than traces of fat at 15.5°, whilst those from olive and cotton oils solidify.

Adulteration of Turkey-red oil with *mineral or rosin oil* would be detected by an estimation of the unsaponifiable matter.

The following simplified method of examining sulphonated oils has been devised by Hart (*J. Ind. Eng. Chem.*, 1917, 9, 850):

Fat.—A solution of the oil is titrated with N/2 sulphuric acid, (Methyl Orange as indicator), and the alkalinity (from the soap) expressed in mg. of potassium hydroxide per grm. The saponification value is determined in another portion of the sample, and the sum of the two results, divided by the neutralisation value of the fatty acids, gives the required percentage of fat. If the neutralisation value of the fatty acids is not known, the average value of 190 is taken.

Ammonia.—A portion of the solution is boiled with a measured excess of N/2 alcoholic sodium hydroxide solution, and, after removal of ammonia, the liquid is titrated with N/2 sulphuric acid. The

alkalinity of a second portion is then determined, without boiling with sodium hydroxide, and the difference between the results calculated into ammonia.   Allowance must be made for the fat corresponding to the ammonium soap present.

Combined Sulphuric Anhydride.—The oil is decomposed by boiling it with a measured quantity of standard sulphuric acid

$$2NaSO_3.O.C_{17}H_{32}CO_2Na + H_2 SO_4 + 2H_2O = Na_2SO_4 + 2NaHSO_4$$
$$+ 2HO\ C_{17}H_{32}.COOH.$$

It is then titrated with standard alkali (Methyl Orange as indicator), and the net change in the acidity is equal to the difference between the total alkalinity (due to the soap) and the acidity (due to the sodium bisulphate).

The total alkalinity of the original sample is estimated as described above, and from these data the acidity corresponding with the sodium bisulphate, or combined sulphuric anhydride, is calculated.

Schultz (*J. Amer. Leather Chem. Assoc.*, 1918, **13**, 190) has suggested certain modifications of this method.   In his opinion it may be regarded as trustworthy; although it yields a somewhat higher value for fat than the method of the American Leather Chemists' Association Committee.

Standards for Sulphonated Oils.—The following specification has been recommended by a committee of the Amer. Leather Chem. Assoc. as a basis for the sale of sulphonated oils: "The standard shall be 70% of total fatty oil.   Any oil tendered which tests 71% or over shall be paid for at a *pro rata* increase calculated as from the 70% standard.   Any oil which tests under 70%, but is 68% or over, shall be subject to a reduction of $1\frac{1}{2}$ times the shortage calculated at *pro rata* price from 70%.   If the test falls below 68% the buyer shall have the right of rejection."

CROTON OIL

(See also p. 111.)   Croton oil is obtained by expression or extraction with alcohol from the seeds of *Croton tiglium*, the yield being about 53 to 56%.   It is a brownish-yellow to dark reddish-brown, viscid oil, with disagreeable odour and acrid burning taste (*British Pharmacopœia*), intensely purgative and vesicatory.

The lighter varieties darken very much with age.   Croton oil differs from castor oil in being soluble in petroleum spirit.   It has

slight drying power and forms no elaidin with nitrous acid. It is composed of the glycerides of tiglic acid and other higher homologues of oleic acid, and of stearic, palmitic, myristic, lauric, caproic, butyric, and acetic acids. Oleic acid itself has not been identified in the oil. Dunstan and Boole (*Proc. Roy. Soc.*, 1895, **58,** 238) have shown that the vesicating constituent is a neutral, resinous substance of empirical formula $C_{13}H_{18}O_4$, which forms but a small proportion of the so-called "croton-oleic acid" from which it is obtained.

Croton oil is more strongly dextrorotatory than castor oil. Rakusin (*Chem. Zeit.*, 1906, **30,** 143), using a Soleil-Ventzke instrument with 200 mm. tube, obtained the following values:

Croton oil, $+14.5°$ to $+16.4°$.
Castor oil, $+ 8.0°$ to $+8.65°$.

The discrepancies in the analytical data for croton oil as obtained by different observers are probably dependent upon the method by which the oil was obtained. Thus, Javillier (*J. Pharm. Chim.*, 1898, **7,** 524) prepared three samples: the first by simple expression, the second by extraction with ether, and the third by digestion at 75° with 95% alcohol; the first two methods being those described by the French Codex of 1884. The yield and character of the products are shown in the following table:

	Expressed oil	Oil extracted by ether	Oil extracted by alcohol
Yield..........................	12.5%	38%	12%
Colour.........................	Pale.	Light brown.	Very dark brown.
Solubility (1 vol. of oil + 2 vols. absolute alcohol)....	Soluble at 75°.	Soluble at 75°.	Soluble in the cold.
Solidification temperature..........	−7°	−7°	−8°
Iodine value........................	109	108	91.2
Saponification value...............	192.9	194.5	260.6
Acid value.........................	27.3	30.9	60.1

The acid value was estimated by dissolving the oil in ether and titrating directly with $N/10$ alcoholic potassium hydroxide.

Dulière (*J. Ann. de Pharm. de Louvain*, 1899, 229 and 278) states that croton oil obtained by extraction with petroleum spirit or by dold expression has the same characteristics as the official oil, but that oils prepared by hot expression or by extraction of the non-cecorticated seeds with ether, differ from it in colour, acidity, and

in absolute degree of solubility alcohol, although the chief chemical constants are practically identical. He gives the following table of constants for this oil:

Sp. gr. at 15°..................................	0.9437
Sp. gr. at 100°.................................	0.8874
Solubility in 92% alcohol.......................	1 in 63
Critical temperature (Crismer)..................	54.8°
Oleo-refractometer degrees, 22°.................	+35
Butyro-refractometer degrees, 27°..............	77.5
Acid value (Burstyn)...........................	21.8
Saponification value...........................	215.6
Reichert-Meissl value..........................	12.1
Acetyl value (Lewkowitsch).....................	38.64
Solidifying-point of mixed fatty acids..........	16.4 to 16.7°

Two samples of croton oil examined by Lewkowitsch (*Analyst*, 1899, 24, 319) gave the following results:

Saponification value...........................	215.0	210.3
Acetyl value...................................	19.82	32.66

The same observer[1] found 0.55% of unsaponifiable matter in several samples of croton oil and 18.6 to 19.0° as the "titer" test of the mixed fatty acids.

Adulteration of croton oil with castor oil would be detected by the increased acetyl value. Hydrocarbons, which are said to be frequently added (Dulière), would lower the saponification value and increase the percentage of unsaponifiable matter.

It is of interest to note that this oil entirely loses its physiological properties when subjected to the process of hydrogenation (*Ber.*, 1909, 42, 1546).

CURCAS OIL

(See p. 111.) This is from the seeds of the "physic nut" or "purging nut" tree, *Jatropha curcas*, a plant chiefly cultivated in the Portuguese colonies, and especially in the Cape Verde Islands. It is yellowish-brown in a crude state, pale yellow when refined, has a faint unpleasant odour, and powerful purgative properties, 10 drops having a greater purgative effect than a tablespoonful of castor oil (Klein). It is only slightly soluble in alcohol, 100 volumes of absolute alcohol at 15.5° dissolving about 2.17 volumes (Archbutt: (*J. Soc. Chem. Ind.*, 1898 17, 1009), but freely soluble in petroleum spirit, by which properties, together with its much lower viscosity, it is readily distinguished from castor oil.

[1] Oils. Fats and Waxes. II. 184.

Acording to Klein (*Zeitsch. angew. Chem.*, 1898, 1012) curcas oil is composed of esters of solid and liquid fatty acids, the former (9 to 10%) consisting of palmitic and stearic acids and the latter of oleic and linolic acids in about equal proportion. No ricinoleic or linolic acid was detected.

Besides its medicinal uses, curcas oil is employed as a lamp oil, and in the manufacture of soap and candles; as a lubricant, however, for which purpose it is also said to be used, it has the disadvantage of drying nearly as rapidly as cottonseed oil. Thin films on glass dried in from 24 to 30 hours at the ordinary temperature, cottonseed oil drying under the same conditions in 18 to 20 hours, and refined rape oil in 48 hours (Archbutt).

With nitric acid (1.375), refined curcas oil gives a pale brown colour, changing to orange on standing; with Halphen's test and with furfural and hydrochloric acid it gives negative results.

Very discordant numbers for the constants of this oil have been published by different observers, which accounts for the wide range shown in the table on p. 111. The results given below were obtained by Lewkowitsch and by Archbutt.

	Lewkowitsch		Archbutt		
	Authentic sample of expressed curcas oil[1]	Com-mercial oil	Commercial oil from Lisbon		
			Crude	Refined	Refined
Sp. gr. at 15.5°...................	0.9204	0.9204	0 9205	0.9205	0.9205
Viscosity (absolute) at 15.5° (cotton-seed oil 0.82–0.91)...............	(0.864)	....	0 858	.... Turbid, 4.4° Solid. 3°	0.878
Solidifying-point, °.................	−8°	....	....		....
Melting-point, °....................	−4°	....	....	......	......
Free (oleic) acid, %...............	(4.46)	....	11.8	0.26	0.47
Unsaponifiable matter, %..........	....	....	....	0 56	....
Maumené test, °....................	(65)°	....	67.5°	66.6°	....
Specific temperature test..........	(138)	....	144 0	145.0	......
Iodine value.......................	98.3	100.2	98.0	99 1	100.0
Saponification value...............	193.2	191.2	192.8	192.9	192.2
Hehner value......................	95.5	95.6	....	....	95.2
Acetyl value......................	7 5	9.02	14.03	....	9 82
Reichert-Meissl value.............	0.55	0.22	....	....	0.28
Mixed Fatty Acids					
Saponification value...............	....	....	....	202.4	....
Melting-point, °...................	....	....	....	27.5°	....
Solidifying-point (titer test), °.......	27.7°–28 6°	27.5°	....	....	....

[1] The numbers in parentheses are by Archbutt.

Klein obtained the following numbers in the examination of specimens of curcas oil which he extracted from the seed; sp. gr. at 15°, 0.9199 to 0.9240; refractive index at 25°, 1.4686 to 1.4689; iodine value 109.1 to 110.4; saponification value, 197.0 to 203.6; m. p. of mixed fatty acids, 29.5° to 30.5°; solidifying-point of fatty acids, 25.75° to 26.5°.

Seed from the Gold Coast and S. Africa examined at the Imperial Institute (*Bull. Imp. Inst.*, 1921, **19,** 288) yielded 33% and 31.9% of oil, respectively.

The oil from the Gold Coast seed had the following characters:

Sp. gr. at 15°/15°	0.9191
Acid value	4.5
Saponification value	191.6
Iodine value	98.7
Acetyl value	25.4
Reichert-Meissl value	0.59
Solidification point of fatty acids	28.7°

The efflux velocity (Redwood) at 70° F. of three samples varied from 284 to 298 seconds, as compared with 3888 seconds for commercial castor oil.

Thin films of curcas oil dried in 26 hours at 100°, whereas castor oil was unaffected. These results show that curcas oil cannot replace castor oil as a lubricant for aeroplane engines.

Curcas oil is said to be used as an adulterant of olive oil in Portugal, but in view of its purgative properties this seems unlikely.

GRAPE SEED OIL

(See p. 111.) Grape seeds contain 6 to 20% of oil, which, when obtained by cold expression from fresh seeds, is golden-yellow and sweet, but that from seeds which have been stored for some time is darker and slightly bitter. It is an edible oil. The oil from a second hot-pressing is brown, with a pronounced bitter taste; it is used, after refining, as a lamp oil (*Chem. Rev. Fett Ind.*, 1903, **10,** 219).

It dissolves at 70° in an equal volume of acetic acid (sp. gr. 1.0562), the solution becoming turbid at 66.5°. It is moderately soluble in alcohol. It gives the elaidin reaction. Horn has suggested that it might be used as a substitute for castor oil in Turkey-red oil manufacture. A large quantity could be obtained. The numbers given in the table on p. 111 are based upon the results obtained by Horn

(*Mittheil. Tech. Gerwerbe-Museums*, 1891, 185) and De Negri and Fabris (*Ann. del. Lab. Chim. Centr. del. Gabelli*, 1891-2, 225). The following quite different numbers have been since published by Ulzer and Zumpfe (*Oester. Chem. Zeit.*, 1905, 8, 121).

Sp. gr. at 15°..	0.9215
Butyro-refractometer reading at 50°................	54.5
Refractive index....................................	1.4623
Iodine value..	142.8
Saponification value................................	190.0
Acetyl value of the fatty acids.....................	43.7
Maumené value......................................	81° to 83°

Eleven samples obtained by expressing and by extraction of the seeds have been examined by André (*Comptes rend.*, 1921, 172, 1296) with the following results: sp. gr. at 20°/20°, 0.9170 to 0.9334; n_D^{19}, 1.4708 to 1.4772; saponification value, 171.0 to 191.1; iodine value, 94.3 to 135.0; and acetyl value, 13.3 to 49.3.

Refined oil expressed from the seeds of the Concord grape had the following characteristics (Rabak, *J. Ind. Eng. Chem.*, 1921, 13, 919): sp. gr. at 25°, 0.9204; solidification point, −22° to −24°; acid value, 0.74; saponification value, 192.2; and iodine value, 135.8.

The composition of this oil was approximately: linolin, 53.6; olein, 35.9; palmitin, 5.2; stearin, 2.2; and unsaponifiable matter, 1.2%. About 1000 tons of these seeds are expressed each year in the United States.

The earlier observers inferred that this oil resembles castor oil in containing a large proportion of hydroxy-acids, and that it also contains erucic acid. Ulzer and Zumpfe found it to consist chiefly of the glyceride of linolic acid, with about 10% of solid glycerides, and smaller quantities of the glycerides of oleic, ricinoleic and linoleic acids. No erucic acid was detected.

André has shown (*Comptes rend.*, 1921, 172, 1413) that there is no proof that the high acetyl value of grape seed oil is due to ricinoleic acid. Hydroxy-acids could be separated by fractional crystallisation of the lithium salts of the mixed fatty acids from dilute alcohol. The average yields were: solid acids, 12.5; liquid acids, 62.5, and viscous hydroxy acids, 25.0%. These hydroxy acids had iodine value 110 and a molecular equivalent of 277, which is much too low for ricinoleic acid.

VI. CACAO BUTTER GROUP

Bassia Tallow.
Borneo Tallow (Tangkawang Fat).
Cacao Butter.
Chinese Vegetable Tallow (Stillingia Tallow).
Cotton Oil "Stearine."
Goa Butter (Kokum Butter).

Laurel Oil.
Mafura Tallow.
Nutmeg Butter.
Palm Oil.
Phulwara Butter.
Piney Tallow (Malabar Tallow).
Shea Butter (Galam Butter).

BASSIA TALLOW

(For constants see p. 111.)   This fat, as met with in commerce, is a mixture of the fats obtained from the seeds of *Bassia longifolia* and of *B. latifolia*, the former being termed *Mohwah butter* or *Mowrah seed oil*, and the latter *Mahua butter or Illipé butter*.   It is used as an edible fat and in the manufacture of soap and candles.

Bassia Longifolia and Bassia Latifolia.—The seeds of *Bassia longifolia* and *Bassia latifolia* are very similar and are much confused not only on account of admixture in commercial samples but more especially because they are commonly known under the same names, such as "Mowrah," "Mohwrah," "Mahua" and "Illipe;" the latter name being also applied to a very large number of exotic fats and ceases to have any designative value.

Bolton and Revis (see *Fatty Foods*, p. 183 *et seq.*) have endeavoured to draw some better line of distinction between the fats of this group and suggest that less confusion would arise if they were referred to as "Latifolia Fat" and "Longifolia Fat."

Bassia longifolia occurs in Southern India *only*.   The seeds are somewhat similar to those of *B. latifolia*, but as a general rule are slightly longer and narrower, although this does not hold true in every case.

The kernels, which represent about ¾ of the weight of the seed, contain some 55% of fat.

In all probability the fat from these seeds yielded the original " Illipé butter."

Bassia latifolia occurs mainly in Central India—from Western Bengal to Burma—but does not extend to Southern India.   The seeds are rather more round and shorter than those of *B. longifolia* and larger than those of *B. butyracea*.   As in the case of *B. longifolia* the kernel represents ¾ (or rather more) the weight of the seed and contains from 57–60% of fat.

Bassia butyracea.—The seeds of *B. butyracea*, which occurs in the sub-Himalayan districts—from the Ganges to Bhutan—are very similar in appearance to *B. longifolia* and *B. latifolia* except that they are much smaller.

The fat obtained from the seeds is known as "Phulwa," the name "Phulwara" being applied to the seeds only. The seeds contain some ¾ of their weight of kernel, which kernel has a fat content of some 66%. This fat is one of the most common adulterants of ghee and on this account has actually been given the name of "Ghee" in some text-books. Bolton and Revis, with a view to differentiating between the fats obtained from the three foregoing seeds examined samples of authentic origin and, having extracted the fat themselves by means of petroleum spirit, obtained the figures given in the following table:

Determination	Bassia latifolia	Bassia longifolia	Bassia butyracea
Ref. index at 40° (Zeiss butyro-refractometer)	47.7	49.3	47.8
Iodine value (Wijs)	59.4	62.6	42.6
Saponification value	192.2	189.8	188.2
Sp. gr., 99°/15	0.8595	0.8624	....
Free fatty acids (as oleic)	24.6%	3.3%	8.74%
Unsaponifiable matter	....	....	1.36
Baryta value:			
(a) Total	263.0	258.2	257.3
(b) Insoluble	252.0	252.8	255.7
(c) Soluble	11.0	5.4	1.6
$b - (200 + c)$	+41.0	+47.4	+54.1
Reichert-Meissl value	....	....	1.31
Polenske value	....	....	0.65

Shea butter or Karité butter is obtained from the seeds of *Butyro-spermum* (or *Bassia*) *Parkii*, a tree largely grown in West Africa, French Soudan, etc. The general appearance of the seed is not unlike that of *B. longifolia*, *B. latifolia* and *B. butyrospermum*, though so very considerably larger in size as to render it impossible to be confused with these.

The whole seeds have a varying content of fat—amounting to 33 to 45% of its weight which is equal to 50–60% of the kernel, the latter being the portion usually imported.

Originally the fat found an outlet for the manufacture of soap and candles, but of late years, owing to improvements in the methods of deodorising and refining, its use as an edible fat in the form of a lard substitute or pastry fat has been very considerable. The "stearine" has been utilised to a limited extent as a chocolate fat and the "oleine" for baking purposes.

One of the disadvantages of its use for edible purposes was at one time its large content of unsaponifiable matter—(5–9%)—but manufacturers have now learned how to select seeds giving the lowest yield of unsaponifiable matter, and methods of removing a proportion of the latter have come into use. The figures in the following tables were obtained by Bolton and Revis.

SHEA NUT OIL

Estimation	Usual limits	Typical specimen
M. p., °, incipient fusion................	29° to 32°	....
M. p., °, complete fusion................	37° to 42°	41.2°
Solidifying point, °......................	25° to 30°	26.8°
Saponification value....................	180 to 190	186.9
Ref. index at 40° (Zeiss butyro-refractometer)	55.5 to 56.5	56.3
Iodine value (Wijs).....................	57 to 63	58.93
Sp. gr., 15°/15.........................	....	....
Sp. gr., 99°/15.........................	....	....
Free fatty acids (as oleic)................	2% upwards	8.29%
Unsaponifiable matter....................	5 to 9%	7.56%
M. p. of fatty acids °....................	....	....

Estimation	Shea nut "stearine"	Shea nut "oleine"
M. p., °, incipient fusion................	40.0°	....
M. p., °, complete fusion................	55.5°	....
Solidifying point, °......................	34.2°	24.0°
Saponification value....................	179.7	181.6
Ref. index at 40° (Zeiss butyro-refractometer)	52.7	58.7
Iodine value...........................	51.9	62.3
Free fatty acids........................	3.4%	5.89%
Unsaponifiable matter....................	6.25%	7.72%
Reichert-Meissl value...................	....	2.60
Polenske value.........................	....	0.72

Bassia toxisperma (Mimusops Djave) produces seeds which are commonly known as "Njave" or "Djave," being the "mahogany nuts" of the Gold Coast Colony.

The nuts are about $2\frac{1}{2}$–3 in. long and $1\frac{1}{4}$ broad, having a bright polished mahogany-coloured shell and a long oval hilum on one side. They are similar to, though rather larger and more pointed at the extremities than, shea nuts. They contain about half their weight of a kernel, in which there is 65 to 70% of fat.

As far as the present reviser is aware the fat has not been used for edible purposes, and this is due to the fact that it usually contains traces of hydrocyanic acid produced by the enzymic decomposition of the non-fatty portion. It would be a comparatively easy matter to free the fat from this poison, and in the event of no other unwholesome substance revealing itself, there seems to be no reason why this fat should not find a use for dietetic purposes.

The following figures have been obtained on a sample of the oil extracted from the seeds with petroleum spirit by Bolton and Revis.

Solidifying point	21.0°
Saponification	184.2
Ref. index at 40° (Zeiss scale)	51.8°
Iodine value (Wijs)	65.1
Sp. gr. $99/15$	0.8578
Free fatty acids (as oleic), %	9.27
Unsaponifiable matter, %	3.86
M. p. of fatty acids	52.8°
Solidifying point of fatty acids	47.8°

Bassia Mottleyana, Nat. Ord. *Sapotaceæ*.

The seeds, which are also known as katio, katiau, ketzian and by various other names, are like those of *B. latifolia* but very much smaller. According to Brooks (*Analyst*, 1909, 39, 207) the tree grows abundantly in the swamps of Sadong and Saribas Districts. This author states that they are at present of no commercial value, but are highly prized by the natives for cooking and other purposes.

The average figures of an oil prepared by the Dyaks are given in the table below. This oil had a bright yellow colour, sweet taste and pleasant odour of almonds.

Brooks has found the kernels to contain 47.5% of oil, whilst another sample examined by Bolton and Revis had a fat content of 56%, and the proportion of kernel amounted to 75% of the weight of the whole seed, 100 of which weighed 30 grm.

Brooks describes the oil prepared by the Dyaks as having a pleasant odour of almonds, which neither the Imperial Institute nor Bolton and Revis have found to be true of oils which were extracted from the seeds in the laboratory. The native-prepared fat was, however, found to have a pronounced smell of almonds, and this was investigated by the Imperial Institute who found no prussic acid, but proved the presence of benzaldehyde, which they suggest had been added for the purpose of flavouring or scenting the oil.

OIL FROM BASSIA MOTTLEYANA

Description of sample	Dyak or native make			Extracted from seeds	
Observer	Brooks	Bolton and Revis	Imperial Institute	Imperial Institute	Bolton and Revis
Solidifying point.............	14.0	15.0	....	....	....
Acid value.................	1.8	1.7	2.3	77.9	13.8
Sp. gr., 15°/15°.............	0.917	0.9174	....	....	....
Sp. gr., 100°/15.5°...........	....	....	0.864	0.885	....
Iodine value................	63.2	66.5	65.0	65.0	65.2
Ref. index..................	53.4	....	....	....	52.3
Saponification value..........	189.5	188.9	191.5	191.0	192.1
Unsaponifiable matter...... ..	0.41	....	....	....	....
Reichert-Meissl value...	....	....	0.6	0.8	....
Titer test.........	....	....	36.3°	36.4°	....

BORNEO TALLOW

During recent years very large quantities of Borneo tallow have found their way on to the European market in the form of cacao-butter substitutes, the fat being obtained from the seeds of several different kinds of plants belonging to the order *Dipterocarpaceæ*, chiefly *Shorea stenoptera* (a native of North West Borneo), *Shorea ghysbertiana, Shorea aptera* and *Shorea robusta* as well as *Isoptera borneensis* and species of *Hopea*. The seeds are usually sent into this country under the name of "Pontianak illipé nuts," being distinguished by the prefix "large" or "small," this not conveying any botanical distinction, but being purely a commercial differentiation of the dimensions of the seed.

The cacao-butter substitute is commercially known as "green butter," but it must be carefully borne in mind that this name also includes the fat of a number of similar exotic nuts.

The fat obtained from certain of these seeds is so similar in physical and analytical properties to true cacao butter that the problem

of distinguishing it from cacao butter is of the highest difficulty. According to Geitel (*J. prakt. Chem.*, **36**, 515), it consists chiefly of the esters of stearic and oleic acids, but Klimont (*Monatsh. Chem.*, 1904, **25**, 929) has isolated from it oleodistearin and oleodipalmitin. The commercial fat has been found to contain from 8 to 10% of free (stearic) acid. It is used in Europe in the manufacture of soaps and candles. Various tested have been put forward with the object of detecting its presence, one of the most important having been suggested by Halphen (*J. Pharm. Chim.*, 1908, **28**, 345). His test has been investigated by Bolton and Revis (*Analyst*, 1913, **38**, 201) who, not having found it altogether satisfactory, have modified it in the following manner: 1 grm. of the clear filtered fat is dissolved in 2 c.c. of a mixture of equal parts of carbon tetrachloride and petroleum spirit (distilling below 40°), and 2 c.c. of this solution are placed in a test-tube about 6 in. long and ¼ in. in diameter. The tube is cooled in water and a solution of bromine in an equal volume of carbon tetrachloride added drop by drop, with constant shaking, until the colour of the bromine is permanent. The greatest care must be taken that only 1 drop in excess is allowed. The tube is then corked and allowed to stand. If, after the expiration of 15 minutes, the solution is perfectly clear, cacao butter is not present, or there is less than 10%. If the solution shows any turbidity, the presence of cacao butter is indicated, except in the case of one—somewhat rare—cacao butter substitute obtained from a species of *Gutta* nut. This one exception, however, does not give quite the same turbidity as cacao butter, and can easily be distinguished as described below.

The method can be made roughly quantitative by making mixtures of cacao butter and some solid fat of low iodine value (such as coconut oil or coconut "stearine," if an actual "green butter" is not to hand), and comparing the turbidities produced by these mixtures and the sample under examination.

After the turbidity has been compared, 2 c.c. of petroleum spirit are added to the tubes, which, after mixing by inversion, are allowed to stand all night, when the cacao-butter turbidity settles out as a very fine canary-coloured precipitate, easily distinguished from the slight flocculent precipitate which "green butters" under these circumstances usually throw down. It is to be also noted that cacao butter is completely soluble in the carbon tetrachloride-

petroleum spirit mixture in the strength given above, whereas "green butters" usually become turbid almost immediately, and on standing for 2 hours usually throw down a considerable precipitate. Care must therefore be taken that the solution used for the test is quite clear.

The fat mentioned above, which might possibly be mistaken for cacao butter, may be distinguished from true cacao butter as follows: the solution of the fat, after treatment with the bromine, is allowed to stand for 15 minutes, and the turbidity is then carefully examined by transmitted light. The turbidity due to cacao butter is absolutely non-flocculent, and any appearance of flocculent particles is characteristic of the other fat. If now to the brominated solution are added 2 c.c. of petroleum (fraction of petroleum spirit distilling between 90° and 100°) and the whole mixed, any turbidity due to cacao butter entirely dissolves, whilst the turbidity due to this other fat remains quite insoluble.

By this means 5% of this fat may be detected in admixture with 95% of cacao butter or "green butter." More than 10% of this fat produces such a heavy flocculent precipitate that it could not possibly be mistaken.

Since this test was put forward difficulties have arisen in that many of the commercial products now often contain proportions of *hydro-genised* fats which considerably mask, and in some cases, vitiate the test.

CACAO BUTTER. OIL OF THEOBROMA

(See also this volume, p. 111, and volume VI.) This oil is expressed from the beans or seeds of the cacao tree, *Theobroma cacao*, from which ordinary cocoa is obtained, and must not be confused with coconut oil from *Cocos nucifera*. It is obtained in large quantities as a by-product in the manufacture of chocolate.

The percentage of cacao butter in the roasted nibs or beans has been carefully estimated by Davies and McLellan (*J. Soc. Chem. Ind.*, 1904, **23**, 481) by extraction of the powdered nibs with petroleum spirit. Beans from Ecuador, Venezuela, Dutch Guiana, Brazil, the West Indies, Africa, and Ceylon were examined. The average percentages of fat in the different sorts ranged from 51.33 to 58.23, the average of the whole being 54.44.

Cacao butter is a yellowish solid, gradually turning white on keeping. At the ordinary temperature it may be broken into fragments, but softens in the hand and melts in the mouth. It melts between 30° and 34° (rarely at 29°) to a transparent yellowish liquid, which congeals again at 20.5°, the temperature rising to about 27°. It has an agreeable odour, tastes like chocolate, and does not readily become rancid. Lewkowitsch (*J. Soc. Chem. Ind.*, 1899, **18**, 556), however, has shown that cacao butter, if exposed to the combined action of sunshine, air, and moisture for a few days, becomes bleached and rancid like any other fat. It dissolves in 20 parts of hot alcohol, separating almost completely on cooling, and is also dissolved by ether and ethyl acetate. It is largely used as the fat in the manufacture of chocolate creams, and in pharmaceutical preparations and cosmetics.

Cacao butter chiefly consists of the propenyl esters of stearic, palmitic, oleic, and linolic acids. Kingzett (*J. Chem. Soc.*, Trans., 1878, **33**, 38) obtained from cacao butter an acid of the formula $C_{64}H_{128}O_2$, which he named theobromic acid, but neither Traub (*Arch. Pharm.*, (3), **21**, 19) nor Graf (*Ibid.*, (3), **26**, 830) were able to find any fatty acids of higher molecular weight than arachidi acid. Hehner and Mitchell (*Analyst*, 1896, **31**, 321) found 40% of stearic acid; Farnsteiner (*Zeitsch Nahr. Genussm.*, 1899, **2**, 1) obtained 59.7% of saturated acids, 31.2% of oleic acid, and 6.3% of other acids. Klimont (*Monatsh.*, 1902, **23**, 51; 1905, **26**, 563) believes these acids to exist mainly in the form of mixed esters. Matthes and Rohdich (*Ber.* 1908, **41**, 19) have found in the unsaponifiable matter two phytosterols, identical, respectively, with the sitosterol and stigmasterol isolated by Windhaus from calabar bean fat.

The following results have been obtained in the examination of the mixed fatty acids of cacao butter (see also p. 111):

		Observer
Solidifying-point ("titer" test)	48.3°–49.2°	Lewkowitsch.
Refractive index at 60°	1.422	Thoerner.
Neutralisation value	190	Thoerner.
Iodine value	32.6–39.1	De Negri and Fabris, Thoerner.

Cacao Butter Adulterants.—The adulterants which should be looked for in cacao butter are numerous, and include coconut and palm-nut oils, and the "stearines" prepared from them (a mixture of $\frac{2}{3}$ palm-nut "stearine" and $\frac{1}{3}$ coconut "stearine" is said to be a favourite substitute), tallow and lard, stearic acid, sesame and other vegetable oils, beeswax and paraffin wax. For the detection of these adulterants the most important estimations are the *iodine value, saponification value, Reichert-Meissl value, acid value,* and *sp. gr.,* together with the *m. p. of the fat and its mixed fatty acids,* or the "*titer test*" of the acids.

Coconut and palm-nut oils and "stearines" would lower the iodine value and sp. gr., raising at the same time the saponification value and Reichert-Meissl value. They would also lower the "titer test" of the fatty acids.

Tallow, beyond somewhat lowering the sp. gr., would cause scarcely any change in the other values. It may be detected by Björklund's test (see p. 249) and the phytosteryl acetate test (p. 386), the latter of which would also have to be applied for the detection of lard, although the presence of lard would have some tendency to raise the iodine value.

Stearic acid would be detected by an estimation of the acid value which, in genuine cacao butter, does not usually exceed about 2.0.

Most **vegetable oils** would lower the sp. gr. of the fat and the "titer test" of its mixed fatty acids, and would raise the iodine value; cottonseed and seame oils would be detected by their characteristic colour indications, arachis oil by its arachidic acid, etc.

Beeswax and paraffin wax would be easily detected; the former would raise the acid value and m. p. of the fat, lowering at the same time the iodine and saponification values, and both beeswax and paraffin wax would increase the amount of unsaponifiable matter, which in genuine cacao butter is quite small.

According to Sachs (*Chem. Rev. Fett Ind.,* 1908, **15,** 9, 30), various exotic fats have, of recent years, been used as substitutes for cacao butter in the manufacture of chocolate, the chief of these being Dika or Gaboon fat, Tangkawang fat (Borneo tallow) and Illipé fat (see p. 240).

Dika fat (Lewkowitsch *Analyst,* 1905, **30,** 394) resembles coconut oil in saponification value (245) and iodine value (5.2), and also *in the absence of stearic acid* (Lewkowitsch found no stearic

acid in dika fat and only 1% (Oils, Fats and Waxes, Vol. II, p. 518) in coconut oil), but it differs from coconut oil in its Reichert-Wollny value (0.42%). *Borneo tallow*, according to the results obtained by Klimont (*J. Soc. Chem. Ind.*, 1904, 23, 1152), closely resembles cacao butter; Illipé fat, on the other hand, has a considerably higher iodine value (53.4 to 67.9) (see Borneo tallow, p. 244).

Sachs states that a mixture of 75% of coconut "stearine" and 25% of Japan wax has given good results as a cacao butter substitute; such a mixture would have about the same m. p. as genuine cacao butter, but would be readily distinguished by the much lower iodine value and higher saponification value and Reichert-Meissl value. Posetto (*Giorn. di Farm. Chim.*, 1901, 337) examined a substitute of this nature, sold as "vegetable butter" or "cacao butter S." It had a faint tallow-like smell and taste, and had the following constants:

M. p.	34° to 35.5°
Iodine value	7.8
Saponification value	237.0
Reichert value	5.50
Free acid	nil

Posetto concluded that it was a mixture of coconut oil 70 to 75%, Japan wax, 30 to 25%. Another mixture said to be used is composed of 60% coconut "stearine" and 40% Borneo tallow.

Björklund's Ether Test.—3 grm. of the fat are shaken in a well-corked test-tube with twice the weight of ether at 18°. If wax be present, the solution will be turbid and will not become clear even on warming. Genuine cacao butter will dissolve to a clear solution. If a clear solution is obtained, the tube is immersed in water at 0°, and the number of minutes noted which elapse before the liquid becomes turbid, also the temperature at which the solution again becomes clear on warming. The following are Björklund's observations:

	Turbidity at 0° after minutes	Clear solution at °
Pure cacao butter	10–15	19–20
Cacao butter + 5% beef tallow	8	22
Cacao butter + 10% beef tallow	7	25

Lewkowitsch (*J. Soc. Chem. Ind.*, 1890, **18,** 557) found that cacao butter containing as much as 10% of tallow will dissolve in 2 parts of ether at 18°, although requiring a little longer than the genuine butter does, and that the chief indication to be relied upon is not so much the time required for crystallisation to begin, as this varies with different samples of cacao butter, but the characteristic way in which genuine cacao butter crystallises as compared with adulterated samples. With genuine samples, distinct tufts of crystals appear at the bottom and sides of the tube, whereas 5% and more of tallow are recognised by flocks separating from the chilled solution.

The following tests recommended by the Committee were approved as tentative methods at the Annual Meeting of the Association of Official Agricultural Chemists, November, 1922 (*J. Assoc. Off. Agric. Chem.*, 1923, **6,** 278):

I. CRICITAL TEMPERATURE OF SOLUTION IN ACETIC ACID.— *Reagents.*—(*a*) Glacial acetic acid, as free as possible from water; (*b*) N/10 potassium hydroxide solution.

Apparatus.—Insert thermometer reading to 0.1° into a cork that fits a 6 × ¾ inch test tube. The thermometer should extend far enough into the tube that the bulb will be covered by 10 c.c. of liquid. Place the test tube in a larger tube (4 × 1¼ inches), containing glycerin, and hold firmly in place with a cork having a groove cut in the side to equalise the pressure when heat is applied.

Determination.—Filter a portion of the sample to be examined through a dry filter paper in an oven where a temperature of about 110° is maintained, to remove traces of moisture. Allow the filtered sample to cool until barely warm, and weigh (a pulp balance is accurate enough) 5 grm. of the sample and 5 grm. of the acetic acid reagent (*a*) into the test tube. Insert the cork holding the thermometer and place the test tube in the glycerin bath. Heat and shake the apparatus frequently until a clear solution of the fat and acetic acid is obtained. Allow the solution to cool, with constant shaking, without removing from the glycerin bath. Note the temperature at which the first sign of turbidity appears. Make a similar test with the same acetic acid on a sample of pure cacao butter. Free fatty acids lower the turbidity temperature. A correction must therefore be made for the acid value of the sample.

Correction Factor.—If the strength of the acetic acid reagent is such that the turbidity temperature of the pure cacao butter is approximately 90°, one unit of acid value will cause a reduction of 1.4° in the critical temperature of dissolution. If the turbidity temperature is approximately 100°, one unit of acid value will cause a reduction of 1.2°. For intermediate temperatures the reduction is proportional.

Determine the acid value (mgrm. of potassium hydroxide required to neutralise the free fatty acids in 1 grm. of the sample) of both the sample and the pure cacao butter. Multiply the acid value by the correction factor and add the result to the observed turbidity temperature. The figure obtained is the true critical temperature of solution. If the true critical temperature of dissolution of the sample is lower by more than 2° than that of the pure cacao butter, adulteration with coconut, palm kernel, cottonseed oils or stearines, maize oil, arachis oil or other vegetable oils is indicated.

II. ACETONE—CARBON TETRACHLORIDE TEST.—*Reagent.*—A mixture of equal parts of acetone and carbon tetrachloride.

Determination.—Dissolve 5 c.c. of the warm fat, which has been previously filtered through dry filter paper in an oven at about 110° to remove traces of moisture, in 5 c.c. of the acetone and carbon tetrachloride reagent in a test tube. Allow the solution to stand in ice water for 20–30 minutes. Run a blank on a sample of pure cacao butter at the same time. If hydrogenated oil, tallow, oleostearine or paraffin is present, a white flocculent precipitate will soon appear. If the water is cold enough, cacao butter may solidify. If a precipitate is formed, remove the sample from the ice water and allow it to remain at room temperature for a time. Solidified cacao butter will soon melt and go into solution, but, if the precipitate is due to any of the above-mentioned possible adulterants, a much longer time will be required for it to go into solution.

A method for the detection of coconut oil in butter, applicable also to lard and cacao butter, has been based by L. Robin (*Ann. Chim. Anal.*, 1906, **11**, 454, and **12**, 181) upon the almost complete solubility of coconut oil fatty acids in alcohol of 56.5% strength and the very slight solubility of the fatty acids from butter and cacao butter. 5 grm. of the fat are saponified by boiling for about 5 minutes with 25 c.c. of alcoholic potassium hydroxide, the operation being conducted in a flask graduated at 150 c.c. attached to a

reflux condenser.   After cooling, sufficient water is added to reduce
the alcoholic strength to 56.5%, and a volume of N/2 hydrochloric
acid (prepared with 56.5% alcohol) sufficient exactly to neutralise
the alkali and liberate the fatty acids from the soap.   The volume
of acid required is ascertained by a previous titration.   The contents
of the flask are then made up to 150 c.c. at 15° with 56.5% alcohol,
well mixed, allowed to stand for at least half an hour, and filtered.
50 c.c. of the filtrate are titrated with N/10 alkali, phenolphthalein
being used as indicator, and the result calculated to c.c. per 1 grm.
of fat represents *fatty acids soluble in 56.5% alcohol*.   The author of
the process states that if even 5% of coconut oil is present in cacao
butter, the "alcohol-soluble" number will be not less than 3, whilst
the ratio of the alcohol-soluble number to the saponification value
of the fat will be less than 60.   A ratio of 45 to 60 corresponds with
the presence of 5 to 10% of coconut oil, a ratio of 35 to 45 with 10
to 15%, and a ratio of 25 to 35 with 15 to 20%.

Robin's analytical results are summarised in the following table:

	Pure cacao butter (9 samples)	Cacao butter to which coconut oil had been added to the extent of		
		5%	10%	15%
Saponification value (a)	191.0–195.4	195.1–199 8	199.0–204.3	205 0–205 6
Alcohol-soluble number (b)	2.30–2.81	3.56–4.10	4 50–5.47	5.76–6.79
Ratio a/b	69–84	48–55	36–45	30–35

For the detection of coconut oil by means of the "ethyl ester value"
(Hanus and Stekl's method, see under "Coconut Oil," p. 261.

Tate and Pooley (*Analyst*, 1921, **46**, 229) have based a method
of detecting and estimating illipé butter in cacao butter upon the
calculation of "factors" obtained by multiplying together a series
of constants obtained under standard specified conditions.

For example, the average values for 14 samples of pure cacao
butter and 16 samples of pure illipé butter were as follows:

	SP. GR. AT 60°	SP. GR. AT 99°	VISCOSITY AT 60°	M. P., °	IODINE VALUE	M. P. REFRACTION OF FATTY ACIDS	N_D^{40}
Cacao butter	0 8825	0.8575	99.9	30.9	35.9	48.4	1.4569
Illipé butter	0.8826	0 8577	103.7	33.2	31.5	52.8	1 4568

For 12 individual samples the products of these factors were as
follows:

Cacao butter...... 3347, 3266, 3252, 3251, 3149, 3191, 3169, 3149, 3130, 3123, 2972, 2839
Illipé butter..... . 4771, 4714, 4652, 4535, 4503, 4487, 4463, 4397, 4279, 4112, 3901, 3890

The respective average "factors" calculated from these results were: cacao butter, 3150; and illipé butter, 4403. In applying this method of calculation to known mixtures of cacao butter with 10 to 90% of illipe butter the results agreed within 4.2% of the actual amounts present. A correction factor for this error is given in the following table:

Illipé butter % observed.....	0	10	20	30	40	50	60	70	80	90	100
Correction—Add...........	0.0	1.7	3.0	3.7	4.0	4.2	3.9	3.2	2.2	1.1	0.0

CHINESE VEGETABLE TALLOW (STILLINGIA TALLOW)

(For constants see p. 111.) This fat is obtained from the fruits of a variety of plants, the most important of which is the Chinese tallow tree, *Stillingia sebifera (Croton sebiferum L.)*. It is largely employed in the manufacture of soap and candles.

The fat is found as a coating, about 0.5 mm. thick, on the seeds, from which it is melted by steam heat. The seeds themselves contain a strongly drying oil (stillingia oil) of quite a different character from the fat which coats them, and some of this is liable to be contained in the commercial tallow. Its presence would be shown by its high iodine value and rotatory power on polarised light.

Commercial Chinese vegetable tallow is a white or greenish fat, without taste or smell, the analytical values of which vary considerably owing to its being obtained from different plants and prepared in different ways. It is believed to consist of esters of palmitin and olein, and these exist, according to Klimont (*Monatsh. Chem.*, 1903, **24**, 408), partly as the mixed ester oleodipalmitin. A sample tested by Hehner and Mitchell contained no stearin. Valenta, by the lead-salt-ether method, obtained 35.56% of oleic acid and 64.44% palmitic acid.

COTTON OIL "STEARINE"

This is the name given to the soft fat that separates when cotton-seed oil is chilled. It is utilised in the manufacture of margarine and of soap. It consists chiefly of palmitin and a little stearin, with olein and linolin (see "Cottonseed Oil").

GOA BUTTER (KOKUM BUTTER, MANGOSTEEN OIL)

(For constants see p. 111.) This fat is expressed from the seeds of the East Indian plant, *Garcinia indica*. It is used locally as a food, whilst the commercial product is manufactured into soap. It consists chiefly of the mixed glyceride, oleo-distearin (Heise).

LAUREL OIL

(For constants see p. 111.) This is a butter-like fat of greenish-yellow colour, slightly bitter taste, and peculiar aromatic odour, obtained from the berries of the laurel tree, *Laurus nobilis*, which yield about 25%. It consists largely of trilaurin, with probably a small amount of olein and linolin. It is employed in the preparation of veterinary medicines.

MAFURA TALLOW

(For constants see p. 111.) This is a light yellow fat obtained from the seeds of *Mafureira oleifera*. It consists of glycerides of solid fatty acids (71.4%) and of liquid fatty acids (23%) (De Negri and Fabris). It is used in the manufacture of soap and candles.

NUTMEG BUTTER

(For constants see p. 111.) This is a yellow tallow-like fat obtained from the seeds of the *Myristica officinalis*, the yield being about 20 to 25%. As expressed, it consists of a fixed oil with 8 to 10% of an essential oil (nutmeg oil). The glyceridic portion is composed chiefly of myristin and olein, with a small proportion of butyrin (Jean). The fat is used in the manufacture of perfumes and for medicinal preparations.

PALM OIL

(See also page 111.) Palm oil is the product of several species of palm, but particularly of *Elæis guineenis* and *E. melanocca*. The former is indigenous to tropical W. Africa, and forms vast forests whence the European supply of palm oil is derived; *E. melanocca* is cultivated in S. America and the W. Indies. Palm oil proper is obtained from the outer fleshy coating of the seed, the palm-nut or palm-kernel oil having a different composition.

Palm oil varies in consistence from that of soft lard to that of the hardest tallow, and its m. p. is correspondingly variable. Soft oil is obtained from the fresh fruit, and hard oil from fruit which has been stored.in the ground and has undergone fermentation. Hard oil, besides being much decomposed and more or less dark in colour, usually contains dirt which has become mixed with the fruit during storage. Pure fresh palm oil has an agreeable and quite characteristic smell, and is of a bright orange colour; but the oil of commerce, owing to the crude method of manufacture, often has a "stink almost indescribable" and every shade of colour between golden-yellow and black. Inferior kinds are further deteriorated by adulteration, a fine red earth being used at Saltpond, and overripe plantains and sour "kanki" in the Chama district of the Gold Coast (*Kew Bulletin*, July, 1891, on "African Palm Oil." See *J. Soc. Chem. Ind.*, 1891, 10, 707). Lagos furnishes the purest and most highly valued palm oil for some purposes; Accra and Saltpond inferior are less valuable sorts.

The colour of commercial palm oil becomes pale after keeping, especially upon exposure to light and air, the oil at the same time becoming rancid; but refined neutral palm oil may be kept for years without developing acidity or rancidity.

According to Allan (*Chem. Trade J.*, 1922, 505), the colouring matter can be separated from the unsaponifiable matter as an orange brown crystalline substance (m. p. $170°-172°$). It dissolves with difficulty in alcohol and ether, but is readily soluble in acetone. It is very susceptible to oxidation and is oxidised even by exposure to air, the product of oxidation having a strong violet colour. It contains an unsaturated ethylene double linkage and can be bleached by saturating that bond with nascent hydrogen.

Palm oil is eaten as butter by the natives of the Gold Coast, and is used for anointing their bodies. In this country it is used for the manufacture of soap and candles, and in the manufacture of tin-plates. It is also a common ingredient of railway wagon-axle greases. It is used in the United States for soap making and dipping tin-plate.

In chemical composition palm oil consists essentially of palmitin, olein, and free palmitic acid, with small quantities of stearin, linolin, and another fat. According to Nordlinger (*J. Soc. Chem. Ind.*, 1892, 11, 445), the solid fatty acids contain 98% palmitic acid, 1%

stearic acid and 1% heptadecylic acid, the latter having been since resolved by Holde (*Ber.*, 1905, **38**, 1247) into palmitic acid and an acid of much higher molecular weight.

The following results have been obtained by examination of the mixed fatty acids of palm oil:

		Observer
Sp. gr. at 98°–99°/15.5°.............	0.8369	Allen.
Sp. gr. at 100°/100°.......... . ..	0.8701	Archbutt.
Solidifying-point (titer test)....... ..	35.8°–47.6°; usually 44°–45°	Various.
Iodine value.......	53.3 49.2–58.9	Thoerner. Tipler.[1]
Iodine value of liquid fatty acids.......	95–99	Lewkowitsch, Tolman and Munson.

[1] 14 samples, see p. 258, omitting two very acid and rancid oils which absorbed only 23.7 and 33.3%, respectively.

Commercial Palm Oil.

Palm oil as met with in commerce varies greatly in quality. It contains almost always more or less water and solid impurities. Some of the irregular oils occasionally contain 25 or 30%, but the usual range is from 2 to 16%, whilst most of the regular oil does not contain more than 5 or 6%. It is usual to sell palm oil on the assumption that 2% of such foreign matters are present; an allowance is made for excess over this.

Water is best estimated by exposing 10 grm. of the sample to a temperature of 110° for an hour or two, and noting the loss of weight (see "p. 440"). If the residual oil be then dissolved in warm petroleum spirit, the *solid impurities* will settle to the bottom, and can be filtered off, washed with a little ether, dried, removed from the filter, and weighed. After weighing, the residue may be ignited, when the ash will indicate with sufficient accuracy the proportion of *sand* and mineral matters, and loss of weight will give that of the *organic matter*. In many cases the water can be estimated with sufficient accuracy by noting the volume of the aqueous layer which separates when the undried sample is dissolved in petroleum spirit, or simply kept melted in a graduated tube immersed in hot water.

Palm oil is not, as a rule, adulterated with other fats, but it frequently contains a large proportion of *free fatty acids*. The

free acid raises the solidifying-point of the oil, and causes it to have a corrosive action upon iron and steel, especially in the presence of water. Axle grease made from acid palm oil may seriously pit and corrode the metal of bearings and journals, unless the free fatty acid be neutralised (Archbutt and Deeley, Lubrication and Lubricants, p. 214).

The following proportions of free fatty acid, calculated as palmitic, have been found in palm oil:

Kind of oil	Palmitic acid, %		Kind of oil	Palmitic acid, %
	Archbutt	A. N. Tate		L. Archbutt
Saltpond..........	78.9	84.0	Fernando Po.......	40.5
Unknown..........	72.0	....	Half-jack........ ·	35.7
Refined...........	55.8	....	Half-jack..........	24.4
Brass.............	53.2	65.0	Bonny.............	21.5
New Calabar......	52.2	49.0	Lagos.............	11.9

Lewkowitsch states that he has found from 50 to 70% of free (palmitic) acid in a large number of commercial palm oils.

The following results obtained by the analysis of typical samples of palm oil, from which the water and impurities were removed, were communicated to Allen by A. Norman Tate:

	Brass	Benin	Lagos	New Calabar	Old Calabar	Grand Bassa
Sp. gr. at 15°...........	0 9213	0.9228	0.9203	0 9269	0.9209	0.9245
Saponification value....	200.2	198 3	196 6	199.7	197 2	201.2
Fatty acids, %..........	96–97	96–96.5	94–97	94–97	94.2–95	95.5–96.5
Fatty acids; solidifying point	44.4–45.8	45.0–45.5	44.5–45.5	44.2–45.5	44.2–45 5	41.5–42.3
Fatty acids; combining weight...............	273.4	273.7	272.7	273 2	273.2	273.0

Analyses of 16 samples, representing various brands of palm oil, made by Mr. F. C. Tipler, chemist of the London and North Western Railway Co., and kindly communicated by him, are given in the table on p. 258.

Analyses of the pulp and kernel fats derived from the fruit of various species of Brazilian palms are given under Palm-kernel Oil (p. 270).

ANALYSES OF PALM OIL (*Tipler*)

Description	Lagos	Emoe	Qua Eboe	Bonny	Old Calabar	Benin	Forcados	Victoria	Cameroon	New Calabar	Accra	Half Jack	Red Sierra Leone	Congo	Saltpond	Basta
Colour	Orange yellow	Orange yellow	Orange yellow	Orange yellow	Orange yellow	Yellow	Yellow	Orange yellow	Brownish yellow	Greenish yellow	Light brownish yellow	Deep orange yellow	Deep orange yellow	Dirty yellowish brown	Light brownish yellow	Dirty greenish yellow
Odour	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Rancid	Very rancid	Satisfactory	Satisfactory	Very rancid and objectionable	Rancid and sickly	Fairly satisfactory
Water (loss at 105°–110°)	0.55%	0.77%	0.17%	0.59%	0.75%	1.61%	1.43%	1.00%	0.81%	1.20%	1.45%	2.49%	1.31%	2.18%	1.78%	3.98%
Matter insoluble in ether	0.015%	0.079%	0.008%	0.116%	0.180%	0.319%	0.084%	0.016%	0.069%	0.239%	0.114%	0.175%	0.081%	0.246%	0.041%	1.040%
Containing ash	0.004%	0.056%	0.002%	0.062%	0.037%	0.267%	0.057%	0.005%	0.004%	0.133%	0.075%	0.104%	0.018%	0.237%	0.023%	0.433%
Sp. gr. at 100°/100°	0.8718	0.8774	0.8713	0.8717	0.8702	0.8720	0.8720	0.8725	0.8713	0.8724	0.8735	0.8713	0.8711	0.8794	0.8897	0.8747
M. p., ° (Bensemann's method) Incipient fusion	25°	32°	28°	34°	28°	34°	40°	32°	30°	42°	35°	23°	30°	45°	46.5°	43°
Complete fusion	42°–45°	49°	48°	51°	48°	49°	50°	52°	50°	51°	51°	48°	50°	55°–60°	55°–60°	55°–60°
														Insoluble matter interferes.		
Free (palmitic) acid	11.26%	24.58%	9.22%	10.24%	24.58%	37.89%	36.86%	18.94%	17.92%	48.13%	36 86%	21.50%	21.50%	76.29%	83.46%	70.14%
Saponification value, %	19.0	19.5	19.3	19.3	19.8	19.6	19.9	19.5	19 4	19.6	19.6	19 5	18.9	20.1	20.4	19.6
Iodine value (Wijs)	57.5	53.0	56.5	53.7	53.0	52.0	52.5	53.5	53.7	50.2	54.7	56.7	55.7	33.0	20.4	48.7
Mixed Fatty Acids																
Iodine value	58.3	50.2	58.3	55.0	55.0	53.2	50.2	50.3	53.7	53.5	49.2	56.5	54.7	33.3	23.7	49.0
Titer test, °	44.0°	42.3°	43.9°	44.3°	44.6°	44.6°	44.7°	44.8°	44.6°	44.9°	44.1°	40.4°	43.0°	47.0°	47.6°	40.9°

Palm olein is obtained by subjecting palm oil to hydraulic pressure in the same way that lard oil is made from lard. It usually has a sp. gr. of about 0.914, and solidifies at 10°.

PHULWARA BUTTER

(For constants see p. 111.) This fat is derived from the seeds of the Indian butter tree, *Bassia butyracea*. It is used locally as a food, whilst the exported product is made into soap. (See also p. 111, **Bassia tallow**.)

PINEY TALLOW (MALABAR TALLOW)

(For constants see p. 111.) This is a light green fat obtained from the seeds of the Indian plant, *Valeria indica*. It is used for illuminating purposes, and in the manufacture of soap.

SHEA BUTTER (GALAM BUTTER)

(For constants see p. 111.) This is a butter-like, grayish-white fat, obtained from the seeds of *Bassia Parkii*, used in the manufacture of soap and candles. (See also p. 111, **Bassia tallow**.)

VII. COCONUT OIL GROUP

Coconut Oil.	Macassar Oil.
Japan Wax.	Myrtle Wax.
Palm-nut Oil	Palm-kernel Oil.

COCONUT OIL

(See also p. 112.) Coconut oil is obtained by expression or extraction from the white pulp ("copra") of the common coconut, the seed of *Cocos nucifera* and *C. butyracea*. It is a white or but slightly coloured fat, having the characteristic odour and taste of coconut, and the consistence of butter or soft lard. The commercial product becomes easily acid and rancid, and then has a bad taste and odour. If properly prepared, however, it is equal in neutrality and keeping qualities to other oils and fats, and it does not become rancid any sooner than other fats if properly stored in full vessels protected from light and air (*J. Soc. Chem. Ind.*, 1906 **25**, 381). Brill and Parker (*Philippine J. Sci.*, 1917, **12**, 95) have shown that the rancidity of coconut oil does not stand in any relationship to the acidity. The "oxidisability value" (p. 45), however, is useful as a confirmatory

test, although certain oils which are unmistakably rancid give a low result in this test. The excessive acidity met with in commercial samples is frequently developed in the fat previous to its expression from the copra, through the latter being allowed to ferment, as in the case of palm oil and other fats. Lewkowitsch has found from 5% to 25% of free fatty acid, calculated as oleic acid. The sp. gr. of coconut oil is higher than that of the majority of vegetable fats. Allen observed a range of from 0.868 to 0.874 at $\frac{98°-99°}{15.5°}$; Crossley and Le Sueur obtained values from 0.903 to 0.9042 at $\frac{100°}{100°}$.

Coconut oil has a peculiar and highly complex chemical composition. It is chiefly composed of laurin and myristin, but contains also six other glycerides, including caproin, caprylin, caprin, palmitin, stearin and olein. (See Ulzer, *Chem. Rev. Fett Ind.*, **6**, 203; Blumenfeld and Seidel, *J. Soc. Chem. Ind.*, 1900, **19**, 914; Jensen, *Zeitsch. Nahr. Genussm.*, 1905, **10**, 265; Haller and Youssoufian. *Compt. rend.* 1906, **143**, 803; Paulmeyer, *J. Soc. Chem. Ind.*, 1907, **26**, 881.) Very little stearin is present; Lewkowitsch found only 0.99% of stearic acid (Oils, Fats and Waxes, II, 518), Hehner and Mitchell none. The volatile acids are chiefly capric and caprylic. Elsdon (*Analyst*, 1912, **38**, 8) by the method of alcoholysis arrives at the conclusion that the composition of the mixed fatty acids is approximately as follows:

Caproic acid....	2 per cent.	Myristic acid.........	20 per cent.
Caprylic acid...	9 per cent.	Palmitic acid.........	7 per cent.
Capric acid.....	10 per cent.	Stearic acid..........	5 per cent.
Lauric acid.....	45 per cent.	Oleic acid...........	2 per cent.

100

Coconut oil is used for making candles and soap. It is an excellent illuminant, emitting no smoke, and is largely used for making night-lights. It forms a hard and white soap, the aqueous solution of which is not readily precipitated by common salt; hence this soap is available for use with sea-water (marine soap).

Coconut oil and the "stearine" made from it are also used as substitutes for, and adulterants of, butter, lard, and cacao butter. By treatment with alcohol and animal charcoal a neutral coconut oil is produced, which is sold under such names as "vegetable butter,"

"vegetaline," "lactine," "nucoline," "laureol," etc. When well prepared, these products are white, of about the consistence of butter, of agreeable, sweet flavour, and, according to Jean (*Soc. Chem. Ind.*, 1891, 10, 275), free from tendency to become rancid. Coconut oil is frequently used in the preparation of margarine.

		Observer
Sp. gr. at 98°–99°/15.5°.....................	0.8354	Allen.
Solidifying-point ("titer" test)...............	21.2°–25.2°	Lewkowitsch.
Refractive index at 60°.....................	1.4295	Thoerner.
Saponification value.......	258	Thoerner.
Mean combining weight...	196–204	Alder Wright.
Iodine value................................	8.4–9.3	Various.

Coconut "oleine" is used as a lubricant, usually as an ingredient of blended oils.

The data given on pp. 112 and 273 have been obtained from the mixed fatty acids of coconut oil.

Coconut oil is alleged to be liable to adulteration with suet, beef marrow, and other animal greases, as also with almond oil and wax. These would be detected by the reduced sp. gr. at the temperature of boiling water and the reduced saponification and Reichert-Meissl values. Indeed, there is no addition likely to be made in practice, excepting that of palm-nut oil, which, if in notable proportion, would not be detected by these tests. The same methods, if used with discretion, will equally serve to estimate the approximate proportion of the adulterant. *Palm-nut oil* cannot be detected by the above or any other satisfactory method, but as it is employed for the same purposes as coconut oil, the substitution has little practical importance.

Hanus and Stekl (*Zeitch. Nahr, Genussm.*, 1908, 15, 577) have proposed a new constant for the detection of coconut oil in other oils and fats, which they name the "ethyl-ester value." 5 grm. of the melted and filtered fat are weighed into an Erlenmeyer flask of about 200 c.c. capacity (14 cm. high and 7 cm. wide) heated for 15 minutes in a thermostat at 50°, then rapidly mixed with 30 c.c. of N/10 alcoholic potassium hydroxide, vigorously shaken until quite clear,

and again heated in the thermostat until the lapse of 10 minutes from the time of adding the alkali. To the liquid are next added 2 c.c. of dilute sulphuric acid of such strength as to neutralise exactly the 30 c.c. of alkali, sufficient water to make the volume up to 140 c.c., and a few fragments of pumice stone. The flask is fitted with a cork and bulb tube, connected with an inclined condenser 70 cm. long, and the liquid rapidly distilled. The first 30 c.c. of alcoholic distillate are collected in a graduated cylinder, and the next 100 c.c. of aqueous distillate in a 100 c.c flask. The distillation should be finished within 25 minutes. The latter (aqueous) fraction is rinsed into an Erlenmeyer flask, sufficient alcohol being used to bring the esters into solution, the free fatty acids are neutralised, and the esters are saponified by heating for about 45 minutes under a reflux condenser with 40 c.c. of N/2 alcoholic potassium hydroxide. When cold, the excess of alkali is titrated with N/10 hydrochloric acid, the result giving the number of c.c. of N/10 alkali required to saponify the respective esters from 5 grm. of fat. The "ethyl-ester values" of the following fats were determined:

	Ethyl-ester value
Coconut oil, 5 samples..............................	41.45 to 45.30
Palm-nut oil, 1 sample..............................	23.15
Cow's butter, 15 samples............................	7.1 to 13.4
Margarine, 5 samples................................	1.70 to 3.00
Lard, 4 samples.....................................	2.70 to 3.20
Cacao butter, 3 samples.............................	1.30 to 1.60

It appears from these results that the method is capable of detecting a small percentage of coconut oil in margarine, lard, or cacao butter, but not less than 15% could be detected in cow's butter. If coconut oil alone is present, the numbers afford a means of approximately estimating the proportion, but the presence of palm-nut oil would upset the calculation. For other tests used for the detection and estimation of coconut oil see **Butter**, p. 374.

Coconut "oleine" and coconut "stearine" are products obtained by submitting coconut oil to hydraulic pressure. The following figures, obtained in Allen's laboratory from samples supplied to him

by Price's Patent Candle Company, show the relative physical and chemical characters of the two products:

	Oleine	Stearine
Sp. gr. at $\frac{98.5°}{15.5°}$	0.8710	0.8696
Sp. gr. at $\frac{60°}{15.5°}$	....	0.8959
Sp. gr. at 15.5°	0.9262	solid
M. p.	....	28.5°
Solidifying-point	4°, rising to 8°	21.5°, rising to 26°
Saponification value	261	259
Reichert value	5.6	3.1

Sachs (*Chem. Rev. Fett Ind.*, 1908, 15, 9, 30) obtained the following values from a sample of commercial hard coconut "stearine," said to be a favourite substitute for cacao butter.

Sp. gr. at 100°	0.8700
M. p.	29.3°–29.5°
Solidifying-point	26.5°
Saponification value	252
Iodine value	4.01–4.51
Reichert-Meissl value	3.4

Mixed Fatty Acids

M. p.	28.1°
Solidifying-point	27.4°
Mean molecular weight	209

The following results were obtained by Archbutt in the examination of a sample of commercial coconut "oleine."

Sp. gr. at 15.5°	0.9290
Sp. gr. at 100°/100°	0.8958
M. p.	18°
Solidifying-point ("titer" test)	11°, rising to 13°
Viscosity (absolute) at 15.5°	0.68 (rape oil, 1.15)
Viscosity (absolute) at 100°	0.052 (rape oil, 0.086)
Saponification value	257.7
Iodine value	13.4
Free (oleic) acid	0.2%
Unsaponifiable matter	2.6%

JAPAN WAX

(See also p. 112.) Japan "wax" is a fat contained between the kernel and outer skin of the berries of several species of *Rhus*, the most important of which are *Rhus succedanea* and *R. vernicifera*, which flourish chiefly in the western provinces of Japan, and are now also cultivated in California.

The wax is extracted by steaming and pressing the crushed berries, after separating the husk, the flow of the last portions of wax being sometimes accelerated by the addition of a little perilla oil. The berries yield in this process about 15% of a coarse, greenish, tallow-like mass, which is refined by melting, pressing it through strong cotton sacks and allowing it to drop into cold water. The flakes of wax thus obtained are bleached in the sun and, if necessary, remelted. Ahrens and Hett obtained 25% of fat by boiling the berries with water and finally extracting them with ether.

The purified fat is a yellowish-white, straw-yellow, or greenish-yellow, wax-like mass, having a smell recalling at once that of tallow and of some kinds of beeswax. Under ordinary circumstances melts at 51° to 53°, but a recently solidified sample melts at a considerably lower temperature. Its solidifying point is about 41°, the temperature rising to 48 to 49° in the act of solidification.

The sp. gr. at the ordinary temperature is about 0.990, whilst in a melted state at a temperature of 98° to 99° it is 0.875 to 0.877, compared with water at 15.5°. Thus, in the solid state it agrees in specific gravity with the true waxes, and in the melted condition it is considerably heavier than the true waxes or the ordinary vegetable fats.

Kleinstück,[1] who investigated the subject minutely, found that the closeness with which the sp. gr. of Japan wax approximates to that of water, coupled with its high coefficient of expansion, gives rise to the curious phenomenon of its floating in water at temperatures above 18°, and sinking below 15°. This behaviour is, however, modified by the fact that, like other similar substances, it is at first abnormally light after being melted and allowed to solidify, regaining its normal sp. gr. only after some time. The following table gives Kleinstück's results:

[1] *Chem. Zeit.*, 1890, 14, 1303.

| Temperature, | Sp. gr. compared with water at 4° | | |
	Japan wax		Water
	Of normal sp. gr.	After recent fusion	
6.5	....	1.00237	0.99995
7.2	1.00737	....	0.99991
17.0	....	0.99123	0.99884
17.5	0.99846	....	0.99875
23.0	....	0.98747	0.99762
26.5	0.98615	0.98683	0.99674

Japan wax is completely soluble in boiling alcohol, but is almost completely deposited on cooling. The variable hardness of the commercial wax is said to be due to the presence of the perilla oil used in its extraction. This will also influence the iodine value, since perilla oil is a strongly drying oil having an iodine value of upwards of 206.

Japan wax is readily and completely saponifiable, yielding glycerol, and hence is distinct in constitution from the true waxes, which yield monatomic alcohols when saponified (p. 87). It is composed chiefly of palmitin and more or less free palmitic acid. It also contains small quantities of saturated di-carboxylic acids of high m. p., of which an acid having the formula $C_{19}H_{38}(COOH)_2$, melting at 117°–117.5°, and its two lower homologues have been identified by Schaal.[1] The acid melting at 117°, to which they attributed the formula $C_{20}H_{40}(COOH)_2$ and named "Japanic acid," had previously been isolated by Geitel and van der Want (*J. prakt. Chem.*, 1900, 61, 151) and found to exist in combination with palmitic acid as a mixed glyceride. The latter observers also found a small quantity of oleic acid, and about 5 to 6% of soluble fatty acids which, in their opinion, had been produced by the action of the oxidising agents used to bleach the wax.

From 5.4 to 14.9% of free (palmitic) acid have been found in commercial Japan wax. Ahrens and Hett found from 5.1 to 5.5% in wax which they extracted in the laboratory.

The following results have been obtained by the examination of Japan wax and its fatty acids, in addition to those given in the table on p. 112.

[1] *Ber.*, 1907, 40, 4784.

		Authority
Unsaponifiable matter, %.............	1.48 to 1.63	Geitel and Van der Want.
Glycerol, %.........................	11.59; 13.50; 14.71	Allen.
Glycerol, %.........................	10.9	Mitchell.
Fatty acids, insoluble, %.............	90.62; 90.66 ⎱	Geitel and van
Fatty acids, soluble, %...............	5.96; 4.66 ⎰	der Want.
Fatty acids, soluble, %...............	8.40	Allen.
Properties of Insoluble Fatty Acids.		
Sp. gr. at 98 to 99°/15.5°.............	0.848	Allen.
M. p..............................	56° to 57°	Allen.
Solidifying-point....................	53° to 56.5°	Allen.
Combining weight...................	257.5 to 259.3	Allen.

That the constitution of Japan wax is peculiar is evident from the study of the products of its saponification, and is shown also by its high sp. gr. both in the solid and liquid state, in which characters it differs widely from the majority of solid fats. The sp. gr. of the insoluble acids, considered in conjunction with their mean combining weight, renders it doubtful whether these fatty acids really consist of palmitic acid, and it may be noted that Hehner and Mitchell (*Analyst*, 1896, **21**, 328) in working out their process for the estimation of stearic acid in fats found that the fatty acids prepared from Japan wax, while possessing apparently the properties of palmitic acid, prevented the crystallisation of stearic acid in an anomalous manner. The percentage of glycerol produced by saponification of the wax, as estimated by the permanganate process in two of the samples examined by Allen, is notably in excess of that yielded by tripalmitin, especially in the sample which gave the highest result, the glycerol from which sample was estimated several times with great care. Whether this high proportion was real or due to some unusual constituent which rendered the estimation by permanganate inaccurate was not ascertained. Any considerable proportion of a diglyceride containing palmitin and a dibasic acid would raise the proportion of glycerol and would also explain the relatively low combining weight of the insoluble fatty acids.

Japan wax is stated to be frequently adulterated with water, with which it is capable of forming a sort of emulsion when the two are agitated together a little above the m. p. of the wax.

La Wall (*Amer. J. Pharm.*, **69**, 18) found a number of samples adulterated with 20 to 25% of starchy matter. The sp. gr. of the

adulterated wax was only slightly higher than that of the genuine article. Such adulteration would be readily detected by means of ether, in which the wax would dissolve, leaving the starch.

The addition of tallow would be detected by the lowered m. p. and increased iodine value; in fact, the characteristic properties of Japan wax would render the detection of adulteration easy.

MACASSAR OIL

(For constants see p. 112.) Macassar oil is a soft fat, forming 60 to 70% of the seed-kernels of *Schleichera trijuga*, a tree growing in India and the East Indies. It is used locally for cooking, illuminating, and medicinal purposes, and has long been esteemed in Europe as a valuable hair restorer. It consists of esters of lauric, palmitic, arachidic and oleic acids, with small quantities of acetic and butyric acids. Its odour is largely due to the presence of a small amount (0.3 to 0.05%) of hydrocyanic acid.

Wijs found 3.12% of unsaponifiable matter in this fat. Of the non-volatile fatty acids, 45% were saturated and 55% unsaturated (liquid) acids; the latter had an iodine value of 103.2. van. Itallie found the sp. gr. of the mixed insoluble fatty acids 0.922 at 15°.

MYRTLE WAX

(For constants see p. 112.) This is a greenish-white fat, of wax-like appearance, separated from the berries of different kinds of *Myrica* (*M. cerifera*, *M. caroliensis*, etc.). It contains glycerides of myristic, palmitic, and oleic acids, palmitic acid being the predominating fatty acid. Besides the figures on page 112, the following have been published:

	Smith and Wade	Allen
Sp. gr. of solid fat at $\frac{22°}{15.5°}$	0.9806	. . . . . .
Solidifying-point	45°	39.5°
Refractive index, 80°	1.4363	. . . . . .
Acid value	30.7	. . . . . .
Free (palmitic) acid, %	. . . . . .	0.12
Glycerol, %	. . . . . .	13.38
Mixed Insoluble Fatty Acids		
Sp. gr. at 98–99°/15.5°	. . . . . .	0.837
Solidifying-point	. . . . . .	46°
Combining weight	. . . . . .	243.0

PALM-NUT OIL. PALM-KERNEL OIL

(See also p. 112.)   This oil is obtained by expression or extraction from the fruit-kernels or nuts of the oil-palm, and is entirely different in composition from palm oil (p. 254), which is obtained from the fleshy covering of the nuts.

Palm-nut oil varies from white to primrose-yellow or pink in colour, with a characteristic odour recalling that of violets, but not unlike that of coconut oil, which it resembles closely in every respect. The sp. gr. is high, ranging from 0.866 to 0.873 at 99° (compared with water at 15.5°).   The m. p. is from 26° to 30°, solidification occurring at 18° to 20°, and the temperature again rising pretty constantly to 25° or 26°.

Palm-nut oil contains a large proportion of esters of lower fatty acids, the composition of a sample analysed by Oudemans (*J. prakt. Chem.*, [2], **11**, 393; Watts Dict. of Chemistry, 7, 890) being given as:

Olein...	26.6%
Stearin, palmitin, and myristin.......................	33.0%
Laurin, caprin, caprylin, and caproin.................	40.4%
	100.0%

Valenta (*J. Soc. Chem. Ind.*, 1889, **8**, 806) found the oil to be composed of the same esters as stated by Oudemans, with the omission of stearin, but that present in largest proportion was found to be laurin.   Blumenfeld and Seidel found 4.53% of volatile fatty acids capable of distillation in a current of steam (*J. Soc. Chem. Ind.*, 1900, **19**, 914).

It is worthy of notice that all the fatty acids of which the esters are said to be present contain an even number of carbon atoms.   The same remark applies to coconut oil, which has a very similar composition (see page 260), but usually contains a larger proportion of lower fatty acids.   Thus, the saponification value of palm-nut oil is usually about 247, but differs somewhat with the mode of preparation.   If it is extracted from the palm-kernels by a solvent instead of by pressure, the proportion of higher fatty acids is increased, and the m. p. and saponification value of the product are respectively raised and lowered in proportion.   Palm-nut oil is stated to be sometimes adulterated with, or substituted by, lard or tallow, coloured with turmeric and scented with orris root.   With modified figures for the saponi-

fication value and distillate-acidity, the method of examining coconut oil for such adulterants fully applies to palm-nut oil.

Ellis and Hall (*J. Soc. Chem. Ind.*, 1919, **38**, 128T) examined a large number of oils expressed from palm-kernels under typical conditions. Of these oils 574 showed an average iodine value of 18.1 and 1236 a value of 18.6. The normal range for the iodine value lies between 16 and 23.

Palm-nut oil is largely used for soap-making, mixed with other fats. The commercial oil contains free fatty acids, sometimes in very large proportion. Valenta found from 7 to 58% in different samples.

The mixed fatty acids of palm-nut oil have given the following results (see page 112):

		Observer
Solidifying-point ("titer" test)..............	20 to 25.5°	Lewkowitsch.
Refractive index at 60°.................... .	1.431	Thoerner.
Iodine value...................	12.0	Thoerner.

Sachs (*Chem. Rev. Fett Ind.*, 1908, **15**, 9, 30) obtained the following results in the examination of *palm-nut* "stearine," which is used, in admixture with other vegetable fats, as a substitute for cacao butter:

Sp. gr. at 100°.....	0.8700
Solidifying-point...............................	28°
M. p...	31.5 to 32°
Saponification value...........................	242
Iodine value..................................	8
Reichert-Meissl value..........................	2.2
Mixed Fatty Acids	
M. p...	28.5°–29.5°
Solidifying-potint..	28.5°
Mean molecular weight.........................	211

Fats from Other Palms.—In addition to the fats derived from the fruit of the ordinary palm, fats derived from other species of palm, and in particular those growing in the forests of Brazil, have, during the last few years, become commercial products.

Some of these fats have been examined by Bolton and Hewer (*Analyst*, 1917, **42**, 35), who gave the following particulars of their characteristics.

1. *Elæis Guineensis.*—The fats from the pulp and kernels of the fruit show considerable differences from the fats of the African palm fruit.

2. *Astrocaryum vulgare.*—The oil expressed from the pulp has the consistence of butter.

3. *Astrocaryum species.*—The kernel fat could be used as a substitute for cacao butter.

4. *Acrocomia sclerocarpa.*—The fat from the fruit pulp of this palm, which grows in the forests of Paraguay, resembles palm oil. The kernel oil would be suitable for margarine

5. *Maximiliana regia* (Anajá or kokerite palm) yields an odourless white fat. ·

6. *Cocos syagrus.*—The two types of this tree produce very similar fats.

7. *Attalea funifera* yields a kernel fat resembling coconut nut oil but of softer consistence.

8. *Œnocarpus Batava.*—The oil from the fruit pulp of this tree closely resembles olive oil and is suitable for a salad oil.

The following analytical values were given by typical specimens of these fats. The close similarity in the characteristics of these palm fats makes it practically impossible to ascertain the origin of a given sample.

Palm oils	M. p. Begins	M. p. Complete	Solidification point	Saponification value	Refractive index (Zeiss) 40°	Iodine value	Free fatty acids %	Unsaponifiable %
	°	°	°					
1. Pulp.............	22–24	30–30.5	21.9	197.1	48 5– 51.5	78.1– 88.3	29.8– 20.5	....
Kernel.............	28.5– 28.0	30.2– 31.0	27.3– 27.8	231.4– 220.2	40.5– 42.7	25.5– 31.6	0 55– 0 33	0.75
2. Pulp.............	27.0	35.0	......	220.2	52.5	46.4	43.8	....
Kernel.............	29.4– 30.0	30.6– 32.5	28.6	240– 245.2	36.3– 37.3	12.2– 13.9	0.54– 1.65	....
3. Kernel.............	33.0	34.0	32.5	237.0	36 8	12.4	0.36	....
4. Pulp.............	......	......	24.9	189.8	40.5	77 2	55.8	....
Kernel.............	21.0	22–25.8	19.4– 24.9	237–246	37.2– 40 1	16.30	0.4–4.7	....
5. Kernel.............	26.0	28.5	......	240.9	38.3	16.56	0.33	....
6. Blunt fruit, kernel....	23 0	29.0	26.8	252.5	37.4	12.5	3.2	....
Pointed fruit, kernel..	23 0	28.7	......	......	36.2	13.4	2.97	....
7. Kernel.............	22.2	26.1	22.7	246.9	37.1	16.3	2 80	....
8. Pulp	......	......	7.0	191.8	52.5	78.2	0.48	1.1

Curua Palm Oil.—Curua fruits (*Attalea spectabilis*) from Brazil contained 13.2% of kernel which yielded 65.9% of a semi-solid

greenish fat with the following values (*Bull. Imp. Inst.*, 1920, **18,** 172):

Sp. gr. at 100°/15°................................ ... 0.8693

Refractive index, $n \frac{40}{D}$ 1.447

M. p.. .... 23.6
Solidification-point of fatty acids.................... 24.6
Acid value....................................... 1.2
Saponification value....... .... 259.5
Iodine value.......... ... . 8.9
Reichert-Meissl value.. .... 6.26
Polenske value........................... .. .. 15.6
Unsaponifiable matter............................... 0.36%

VIII. LARD OIL GROUP

Lard Oil.   Tallow Oil.
Neatsfoots Oil   Egg Oil.

LARD OIL

(See p. 112.)   Lard, especially the softer kind, subjected to hydraulic pressure yields a considerable quantity of fluid called "lard oil," or "lard oleine," whilst the solid portion constitutes "pressed lard," or "lard stearine."   Consequently, the m. p. and other characters of lard oil depend much on the temperature at which the pressing is conducted, winter-pressed lard oil naturally containing less of the solid constituents of lard than that expressed at a higher temperature.

Prime lard oil is a nearly colourless, pale yellow or greenish coloured oil, having but little odour, and composed of the glycerides of chiefly oleic, stearic, and palmitic acids, with some linolic and perhaps linolenic acids.   It usually thickens at about 4°, and becomes solid at −4°, but some samples exhibit wide departures from these limits.   A specimen of pure winter-pressed oil examined by Henry began to deposit flakes at −8°, was thick at −10°, and solid at −12°.   It did not remelt completely until the temperature reached +7°.   On the other hand, a sample tested by Duyk (*Bull. de l'Assoc. Belge*, 1901, **15,** 18) began to crystallise at +10°.   Commercial lard oil varies in character from the nearly neutral sweet oil above described to the acid, rancid, and offensive-smelling lard oils of deep brown colour called "Extra No. 1," "Extra No. 2," and "Extra No. 3" (Schweitzer and Lungwitz).

In many of its characteristics lard oil closely resembles olive oil, particularly in its behaviour with nitric acid, in the elaidin-test, and the temperature produced by strong sulphuric acid.

Lard oil is extensively employed as a lubricant. The chief adulterants affect its viscosity and non-drying characters, and therefore its value for lubricating. Lard oil is often employed in lighthouse and signal lamps, and a small percentage of free acid or of cottonseed oil affects, injuriously, its quality for these purposes.

The *acidity* of lard oil, calculated as oleic acid, should not exceed 2%. Of 47 samples tested by Jenkins (Private communication) 40 satisfied this condition, and the average acidity of the whole was 1.56%.

> 10 samples contained between 0 and 1%.
> 30 samples contained between 1 and 2%.
> 5 samples contained between 2 and 3%.
> 2 samples contained between 4 and 6%.

Of 14 samples examined by Archbutt,

> 1 sample contained   0.85%.
> 11 samples contained from   1.0 to 2.0%.
> 2 samples contained   6.7%.

4 samples examined by Tolman and Munson contained from 0.28 to 1.28, and 4 by Sherman and Snell from 0.74 to 2.64% of free oleic acid.

The *sp. gr.* of genuine American lard oil at 15.5° ranges from 0.913 to 0.919, according to Schweitzer and Lungwitz (*J. Soc. Chem. Ind.*, 1895, 14, 129) and the results published by other chemists fall within these limits. Of 47 samples of commercial lard oil examined by Jenkins and believed to be genuine, only one sample had a higher sp. gr. (0.921); the remainder ranged from 0.914 to 0.919, the average being 0.9172. Adulterants, such as cottonseed oil, maize oil, and fish oils, would raise the sp. gr.

The *oleo-refractometer* is a valuable instrument for examining lard oil, the recorded deviation caused by which ranges from −1° to +5.5°. All fixed oils likely to be added as adulterants, except arachis, neatsfoot, and tallow oils, would increase the refraction (see page 61).

The average *viscosity* of commercial lard oil is about the same as that of olive oil, but it varies between rather wide limits. The efflux time of 45 samples examined by Jenkins ranged from 356 to 534 seconds for 50 c.c. at 15.5° from Redwood's viscometer, the average being 437 seconds. Olive oil from the same viscometer at 15.5° required 426 seconds. The majority of the samples fell within a narrower range, as is shown below.

6 required from 356–399 seconds.
9 required from 400–422.5 seconds.
17 required from 427–449 seconds.
7 required from 451–466 seconds.
3 required from 477–495 seconds.
3 required from 508–534 seconds.

The *Maumené thermal value* (50 c.c. of oil and 10 c.c. of 97% sulphuric acid) ranges from about 40° to 46°, practically the same as in the case of olive oil. This is, therefore, a valuable test, since most oils likely to be added as adulterants would increase the temperature indication.

The *iodine value* of genuine lard oil depends largely on the proportion of olein. The interpretation to be placed upon the result of this test must, therefore, depend upon the congealing-point of the oil. Schweitzer and Lungwitz, who have investigated this relation, ascertain the congealing-point as follows: The oil is poured into a wide-mouthed bottle, immersed in a freezing-mixture of ice and salt, and stirred vigorously with a thermometer; the temperature is noted at which the oil shows the first sign of becoming cloudy. Any (American) lard oil with higher iodine value than 70 should not show signs of cloudiness above 40° F. The lard oil having iodine values of from 60 to 70 are generally pasty at 40° F.

The following table is taken from Schweitzer and Lungwitz's paper:

Sp. gr. at 15°/4°	Iodine value	Congealing-point
0.9136	78.8	25° F.
0.9146	76.4	28° F.
0.9174	76.0	28° F.
0.9151	71.5	35° F.
0.9159	67.8	40° F.
0.9160	63.9	42° F.
0.9186	62.8	Solid at 40° F.

Probably the iodine values of most genuine lard oils would fall between 67 and 82.

The *saponification value* is about 193 to 198. Adulteration with rosin oil, mineral oil, or rape oil would lower this value. Rosin oil or mineral oil, if present, would be found in the *unsaponifiable matter* which, in genuine lard oil, does not exceed about 0.6%.

The *flash-point* (closed test) of a genuine sample of lard oil was found by Jenkins to be 480° F.

The *"titer" test* of the mixed fatty acids ranged from 27° to 33° in 46 samples examined by Jenkins, and Duyk (*Bull. de l'Assoc. Belge*, 1901, **15**, 18) found the sp. gr. at 100° to be 0.885.

4 samples of genuine lard oil examined by Tolman and Munson (*Bull.* No. 77, United States Dept. of Agriculture) gave the following results:

	1	2	3	4
Sp. gr. at 15.5°........................	0.9148	0.9145	0.9160	0.9175
Butyro-refractometer reading at 15.5°...	67.4	67.4	69.5	66.8
Saponification value....................	195.7	195.3	197.7	196.2
Iodine value...........................	75.9	77.2	69.7	72.5
Iodine value of ⎰ estimated..........	94.0	....	95.8	93.9
Liquid fatty acids ⎱ calculated..........	98.9	101.3	101.3	97.9
Solid fatty acids, %....................	18.9	19.3	26.68	21.43
M. p. of mixed fatty acids..............	33.2°	34.2°	38.4°	35.8°
Free (oleic) acid, %....................	0.75	0.78	0.28	1.28

Cottonseed oil, unless it has been heated, would be detected by Halphen's colour test; *sesame oil* by the furfural test. Vegetable oils as a class would be detected by the *phytosterol acetate* test. Some vegetable oils would be indicated by the appearance of a well-defined band in the absorption spectrum, near the line B. Genuine lard oil gives no absorption bands.

For the detection of *arachis oil*, Renard's process must be used (see under "Arachis Oil"). Hehner and Mitchell's insoluble bromide test would prove the presence of *fish oils* or *linseed oil*.

The oxidation test described under **Olive Oil** is usefully applied to lard oil intended for lubricating.

NEATSFOOT OIL

(See also p. 112.) Neatsfoot oil is obtained by boiling the feet of oxen in water until all the oil has risen to the surface. It is usually the custom in rendering establishments to use the whole leg below the knee, and no doubt the majority of the neatsfoot oil of (American) commerce is made in this manner (Lythgoe). The commercial

oil also often includes that from the feet of sheep and horses. 10 ox-feet yield from 2 to 2.5 pints of oil.

Pure neatsfoot oil has a pale golden-yellow colour, a not unpleasant odour of beef fat, and slowly deposits "stearine" on standing. The portion which remains fluid at a low temperature is used as a lubricant for clocks. The commercial oil is largely used for leather dressing and to some extent as a lubricant, chiefly in admixture with mineral oils.

Neatsfoot oil is composed chiefly of olein, with some palmitin and stearin. No glyceride of a fatty acid less saturated than oleic is present in any quantity (Coste and Shelbourn). The unsaponifiable matter does not exceed 0.7% and consists chiefly of cholesterol and a pigment which tints the oil yellow.

Neatsfoot oil is extensively adulterated with bone oil, fish, seed, and mineral, oils. If carefully separated from foreign matters soon after boiling, it contains very little free fatty acid, and if preserved under proper conditions very little hydrolysis of the oil occurs. Excessive acidity of the commercial oil must, therefore, be due either to adulteration or to want of proper care in manufacture.

The most complete investigation of this oil has been made by Coste and Shelbourn (*J. Soc. Chem. Ind.*, 1903, **22,** 775) who prepared a number of samples in the laboratory from the feet of different breeds of oxen and from a calf's feet. A summary of their results is given in the following table, together with some results by other authorities with commercial oils believed to be genuine:

	Coste and Shelbourn. Oil prepared in laboratory	Gill and Rowe. American oil. 5 samples	Lythgoe. American oil. 4 samples	Holde and Stange. 10 genuine oils
Sp. gr. at 15.5°....................	0.9151–0.9181	0.914–0.919	0.9133–0.9148	....
Butyro-refractometer, 20°.........	63.0–64.6	....	63.3–63.6	....
Saponification value..............	193.6–199.7	....	....	196–199
Iodine value.....................	66.4–73.1	67.1–72.9	71.3–73.0	66–74
Hehner value.....................	94.8–95.9	....	....	....
Reichert-Meissl value........... ..	0.9–1.2	....	....	....
Maumené test (100% acid used)...	....	42.2°–49.5°	....	....
Unsaponifiable matter...........	0.12–0.65	....	....	....
Mixed Fatty Acids				
Sp. gr. at 100°/100°..............	0.8713–0.8739	....	....	....
Titer test.......................	16°–26.5°	....	....	....
Solidifying-point	24.5–29.2	....	....	....
Neutralisation value.....	103.4–206.3	....	....	....
Iodine value.............	71.0–77.0	63.6–69.5	....	....

A. Bruno (*Ann. Falsific.*, 1921, **14**, 137) obtained the following values with samples prepared in the laboratory:

	Sp. Gr. at 15°	$N\frac{22}{d}$	Saponific- tion Value	Iodine Value	Acidity as Oleic Acid, %
Sheep-foot oil...	0.917	1.46805	194	84.0	0.34
Ox-foot oil......	0.9169	1.4675	194	75.3	0.87

A number of samples of neatsfoot oil examined by Eckart (*Zeitsch. Untersuch. Nahr. Genussm.*, 1922, **44**, 1) gave the following analytical values:

Sp. gr. at 50°/50°.............. . . 0.9026 to 0.9049
Solidification point................... −2° to +4°
Acid value......................... 0.1 to 6.3 (bleached oil)
Saponification value............. ..... 191.8 to 196.2
Hehner value...................... 93.3 to 96.6
Reichert-Meissl value............... 0.4
Iodine value...................... 57.4–72.3
Acetyl value...................... 7.7–9.3
    Fatty Acids
M. p.............................. 29.5°–41.2°
Neutralisation value.... 195–202
Mean molec. equivalent............. 278–288

The average composition of these oils was as follows: stearic acid, 2 to 3; palmitic acid, 17 to 18; oleic acid, 74.5 to 76.5; glycerol, 5 to 10; and unsaponifiable matter, 0.1 to 0.5%. The unsaponifiable matter consisted of cholesterol.

The *oleo-refractometer* should be of great value in examining samples of neatsfoot oil. The presence of seed oils and fish oils would be readily detected by its means. Sheep's-foot oil is the standard oil used in this instrument.

Observation of the sp. gr. and iodine value, together with the Maumené test, would serve to detect many of the most objectionable adulterants. Rape oil would reduce the saponification value. Fish oils and linseed oil would be shown by the insoluble bromide test. Mineral and rosin oil would be found in the unsaponifiable matter. Bone oil would be detected, most likely, by the ash, and probably would increase the amount of free fatty acid. Vegetable oils, as a class, would be found by the phytosteryl acetate test.

TALLOW OIL

(See p. 112.) Tallow oil, or tallow "olein," is obtained by submitting tallow to hydraulic pressure, and its characteristics differ, as in

the case of lard oil, according to the temperature at which it has been expressed. It is largely used as a lubricating oil, especially in admixture with mineral lubricating oils. "Ox" oil should be tallow oil expressed from beef tallow. "Animal" oil might contain the fat of other animals. The name "tallow oil" is sometimes incorrectly applied to crude oleic acid, and care has to be taken that such oil is not inadvertently purchased for lubricating purposes.

Gill and Rowe (*J. Amer. Chem. Soc.*, 1902, **24**, 466) give the analytical constants of 3 samples of tallow oil, as follows:

Sp. gr. at 100°............................	0.794
"Titer test".................................	35° to 37.5°
Maumené test (100% H_2SO_4 used)...............	35°
Iodine value.................................	55.8 to 56.7
Iodine value of mixed fatty acids.................	54.6 to 57.0

Two samples of "refined animal oil" examined by Archbutt gave the following numbers:

	1	2
Sp. gr. at 15.5°............................	0.9187	0.9187
Relative efflux time (seconds) at 15.5° ⎫	602	556
(Refined rape oil, 600–630 seconds) ⎭		
Free (oleic) acid...........................	0.20	0.25
Maumené test (97% H_2SO_4 used)...............	40.5°	42.5°
Saponification value........................	199.6	193.5
Iodine value................................	60.4	59.7

On cooling to 50° F., no crystals formed in 3 hours, but on lowering the temperature to 46° F. crystallisation commenced, and slowly continued until the oil ceased to flow.

8 samples of animal oil, believed to be genuine, examined by Dunlop (*Analyst*, 1907, **32**, 319), had iodine values ranging from 66.3 to 77.6 and sp. grs. (15.5°) from 0.914 to 0.9165. The efflux times of 50 c.c. from Redwood's viscometer at 21.1° ranged from 330 to 460 seconds. Dunlop states that oils of this character are far from common, and that out of more than 40 samples of commercial animal oil tested by him, at least half had a sp. gr. of 0.9170 to 0.9215 and iodine values of 90 to 116. Many of these oils were adulterated with seed or fish oils and had marked drying properties, unfitting them for

lubrication; others, of lower sp. gr., were adulterated with mineral oil. The amount of free fatty acid ranged from 0.70 to 22.0%. The Zeiss refractometer is useful as a sorting test, a reading higher than 61 at 25° indicating either a high iodine value or the presence of mineral oil.

Dunlop points out that a high iodine value may be due to the presence of horse oil, four samples of which he prepared from the fat obtained from different parts of the horse. These oils ranged in iodine value from 90 to 115, in sp. gr. at 15.5° from 0.9182 to 0.9212, were lower in viscosity than the genuine animal oils, and had objectionable drying properties. To decide whether a high iodine value is due to the presence of horse oil or a seed oil, the phytosteryl acetate test would be necessary.

To test the drying property of tallow oil, Dunlop recommends exposing 2 drops on a $\frac{1}{4}$ plate negative glass for 24 hours to a temperature of 95° to 97°. Genuine tallow, lard or neatsfoot oil does not gum to any appreciable extent under these conditions, but many "animal oils" of higher sp. gr. than 0.9170 gave sticky films. Hehner and Mitchell's insoluble bromide test also gives valuable information, even when used qualitatively, since genuine tallow and lard oils give little or no deposit, whilst the presence of even 5% of whale or similar oil is indicated by a very distinct precipitate of the bromine compound.

EGG OIL

This oil, which is used in ointments and cosmetics, also in Russia for cooking, is obtained from the yolk of hard-boiled hens' eggs, either by pressure or by solvents. The yolks contain from 25 to 35% of oil, according to Paladino and Toso (*Analyst*, 1896, **21**, 161). Kitt (*Chem. Zeit.*, 1897, **21**, 303) obtained 19% of oil by extraction with ether.

Egg oil has an orange-yellow colour, is partly solid at ordinary temperatures, gives the Hager-Salkowski indication for cholesterol, and yields a solid elaidin. According to Kitt, the oil is composed chiefly of the glycerides of oleic acid (82%) with palmitic and stearic acids. It contains cholesterol and lecithin. The results obtained by the above named chemists are given in the following table:

	Paladino and Toso	Kitt
Sp. gr................................	0.9156 at 20°	0.9144 at 15°
Solidifying-point......................	8°–10°	....
M. p................................	22°–22.5°	....
Saponification value..................	185.2–186.7	190.2 (mean)
Iodine value.........................	81.2–81.6	72.1 (mean)
Hehner value.........................	....	95.16
Reichert-Meissl value.................	....	0.4
Free (oleic) acid.....................	....	0.6
Cholesterol, %.......................	....	1.5
Mixed Fatty Acids		
M. p................................	34.5°–35°	36°–39°
Saponification value..................	....	194.9 (mean)
Iodine value.........................	....	73.7 (mean)

IX. TALLOW AND BUTTER GROUP

Beef Fat.   Horse Fat.
Butter Fat.   Lard.
Bone Fat.   Mutton Fat.

Tallow.

BEEF FAT

(See also p. 112.) Beef fat is more solid than lard, though it differs in consistence as well as in chemical composition with the part of the animal from which it is obtained. It is largely used in the preparation of oleomargarine for the margarine industry, and also as an adulterant of lard (see under "Tallow").

BUTTER FAT

(See special article.)

BONE FAT.   BONE GREASE.   BONE TALLOW

(See p. 112.) Bone fat is obtained by boiling bones with water and skimming the oil; by steaming bones in closed digesters; or by extraction with solvents. It is chiefly used for making soap and candle.

Bone fat ranges in colour from drab to deep brown, has a characteristic odour, frequently contains a large proportion of free fatty acids, and usually contains lime soaps in solution, besides more or less calcium phosphate, sand, dirt, and water. Its fatty acids usually solidify at about the same temperature as those of lard, though the best samples approach ordinary tallow in this respect. These variations in quality largely depend upon the kind of bones the fat is obtained from, the length of time they have been kept before being treated for the extraction of the fat, the process of extraction employed, etc. Bullocks' hollow shank bones yield the best fat (Carpenter). The following results were obtained by Eckart (*Zeitsch. Unters. Nahr. Genussm.*, 1922, **44**, 1) in the examination of samples of bone fat extracted by different methods:

Sp. gr. at $50°/30°$	$0.9009-0.9034$
M. p.	$44°-45°$
Solidification point	$32.6°-33.8°$
Acid value	$0.3-0.6$
Saponification value	$189.6-195.2$
Hehner value	$94.1-95.6$
Reichert-Meissl value	$0.2-1.7$
Iodine value (Hanus)	$49.1-95.6$
Acetyl value	$12.0-14.8$
Fatty Acids	
M. p.	$42.5°-44°$
Mean molec. equivalent	$278.8-284.8$

Marrow fat gave very similar results.

The average composition of ox bone fat was as follows: stearic acid, 19 to 21; palmitic acid, 20 to 21; oleic acid, 53 to 59; glycerol, 5 to 10; and unsaponifiable matter about 0.5%.

In 10 samples of commercial bone fat analysed by Valenta (*Zeitsch. Chem. Ind.*, 1887, 265) the ash ranged from 0.11 to 2.01%; water from 1.33 to 3.08, except in one very impure, nearly black sample, which contained 6.31%; the total fatty acids ranged from 89.8 to 93.7%; the free fatty acids from 14.8 to 26.5%; the iodine value from 48 to 55.8; the saponification value from 200 to 207; and the m. p. of the fatty acids from $41.5°$ to $42.7°$.

According to Shukoff (*Chem. Rev. Fett Ind.*, 1901, **8**, 229), the following varieties are recognised in Russian commerce: *Benzine bone fat* (Petrograd), a very pure fat, containing from 0.05 to 1.0% of water; *benzine bone fat from S. Russia*, usually very impure,

containing water and impurities 3 to 4%, free acids 30 to 40%; "titer" test 40 to 42°; *benzine horse-bone fat*, containing 3 to 4%, of water and impurities, titer test 38.2°; *white natural bone fat* (Petrograd) from the gelatine factories, containing 0.3 to 1.5% of water and impurities, 20 to 30% of free fatty acids, titer test 40° to 45°.

In 379 samples of bone fat examined by Schestakoff (*Ibid.*, 1902, **9,** 180) the free fatty acids ranged from 8.3 to 56.2%.

Marrow fat from ox bones, prepared by Dunlop (*Analyst*, 1907, **32,** 318), was light yellow, resembled hard lard in consistence, and had the following characteristics: iodine value, 52.0; butyro-refractometer reading at 25°, 55.3; saponification value, 196.3; free fatty acid, 0.22%.

For the valuation of bone fat, Shukoff and Schestakoff recommend the following procedure (*Chem. Rev. Fett Ind.*, **5,** 5-8 and 21-23:

Water.—Dry 5 grm. at 100° to 110° until constant in weight; owing to the tenacity with which the lime soaps retain water, over 24 hours' drying may be required. The water can also be estimated by difference.

Fat, and Non-fatty Impurities.—10 grm. are gently melted on the water-bath, and heated for about an hour with 3 to 5 drops of hydrochloric acid, with frequent stirring, to decompose the lime soaps. The fatty matter is then dissolved out with 40 c.c. of petroleum spirit, which is poured through a tared filter-paper into a weighed flask. The insoluble matter is rinsed on to the filter, well washed with petroleum spirit, dried, and weighed. The fatty matter is estimated by distilling off the solvent and drying the residue at 100 to 110° until constant in weight.

Ash.—This is estimated by careful combustion of a weighed quantity of fat. The calcium in the ash, existing chiefly as carbonate and oxide, is estimated by titration, and the corresponding amount of lime soaps calculated from the result, 260 being taken as the average molecular weight of the fatty acids. When sand, calcium phosphate, etc., are present, a quantitative analysis of the ash may be necessary, but this is seldom required.

Unsaponifiable Matter.—When the bone fat is intended for soap-making, the unsaponifiable matter should be estimated, as any amount in excess of that natural to the fat, say 2%, must be regarded as an impurity.

"Titer" Test.—The titer test of the mixed fatty acids is estimated by Dalican's process, as in the case of tallow and other fats.

HORSE FAT

(See also p. 112.)   The fat of the horse is light or dark yellow in colour, and varies in consistence according to the part of the animal from which it has been obtained.   It consists of the esters of oleic and linolic acids (the latter constituting about 10% of the total fatty acids), and of saturated fatty acids of which palmitic acid is probably the chief constituent.   Horse fat is sometimes used as an adulterant of lard and tallow.

The following results of examination of horse fat and oil have been published by Dunlop (*Analyst*, 1907, **32**, 318):

Fat or oil from	Colour and consistence	Sp. gr. at 15.5°	Butyro-refractometer, 25°	Iodine value	Saponification value	Reichert-Wollny value	Unsaponifiable matter, %	Free (oleic) acid, %
1 Belly........ . . .	Orange-yellow, butter-like	....	59.8	85.66	198.4	......	0.54	8.80
2 { Neck ("mane") ...	Light yellow, part liquid	....	61.2	86.70	199.1	....	....	0.56
3 { Neck after filtration at 12.2°.	Lemon-yellow oil	0.9182	61.8	90.10	... ..	0.30	0.46	.....
4 { Neck ("mane")....	Light yellow, part liquid	... ...	61.2	90.07	.....	. ...	....	.....
5 { Neck after filtration at 8.9°.	Lemon-yellow oil	0 9184	61.8	93.11	195.6	0.20	0.50	1 20
6 { Kidney bed.......	Orange-yellow, part liquid	... ..	66.0	110.65	......	.....	.....	.....
7 { Kidney after filtration at 13.3°.	Orange-yellow oil	0.9212	66.7	114.85	196.3	0.35	0.68	.....
8 Oil from neck fat.	Lemon-yellow oil	0.9211	66.0	112.85	196.3	. ...	0.42	0.46

Dunlop calls attention to the high iodine value, especially of the fat from the kidney bed, which, in the case of most animals, gives a low value.   The drying properties of horse fat are very marked, especially at high temperatures.   The oils numbered 4 and 5, when exposed to the air in thin films on glass at 95 to 97°, became sticky in 2 hours, and dried to a varnish in 4 hours.   No. 5 sample, tested in Redwood's viscometer, required 286 seconds for the outflow of 50 c.c.

at 21.1°. No stearic acid was found in Nos. 1 and 4 samples by Hehner and Mitchell's method.

LARD

(See special article.)

MUTTON FAT

(See also page 112.) Mutton fat is, as a rule, more solid than beef fat, but varies in composition and general characteristics according to the part of the sheep from which it is derived (see under Tallow). The fat from the region of the kidney, for instance, is hard, whilst that from the neck is almost fluid. Besides its use as a food, mutton fat is employed in the manufacture of soap, candles, and lubricants. It is also used as an adulterant of lard and butter.

TALLOW

(See also page 112.) Tallow is the fat of certain ruminant animals, separated from the enveloping membrane of the tissue by the process of melting out or "rendering." Tallow is classed commercially as "beef" and "mutton" tallow, but each of these may comprise the fat of other animals besides the ox and sheep.

Pure tallow is white and almost tasteless, but much of that in commerce has a yellow colour and a disagreeable rancid flavour.

In chemical composition, tallow is composed essentially of the glycerides of palmitic, stearic, and oleic acids, but these do not wholly exist as simple esters, as was formerly believed. Hansen (*Arch. Hyg.*, 1902, **42**, 1) has isolated from beef and mutton tallow palmito-distearin, stearo-dipalmitin, oleo-dipalmitin and oleo-palmito-stearin. On the other hand, Bömer (*Zeitsch. Nahr. Genussm.*, 1907, **14**, 90) has found about $1\frac{1}{2}\%$ of tristearin in beef tallow, 4 to 5% in pressed beef tallow, and 3% in mutton tallow. According to Farnsteiner (*Ibid.*, 1899, **2**, 1) the unsaturated acids include a small amount of linolenic acid. Hehner and Mitchell (*Analyst*, 1896, **21**, 328) found 50.62% of stearic acid in a sample of beef "stearine" of iodine value 2.0. In several samples of beef tallow, Lewkowitsch (Oils, Fats and Waxes, II, 639) found from 21 to 22% of stearic acid. The following table of results by Hehner and Mitchell shows the percentage of stearic acid, etc., found in the fat from different parts of a Scotch sheep 18 months old:

Fat from	Stearic acid in fat, %	Stearic acid in saturated fatty acids, %	Iodine value of fat	M. p. of mixed fatty acids
Kidney.....	$\left\{\begin{array}{c}26.2\\27.7\end{array}\right\}$	58.0	48.16	45.6°
Back...........	24.8	78.0	61.3	41.4°
Neck...........	16.4	36.0	48.6	42.2°
Breast..........	About 1	3.0	58.2	33.8°
Ham...........	Nil	Nil	50.6	40.8°

The ham fat was fluid, and that from the breast was almost fluid, at the ordinary temperature.

The following values have been recorded for the fatty acids of tallow (see also page 112):

	Beef tallow	Mutton tallow	Authority
Sp. gr. at 100°/100°........	0.8698	....	Archbutt.
Solidifying-point (titer test).	38.3°–46.3°	41.5°–48.3°	Lewkowitsch.
	Usually 43°–45°	Usually 43°–46°	....
Refractive index at 60°.....	1.4375	1.4374	Thoerner.
Saponification value.......	197.2–201.6	210	....
Iodine value.......... ...	26–41	34.8	....
Iodine value of liquid fatty acids.................	92–93	92.7	Tortelli and Ruggeri; Wallenstein and Finck.

Examination of Commercial Tallow.—The tallow of commerce frequently contains a considerable amount of *free fatty acid.* Thus Deering (*J. Soc. Chem. Ind.*, 1884 3, 540) found in 25 samples of tallow from various sources the proportions of free acid shown in the following table:

Number of samples	Source	Free (oleic) acid, %		
		Highest	Lowest	Average
13	Russian......................	12.20	2.20	5.48
4	Australian beef....................	8.85	1.75	4.47
4	Australian mutton..................	7.15	0.85	3.91
2	Town tallow......................	6.95	4.55	5.75
1	Unknown........................	2.10	....	....
1	Town tallow, 6 years old............	25.0	....	....

88 samples examined by Archbutt gave the following results:

Number of samples	Source	Free (oleic) acid, %		
		Highest	Lowest	Average
55	Home melted......................	11.90	1.40	4.89
9	Australian mutton..................	12.84	1.00	4.84
11	South American beef...............	7.60	0.70	2.07
12	Unknown.........................	10.60	1.30	4.65
1	Unknown	83.60	....	....

227 samples of tallow, supplied to a specification limiting the free (oleic) acid to 4.0%, contained a minimum of 0.5%, a maximum of 26.2%, and an average of 2.86% of free (oleic) acid (Archbutt and Deeley. *Lubrication* and *Lubricants*, 2nd Ed., p. 212).

The free acid in 36 samples of Australian tallow examined by Norman Tate ranged from 1.20 to 4.70, and in 277 samples reported by Schestakoff (*Chem. Rev. Fett-Harz-Ind.*, 1902, 9, 180) the free acid found was as follows:

Number of samples	Description	Maximum, %	Minimum, %
158	Mixed tallow............	56.2	8.3
65	Ox tallow..............	27.0	0.1
54	Mutton tallow....	10.7	0.33

Large proportions of free acid may be due to adulteration of the tallow with wool-grease acids or solid-fatty acids from cottonseed oil, but they are usually due to hydrolysis of the tallow itself having occurred previous to the rendering of the fat. From whatever cause produced, free acid is objectionable and depreciates the value of the tallow to the maker, of soap and candles besides unfitting it for use as a lubricant.

Tallow frequently contains more or less water, infusible substances, and mineral impurities, and has been occasionally purposely adulterated with starch, china clay, whiting, barium sulphate, etc. Fats of greater fusibility, especially bone fat, may be present, and wool-grease acids and cottonseed "stearine" have been extensively

used. Cakes of tallow are said to have been met with the interior of which consisted of inferior fats.

The presence of *water, starch*, and *insoluble substances* generally can be detected and their proportion roughly ascertained by melting a fair sample of the tallow in a graduated cylinder heated in a water-bath, and reading off the volume of impurities which settle out. The insoluble matter in samples of tallow representing large lots is usually under 0.2%, and the water rarely exceeds 1.0 to 1.5%. *Water* can be accurately estimated as described under "Lard." *Insoluble impurities* can be estimated by dissolving 10 to 20 grm. of the tallow in ether or petroleum spirit, filtering the solution through a tared filter-paper, well washing the paper and contents with the solvent to remove fat, drying at 100°, and weighing. The residue on the filter may be examined under the microscope, when *starch, gelatinous matter*, or fragments of *tissue* will be readily recognised. Starch may also be detected by boiling the residue with water and testing the solution with iodine. *Lime soap* will be detected by warming the residue with dilute hydrochloric acid, when globules of fatty acids will rise to the top of the liquid, which, after filtration, may be neutralised and tested for calcium with ammonium oxalate. Any effervescence of the residue on addition of hydrochloric acid will probably be due to *whiting*.

For the detection of foreign fats, paraffin wax, rosin oil, the quantitative reactions and a few special tests usually suffice.

The *saponification value* of tallow may range from 192.5 to 198, and averages about 195. Paraffin wax would lower this value; palm-nut and coconut oils would raise it. Bone fat, cottonseed oil, and cottonseed "stearine" do not affect this constant.

The *iodine value* of genuine tallow has been found to range from about 33 to 48, but the usual range is from 40 to 45. A value higher than 48.0 would be suspicious, and might be due to the presence of cottonseed oil or "stearine," horse fat, or bone fat. An abnormally low value might indicate paraffin wax, coconut oil, or palm-nut oil.

Smetham (*J. Soc. Chem. Ind.*, 1899, **18**, 330) has published the iodine values of 1000 samples of commercial tallow, estimated by Hübl's method. Unfortunately, no attempt was made to discriminate between pure and adulterated samples, but as tallow is not often adulterated, the averages of such a large number of samples

cannot be far from the averages of pure tallow of the respective kinds.

Number of samples	Description	Average iodine value
592	Home melted..................	42.81
46	North American................	46.03
5	South American................	41.02
62	Australian, unclassified...........	43.61
69	Australian mutton..............	42.83
13	Australian beef.................	45.17
6	Beef.........................	41.42
12	Mutton.......................	41.61
195	Unclassified....................	43.61

Cottonseed oil and cottonseed "stearine," besides being indicated by the raised iodine value, would probably be detected by Halphen's colour test. The nitric acid test must be used with caution, since it has been observed that tallow which has not been washed and purified and which, therefore, contains particles of blood, etc., acquires a light brown colour when agitated in a melted state with ⅕ of its volume of nitric acid (sp. gr. 1.38). L. Mayer (*Dingl. polyt. J.*, 1883, 247, 305) recommends an examination of the "oleine" obtained by allowing the melted tallow to crystallise for 18 hours at 35° and then squeezing the liquid portion through filter cloth. The iodine value of this should not exceed 55 if the tallow be genuine, but in presence of cottonseed oil or stearine a much higher value will be obtained. A more scientific test would be the estimation of the *iodine value of the liquid fatty acids*, those of tallow absorbing 92 to 93% of iodine, whilst the liquid acids from cottonseed oil absorb nearly 150%. Vegetable oils and fats generally would be detected by the *phytosteryl acetate* test (page 386).

Tallow has been occasionally met with which has been largely adulterated with the distilled *fatty acids from wool grease*. Mayer (*loc. cit.*) has described a sample which consisted almost exclusively of such fatty acids. It had a very high acid value, smelt strongly of wool grease, yielded only 0.2% of glycerol on saponification, and when the aqueous solution of the soap was shaken with ether and the ethereal solution separated and evaporated, a considerable

amount of unsaponifiable matter containing cholesterol was obtained which gave a violet colouration, changing to blue, when evaporated with concentrated hydrochloric acid and ferric chloride. Mayer states that 5% of wool grease can be detected in tallow by this method. The fatty acids separated from the soap formed in the above process turned yellow in a few days, and after several months had acquired a deep orange-yellow tint.

The presence of *bone fat* would be indicated by an excessive amount of *ash*, containing calcium phosphate. In 5 samples of bone fat examined by Valenta the amount of ash ranged from 0.11 to 2.01%, averaging 1.32%. Genuine tallow leaves a mere trace of ash. Tallow containing bone fat would most probably be very acid.

Horse fat would tend to make tallow yellow in colour and soft. It would raise the iodine value and would also lower the "titer test" of the mixed fatty acids. Horse fat contains no stearin. It has marked drying characters, and the intense yellow colour of ethereal solutions of the unsaponifiable matter appear to be characteristic of this fat (Dunlop, *Analyst*, 1907, **32**, 317).

Paraffin wax, which is sometimes added to soft tallow and usually reveals its presence by reducing the saponification value, can be estimated by separating the *unsaponifiable matter*, which, in genuine tallow, does not exceed 0.4 to 0.6%. The same process would indicate the presence of *rosin oil* and also *wool fat*.

Palm-nut and coconut oils, besides raising the saponification value, would increase the *Reichert-Meissl value* and reduce the *Hehner value*.

The varying quality and frequent adulteration of tallow some years since caused the French candle manufacturers to adopt a process of analysing samples for the relative proportions of oleic and solid fatty acids. This they effect by Dalican's method, which consists in estimating the solidifying point of the mixed fatty acids by the "titer test" (see p. 73). The lowest permissible solidifying point of the acids is often fixed at 44°, corresponding to a mixture of oleic and solid fatty acids in equal proportions. The following table by F. Dalican shows the approximate yield of *solid fatty acids* ("stearic acid") from 100 parts of tallow. The corresponding *oleic acid* may be found by subtracting the percentage of solid acids from 95.00.

Solidifying point; °	Solid acids; %	Solidifying point; °	Solid acids; %	Solidifying point; °	Solid acids; %
40.0	35.15	43.5	44.65	47.0	57.95
40.5	36.10	44.0	47.50	47.5	58.90
41.0	38.00	44.5	49.40	48.0	61.75
41.5	38.95	45.0	51.30	48.5	66.50
42.0	39.90	45.5	52.25	49.0	71.25
42.5	42.75	46.0	53.20	49.5	72.20
43.0	43.70	46.5	55.10	50.0	75.05

The "titer test" of tallow used for making railway wagon axle grease should not fall below 41°.

X. WHALE OIL GROUP

Codliver and Allied Oils.	Herring Oil.
Shark-liver Oil.	Seal Oil.
Menhaden Oil.	Whale Oil.
Sardine Oil. Japan Fish Oil.	Porpoise Oil.

CODLIVER OIL

(For constants see p. 113.)   Strictly speaking, codliver oil is the oil obtained from the liver of the cod, *Gadus morrhua*, but the closely analogous oils obtained from the livers of other species of *Gadus* and of the *Gadidæ* family, such as the ling, coalfish, hake, haddock, and whiting, are frequently mixed with codliver oil and cannot in the present state of our knowledge be distinguished from it.

The best Norwegian codliver oil (*U. S. Consular Report* No. 1843, Jan. 6, 1904) is extracted from the fat livers of the cod caught in the early part of the winter fisheries in the Lofoden Islands.   At this season of the year cod is about the only fish caught in that locality, and there is little opportunity of mixing other fish oils with it.   The Finmark oil is more liable to be mixed, as the cod caught there are accompanied by large numbers of haddock, ling, and other fish (Mann, *Pharm. Jour.*, 1903, **71**, 840).   Newfoundland codliver oil is considered inferior to Norwegian for medicinal purposes, and is sometimes largely adulterated with menhaden and seal oil (Sage *Chemist and Druggist*, 1903, **62**, 571).   Lewkowitsch states that commercial "Coast cod oil" is a liver oil which may have been obtained from any fish which the trawler's nets bring up from the

open sea; it may, therefore, contain oil from the shark, dogfish, etc., in addition to those mentioned in the first paragraph.

Several qualities of codliver oil are recognised in commerce: pale, used only in medicine; light brown, an after-yield, of inferior quality, but still largely used in medicine; and dark brown, or tanners' oil, obtained by roughly boiling down the livers remaining from the foregoing processes.

The purest codliver oil has a pale yellow colour, and is never quite colourless unless artificially bleached. It is limpid, has a slight odour and taste, and a faint acid reaction. If prepared at a high temperature, or if the livers be allowed to putrefy partially, the acid reaction is more decided and the colour pale or dark brown, the darkest varieties being transparent only in thin layers, and having a repulsive, fishy odour, and bitterish, acid taste.

The composition of codliver oil is very complex and not yet fully known. By fractionating the methyl esters of the fatty acids in *vacuo*, Bull (*Chem. Zeit.*, 1899, 23, (2), 996 and 1043; *Berichte*, 1906, 39, 3570) found that about 80% distilled over below 240°, and from these he obtained the saturated acids, myristic and palmitic, with a small quantity of stearic acid, the unsaturated acids, oleic and erucic, and two new acids, to one of which he gave the formula $C_{16}H_{30}O_2$, and to the other $C_{20}H_{38}O_2$. The latter he named *gadolinic acid;* it is said to occur in large quantity. By the sodium salt and ether method Bull has also isolated from Norwegian codliver oil from 17 to 21% of highly unsaturated acids, absorbing from 306 to 324% of iodine, which he states belong mainly to the series $C_nH_{2n-8}O_2$. (See also under "Sardine Oil.") These various acids exist as glycerides. Allen recorded the presence of a sensible quantity of cholesterol and of volatile fatty acids. The latter however, appear to be secondary products, due to putrefactive changes in the livers, and are not met with in medicinal codliver oil.

The following bases have been isolated from codliver oil: butylamine, isoamylamine, hexylamine, dehydrolutidine, morrhuine, and aselline. Trimethylamine, derived probably from the decomposition of the liver tissue, has also been detected.

The presence of biliary compounds, as stated by earlier investigators, is now denied.

Codliver oil contains traces of iodine and sometimes of bromine, but the form in which these elements exist is unknown. The

proportion of iodine, judging from the statements of different investigators, is variable. The question has been reinvestigated by E. C. Stanford, who found the proportion of iodine to be extremely minute, ranging from 0.138 to 0.434 mg. per 100 grm., with an average of 0.322. The proportion in the flesh of dry codfish and herrings is considerably larger than in codliver oil.

The mixed fatty acids of codliver oil have been found to possess the following characters:

		Authority
Refractive index at 60° F....................	1.4521	Thoerner.
Solidifying-point (titer test)		
Norwegian oil...........................	13.3°–13.9°	Lewkowitsch.
Medicinal oil...........................	17.5°–18.4°	Lewkowitsch.
Coast cod oil...........................	18.7°–19.3°	Lewkowitsch.
Dark unracked oil.......	22.5°–24.3°	Lewkowitsch.
Iodine value............................	164–171	Parry.
Mean molecular weight...................	287–290	Parry.

Examination of Codliver Oil.—Codliver oil to which iodine or compounds of iodine have been purposely added is employed in medicine. These additions are dissolved on agitating the oil with alcohol, and can be detected in the alcoholic solution by the usual tests. The ash left on igniting natural codliver oil contains no trace of iodine, but if an iodide has been added it will be found in the incombustible residue. The usual proportion of iodine in iodised codliver oil is about 0.1%.

A ferrated codliver oil is also employed, containing about 1% of ferrous oleate.

Good *medicinal codliver oil* should deposit no solid fat at 0° (*Pharm. Germ.*), but a granular crystalline deposit is often produced on cooling oils of the lower qualities.

The *British Pharmacopœia* describes codliver oil as pale yellow, with a slight fishy, but not rancid, odour. It states that it is the oil extracted from the fresh liver of the cod, *Gadus morrhua*, by the application of a temperature not exceeding 180° F. (82.2°); and from which solid fat has been separated by filtration at about 23°F. (−5°). It states that no solid fat should separate on exposure of the oil for 2

hours to a temperature of 32° F. (0°), but no test is given by which the oil from *Gadus morrhua* can be distinguished from allied oils.[1]

As previously stated, the "codliver oil" of commerce is in practice obtained from several members of the *Gadidæ*, or cod family; and, as long as it is produced from these fish solely, little exception can be taken. The livers of various other fish are, however, apt to be employed, and the detection of the substitution is very difficult. Adulteration with fish oils, such as menhaden oil, with blubber oils, such as porpoise, seal, and whale oils, and with mineral and rosin oils is also practised.

The constants of a number of fish-liver oils other than codliver oil, many of which were prepared from the fresh livers by Thomson and Dunlop and were, therefore, undoubtedly genuine, are given in the table on p. 297. Thomson and Dunlop,[2] who have studied the question carefully, are of opinion that, so far as present knowledge goes, taking into consideration the wide limits of variation of cod oils and the small amount of information we possess of the others, coal-fish. haddock, hake, ling, whiting, and skate liver oils are practically undistinguishable from each other and from codliver oil by chemical or physical tests. They also believe the detection of seal oil to be almost impossible by chemical methods, and that of whale oil difficult. The smaller yield of brominated glycerides, however, enables seal and whale oils to be detected and may eventually be found useful in detecting some of the others, such as coalfish oil. The liver oils, such as shark and dogfish, which contain large amounts of unsaponifiable matter, may be detected by means of this characteristic, if present in sufficient proportion, and porpoise oil can be easily detected, even in small proportion, by means of its high saponification and Reichert values.

The *sp. gr.* of codliver oil ranges from about 0.922 to 0.930 at 15.5°, the darker varieties being generally the heavier. The United States Pharmacopœia demands a sp. gr. of 0.918 to 0.922 at 25°, which corresponds with about 0.923 to 0.927 at 15.5°. The oil from fish allied to the cod is sometimes of a slightly higher sp. gr. Thus, that

[1] The United States Pharmacopœia describes codliver oil as "a fixed oil, obtained from the resh liver of *Gadus morrhua* Linné and of other species of *Gadus.*"
[2] Papers read before the Association of Public Analysts of Scotland, June, 1905, and Jan., 1906.

prepared in Grimsby from a mixture of the livers of cod, haddock, ling and whiting has a sp. gr. of 0.930; whilst the product obtained in Aberdeen from haddock livers has a sp. gr. of 0.931, is somewhat less viscous, and develops more heat with sulphuric acid than the other varieties of codliver oil. A sample of very much decomposed (44% free acid) brown codliver oil·examined by Bull had a sp. gr. of 0.941. It is evident that the sp. gr. affords no reliable indication of the presence of other fish oils in codliver oil.

The *iodine value* (Wijs) usually ranges from about 154 to 170, but a value as high as 181 has been recorded (Wijs). With reference to some of the very low numbers, below 154, which have been published, it may be noted that values estimated by the Hübl method are from 6 to 10% lower than those by the Wijs method for this oil, also that the oil from decomposed livers has a lower in iodine value than that from fresh livers.

The *saponification value* ranges from about 179 to 190. A lower value might be due to shark liver or dogfish liver oil, if accompanied by an excessive amount of the kind of unsaponifiable matter characteristic of those oils, or it might indicate the presence of rosin or mineral oil, which would be found wholly in the unsaponifiable matter. An abnormally high value might be due to porpoise oil.

The *refractometer* is of limited use, except as a rapid sorting test, and in this respect it is inferior to the iodine value. Dowzard (*Pharm. J.*, 1898, 532) found the refraction of 13 samples of Newfoundland and Norwegian and 1 sample of English codliver oil to range from +43.5 to +45.0 when tested in Amagat and Jean's *oleo-refractometer* at 22°, whilst 3 samples of pale seal oil ranged from +32.0 to +32.5, and he gave a table showing that 20% and upwards of seal oil could be detected by this instrument. But Pearmain's numbers (+40 to +46 for codliver oil and +30 to +36 for seal oil) show a much wider range for each oil and a much smaller difference between the two oils. Further tests of authentic samples with this refractometer seem desirable. Utz (*Zeits. öffentl. Chem.*, 8, 304) states that Newfoundland and Norwegian oils can be distinguished by means of the butyro-refractometer, and gives the following values. For comparison, results by Lythgoe (*J. Amer. Chem. Soc.*, 1905, 27, 887), Liverseege (*Analyst*, 1904, 29, 210), and Thomson and Dunlop are also given.

Description of oil	Newfoundland		Norwegian		West coast	East coast	Unknown	Unknown
Observer	Utz	Liverseege	Utz	Liverseege	Thomson and Dunlop			Lythgoe
15°	80 8–81.5	....	82.0–86.7	....	....	......	....	82.5–85.1
20°	77.5–78.1	....	78.6–83.2	....	....	......	....	79.3–81.9
25°	....	76.3–79.0	....	79.7–80.0	75.7	78.0	76.0–76.5	76.2–78.8
40°	... .	....	....	....	66.7	69.0	67.0–67.5	....

The *Reichert-Meissl* value of genuine codliver oil should not exceed about 0.4. A higher number would indicate that the oil had been prepared from livers which had undergone putrefaction, and in this case the iodine value would be lower and the sp. gr. higher. In illustration of this, Thomson and Dunlop give the following results:

EFFECT OF OXIDATION ON CODLIVER OIL

	Sample A		Sample B	
	Fresh	After oxidation	Fresh	After oxidation
Sp. gr. at 15°...................	0.9263	0.9321	0.9248	0.9378
Butyro-refractometer at 25°....	78.0	79.0	75.7	77.3
Iodine value (Wijs)...........	167.3	164.2	153.7	143.4
Saponification value..........	187.9	190.7	186.0	197.0
Reichert-Wollny value........	0.4	1.4	0.5	3.3
Free (oleic) acid..............	1.20	3.01	0.20	2.25

An abnormally high value might be due to the presence of porpoise oil, which has such a high Reichert value that a very small quantity would betray its presence.

The *unsaponifiable matter* in genuine codliver oil contains cholesterol, and does not exceed 1.5%. A higher percentage would indicate the presence of shark-liver oil, dogfish, sunfish, mineral, or rosin oil. The presence of phytosterol would prove the presence of vegetable oil.

Free fatty acid in fresh codliver oil should be very trifling in amount; medicinal oil should not contain more than 1 to 1.5% as a maximum; but in dark coloured, partially decomposed oils the acids may amount to 20 or 30% or even more.

The *yield of insoluble brominated glycerides* from some fish oils, notably seal oil, is much lower than from codliver oil and is the most

characteristic test yet discovered for the detection of these oils. In the following table, some results by Hehner and Mitchell, Walker and Warburton, and Lewkowitsch are summarised in the first column, and in the second Procter and Bennett's "Bromide Values" are given. These figures show the possibilities of the methods and the desirability of collecting further data:

Kind of oil	Percentage yield of brominated glyceride by Hehner and Mitchell's method	"Bromide value" (Procter and Bennett)
Codliver, brown...................	....	60.4
Codliver, undescribed...........	34.5–42.9	....
Codliver, Newfoundland.........	31.6	49.0
Codliver, Möller's...............	....	42.1
Menhaden......................	....	53.3–59.9
Fresh herring...................	....	44.8
Whale.........................	15.7–25.0	27.3–37.4
Coalfish.......................	....	29.8
Seal..........................	....	13.9–14.1
Shark-liver....................	20.2–22.0	16.5
Japan fish.....................	21.6	....
Linseed.......................	23.1–37.7	24.8

As most vegetable oils other than linseed yield no bromoglycerides, or only very small amounts, a low yield might be due to the presence of a vegetable oil. The phytosteryl acetate test would decide the question.

The British Pharmacopœia gives the following colour test:

"A drop of sulphuric acid added to a few drops of the oil on a porcelain slab develops a violet coloration."

In the United States Pharmacopœia the following three tests are given:

1. "If 1 drop of the oil be dissolved in 20 drops of chloroform and the solution shaken with 1 drop of sulphuric acid, the solution will acquire a violet-red tint, rapidly changing to rose-red and, finally, brownish-yellow." (In the German Pharmacopœia the oil is directed to be dissolved in carbon disulphide instead of chloroform.)

2. "If a glass rod moistened with sulphuric acid be drawn through a few drops of the oil on a porcelain plate, a violet colour will be produced."

3. "If 2 or 3 drops of fuming nitric acid be allowed to flow alongside of 10 or 15 drops of the oil, contained in a watch-glass, a red

colour will be produced at the point of contact. On stirring the mixture with a glass rod, the colour becomes bright rose-red, soon changing to lemon-yellow (distinction from *seal oil*, which shows at first no change of colour, and from *other fish oils*, which become at first blue and afterwards brown and yellow)."

In regard to the above tests, it may be remarked that the violet coloration produced by sulphuric acid is characteristic, not of cod-liver oil alone, but of liver oils generally. Rancid oils do not give the violet colour, but only the red. Thomson and Dunlop have obtained the violet colour with porpoise and seal oils which they extracted themselves from the blubbers and, therefore, the test is not exclusively characteristic even of liver oils. The reaction has been shown by Drummond and Watson (*Analyst*, 1922, **47,** 341) to stand in some relationship to the vitamin content, and they have devised a quantitative method of applying the test (see p. 43). As regards the test with fuming nitric acid, Tolman has shown that it is liable to give misleading results with perfectly genuine codliver oils of American origin. A variety of other colour tests has been proposed, but as they are more likely to mislead than to afford reliable information respecting the genuineness of codliver oil it is not thought worth while to describe them. Reference may be made, however, to the differences which Chapman has observed (*Analyst*, 1917, **42,** 161) in the colour reactions given by codliver oil and shark liver oil containing spinacene.

Skatel-iver oil, obtained from *Raia batis*, has been proposed as a substitute for codliver oil. It is bright or golden yellow in colour, is neutral in indication, and has a slightly fishy odour and taste. It darkens but little under the influence of chlorine, and is said to give an odour of valeric acid when heated with a solution of alkali. A sample examined by Thomson and Dunlop gave the results shown in the table on p. 297.

SHARK-LIVER OIL. SHARK OIL

(See also pages 113 and 299.) The shark oil known in commerce is chiefly obtained from the liver of the basking shark (*Cetorhinus (Selache) maximus*), chiefly caught off the coast of Norway, but the dogfish and several allied fish also contribute to it.

Shark oil has been largely employed in tanneries and as a substitute for codliver oil, but in England it is now almost disused.

SOME FISH-LIVER OILS OTHER THAN CODLIVER

Kind of oil	Brusmer	Coalfish			Haddock		Hake	Hoi	Ling			Skate	Whiting
Authority................	Liver-seege	Bull	Bull	Thomson and Dunlop	Liver-seege	Thomson and Dunlop	Thomson and Dunlop	Liver-seege	Bull	Liver-seege	Thomson and Dunlop	Thomson and Dunlop	Thomson and Dunlop
Particulars of source........	Nor-wegian	Aalesund, clear	Aalesund, clear	Prepared in laboratory from the fresh liver	....	Prepared in laboratory from the fresh liver	Prepared in laboratory from the fresh liver	Nor-wegian	Aalesund, clear	....	Prepared in laboratory from the fresh liver	Prepared in laboratory from the fresh liver	Prepared in laboratory from the fresh liver
Sp. gr. at 15°...............	....	0.9268	0.9254	0.9261	....	0.929	0.9256	....	0.9200	....	0.924	0.9298	0.929
Sp. gr. at 15.5°............	0.923	....	....	....	0.934	....	....	0.919	....	0.923	....	....	....
Butyro-refractometer at 25°..	75.0	....	....	77.0	84.0	81.0	76.0	73.7	....	74.0	75.0	82.5	81.0
Butyro-refractometer at 40°.	66.3	....	....	....	74.3	72.0	....	64.7	....	65.0	....	73.5	72.0
Valenta test, °[1]............	108°	....	....	....	73°	....	....	113°	....	105°	....	....	....
Free (oleic) acid, %........	0.05	3.6	10.9	0.27	0.3	2.37	1.05	0.05	5.5	0.05	0.34	0 33	0.65
Unsaponifiable matter, %....	....	....	1.83	1.14	1.0	1.30	1 38	....	2.23	....	1.0	1.08	1 06
Iodine value,[2]	138 H	162.2	....	161.1 W	179 H	186.4 W	154.0 W	124 H	132.6	133 H	151.8 W	191.1 W	....
Saponification value......	183	183.7	186.2	187 2	193	187.2	190.7	169	184.1	188	187.2	187 9	187 9
Specific temperature reaction.	....	....	....	257	....	300	....		....	....	232	322	317

Hoi note: If this is the piked dogfish, as suggested by Prof. Bridge, it belongs to the shark-liver oils.

[1] The acid used gave 65° with butter fat, and 94°–96° with codliver oil.

[2] H = Hübl.
W = Wijs.

Owing to frequent adulteration, the physical and chemical characters of shark oil have been misstated by many authorities. Thus it has been alleged to be of very low sp. gr., a character in all probability really due to the presence of a large proportion of mineral oil or similar adulterant.

It has been shown by Tsujimoto, however (*J. Ind. Eng. Chem.*, 1916, **8**, 289), that a hydrocarbon (or hydrocarbons) is a normal constituent of the liver oil of several species of Japanese sharks. He termed this compound *squalene*, and it appears to be analogous to the hydrocarbon termed *spinacene* which Chapman (*J. Chem. Soc.*, 1917, **111**, 56; *Analyst*, 1917, **42**, 161) isolated from the liver oils of two species of Portuguese sharks of which it was the main constituent. It is an unsaturated hydrocarbon, $C_{30}H_{50}$, yielding a dodecabromide $C_{30}H_{50}Br_{12}$. It is optically inactive, does not solidify at $-20°$, has a sp. gr. of 0.8641 at $15°/15°$, and when exposed to the air absorbs oxygen rapidly, forming a hard film resembling linoxyn.

It is probable that some, at least, of the shark oils previously reported to be adulterated with mineral oil have been oils which contained this hydrocarbon.

Ordinary shark oil is peculiar in yielding a very notable proportion of unsaponifiable matter, consisting in great part of cholesterol. If the sample be saponified in the usual way, and the aqueous solution of the soap agitated with ether, the separated ethereal layer leaves, on evaporation, a nearly colourless crystalline mass, which, if dissolved in boiling alcohol, deposits abundant plates of cholesterol, which yield the characteristic colour-reactions.

Analyses of a number of shark-liver and some other oils are given in the following table. It will be noticed that the percentage of unsaponifiable matter is irregular.

Shark oil has been found to yield from 20 to 22% of an insoluble brominated ester by Hehner and Mitchell's process, and the "bromide value" of a specimen examined by Procter and Bennett was found to be 16.5—much lower than that of codliver oil.

In regard to the three last-named oils in the following table, the "dogfish" is probably *Acanthias vulgaris*, the piked dogfish, a small shark frequently seen in shoal water on British coasts. The "crampfish" may be one of the electric rays, *Torpedo*. The "sunfish" may be the basking shark, which floats with its dorsal fin above the

ANALYSES OF SHARK OIL, ETC.

Authority	Description	Sp. gr.		Butyro-refrac-tometer. 25°	Unsaponi-fiable mat-ter. %	Free (oleic) acid, %	Iodine value	Saponifica-tion value	Hehner value	Acetyl value
		15°	15.5°							
Allen...............	Japanese...........	......	0 9260	....	2.82	....	....	177.3	....	....
Allen....	Crude..............	......	0.9185	....	8.70	....	....	169 6	....	....
Allen...............	Refined............	......	0 9285	....	0.70	....	....	197.6	....	....
Allen...............		......	0.9143	....	10.25	....	....	153.0	....	....
Allen		......	0.9136	....	17.30	....	....	140.0	....	....
Allen...............		......	0.9113	....	10.34	....	....	140.0	....	....
Bull	Norwegian (Finmark)	0.9105	....	....	21.18	3.1	III 9	146.1	....	....
Bull...	Norwegian (Finmark)	0.9130	....	....	21 08	1.3	114.9	148 5	....	....
Bull	Japanese...........	0.9156	....	....	14 39	0.75	128.3	163.4	....	....
Bull...............	Japanese...........	0.9177	....	....	12.54	0.44	136.0	163.5	....	....
Bull	Dark Japanese........	0.9166	....	....	2 43	19.9	116 3	183.2	....	....
Lewkowitsch	Arctic..............	0 9163	......	....	10.2	....	114.6	161.0	86.9	11.9
Thomson and Dunlop	....	....	....	72 0	15 28	....	....	....	....	....
Tsujimoto..........	Japanese	0.8664	....	....	....	....	309	28 2	......	....
Thomson and Dunlop	Dogfish oil, prepared in laboratory from the fresh liver	0.9179	....	71.2	8.40	trace	126.4	169 7	....	....
Bull..	Crampfish oil, American	0.9090	....	....	21.97	0.39	107.3	148.2	....	....
Bull	Sunfish oil, American..	0.901	..	....	24.12	1.07	102.7	147.6	.. ..	... ...

water like the true sunfish, *Orthagoriscus mola;* the latter is not a shark.

The liver oils from 12 species of Japanese sharks examined by Tsujimoto (*J. Chem. Ind. Tokyo*, 1918, **21**, 1015) had iodine values ranging from 91.3 to 236.6; those of low sp. gr. (below 0.9 at $15°/4°$ invariably contained the hydrocarbon squalene (see p. 97).

Three specimens of oil from the liver of the basking shark (*Cetorhinus maximus*) contained 41.92 to 55.51% of unsaponifiable matter, consisting largely of the unsaturated hydrocarbon squalene. This hydrocarbon forms hexahydrohalides of the general formula $C_{30}H_{50}.6HX$, which may be crystallised and serve for the identification of the hydrocarbon.

MENHADEN OIL

(See p. 113.)   This oil is obtained from *Alosa menhaden*, a North American fish allied to the herring.   It is derived from the whole body of the fish, by boiling with water and pressing.   It resembles codliver oil in many respects, and is used to adulterate Newfoundland codliver oil (Sage).   It is chiefly employed for dégras and as a currying oil.   Sometimes it is added as an adulterant to linseed oil, and is used as a substitute for that oil in printing inks.   Some constants and variables of menhaden oil are given in the following table:

Authority	Thomson and Ballantyne	Bull		Liverseege
Description	Brown	Extra refined	Natural pressed	
Sp. gr. at 15°..................	....	0.9311	0.9284	....
Sp. gr. at 15.5°.................	0.9311	....	....	0.931
Butyro-refractometer, 25°.......	....	....	....	80.7
Butyro-refractometer, 40°.......	....	....	....	71.3
[1] Valenta test, °...............	....	....	....	78°
Free (oleic) acid, %...........	7.57	nil	5.4	0.25
Unsaponifiable matter, %.......	1.60	1.43	2.15	0.6
Iodine value (Hübl)............	160.0	172.6	139.2	174.0
Saponification value...........	189.3	188.75	193.0	193.0

[1] The acid used gave 65° with butter fat, and 94° to 96° with codliver oil.

Twitchell (*J. Ind. Eng. Chem.*, 1917, **9**, 581), using his method of determining the composition of fatty acids by the lowering of the m. p. on adding a known amount of the mixture to a pure acid of known m. p. (see p. 519), found menhaden oil fatty acids to have the following composition: palmitic acid, 22.7; myristic acid, 9.2; stearic acid, 1.8; unsaturated acids with 18 carbon atoms, 24.9; with 20 carbon atoms, 22.2; and with 22 carbon atoms, 20.2%.

Adulteration with mineral or rosin oil would be detected by estimating the unsaponifiable matter, which in genuine menhaden oil does not exceed about 2%.

SARDINE OIL. JAPAN FISH OIL

(See p. 113.) Sardine oil is obtained from species of sardines belonging to the family *Clupeidæ*. According to Tsujimoto (*J. College of Engineering*, Tokyo Imp. University, 1906, **4**, 1), Japanese sardine oil is obtained from *Clupanodon melanosticta* T. and S., and does not possess the low iodine value commonly attributed to it. Three authentic samples examined by him had (Wijs) iodine values of 180.7, 180.6, and 187.3, respectively (see table below). These samples were greenish-brown to reddish-brown in colour, and all deposited large quantities of "stearine" at low temperatures. The iodine values of the samples examined by Bull were probably estimated by the Hübl method, and one, at any rate, of the samples (the last), besides being a badly decomposed oil, was of very suspicious quality.

Tsujimoto obtained from the mixed acids 44.2 to 47.1% of an insoluble octobromide derived from an acid of the formula $C_{18}H_{28}O_2$, belonging to the series $C_nH_{2n-8}O_2$ (to which he gave the name of *clupanodonic acid*) which constituted about 13 to 14% of the mixed fatty acids from the oil. The free acid liberated from the bromide was a pale yellow liquid with a fishy smell. It had an iodine value of 344.4, and oxidised in the air, forming a dry varnish. No insoluble hexabromide was obtained. The same acid was found in herring oil (3.8 to 6.5%) and in whale oil (8.39%). Bull (*Chem. Zeit.*, 1899, **23**, 1044) had previously assumed the existence of highly unsaturated acids of the $C_nH_{2n-8}O_2$ and $C_nH_{2n-10}O_2$ series in fish oils, and had

isolated from a large number of different kinds of oil by the sodium salt and ether method variable percentages of acids absorbing more than 300% of iodine. A sample of Japan fish oil examined by Walker and Warburton (*Analyst*, 1902, **27**, 937) gave 21.6% of an insoluble bromoglyceride, and the mixed fatty acids from the same sample gave 23.2% of an insoluble bromide by Hehner and Mitchell's process. Fahrion (*Chem. Zeit.*, 1893, **17**, 938) isolated from European sardine oil a highly unsaturated liquid fatty acid (*jecoric acid*), $C_{18}H_{30}O_2$, isomeric with linolenic acid, and 13.6% of palmitic acid, but jecoric acid was not present in a specimen of the Japanese oil examined by him. This is in accordance with the fact that the iodine value of the European oil is lower than that of the Japanese oil.

When exposed to the air European sardine oil becomes viscous and resinous, but, unlike the Japanese product (*supra*), does not form a dry film of varnish.

The Japanese sardine oil of commerce is obtained by boiling the entire fish with water and pressing the mass. It is liable to be mixed with other fish oils. It is principally used in commerce for making soap and dégras.

Authority	Source and description	Sp. gr. 15°	Sp. gr. 15.5°	Refractive index, 20°	Unsaponifiable matter, %	Free (oleic) acid, %	Iodine value W = Wijs	Saponification value	M. p. of mixed fatty acids
Bull........	Japan, clear......	0.9283	......	......	1.96	1.1	134.1	189 0	......
Bull........	Japan, white......	0.9338	......	......	1.55	1.1	162.4	193.7	......
Bull........	Japan, white......	0.9279	......	......	1.9	6.0	156.2	191.9	......
Bull........	Japan, white......	0 9272	......	......	1.81	7.2	138.3	191.4	......
Bull........	Japan, pale brown	0.9324	......	......	0.95	6.9	171.3	190.6	......
Bull........	Japan, turbid.....	0 9155	......	......	2.27	17.3	104.0	178 8	......
Tsujimoto...	Chita...........	......	0.9347	1.4808	......	0.66	180 7W	195.8	35.4°
Tsujimoto...	Chōshi...........	......	0.9318	1.4802	......	4.11	180.6W	196.2	36.2°
Tsujimoto..	Hakodaté........	......	0.9316	1.4807	......	2.58	187.3W	194.8	35.8°

HERRING AND OTHER FISH OILS

The following characteristics of commercial herring oil have been published by Bull. Figures obtained with sturgeon oil and "whitefish" oil are added.

Kind of oil	Sp. gr. $15°$	Free (oleic) acid, %	Unsaponifiable matter, %	Iodine value	Saponification value
Herring oil, white, Japanese......	0.9215	0.9	10.68	131.0	170.9
Herring oil, white, Japanese......	0.9222	4.1	7.75	141.4	175.9
Herring oil, clear, Japanese.......	0.9254	5.4	·1.58	142.0	188.3
Herring oil, clear, Japanese.......	0.9310	7.9	2.15	131.8	193.7
Herring oil, turbid, Japanese......	0.9202	6.0	1.33	134.2	184.6
Herring oil, cold-filtered, Japanese.	0.9202	7.3	1.39	135.5	184.7
Herring oil, brown, English.......	0.9391	20.2	2.64	132.7	184.8
Sturgeon oil, American...........	0.9236	0.11	1.78	125.3	186.3
Whitefish oil, Finmark...........	0.9268	2.0	1.75	127.4	201.6

SEAL OIL

(For constants see page 113.) This oil is rendered in Greenland from the blubber of different species of seal, *Phoca grœnlandica*, etc., and is subsequently refined in Denmark Chemically it is composed of glycerides of saturated fatty acids (palmitic acid) and unsaturated fatty acids, including oleic and physetoleic acids (Ljubarsky). Linolic and still more unsaturated fatty acids have also been found in seal oil. Thus, Bull obtained from 2 samples 7.78 and 11.96% of highly unsaturated acids absorbing, respectively, 306.1 and 330.3% of iodine. Procter and Bennett obtained a much smaller yield of insoluble brominated esters from seal oil than from codliver oil (see under **Codliver Oil**).

Commercial seal oil varies in colour from very pale yellow ("Water white") to dark brown, and from the figures which have been published by several observers it appears to be very uniform in character. Thus, the published sp. gr. numbers at 15° to 15.5° range between the narrow limits of 0.9238 to 0.9267, and the iodine values, estimated by the Hübl method, between 132 and 152. A sample rendered in the laboratory by Thomson and Dunlop had a Wijs iodine value of 162.6. The published saponification values range from 187.5 (Bull, Sandefjord oil) to 196.2 and the percentages of unsaponifiable matter from 0.38 to 1.00, except that in the Sandefjord sample of low saponification value Bull found 1.8% of unsaponifiable matter.

Seal oil readily oxidises and is unsuitable for use as a lubricant. It evolves rather less heat with sulphuric acid than codliver oil.   At 15.5° it has about 3/5 of the viscosity of refined rape oil.   In the butyro-refractometer the following readings have been obtained:

	25°	40°
Liverseege...	72.7	64.0
Thomson and Dunlop, commercial oil....................	73	64
Thomson and Dunlop, oil rendered in laboratory..........	76.2	.....

Two samples of oil from the Vikare seal, *Phoca fœtida,* examined by Schneider and Blumenfeld (*Chem. Zeit.,* 1905, 29, 53) had distinctly higher sp. gr. and iodine values than the ordinary commercial oil, as is shown below:

	Oil from *Phoca fœtida*	
Sp. gr. at 15°.....................................	0.9321	0.9336
Butyro-refractometer, 20°.......................	87	....
Free (oleic) acid, %...........................	0.24	0.54
Iodine value (Hübl)............................	191.3	193.3
Saponification value.............	188.5	189.0
Hehner value....................................	95.6	95.8
Reichert-Meissl value..........................	1.55	0.96
Mixed Fatty Acids.		
Solidifying-point................................	13.0°	14.0°
Iodine value....................................	195.3	201.8
Neutralisation value............................	196	198

WHALE OIL (TRAIN OIL)

Whale oil proper is from the blubber of the Greenland or Arctic "right" whale, *Balæna mysticetus;* but commercial whale oil includes the oil from the southern right whale, *Balæna australis,* and other species of *Balænidæ* and *Balænopteridæ* (finbacked whales) belonging to the sub-order *Mystacoceti,* or whalebone-yielding whales. The term "train oil," formerly applied to whale oil, is now extended to the oil from the blubber of any marine animals, including seals.

The oils from the different species of dolphin and porpoise (*Delphinidæ*) are glyceridic in nature, like ordinary whale oil, but the

oils from the cachalot, and probably other *toothed* cetaceans, are essentially different both in chemical constitution and practical applications, and hence are described in another section (see page 113).

Whale oil is usually extracted by boiling the blubber with water and skimming the oil from the aqueous liquid and refuse tissue. It is graded according to colour, taste, smell, and acidity; the highest grades being pale coloured, nearly neutral oils, of only slight odour, and the lower grades dark coloured, acid oils, having a marked and offensive "fishy" smell and taste. In the United States crude whale oil is separated by refrigeration and pressing into "winter whale oil," congealing at 36° to 40° F., and "whale foots" or "stearine." Occasionally "spring" and "summer" oils are also produced. By the usual method of pressing, the oil of the "right" whale, taken in high northern latitudes, gives about 8% of "stearine"; that of the whales taken in the vicinity of the equator or south of it, about 15%; humpback or finback whales give 12% (*United States Fish Commission Report*, 1902). The whale oil "stearine," which consists largely of palmitin, is sometimes used for soap-making, though the odour of the product indicates its origin. The oil from the finback whales is considered inferior to that from the "right" whales; some varieties, especially the southern product known in commerce as Bahie whale oil, exhibit strongly marked drying properties. The results of examination of a number of commercial whale oils by Bull (*Chem. Zeit.*, 1899, 23 (2), 1044) are given in the following table:

Description	Sp. gr. at 15°	Free (oleic) acid, %	Unsaponifiable matter, %	Iodine value	Saponification value
Arctic whale oil, refined, American..	0.9234	0.95	2.11	117.4	185.0
Antarctic "right" whale oil, American	0.9257	0.28	1.46	136.0	183.1
Crude white whale oil, American....	0.9222	1.25	1.37	127.4	183.9
Whale oil No. 1, unrefined, Finmark.	0.9181	0.43	2.36	104.0	188.6
Whale oil No. 2, unrefined, Finmark.	0.9182	1.8	3.3	....	188.3
Whale oil No. 3, unrefined, Finmark.	0.9162	13.3	2.42	96.0	185.7
Whale oil No. 4, unrefined, Finmark.	0.9205	29.1	3.4	89.0	182.1
Whale oil No. 1, refined, Glasgow...	0.9214	0.7	2.33	113.2	184.7
Yellow whale oil, refined, Glasgow...	0.9232	5.3	1.89	110.0	185.9
Brown whale oil, refined, Glasgow...	0.9272	18.6	3.22	125.3	160.0
Dark whale oil, refined, Glasgow....	0.9170	49.3	3.03	103.1	178.3

The chemical composition of whale oil is variable. It is composed of esters of saturated and unsaturated acids, some of the latter being highly unsaturated. Hehner and Mitchell obtained 25%, and Walker and Warburton a mean of 15.84% of brominated ester from samples. Bull, by the sodium salt and ether method, found a smaller proportion of highly unsaturated acids in whale oil than in most other marine oils. Tsujimoto found 8.39% of an acid of the $C_nH_{24-8}O_2$ series (see under **Sardine Oil**).

The amount of unsaponifiable matter is variable, but does not exceed 4%. This and the much higher sp. gr. readily distinguish ordinary whale oil from the sperm oils. Adulteration with mineral or rosin oil would, of course, increase the percentage of unsaponifiable matter. Rosin oil is the most likely adulterant. A sample of "whale oil" supplied for oil-tempering steel, examined by the Archbutt, had a sp. gr. of 0.9608 at 15.5°, required only 7.72% of potash for saponification, and contained 60.3% of unsaponifiable matter of sp. gr. 0.981, easily soluble in acetone.

The recorded sp. grs. of genuine whale oil range from 0.917 (Liverseege) to 0.927 (Bull); the saponification values from 188 to 194 (Schweitzer and Lungwitz), the low value of 160 obtained by Bull being exceptional. The range of iodine values is wide, 89 to 136 in the samples examined by Bull, and there was also a fairly wide range in the percentages of highly unsaturated acids which he found by the sodium salt and ether method.

8 samples of whale oil examined by Milrath (*Zeitsch. öffentl. Chem.*, 1907, **19,** 371) in the butyro-refractometer gave readings of 63.1 to 70.2 at 25° and 56.2 to 63.0 at 40°.

The mixed fatty acids of whale oil have been found to possess the following characteristics:

		Authority
Sp. gr. at $\frac{100°}{100°}$	0.8922	Archbutt.
Solidifying-point (titer test)	22.9°–23.9°	Lewkowitsch.
Butyro-refractometer reading, 40°	43.3	Liverseege.
Iodine value	130.3–132.0	Schweitzer and Lungwitz.

Whale oil is liable to adulteration with seal oil, which so nearly resembles whale oil that it cannot be detected by chemical means, except perhaps by a lowering of the "bromide value" (see under Codliver Oil).

Whale oil is used as an illuminant and to some extent as a lubricant. The lower grades are used in leather manufacture and for tempering steel. The characteristics of hydrogenated whale oil, which has been used on the continent as a constituent of margarine, are given on page 501.

PORPOISE OIL

(See also p. 113.) Commercial porpoise oil is derived not only from the black porpoise, *Phocæna communis*, usually caught off the coast of Denmark and in the Mediterranean and Black Sea near Trebizond, but also largely from the beluga or white whale, *Delphinapterus leucas*, caught in the White Sea, the St. Lawrence, and on various parts of the Canadian coasts. The oils from the "grampus" or killer whale, *Orca gladiator*, and the various species known as blackfish, especially *Globicephalus melas*, also rank as "porpoise oil."

Porpoise oil is prepared in much the same manner as whale oil. In some instances, oil of a superior quality drains from the blubber at the ordinary temperature, but the greater part is obtained by boiling the tissue with water. The oil is pale yellow to brown in colour and, according to Schaedler, is composed of the glycerides of valeric, palmitic, stearic, physetoleic, and oleic acids.

The liquid "oleine," obtained from the soft fat of the head and jaw by exposing the fat to a low temperature and straining off the oil which remains fluid, contains a much larger percentage of valerin and of unsaponifiable matter than the body oil. In the case of *G. melas*, the mass of fat taken from the head has the shape of a half watermelon, and the liquid oil obtained from it is known as "melon oil." These jaw oils are specially prepared in America for lubricating watches and other delicate mechanism, and command a high price. The body oils are also used for lubricating.

Porpoise oil is remarkable for the large proportion of valerin which it contains. A sample examined by Allen yielded 5.06% of volatile fatty acids, having a mean combining weight of 104.7 ($C_5H_{10}O_2$ = 102). Chevreul, the original discoverer of valeric acid, which he isolated from porpoise oil and called "phocenic acid," prepared

Description	Porpoise body oil					Blackfish body oil		Porpoise jaw oil					Black-fish jaw oil	Kelley's superfine (American) watch oil
Authority	Allen	Bull	Steen-buch	Schnei-der and Blumen-feld	Thomson and Dunlop	Bull	Moore	Moore	Moore	Moore	Steen-buch	Bull	Moore	Archbutt and Deeley
Source, etc.		American		From *Phocæna communis*				Unstrained	Skimmed and Strained	Skimmed and Strained		American	Skimmed and Strained	
Sp. gr. at 15°................		0.9258	....	0.9334	0.9352	0.9266	....	....	....	....	....	0.9258	....	....
Sp. gr. at 15.5°.............	0.926	....	....	....	....	....	....	....	....	....	....	....	....	0.930
Butyro-refractometer, 25°....		....	....	62.7	54.8	....	....	....	....	....	....	....	....	....
Butyro-refractometer, 40°....		....	....	....	46.3	....	....	....	....	....	....	....	....	....
Free (oleic) acid, %........		nil	....	0.6	0.10	0.38	....	....	....	....	....	2.5	....	....
Total volatile acids, as valeric acid, %		....	....	....	....	....	2.71	1.64	19.91	24.30	....	....	28.17	....
Unsaponifiable matter, %....		3 7	....	....	0.67	2.01	....	....	....	....	....	16.4	....	10.6
Iodine value[1].............		119.4	....	111.2 H	88.3 W	126.9	99.5	76 8	49.6	30 9	....	21.5	32.8	....
Saponification value........	216.0–218.8	195.0	....	224.8	256.6	203.4	197.3	143.9	253.7	272.3	....	269.3	290.0	....
Hehner value...............		....	....	85.5	....	....	93 07	96.50	72 05	68 41	....	....	66.28	....
Reichert value, 2.5 grm......		....	....	....	....	....	5.60	2.08	47.77	56.00	....	....	65.92	....
Reichert-Meissl value.......	11–12	....	46.9	42.1	81.4	....	....	....	....	....	131.6	....	....	115.1
Mixed Fatty Acids.														
Sp. gr. at 15°...............		....	....	0.9121	....	....	....	....	....	....	....	....	....	....
Solidifying-point...........		....	....	18.0°	....	....	....	....	....	....	....	....	....	....
Iodine value...............		....	....	126.0	....	....	....	....	....	....	....	....	....	....
Neutralisation value........		....	....	207.0	....	....	....	....	....	....	....	....	....	....

[1] H = Hübl.   W = Wijs.

barium salts of volatile fatty acids equivalent to 9.63% of valeric acid, so that the composition of the oil is evidently very variable. From a sample of oil from *Globicephalus melas* Chevreul prepared barium salts corresponding to 20.6% of valeric acid, besides a considerable proportion of spermaceti. Hence the oils from the *Delphinidæ* appear to form an intermediate group between those of the sperm whales and the whalebone whales.

The different percentages of volatile acid found is no doubt due to the difference in composition between the body oils and the jaw oils. Steenbuch found valeric acid to constitute 10% of the soluble acids of the body oil and 26% of the acids from the jaw oil. Moore obtained volatile acids equivalent to 19.91 and 24.30% of valeric acid from two samples of jaw oil, but only 2.71% from a sample of body oil.

Owing to its peculiarity of composition, porpoise oil has a high saponification value and Reichert-Meissl value. It is saponified with great facility by means of aqueous potassium hydroxide solution, the product being coloured reddish-brown. In the elaidin test, porpoise oil gives but little solid elaidin. The results of the examination of a number of samples of these oils are given in the table on p. 308.

XI. SPERM OIL GROUP

Sperm Oil. Arctic Sperm Oil. Bottlenose Oil. Dolphin Oil

SPERM OIL

(See p. 113.) Sperm oil proper is obtained from the head-cavities and blubber of the cachelot or sperm whale (*Physeter macrocephalus*). Several other of the toothed whales (*Odontoceti*) yield allied products, and the oil from one of these, namely, the doegling, or bottlenose whale (*Hyperoodon rostratum*) is known under the name of "Arctic sperm oil."

Sperm oil, on cooling, readily deposits crystalline scales of spermaceti. This is removed by filtration, but unless the operation is conducted at a very low temperature a portion of the wax is liable to remain in solution.

In the oil refineries at San Francisco the crude sperm oil is separated by refrigeration and pressing into: 1. "winter sperm oil,"

congealing below 3°, the yield being about 75%; 2. "spring sperm oil," congealing at 10° to 11°, 9%; 3. "taut-pressed oil," melting at 32° to 35°, 5%; and 4. "crude spermaceti," melting at 43° to 46°, 11% (United States Fish Commission Report, 1902).

Sperm oil is a thin yellow liquid, and when of good quality is nearly free from odour. Inferior specimens have an unpleasant "fishy" smell and taste. Its sp. gr. is very low, ranging between 0.875 and 0.884 at 15.5°.[1]

Sperm oil is one of the most valuable oils in commerce. It has been found preferable to any other fixed oil for lubricating the spindles of cotton and woolen mills and for light machinery generally, owing to its limpidity and freedom from tendency to "gum."

Some indication of the peculiar composition of sperm oil was given in 1823 by Chevreul. Chevreul's observations seem to have been wholly forgotten until Allen some years ago called attention to the unique constitution of sperm oil.

Sperm oil gives, on saponification, products very different from those yielded by ordinary oils. When saponified with potassium hydroxide it forms potassium oleate and monohydric alcohols, the nature of some of which is at present unknown. By agitating the aqueous solution of the resultant soap with ether, the higher alcohols are dissolved, and may be recovered by evaporating the solvent. The fatty acids may be isolated by acidifying the soap solution and again shaking with ether. From the residual liquid glycerol can be obtained, though in much smaller proportion than from most other oils and fats. The existence of glycerol has been proved by Fendler (*Chem. Zeit.*, 1905, 29, 555) and Dunlop (*J. Soc. Chem. Ind.*, 1908, 27, 64), whose results are given in the following table:

Oil	Wax alcohols, %	Glycerol, %	Authority
Sperm	39.17	1.32	Fendler.
Cachalot "head"	41.16	2.51	Dunlop.
Cachalot "head"	42.28	1.53	Dunlop.
Cachalot "body"	44.30	1.36	Dunlop.
Arctic sperm	38.02	2.56	Dunlop.
Arctic sperm	39.22	2.26	Dunlop.

[1] *Dealers in sperm and similar oils commonly use a special hydrometer, devised by Casartelli, on the scale of which water is 0° and rape oil 28°. Sperm oil stands at 44° to 46° and southern whale oil at about 24° on the same scale.*

The higher alcohols, isolated in the manner described above, form a pale yellow, solid, semi-crystalline substance, the m. p. of which depends on the completeness with which the oil had been previously purified from spermaceti. They are insoluble in water, but readily soluble in alcohol and ether, and are volatile, apparently without change, in a vacuum, condensing as a perfectly colourless liquid, of 0.830 sp. gr. at 100°, which solidifies on cooling to a crystalline mass. The ether-residue from sperm oil is apparently a mixture of homologous alcohols which, according to Lewkowitsch (*J. Soc. Chem. Ind.*, 1892, **11**, 134) belong for the most part, if not wholly, to the ethylene series. Dunlop published the following results of an examination of the unsaponifiable matter (wax alcohols, etc.) from six authentic samples of sperm oil from which the spermaceti had been removed:

Description	Iodine value (Wijs)	M. p., °	Butyro-refractometer	
			25°	40°
1a. Cachalot oil from "head-matter"......	60.43	32–32.5	....	35.0
1b. Cachalot oil from "body-matter".....	83.17	24.5–25.5	47.0	39.0
2a. Cachalot oil from "head-matter"......	53.7	31.5–32.5	....	35.0
2b. Cachalot oil from "body-matter".....	79.77	23–24	47.0	....
3. Arctic sperm oil......................	80.35	23.5–24	46.7	38.7
4. Arctic sperm oil......................	69.4	23	46.2	38.2
5. Southern sperm oil...................	68.5	26.5	45.7	37.7
6. Southern sperm oil...................	69.37	....	....	....

The following table contains some further results given by the mixed alcohols from Southern sperm (S), Arctic sperm (A), and genuine commercial oil (C) the origin of which was unknown:

	Lewkowitsch	Archbutt
Sp. gr. at $\frac{15.5°}{15.5°}$..........................	....	0.8535–0.8588c
Sp. gr. at $\frac{100°}{100°}$..........................	....	0.8271c
Solidifying-point, °......................	⎰ 23.0–23.4s ⎱ 21.7–22.0A	....
M. p., °...............................	⎰ 25.5–27.5s ⎱ 23.5–26.5A	....
Iodine value...........................	⎰ 64.6–65.8s ⎱ 64.8–65.2A	65.6–69.3c ....
Acetyl saponification value.....	....	184.9s 186.2A

Blakeley and Reilly (*J. Ind. Eng. Chem.*, 1917, 9, 1099) separated alcohols which had an iodine value of 63.9 to 74.1, melted at 20° to 27°, and yielded an acetate with a saponification value of 189.5 to 216.0.

The fatty acids from sperm oil appear to be mainly unsaturated acids of the oleic series, with small quantities of saturated acids and of acids more unsaturated than oleic. Fendler obtained from the mixed fatty acids of an authentic sample of sperm oil, by the lead salt and ether method, 14.22% of saturated acids and 87.58% of unsaturated acids. Bull, by the sodium salt and ether method, obtained from four samples of sperm and Arctic sperm oils quantities of highly unsaturated acids ranging from 3.65% (Arctic sperm) to 7.53% (Southern sperm), and absorbing from 121.2 to 159.5% of iodine.

The following results have been recorded for the mixed fatty acids of sperm and Arctic sperm oils:

	Sperm oil	Arctic sperm oil	Authority
Sp. gr. at 15°....................	0.8999	....	Fendler.
Sp. gr. at 15.5°..................	0.899	....	Allen.
Solidifying-point, °..............	12.4	....	Fendler.
Solidifying-point (Bach), °........	16.1	10.0	Archbutt and Deeley.
Solidifying-point "titer" test, °......	11.1–11.9	8.3–8.8	Lewkowitsch.
M. P., °.......................	18.8	....	Fendler.
M. p., °....	....	10.3–10.8	Lewkowitsch.
M. p., °.......................	13.3	....	Williams.
M. p. (Bach), °..................	21.4	16.1	Archbutt and Deeley.
Iodine value....................	83.2–88.1	82.2–83.3	Lewkowitsch, Williams.
Mean molecular weight...........	281–294	....	Allen.
Mean molecular weight...........	305	....	Williams.
Mean molecular weight..........	237.7	....	Fendler.
Neutralisation value.............	236.2	....	Fendler.

Examination of Commercial Sperm Oil.—The peculiar physical characteristics and chemical constitution of sperm oil afford ample means for its detection and estimation in presence of other oils. This is important, as the high price of sperm oil renders it liable to be mixed with or replaced by other oils.

No means of distinguishing sperm and Arctic sperm oils by chemical tests is known. In commerce they are distinguished by their taste and smell, and the fatty acids of sperm oil appear to have a somewhat higher m. p. than those of Arctic sperm oil, but in other respects they are so much alike that it is convenient to consider them together. Authentic samples of the two oils examined by Archbutt and Deeley (*Lubrication* and *Lubricants*, 1907, p. 325) gave the following results:

Description	1 Finest southern sperm oil	2 Deodorised Arctic sperm oil
Colour......................	Dark golden yellow	Paler than No. 1.
Smell.......................	Slight fishy	Fishy; more pungent than No. 1.
Sp. gr. at 15.5°.............	0.8809	0.8787
Viscosity (absolute) at 15.5°......	0.3915	0.4148
Freezing-point.................	Practically	solid at 0°
Oleo-refractometer reading at 22°..	−13	−13
Free (oleic) acid, %...........	1.2	1.6
Unsaponifiable matter, %.........	39.1	39.7
Maumené test; 50 grm. oil, 10 c.c. of 97% sulphuric acid	46.0°	44.8°
Saponification value............	120.0	125.0
Iodine value...................	84.4	81.5
Mixed Fatty Acids.		
M. p. (Bach), °...............	21.4	16.1
Solidifying-point (Bach), °.......	16.1	10.0
Mixed Alcohols.		
Acetyl saponification value	184.9	186.2

A number of samples of southern and Arctic sperm oil, obtained from reliable sources, have been examined by Dunlop (*J. Soc. Chem. Ind.*, 1908, **27**, 64), whose results are given in the following table:

		Cold test, °	Sp. gr. at 15.5°	Butyro-refrac-tometer, 25°	Free (oleic) acid, %	Wax alco-hols, etc., %	Iodine value (Wijs)	Saponi-fication value
1a	Cachalot oil from "head matter"..................	9.5	0.8779	49.7	4.60	42.28	76.30	140.2
1b	Cachalot oil from "body matter"..................	8.5	0.8772	54.8	1.42	42.14	92.85	124.8
2a	Cachalot oil from "head matter"..................	7.0	0.880	50.0	1.39	41.16	70.35	144.4
2b	Cachalot oil from "body matter"..................	7.0	0.8757	54.6	1.07	44.30	87.90	122.0
3	Arctic sperm oil...........	.....	0.8806	55.2	0.73	38.02	88.75	129.0
4	Arctic sperm oil...........	.....	0.8786	55.3	1 43	39.22	82.80	124.8
5	Southern sperm oil........	.....	0.8791	54.6	1.16	41.16	84.35	129.7
6	Southern sperm oil........	.....	0.8798	......	2.53	39.20	84.37	129.0

The oils numbered 1 and 2, from 2 animals, represent the oil after removal of the spermaceti from the "head" and "body" matter, respectively; these oils are not usually kept separate in practice, but are mixed together, and hence the differences in the iodine and saponification values, though noteworthy, are not of practical importance.

The "*flake test*," *i. e.*, the temperature at which solid matter separates from the oil, was found by Blakeley and Reilly (*J. Ind. Eng. Chem.*, 1917, 9, 1099) to range from 3.3° to 10°.

The *sp. gr.* of genuine commercial sperm oil ranges from 0.878 to 0.884 at 15.5°. In the absence of mineral oil, Dunlop considers that a figure within 0.875 and 0.882 will generally indicate a pure oil. Adulteration with any other fixed oil would raise the gravity, but this could be corrected by the addition of light mineral oil.

The *saponification value* of genuine sperm oil appears to range from about 120 to 137. It would be raised by the addition of a fixed oil and lowered by that of mineral oil, but a mixture of the two might be added having the same saponification value as sperm oil.

The nature and estimation of the saponification products afford the most satisfactory means of detecting adulterations of sperm oil, which, when genuine, yields from 60 to 63% of insoluble fatty acids, and 37 to 42% of ether-residue consisting of higher alcohols. No other animal or vegetable oil, except shark-liver oil and oils from allied *Cetacea* (*e. g.*, bottlenose oil), is known to yield more than 2% to ether, and, with few exceptions (*e. g.*, porpoise oil and some varieties of whale oil), all other fixed oils yield fully 95% of insoluble fatty acids, and from 10 to 12% of glycerol. Hence, in a case of

adulteration of sperm oil with any other fatty oil, estimation of the ether-residue will detect the admixture and approximately estimate the proportion. Some specimens of shark-liver oil yield a considerable proportion of ether-residue, and hence if shark oil is present, the ether process will be rendered inaccurate. Genuine shark-liver oil has a comparatively high sp. gr. (0.911 to 0.929), and has a very high halogen-absorption, besides giving a well-marked violet coloration and great increase of temperature with strong sulphuric acid.

The foregoing process, if used without discretion, would fail in the case of a mixture of mineral oil and a fatty oil in certain proportions, but a careful consideration of the results and further examination of the products will allow of such a mixture being readily distinguished from sperm oil. Thus, from an inspection of the figures in the following table, it appears that whilst the saponification products yielded by sperm oil would be approximately imitated by those given by a judicious mixture of mineral oil with rape oil, in the latter case the sum of the fatty acids and ether-residue would be several units less than 100, and there would be a larger proportion of glycerol produced. Besides, the ether-residue would probably be insoluble in cold rectified alcohol (see below), and to obtain a mixture of the same sp. gr. as sperm oil, so very light a mineral oil would require to be used that it would necessarily be liquid, even at 0°, and would have so low a flash-point that it could without difficulty be detected in, and even distilled out of, the original oil or the ether-residue Sperm oil does not flash below 400° F.

| | Products of the saponification of 100 parts of oil | | | |
| | | | Ether-residue | |
	Fatty acids	Glycerol	Percentage	Characteristics
Sperm oil.................	60 to 64	1.3 to 2.6	37 to 42	Solid; soluble in spirit.
Ordinary fixed oils.........	95 to 96	10 to 11	0.5 to 1.5	
Mineral oil...............	none	none	100	Liquid; insoluble in alcohol.
Rape oil. 60 ⎫ .... Mineral oil, 40 ⎭	57.6	6	40	Liquid; insoluble in alcohol.

Although mineral oils are practically insoluble in rectified alcohol, Nash (*Analyst*, 1904, **29**, 3) has shown that a solution of sperm oil alcohols in absolute alcohol, and even in alcohol of 0.8345 sp. gr.,

unless much diluted, dissolves mineral oil freely.   Absolute alcohol, therefore, must not be used in testing the unsaponifiable matter for mineral oil; but if the unsaponifiable matter from 5 grm. of a sperm-oil sample be normal in amount and completely soluble in 50 c.c. (not less) of cold alcohol of o.834 sp. gr., the sample is most probably genuine.   Dunlop states, however, that even under these conditions a considerable amount of mineral oil may be dissolved and escape detection.   The following tests for mineral oil are, however, available:

Holde's Test.—6 to 8 drops of the oil are boiled in a test-tube for 2 minutes with 5 c.c. of N/2 alcoholic potassium hydroxide, and to the soap solution thus prepared distilled water is added very gradually, with thorough well mixing after each addition, until from o.5 to 15 c.c. in all have been added.   If mineral oil is absent, the solution remains clear, even when mixed with the maximum quantity of water, but the presence of even 1% of mineral oil is said to cause the formation of a turbidity.   Careful observation is needed, since the characteristic feeble turbidity caused by a very small proportion of mineral oil, which appears after the addition of the first few drops of water, disappears again on adding more and may easily be overlooked.   Rosin oil is said not to be detectable in less quantity than 12%.   The higher alcohols in sperm oil do not interfere, since they remain dissolved in the soap solution for some time (Lobry de Bruyn). Dunlop found this test capable of detecting as little as 3.5% of mineral oil.

Flash-point.—Of 93 samples of sperm oil tested by Veitch Wilson the flash-points (closed test) of only 3 samples were below 410° F., *viz.*, 1 sample 400° and 2, 390°.   The others ranged from 410° to 485° F., and the averages were 457.5° F. for southern sperm oil and 446.2° F. for Arctic sperm oil.   Several samples of genuine sperm oil tested by Dunlop in Gray's apparatus flashed at from 410° to 422° F.   A mixture of sperm oil flashing at 416° F. with 5% of "o.865" mineral oil flashed at 361° F., and with 5% of "o.896" mineral oil at 392° F.   A flash-point below 410° F. would be suspicious, and below 400° F. would probably indicate adulteration.

Dunlop points out that the *refractive power of the unsaponifiable matter* may be useful for the detection of mineral oil.   The highest butyro-refractometer reading he has obtained for the mixed alcohols

of genuine sperm oil is 47 scale divisions at 25°. The addition of 10% of "0.865" mineral oil would raise this by about 6 units.

For the detection of fish oils and blubber oils in sperm oil, the estimation of the *yield of insoluble brominated esters* may prove useful. Walker and Warburton obtained from 2 samples of sperm oil only 2.5 and 3.7%, respectively, of brominated esters insoluble in ether, whilst all other fish and blubber oils which have been tested have given a much larger yield. Dunlop obtained the following results by Procter and Bennett's method:

	"Bromide value," = yield % of brominated esters insoluble in a mixture of CCl_4 and alcohol
1. Cachalot oil from "head matter"...........	1.13
2. Cachalot oil from "body matter".........	2.00
3. Cachalot oil from "body matter"......	2.30
4. Arctic sperm oil.................	3.04
5. No. 2 with 10% of whale oil...	3.68

As whale oils were found by Procter and Bennett to yield from 27 to 37% of brominated esters, a greater difference between the yield from oil No. 2 and mixture No. 5 might have been expected. But further experiments are needed. Procter and Bennett themselves obtained 6.3% of brominated esters from the sperm oil which they tested.

In examining sperm oil the *iodine value* is not so useful or so necessary a test as in the case of other oils. The recorded values have a fairly wide range, Dunlop's figures ranging from 70.3 to 92.8 (Wijs), but as these extreme values were obtained from head-matter oil and body-matter oil, respectively, and not from the mixed oil, they must be regarded as abnormal. A range from 80 to 90 would include most genuine commercial sperm oils, though Bull records a value as low as 67.1 (probably obtained by the Hübl method) for an Arctic sperm oil containing 42.61% of unsaponifiable matter and having a saponification value of 122.3. Dunlop has pointed out that there is a relationship between the iodine value of the wax alcohols and that of the oil. This will be seen by comparing the iodine values given in the table on p. 311 with those in the table on p. 113 from the same oils. The difference in the amount of iodine absorbed by

different oils would, therefore, appear to be due partly to the variable composition of the alcohols.

Sperm oil has a much lower viscosity than most fixed oils, and this physical property in absolute measure is given on p. 313. The efflux time of 50 c.c. of sperm oil from Redwood's viscometer has been stated as follows: at 60° F., 177 to 201 seconds; at 70° F., 137 to 164 seconds. Southern sperm oil seems to be rather lower in viscosity than Arctic sperm, but more samples need testing.

The colour indication with sulphuric acid (page 55) is often a useful test for the purity of sperm oil. The genuine oil gives a brown coloration, becoming somewhat darker with a tinge of violet on stirring. Shark-liver oil gives a well-marked violet colour when tested in the same manner, the tint changing to red or reddish-brown on stirring.

Blakeley and Reilly (*J. Ind. Eng. Chem.*, 1917, **9**, 1099) have found that sperm oil containing not more than 4% of oleic acid caused a slight crust to form on the wick when burned in safety lamps of the Davy type, but otherwise gave satisfactory results. In their opinion, therefore, the injurious effects of free fatty acids in sperm oil intended for burning have been over-estimated. In judging as to the suitability of sperm oil for burning in lamps they attach importance to the iodine value and refractive index, as well as to the acidity and other physical properties.

ARCTIC SPERM OIL. DOEGLING OIL. BOTTLENOSE OIL

(See also page 113.) Several species of toothed cetaceans yield an oil analogous to that obtained from the cachalot or sperm whale. The chief of these in economic importance is the product from the doegling or bottlenose whale (*Hyperoodon rostratum*),[1] which is known in commerce as "Arctic sperm oil."

Bottlenose oil deposits more or less spermaceti when cooled, but the yield is not nearly so large as that obtained from the head matter and oil of the sperm whale, though of good quality and high m. p. Bottlenose oil often has a more or less unpleasant odour, but this peculiarity, together with the small proportion of free acid present in the crude oil, can be removed to a great extent by agitation with

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[1] There has been much confusion respecting the bottlenose, at least eight different whales and dolphins having been designated by that name.

a solution of sodium carbonate or by analogous treatment. The refined oil is straw-yellow.

The chemical constitution of doegling oil was first pointed out by Scharling (*J. prakt. Chem.*, 1848), who found it to consist essentially of the ester of a higher monatomic alcohol, dodecyl doeglate, C_{12}-$H_{25}.C_{19}H_{39}O_2$, and hence to yield on saponification dodecyl alcohol and doeglic acid. Further investigation on this point is desirable. Bull thinks that Scharling's doeglic acid ($C_{19}H_{36}O_2$) must have been a mixture of gadolinic acid ($C_{20}H_{38}O_2$) (see under **Codliver Oil**) and oleic acid ($C_{18}H_{34}O_2$).

The wax alcohols, etc., obtained from bottlenose oil by agitating *the aqueous solution of the saponified oil with ether and separating* and evaporating the ethereal solution, have similar characters to the product obtained in a similar manner from sperm oil (see under **Sperm Oil**).

The mixed fatty acids prepared by Allen from several specimens of *bottlenose oil were found to have a sp. gr. of 0.896, their combining* weights ranging from 275 to 294.

Bottlenose oil presents the closest resemblance to sperm oil. In its sp. gr. (0.876–0.881), viscosity, solubility in acetic acid, saponification value, and behaviour with strong sulphuric acid and in the elaidin test, it shows no material differences from sperm oil. On saponification it yields from 61 to 65% of fatty acids, and from 37 to 41% of ether-residue, in this respect very closely resembling true sperm oil. The only differences observed by Allen in the course of a series of very careful comparative examinations of sperm and doegling oils were the slight tendency of the latter to gum or thicken on exposure, and the somewhat higher m. p. of the fatty acids from sperm oil. It has, therefore, been convenient to treat them together in the preceding pages under the "Examination of Commercial Sperm Oil."

DOLPHIN OIL

The oil from the blubber of the blackfish, *Globicephalus melas*, is citron-yellow in colour, deposits spermaceti when cooled, and contains a large proportion of the glyceride of valeric acid. It presents many points of resemblance with porpoise oil (see under **Porpoise Oil**).

XII. BEESWAX GROUP.   SOLID WAXES

Beeswax.	Chinese Insect Wax.
Carnaüba Wax.	Spermaceti.

Wool Fat.   Wool Wax.

BEESWAX[1]

(See also table on page 113.)   Beeswax is the material of which the honeycomb of bees is composed.   To obtain the wax the honey is drained off, the comb pressed, melted in water, the impurities allowed to subside, and the wax allowed to cool or run into suitable moulds.   About 1 pound of wax is obtained from 20 pounds of honey. In the process, as described by Hirschel (*Chem. Zeit.*; 1904, **28**, 212), the bulk of the wax is first separated by treatment with hot water and straining from dead bees, etc., and the residue pressed in layers with straw in a filter-press.   The pressed residue is again boiled with water and pressed, after which there still remains 10 to 15% of wax in the press-cake.   This is extracted with petroleum spirit and known as "*extraction wax*," the former being "*pressed wax*."   3 samples of genuine "extraction wax" examined by Hirschel, previous to bleaching and refining, were dark brown, soft, greasy substances, of unpleasant odour.   They had higher acid values than normal beeswax (23.3 to 27.1) and lower "ratio numbers" (2.46 to 2.95), also much higher iodine values (31.2 to 39.6); the m. p. (61.3° to 62.5°) and sp. gr. at 15° (0.953 to 0.957), though lower than, did not differ greatly from those of ordinary beeswax.   All three samples gave faint indications for rosin, and in Weinwurm's test (page 335) behaved as if containing about 5% of paraffin wax.

Yellow Wax.—Normal beeswax is a tough, compact, solid substance, of a yellowish or brownish colour, with a slight lustre and a finely granular fracture.   Its taste is faint and slightly balsamic, and the odour is honey-like and characteristic.   It does not feel greasy to the touch.

Beeswax can be volatilised almost without change in a vacuum. When distilled under the ordinary pressure, it yields a variety of products, among which acrolein does not appear to occur.   It is insoluble in water, but dissolves readily in fixed oils, carbon disulphide, and in about 10 parts of boiling ether or turpentine.   Accord-

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[1] Bibliographies relating to earlier investigations of beeswax and waxes used for adulterating it are given in *J. Soc. Chem. Ind.*, 1892, **11**, 756, 757.

ing to Hager, ether dissolves only about half the wax at the ordinary temperature, and benzene and petroleum spirit about 27%.

Buchner (*Chem. Zeit.*, 1907, 31, 570) separated beeswax by treatment with cold ether into two portions, giving the following results as compared with the original wax:

	Acid value	Ester value
Original wax..............................	19.5	76.7
30% dissolved by ether.........	40.0	43.8
70% undissolved by ether.........	11.6	87.5

Yellow beeswax is completely soluble in chloroform (Dieterich). It is nearly insoluble in cold alcohol, but dissolves in about 300 parts of the boiling liquid, leaving only a small yellowish-brown residue. On cooling, the solution deposits a whitish crystalline substance, whilst the filtrate is yellowish, and is not rendered turbid by addition of water. The portion soluble in cold alcohol consists of aromatic and colouring matters, together with a small quantity of fatty matter to which the name of cerolein has been given. The portion of beeswax dissolved by a moderate quantity of hot alcohol consists chiefly of cerotic acid and its homologues, whilst the undissolved part is myricin.

Schwalb (*Chem. Centr.*, (3), 16, 354; *Annalen*, 1886, 235, 149) separated from beeswax about 6% of hydrocarbons of the paraffin series, among which he identified heptacosane, $C_{27}H_{56}$, melting at 60.5°, and hentricontane, $C_{31}H_{64}$, melting at 67°. Much larger quantities of hydrocarbons have since been found by Buisine and others (see page 337).

T. Marie (*Compt. rend.*, 1894, 119, 428; *J. Pharm.*, 1896, (6), 3, 107; *Bull. Soc. Chim.*, 1896, (3), 15, 503, etc.) has shown that the free acids of beeswax consist of cerotic acid, mixed with from 30 to 40% of homologous acids, including melissic acid.

Cerotic acid, $C_{26}H_{52}O_2$ (Lewkowitsch), dissolves in hot ethyl alcohol, but is almost wholly deposited on cooling; when quite pure, it forms stellate, microscopic needles, melting at 77.9°. It is easily soluble in warm methylic alcohol and ether. *Melissic acid*, $C_{30}H_{60}O_2$, resembles cerotic acid in appearance, but crystallises more readily and melts at 90.6°. It is readily soluble in hot ethyl

alcohol, chloroform, petroleum spirit, and carbon disulphide, but almost insoluble in warm methyl alcohol and ether.   For the properties of these acids and their derivatives and the method of separating them in a pure state from beeswax, the papers by Marie should be consulted.   The proportion of crude cerotic acid existing in beeswax in the free state usually ranges from 12 to 16%.

Myricin is the chief constituent of beeswax insoluble in alcohol. It is a solid, wax-like body, melting at 64°.   On saponification, it yields a palmitate, myricyl alcohol, and a small quantity of soap from an acid of the oleic series.   Hence myricin has essentially the constitution of myricyl palmitate.

Myricyl alcohol, $C_{30}H_{61}.OH$, may be prepared by heating myricin or beeswax itself in a closed vessel for an hour or two with excess of alcoholic potassium hydroxide, nearly neutralising the excess with acetic acid (phenolphthalein as indicator), and treating the turbid liquid with excess of lead acetate.   The precipitate, consisting of a mixture of lead soaps and myricyl alcohol, is washed, dried, and exhausted with hot ether or petroleum spirit in a Soxhlet extractor tube.   On evaporating the solvent the wax-alcohol is obtained in white glittering crystals, which may be purified by washing with cold alcohol and recrystallisation from ether.   It may also be prepared in a similar manner from carnaüba wax.

Myricyl alcohol is a crystalline silky substance, which melts at 85° to 86° to a colourless liquid, and solidifies to a fibrous mass at about 1° lower.   It is insoluble in water, scarcely soluble in cold alcohol, ether, or benzene, and only slightly soluble in cold chloroform.   It dissolves readily in boiling alcohol, ether, chloroform, benzene, and petroleum spirit.   When fused with potassium hydroxide, or heated to 220° with potashlime as long as hydrogen is evolved, it is converted into potassium melissate, $KC_{30}H_{59}O_2$, which, on solution in water and treatment with an acid, gives melissic acid.

White or Bleached Wax.—By exposure to moisture, air, and light, beeswax becomes decolorised.   It is usually exposed to sunlight in thin cakes, but the bleaching is a slow process.   In order to expose as large a surface as possible, Ramboe (*Chem. Zeit.,* 1896, 20, 1004) has proposed to break the wax up into minute globules by emulsifying it with hot water and pouring the emulsion into cold water to which a little oil of turpentine has been added.

Wax thus subdivided, if previously mixed with bleached wax, can be bleached by sunlight in 3 or 4 days. The addition of bleached wax to the yellow wax is found greatly reduces the time required for bleaching.

Beeswax may also be bleached by cautious treatment with chromic or nitric acid; but chlorine cannot be advantageously employed owing to the formation of chlorinated substitution-products which give rise to hydrochloric acid when the wax is burnt. It may also be bleached by boiling it with a dilute solution of potassium dichromate and sulphuric acid. The wax thus treated has a greenish colour from the presence of chromium compounds, which it holds very persistently, but which may be removed by boiling the product with a solution of oxalic acid. Permanganate bleaching is also employed. It is not every kind of wax which can be effectually bleached. The presence of a small proportion of fatty matter appears to facilitate the process.

The effect of bleaching on the constants of beeswax has been studied by Buisine,[1] Berg (*Chem. Zeit.*, 1902, 26, 605) and others. The *acid value* is raised least by natural bleaching (most by chromic acid bleaching), to a sufficient extent to lower the ratio number and suggest adulteration with stearic acid. Thus, Buchner has recorded the following numbers for chemically bleached wax: acid value, 23.1 to 26.2; saponification value, 95.0 to 98.45; ratio number, 2.70 to 3.20. The *saponification value* of bleached wax is always a few units higher than that of the yellow wax. Berg found the *iodine value* to be lowered by the natural and permanganate methods of bleaching, but, curiously, raised by chromic acid bleaching, except in the case of Italian waxes, which had their iodine values lowered in all cases. Dieterich found the iodine value of bleached wax 4.2 to 4.4. *Buchner's number* is slightly lowered by natural and permanganate bleaching; chromic acid sometimes raises it considerably, sometimes does not alter it, or even lowers it in the case of Italian waxes. Natural and permanganate bleaching either do not affect or slightly raise the *refractive power* of the wax; treatment with chromic acid or any method of bleaching Italian wax lowers· the refractive power. Chromic acid frequently raises the m. p.; other processes lower it a trifle. A Morocco wax bleached by chromic acid had its m. p. raised from 64.5° to 67.5°. Medicus and Wellenstein (*Zeitsch. Nahr. Genussm.* 1902, 5, 1092) found the m. p. of a wax

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[1] *Bull. Soc. Chim.*, 1890, [3], 4, 465, in which detailed results are given of yellow waxes before and after bleaching by several methods; also *Compt. rend.*, 1891, 112, 738.

raised from 62.5° to 63.5° by chromic acid bleaching, that of the mixed free fatty acids being raised from 68° to 69°, and their acid value from 51.47 to 58.83. An ultimate analysis gave $C_{28}H_{56}O_2$ or $C_{29}H_{58}O_2$ for the yellow wax, and $C_{24}H_{48}O_2$, or $C_{25}H_{50}O_2$ for the bleached wax. They attribute the increased acidity to the splitting up of the acids with formation of acids of lower molecular weight. White wax is not completely soluble in chloroform (Dieterich).

Analysis of Genuine Beeswax.—The proportion of crude *cerotic acid* in beeswax can be ascertained by titration with standard acid and phenolphthalein in the usual way, but, owing to the very high combining weight of the acid, the operation must be conducted with extreme care. Hehner (*Analyst*, 1883, 8, 16) recommends that alcoholic potassium hydroxide should be used, and that it should be prepared from pure material and from spirit which has been redistilled from potassium hydroxide. It should be about N/3—that is, 1 c.c. should correspond to 0.3 to 0.4 c.c. of N/1 acid. The alkali should be standardised several times with the acid, and the results should not differ by more than 0.05 c.c. of standard alkali for each 10 c.c. of acid used. 5 grm. of the wax should be heated in a flask with 50 c.c. of methylated spirit which has been redistilled from sodium hydroxide. When the wax is perfectly melted, an alcoholic solution of phenolphthalein is added in not too small an amount. The indicator must not be acid, as is frequently the case, but must previously have been rendered pink by addition of alkali in faint excess. The standard solution of alcoholic alkali is then added, drop by drop, the liquid being kept well agitated until the pink colour becomes permanent, when the volume employed is observed. The combining weight of cerotic acid being 410,[1] a volume of standard alkali corresponding to 1 c.c. of normal acid represents 0.410 grm. of cerotic acid. The percentage of cerotic acid may be found by multiplying the percentage of potassium hydroxide required for neutralisation by 7.31. As the volume of standard alkali required by 5 grm. of wax amounts to only a few c.c., a very finely graduated burette should be employed.

Hehner found by this process, in sixteen samples of English unbleached wax, proportions of free acid, calculated as cerotic acid, ranging from 12.15 to 15.71%, the average being 14.4. 17 samples of

[1] Based on Brodie's formula, $C_{27}H_{54}O_2$. As a matter of fact, the mean molecular weight of the free acid in beeswax has been found by Hehner to be 407.

foreign wax gave very similar results, but showed a somewhat wider variation, the extreme numbers obtained being 12.17% from a dark-brown Mauritian wax, which showed signs of having been burnt in the process of manufacture, and 16.55% from a dark-brown wax from Gambia. In wax bleached by air and light the proportion of free acid is practically unchanged, but in wax bleached by chromic acid mixture it may be increased to 17 or 18%. Thus, in 24 samples of commercial bleached wax Hehner found from 15.5 to 17.6% of free acid calculated as $C_{27}H_{54}O_2$, the average being 16.6% or almost exactly one-sixth of the wax. Hehner's results have been confirmed by Hübl (*Dingl. Polyt. J.*, 1883, 249, 338), who found in 20 samples of yellow wax proportions of free acid ranging from 13.9 to 15.3, the average being 14.6%.

It is evident that the foregoing rapid and simple volumetric process fails to prove the actual nature of the free acid, but by operating on a somewhat larger quantity of beeswax the same method serves as the first step toward the actual isolation of cerotic acid, the quantity obtained being sufficient for the estimation of the m. p. and other data. The unsaponified portion consists principally of *myricin* and hydrocarbons, which can be separated and weighed as such, or its nature and composition may be deduced from the results of its saponification in the following manner:

The experiment by which the proportion of crude cerotic acid in beeswax was ascertained by titration with alcoholic alkali and phenol-phthalein may be extended in such a way as to obtain an estimation of the *myricin*. For this purpose a further exactly known volume of standard alcoholic potash should be run into the flask, the quantity used being equivalent to about 25 c.c. of N/1 acid. A reflux condenser is then attached to the flask, and the liquid briskly boiled for 1 hour, when the solution should be clear, or nearly so. The flask should be shaken at intervals to remove any particles of wax which may have adhered to the sides of the flask above the liquid. The condenser is then detached and the solution titrated back by means of a very accurately standardised burette with N/2 acid. The alkalinity which has been neutralised, expressed in terms of N/1 acid, represents the myricin which has been saponified. 1 c.c. of normal acid, or 0.0561 grm. of potassium hydroxide neutralised, corresponds to 0.676 grm. of myricin. Hübl found 20 samples of yellow wax to require from 7.3 to 7.6% of potassium hydroxide for the saponi-

fication of the myricin, which figures correspond to proportions of that substance varying from 88 to 91.6%. These results fully confirm those of Hehner, who found in sixteen samples of yellow English wax proportions of saponifiable substance expressed as myricin ranging from 85.95 to 89.05, the average being 88.1, and in 24 samples of commercial bleached wax proportions ranging from 85.2 to 89.9%, the average being 87.7%.

When estimated volumetrically by the above method, the free acid expressed as cerotic acid and the esters expressed as myricin together amount to somewhat more than 100%, the average being, according to Hehner, 102.5. It is evident, therefore, that wax requires more alkali for saponification than would be required for a mixture of pure cerotic acid and myricin.

The results above recorded prove that genuine beeswax is of approximately constant composition. Hehner's experiments show that the proportion the cerotic acid bears to the myricin in English beeswax (unbleached) averages 1:6.12, while Hübl finds ratios varying from 1:594 to 1:6.24; in English bleached wax Hehner found an average ratio of 1:5.3.

Adulterations of Beeswax.—Commercial beeswax is liable to contain a number of adulterants, among which the following have been recorded: Water; mineral matters, such as kaolin, gypsum, barium sulphate, and yellow ochre; sulphur; starch and flour; resinous substances, such as colophony, galipot, and burgundy pitch; fatty substances such as stearic acid, stearin, Japan wax, and tallow; paraffin and ozokerite; and vegetable waxes, such as carnaüba wax. Spermaceti is also said to have been used.

Water has been met with in beeswax to the extent of 6%, being purposely introduced. It may be detected and estimated as described under **Lard.**

Mineral matters may be detected and estimated by igniting the wax. They will also remain insoluble on dissolving the sample in turpentine, chloroform, or benzine. As much as 17% of *yellow ochre* has been found in unbleached beeswax.

Starch and *flour* will be left undissolved on treating the wax with warm turpentine. The liquid may be filtered, the residue washed with a little ether, and examined under the microscope with solution of iodine. 60% of starch has been met with. Small quantities of starch or flour may exist in genuine wax that has been rolled or

pressed, the rollers or press being dusted over with flour to prevent the wax from sticking.

Sulphur has been found as an adulterant of unbleached wax. It may be detected by boiling the sample with a weak solution of sodium hydroxide, and adding lead acetate to the cooled liquid, when a black or brown precipitate will be produced if sulphur is present.

Beeswax containing any of the above-named impurities or admixtures should be melted over water, and the melted wax filtered through paper dried in the water-oven before proceeding with the following tests.

As a useful preliminary test, the sample may be dissolved in *chloroform*, in which genuine yellow wax is completely soluble. Incomplete solubility would indicate the presence of paraffin wax, ceresin, carnaüba wax or wool wax (Dieterich). White wax, however, even when genuine, is not completely soluble in chloroform.

J. Werder *(Chem. Zeit.*, 1898, **22,** 38, 59) finds that the Zeiss *butyro-refractometer* may advantageously be employed in the examination of different kinds of wax, especially when the amount of material at disposal is very limited, and that the indications obtained with it are quite as valuable as in the case of oils and fats. Owing to the high m. p. of the wax, it is necessary to work at a higher temperature than usual, preferably 66° to 72°, and then to reduce the results to the normal temperature, 40°. As shown in the annexed table, the figures given by genuine beeswax vary from 42.6° to 45.4°, the great majority of specimens falling between 44° and 45°; and it seems to make little or no difference to the refractive power whether they are tested before or after bleaching. Samples 19 to 24 had previously been examined chemically, and had been rejected on the ground of their abnormal acid and ester values, which were as follows:

Number of sample	Acid value	Ester value
19 .	18.48	66.64
20	127.1	13.4
21	59.08	3.36
22	104.7	. 14.3
23	41.0	57.0
24	106.9	48.1

No. 14 is a product called "Glanzwachs," obtained by adding some of the mixture of stearic and palmitic acids as used in the manufacture of stearin candles (No. 28) to a genuine wax, this being a form of adulteration at one time commonly employed in Switzerland.

Refractive Power of Different Kinds of Wax.

Sample	Temperature of observation	Refraction at 40°
1. Bleached, from Egypt.......	66.0	44.1
2. Bleached, from Turkey...................	67.0	44.8
3. Bleached, from Moldavia..........	66.5	44.2
4. Yellow, from Egypt........., ...	66.0.,	42.8
5. Yellow, from Monte Christo............ ..	71.0°	44.8
6. Yellow, from France............	67.5	44.1
7. Yellow, from Savoy.....................	67.0	42.6
8. Yellow, from California.....	69.5	45.2
9. Yellow, from North Africa................	71.0	45.0
10. Yellow, from Massowah..................	71.5	44.3 ·
11. Yellow, from Italy ⎫	70.0	44.9
12. Yellow, from Italy ⎬ different samples.......	70.0	44.0
13. Yellow, from Italy ⎭	68.5	44.6
14. Yellow, from Mexico ⎫ different samples.....	69.5	44.2
15. Yellow, from Mexico ⎭	67.0	45.3
16. Yellow, from Syria.................... ..	69.5	44.2
17. Yellow, from Casablanca.................	68.0	45.4
18. Yellow, from Smyrna	70.0	44.7
19. Bleached, in chips (professedly genuine).....	70.5	41.3
20. White church candles (professedly genuine).	67.5	32.0
21. White church candles (professedly genuine).	68.0	32.5
22. White church candles (professedly genuine).	68.5	32.6
23. Yellow wax, source unknown..............	66.0	38.3
24. Wax adulterated with No. 28.	65.5	38.8
25. Paraffin.....................	65.0	22.5
26. Ceresin............	77.0	41.0
27. Tallow......	71.5	48.5
28. Stearin candle material.................	70.0	30.0
29. Carnaüba wax........	91.0	66.0
30. Japan wax........	71.0	47.0

The sp. gr. of beeswax is a useful indication of tne presence of foreign admixtures. Great discrepancies occur in the recorded sp. gr. of possible adulterants of beeswax, as determined by various observers, the differences being probably due to the faulty methods of observation. The subject has been investigated by W. Chattaway in Allen's laboratory, with the following results:

1. Hager's method is objectionable, owing to the anomalous contraction caused by sudden cooling of the melted substance.

2. If sudden cooling is avoided, the estimation may be made by immersing the fragment in dilute alcohol or ammonium hydroxide, adjusting the sp. gr. of the liquid until identical with that of the wax, and then ascertaining its sp. gr. by one of the usual methods. To prepare the fragments, a good plan is to melt the wax in a clock-glass or flat-bottomed capsule placed over a beaker of boiling water, and then remove the source of heat and allow the water in the beaker to cool spontaneously. Small blocks can then be cut from the solidified wax with a knife, or cylinders removed with a corkborer. Another good plan is to suck up the melted wax into a piece of quill-tubing, the upper end of which is then closed by the finger, while the lower is immersed in cold water. This causes the wax to set at the orifice of the tube, and so closes it. The tube is then supported in a vertical position, and the contents allowed to solidify spontaneously. Owing to the mode of cooling, the wax forms a smooth cylindrical stick, readily removable from the tube; the central portion is always free from cavities and air-bubbles. The cubes or cylinders are painted over with a wet brush to prevent the adherence of air-bubbles, and then cautiously lowered (not dropped) into the spirit by means of a pair of forceps or a glass rod bent into the form of a hoe.

3. In the case of a crystalline substance, such as spermaceti or Chinese wax, the estimation of the sp. gr. of the solid substance is very unsatisfactory, but the difficulty is wholly avoided if the observation is made with the melted wax at the temperature of boiling water.

The *melting point* and *solidifying point* of a sample of wax will often afford valuable information; but unfortunately the figures recorded as the m. p. of various waxes exhibit great discrepancies, owing to the different methods employed.

The following table shows a number of results obtained in Allen's laboratory by the examination of specimens of waxes and analogous bodies. The sp. grs. were estimated by the methods just indicated, the m. p. by the first method on page 52 and the solidifying points by Dalican's method, page 73:

Substance	Sp. gr.; water at 15.5° = 1		Temperature of change of physical state; °	
	At 15–16°	At 98–99°	M. p., °	Solidifying point, °
Beeswax, yellow...............	0.963	0.822	63.0	60.5, no rise
Beeswax, chemically bleach-ed......................	0.964	0.827	63.5	62.0, no rise
Beeswax, air-bleached.......	0.061	0.818	63.0	61.5, no rise
Spermaceti, bottlenose......	0.942	0.808	49.0	48.0, no rise
Carnaüba wax...............	....	0.842	85.0	81.0, no rise
Chinese insect wax..........	....	0.810	81.5	80.5, no rise
Japan wax..................	0 984–0.993	0.875–0.877	51–53	41.0, rising to 48
Myrtle wax.................	....	0.875	40.5	39.5, no rise
Tallow, pressed.............	....	0.861	44.5	32.5, rising to 34
Suet, beef..................	0.944	0.860	49.0	32.5, rising to 34.5
Stearic acid................	....	9.830	56.5	54.5, no rise
Colophony.................	1.074	....	....	....
Paraffin wax...............	0.909	0.753	54.5	54.0, no rise
Ozokerite, refined..........	....	0.753	61.5	60.0, no rise

The following table gives the sp. gr. and m. p. of waxes and some other substances, as estimated by other observers:

Substance	Sp. gr. at 15°–15.5°	M. p., °	Solidifying point, °
Beeswax, yellow.....................	0.959–0.970	62.5–64.5	60.5–63.5
Beeswax, bleached..................	0.966–0.968[1]	62–70	61.6
Spermaceti........................	0.905–0.960	41–46	41–47
Carnaüba wax......................	0.995–1.000	83–86	....
Japan wax.........................	0.976–0.993	50.4–53.4	48.5–51
Tallow............................	0.937–0.953	38–49	27–36
Stearic acid.......................	0.964–0.986	58–65	....
Colophony	1.070–1.090	....	....
Paraffin wax ⎫ Ceresin ⎭	0.868–0.915	48–72	....

[1] 24 samples examined by Hehner, the m. p. of which ranged from 63.4° to 64.4°.

The most valuable method for the examination of beeswax is based upon the researches of Hehner and of Hübl, and consists in a careful estimation of the *acid value* and *saponification value* of the sample. Hehner's method of operating has already been described on p. 324; Hübl's was substantially the same. Numerous modifications have since been proposed.

Thus, Henriques (*Zeit. angew. Chem.*, 1895, 721; 1896, 221) has proposed a method of cold saponification, in which the wax (3 to 4 grm.) is dissolved in 25 c.c. of warm petroleum spirit (boiling at 100°–150°), titrated with N/2 alcoholic sodium hydroxide, made

with 96% alcohol, for estimating the acid value, then mixed with N/1 alcoholic sodium hydroxide and allowed to stand for 24 hours in the cold, the saponification value being estimated by titrating the excess of alkali. There appears to be no advantage in this process, and it is slower than the ordinary method. The acid values estimated by it are lower than those estimated by Hehner's method (*Dieterich, Buchner*). Cohn (*Zeit. öffentl. Chem.*, 1904, **10,** 404) finds 3 hours' boiling with alcoholic potassium hydroxide under a reflux condenser necessary to ensure complete saponification, but others have shown 1 hour to be sufficient if strong enough alcohol (96 to 98%) be used. Buchner (*Chem. Zeit.*, 1905, **29,** 32) has proposed to use a Soxhlet extractor as reflux condenser, the concentration of the alkali resulting from its use helping the saponification. Eichorn (*Zeit. anal. Chem.*, 1900, **39,** 640) has suggested the use of amyl alcohol instead of ordinary alcohol, in order to carry out the neutralisation and saponification at a higher temperature. Berg (*Chem. Zeit.*, 1907, **31,** 537) states that different waxes require different times for saponification; German seldom less than 2 hours, usually 3 to 3½ hours; Morocco, about 5 hours; East African, up to 6 hours; Chinese and Tonking, up to 8 hours. He thinks every wax contains lactonic anhydrides which are difficult to saponify, differing from Buchner, who believes these substances are of only rare occurrence. In Archbutt's experience, the following method of operating usually gives good results:

8 grm. of the wax are warmed with 70 c.c. of neutralised rectified alcohol until melted, then mixed with neutralised phenolphthalein solution and carefully titrated with N/2 alcoholic potassium hydroxide. This gives the acid value. For ascertaining the saponification value, 5 grm. of wax are boiled under a reflux condenser for at least 1¼ hours with 25 c.c. of N/2 alcoholic potassium hydroxide, made up with alcohol of 95 to 96% strength, and then titrated with N/2 hydrochloric acid and phenolphthalein in the usual way.

The difference between the acid and saponification values was termed by Hübl the "*ester value*," and he found the *ratio*, $\frac{ester\ value}{acid\ value}$, in genuine beeswax to range from 3.6 to 3.8. Adulteration with unsaponifiable matters (paraffin, ceresin) lowers the saponification value without disturbing this ratio; acid substances (stearic acid,

resin), raise the acid value and lower the ratio, foreign waxes or fats raise the ratio as is indicated in the following table:

Substance	Acid value	Ester value	Saponification value	Ratio: $\dfrac{\text{ester value}}{\text{acid value}}$
Beeswax, unbleached..........	17–22	70–82	88–102	3.4–4.2
Beeswax, chemically bleached..	19–25	69–74	95–99	2.7–3.2
Spermaceti..................	traces	....	121–135	....
Carnaüba wax......	3–8	85.4	79–88	29.4
Chinese insect wax...........	traces	....	80–93	....
Japan wax.........	20–33	....	214–238	say 10
Myrtle wax..................	3	....	206–217	say 70
Tallow and "stearine"........	say 2–12	....	193–198	say 15–97
Stearic acid (commercial).....	200	nil	200	....
Colophony...................	180	10	190	....
Paraffin wax, ceresin, and ozokerite.....................	nil	nil one sample	nil	.... one sample

Further investigation has shown that the "ratio-number" of genuine beeswax varies within wider limits than those stated by Hübl, but the range is still narrow enough to afford a valuable distinction between beeswax and the foreign fats and waxes likely to be added to it as adulterants.   In the case of beeswax, the ratio-number is a true "constant;" but in the case of fats, such as Japan and myrtle "waxes," tallow, etc., the figures given in the table as ratio-numbers are accidental numbers depending upon the amount of free fatty acid in the sample, which may range from *nil* upward, and, therefore, the "ratio-numbers" of these fats will be higher the more nearly pure and neutral they are.

It is evident that the estimation of the ratio number alone will not suffice to detect adulteration in every case, as it is possible to prepare, without wax, mixtures having a normal ratio number. Thus, Lewkowitsch calculates that a mixture of Japan wax 37.5 parts, stearic acid 6.5 parts, and ceresin or paraffin wax 56 parts, will give the normal ratio number, 3.71.   The examination must, therefore, be supplemented by other estimations; *e. g.*, iodine value, hydrogen liberated on heating with potassium hydroxide, estimation of the hydrocarbons, and other special tests.

The *iodine value* of genuine yellow beeswax ranges from about 7 to 14; bleached wax has a lower value, since bleaching destroys or modifies the iodine-absorbing substances. Adulteration with tallow or colophony would raise this value; paraffin or ceresin would lower it; Japan wax or carnaüba wax would be without effect. Beeswax could be largely adulterated without the normal iodine value being disturbed.

Japan wax and other *fatty substances* (e. g., tallow, stearin, stearic acid) may be detected by boiling 1 grm. of the sample with 1.5 grm. of borax and 20 c.c. of water, when the aqueous liquid will become milky or gelatinous on cooling. With pure beeswax it remains clear or becomes but slightly turbid, and carnaüba wax and rosin behave similarly.

Japan and *myrtle wax* are denser than *beeswax*, and *tallow* and *stearin* somewhat lighter, but they all agree in having a notably lower m. p. than pure beeswax, and much higher saponification values and "ratio-numbers;" they also yield *glycerol* on saponification. In doubtful cases, an estimation of the glycerol may be made, when the amount found, multiplied by 10, gives the approximate weight of the adulterant. In 2 test mixtures of tallow and wax, containing, respectively, 50.9% and 28.4% of tallow, Benedikt and Zsigmondy found 4.93% and 3.00% of glycerol, corresponding to 49.3% and 30% of tallow.

Free *stearic acid* is readily distinguished from the neutral fats and beeswax by its high acid value; in fact, in the absence of other adulterants, the percentage of stearic acid in a sample of wax might be approximately calculated from the acid value, that of beeswax being taken as 20 and that of stearic acid as 200. As, however, the adulterant commonly used is a mixture of stearic acid, Japan wax, and ceresin, so proportioned as to give normal figures, a special test for stearic acid is required. The following modification of Fehling's test is recommended by Buchner: 3 grm. of the wax are boiled with 10 c.c. of 80% alcohol for a few minutes, and the tube is then immersed in cold water and shaken so that a thick paste results. After standing for 1 hour the mixture is filtered, and the filtrate mixed with a large excess of water or with an alcoholic solution of lead acetate or calcium chloride, which make the test more sensitive. Normal waxes give only a faint opalescence, the cerotic acid dissolved by the boiling alcohol being almost entirely redeposited on cooling

and standing, though after some hours they may show an amorphous deposit, especially in the case of soft African waxes. Buchner regards a wax as genuine in this respect when it shows no deposit of stearic acid after 1 to 2 hours

A quantitative modification of the test (making it applicable to rosin as well as fatty acid) has since been proposed by Buchner (*Chem. Zeit.*, 1895, **19**, 1422): 5 grm. of the sample are treated with 100 c.c. of neutralised 80% alcohol and the flask and contents are weighed. The alcohol is gently boiled for 5 minutes, with frequent agitation. The flask and contents are then cooled, and the solution made up to its original weight by the addition of 80% alcohol, well mixed, corked, and allowed to stand for 12 hours (*Berg*). The solution is then filtered through a ribbed filter, and 50 c.c. of the filtrate are titrated with N/10 potassium hydroxide, with the use of phenolphthalein as indicator. The figures thus obtained are known as *Buchner numbers*. Some results with waxes, fats, and mixtures are given in the following table:

Substance	Buchner's number
Beeswax, yellow	3.6–3.9
Beeswax, white	3.7–4.1
Palm wax	1.7–1.8
Carnaüba wax	0.76–0.87
Japan wax	14.93–15.3
Stearin (from tallow)	1.1
Colophony	150.3
Stearic acid	65.8
Mixtures giving normal ratio numbers:	
1. Stearic acid, stearin and ceresin	21.40
2. Stearic acid, Japan wax and ceresin	17.80
3. Rosin, stearin and ceresin	22.00
Genuine beeswax + 25% mixture No. 1	8.42
Genuine beeswax + 50% mixture No. 1	11.30

According to Bohrisch and Richter (*Pharm. Centralh.*, 1906, **47**, 201, etc.), the Buchner's number of genuine beeswax may range from 2 to 6. These authors, who made a full examination of 73 samples of beeswax from different parts of Germany, found 38 samples adulterated; of these, 34 contained paraffin wax and ceresin and 4 contained stearic acid, tallow or carnaüba wax.

Colophony or *rosin*, like stearic acid, if added to beeswax increases the acid value; and although the acid value of rosin is somewhat

lower than that of stearic acid, its greater solubility in alcohol causes it to increase the Buchner number in greater proportion. Colophony is easily detected in beeswax by means of the *Liebermann-Storch reaction;* it may be estimated by applying Twitchell's process to the mixture of rosin and fatty acids obtained by extracting the adulterated sample with boiling 80% alcohol and filtering the solution when cold.

Paraffin wax, if present to the amount of 3% or more, can easily be detected by saponifying 5 grm. of the sample with alcoholic potassium hydroxide, as in determining the saponification value, and keeping the liquid hot on the water-bath in a corked flask. The paraffin wax will be seen floating on the surface of the liquid or adhering in small globules to the sides of the flask, and the solution, when diluted with hot water, will be turbid. Genuine beeswax gives a clear solution.

According to Weinwurm (*Analyst*, 1897, **22**, 242) 2 or 3% of ceresin or paraffin wax, or 5% of rosin, may be detected as follows: 5 grm. of filtered wax are saponified by means of 25 c.c. of N/2 alkali and the alcohol removed. 20 c.c. of glycerol are run in, the whole warmed in the water-bath till solution is effected, and 100 c.c. of boiling water added. Pure wax gives a clear, transparent, or translucent solution, through which ordinary printed matter may be read with ease. 5% of ceresin or rosin yields a cloudy liquid, and the print is no longer legible; 8% of ceresin causes a decided precipitate. If the solution is clear, 3%, or, if it is opaque, 2% of ceresin is added to another sample of the wax, and the saponification repeated, when the appearance of the soap solution affords an indication of the presence or absence of either impurity.

R. Henriques (*Ibid.*, 1897, **22**, 292) reports favorably on the above process, but simplifies it by applying the Leffmann-Beam alkali and glycerol method of saponification. A piece of wax about the size of a pea is boiled in a test-tube for 3 or 4 minutes with 5 c.c. of alkali gylcerol (see p. 27). The solution, which is at first quite clear, becomes gradually cloudy. After boiling for about the time mentioned, the oil collects in a layer and the underlying fluid becomes clear. The bubbles of the boiling mass also now become smaller and the glycerol begins to distil. As soon as this point is reached the heating is discontinued. The fluid is now poured into another test-tube, in order to separate it from the unsaponified portion; an equal

weight of hot water is added, and the liquid boiled and allowed to cool.   In the case of pure wax the solution will be either quite clear and transparent, or, at any rate, sufficiently translucent to allow of large printed matter being read through it, as described by Weinwurm.   Should, however, on the contrary, as much as 5% of foreign hydrocarbons be present, the fluid will be quite opaque. With an admixture of only 3% of ceresin or paraffin wax, the indication is uncertain, and the further treatment recommended by Weinwurm to meet such cases should be followed.

Lewkowitsch (Oils, Fats and Waxes, II, 772) states that he can recommend Weinwurm's test for pure beeswax, but that turbidity of the solution does not necessarily prove the presence of ceresin or paraffin wax, since it is also produced by carnaüba wax and insect wax.

Paraffin, ceresin, and *ozokerite* are the only adulterants of beeswax which tend to reduce in a notable degree the saponification value.   They also reduce the sp. gr. in a marked manner, but this indication has little more than a qualitative value.   In a sample consisting solely of beeswax and hydrocarbon wax the proportion of the former may be deduced with considerable accuracy from the results of the saponification, each 0.1% of potassium hydroxide required representing 1.053% of beeswax in the sample.

Estimation of Fatty Alcohols and of Paraffin and Ceresin.—An adulteration of beeswax with less than 6% of ceresin or paraffin wax cannot be detected with certainty by any of the ordinary methods, because the relationships between the free fatty acid and saponifiable matters in genuine beeswax vary within somewhat wide limits.

Werder (*Chem. Zeit.*, 1900, 14, 967) has proposed to saponify 2 grm. of the sample of wax with alcoholic potassium hydroxide, dry on sand, extract the dry mixture of soap, sand, etc., with pure dry ether in a Soxhlet extractor and weigh the mixture of alcohols and hydrocarbons.   But, as the residue of unsaponifiable matter obtained from 20 samples of genuine beeswax in this manner ranged from 48.55 to 53.01%, it is evident that at least 4.5% of paraffin wax or wax alcohols could be added to some samples without detection.

A preferable method is a direct estimation of the hydrocarbons present, and a method for doing this was worked out by A. and P.

Buisine (*Bull. Soc. Chim.*, 1890, [3], 3, 576), based upon an observation of Dumas and Stas. The wax is saponified with potassium hydroxide and heated with potash-lime, by which treatment the higher alcohols are converted into their corresponding fatty acids, with evolution of hydrogen, the volume of which serves as a measure of their amount, whilst the hydrocarbons present are left unattacked and can be extracted from the residue with solvents. The following modification of the process has been described by Mangold (*Chem. Zeit.*, 1891, 15, 799): 2 to 10 grm. of the wax are melted in a porcelain basin and intimately mixed, by stirring, with an equal weight of finely powdered potassium hydroxide. The saponified mass, when cold, is powdered in a mortar, intimately mixed with 3 grm. of a mixture (1 part potassium hydroxide, 2 parts lime) for every grm. of wax taken, and then transferred to a thickwalled, pear-shaped bulb-tube, which is heated to 250° for 2 hours. An apparatus for conducting this operation is shown in the sketch. *A* is an iron vessel with a lid fastened down with screws and filled with mercury. The flask *E* is connected, gas-tight, with a Hofmann's burette, *H*, for measuring the hydrogen evolved. *T* is a thermometer and *V* a temperature regulator. *K* is a condensing tube for mercury vapour. It is advisable that the heating at 250° be continued for 3 hours to secure completion of the reaction, after which the flask is allowed to cool, and is broken up to liberate the residual mass, which is then powdered and extracted with petroleum ether in a Soxhlet apparatus. The residue left on evaporation of the petroleum spirit is dried at 110° and weighed.

Fig. 7.

The following are some results obtained by A. and P. Buisine (*Bull. Soc. Chim.*, 1891, [3], 5, 654) in the examination of beeswax and adulterants:
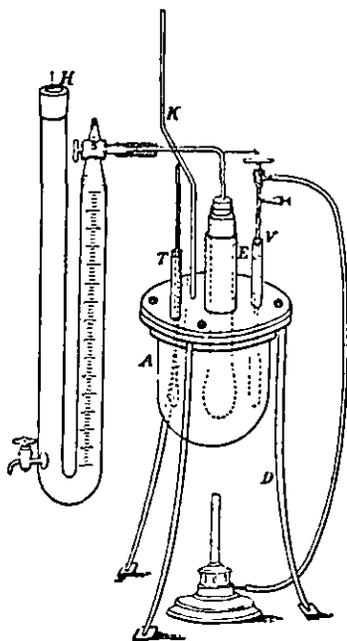
	M. p., °	Acids soluble in water	Acid value	Saponification value	Iodine value	c.c. hydrogen from 1 grm. on treatment with KOH; 0° and 760 mm.	Hydrocarbons, %
Japan wax.............	47–54	2	18–28	216–222	6–7.55	69–71	0
China wax.............	53.3	2	22	218	6.85	72.3	0
Vegetable waxes........	47–54	2	17–19	218–220	6.6–8.2	73–74	0
Carnaüba wax..........	83–84	0	4–6	79–82	7–9	73–76	1.6
Mineral waxes..........	60–80	0	0	0	0–0.6	0	100
Paraffin waxes..........	38–74	0	0	0	1.7–3 1	0	100
Wax from "suint"......	62–66	0	95–115	102–119	13–18.5	0	14–18
Waxy acids from "suint"..............	50–62	0	155–185	159–189	2.6–2.8	0	0
Suet..................	42–50.5	0	2.75–5	196–213	27–40	52–60	0
Stearic acid...........	55.5	0	204	209	4	0	0
Rosin.......	......	0	168	178	135.6	35	0
Yellow beeswax........	62–64	0–1	19–21	91–97	8–11	53–57.5	12.5–14.5
Bleached beeswax.......	63–64	0–2	20–23	93–110 (?)	2–7	53–57	11–13.5

If a measurement of the hydrogen is not required, the powdered mixture of saponified wax and alkali lime may be transferred to a simple boiling tube, which is closed by a rubber stopper and a short piece of bent glass tube, supported vertically in a bath of oil or melted carnaüba wax, and heated to 250° until no more gas is evolved; the temperature is then raised for a short time to 290°. Evolution of gas is ascertained by attaching a short length of rubber tubing to the glass tube and immersing the free end in water, but the rubber tube must not be left permanently attached, otherwise water may be sucked back and cause an explosion. When gas-evolution has ceased, the tube and contents are allowed to cool somewhat and the contents, whilst still hot, are removed, as completely as possible, to a basin by means of a pointed glass rod. If allowed to become quite cold, the mixture sets hard and cannot be removed. The bottom of the boiling tube is finally broken out and what adheres to the sides scraped off as completely as possible. The mixture is then placed in a paper extraction thimble with alternate layers of powdered pumice, the tube and basin are rinsed out with dry ether, which is poured through the thimble in the Soxhlet's tube, and the contents are then thoroughly extracted with dry ether for 4 or 5 hours. The (turbid) ethereal extract will contain a little soap. It is first shaken in a separating funnel with hydrochloric acid to decompose calcium soaps, and after this has been drawn off and washed with water it is shaken with dilute potassium hydroxide solution containing a little alcohol in order to remove fatty acids.

After another washing with water, the ether is distilled off and the hydrocarbons weighed.

The proportion of hydrocarbons which has been found in genuine beeswax by Buisine, Mangold, Kebler, and Ahrens and Hett (*Zeit. öffentl. Chem.*, **5**, 91) has ranged from 11.0 to 17.5%. 15 samples of apparently genuine commercial yellow beeswax examined by Archbutt were found to contain from 12 to 16.7% of hydrocarbons; 6 obviously adulterated samples contained from 19.8 to 55.6%. The process is quite easy to work with a little practice, but is evidently not capable of detecting with certainty less than about 6% of hydrocarbons, owing to the comparative wide variation in the amount obtained from genuine samples.

Spermaceti is not usually an adulterant of beeswax, but occasionally its substitution would be profitable and might be practised. It is the only adulterant which would cause the sample to show less free acid, and yet require an increased proportion of alkali for its saponification, at the same time yielding glycerol and reducing the sp. gr. and m. p. In the absence of carnaüba wax, a direct indication of the presence and proportion of spermaceti may be obtained from an estimation of the m. p. of the higher alcohols of the sample.

From an inspection of the table on page 340, it appears that *carnaüba wax* requires for complete saponification a proportion of alkali not very different from that required by beeswax, but is distinguished from the latter by the smaller (but very variable) proportion of alkali required by the free acid. An admixture of carnaüba wax will be further indicated by the increased sp. gr. and higher m. p. of the sample.

Another proof of the presence of carnaüba wax is obtainable by removing free acid by alcohol and alcoholic potassium hydroxide, saponifying the separated neutral wax, treating the solution with lead acetate, exhausting the precipitate with petroleum spirit, and decomposing the soap with hot hydrochloric acid. Beeswax, when thus treated, yields a product which is chiefly palmitic acid (m. p., 62°), whilst the product similarly obtained from carnaüba wax is largely cerotic acid (m. p., 79°).

Among the hydrocarbons isolated from the wax may be found unchanged *cholesterol*, if the sample had been adulterated with *wool wax*, since Lewkowitsch (*J. Soc. Chem. Ind.*, 1896, **15**, 14) has

shown that cholesterol is practically unchanged by heating for 2 hours with soda-lime at 250°, and that 80% of the total alcohols of wool wax were recovered unchanged.   In presence of wool wax, cholesterol may also be looked for in the unsaponifiable matter. Some results of examination of the unsaponifiable matter from waxes are given in the following table (Archbutt and Deeley):

	Unsaponifiable matter from		
	Beeswax	Carnaüba wax	Wool wax
Sp. gr. at $\frac{100°}{100°}$	0.8239	0.8426	0.957
M. p.	75°–76°	85°	44°–48°
Iodine value	....	....	35–40
Saponification value of mixed acetates	9.9–10.3	12.3	15.0–16.1

For the detection of *artificial colouring matters*, Lemaire (*J. Soc. Chem. Ind.*, 1904, 23, 840) recommends the following tests:

A small fragment of the wax is dissolved in chloroform, and 2 or 3 drops of hydrochloric acid are added to the solution.   The production of a rose-red colour indicates artificial colouring matter. Another portion is saponified by boiling with sodium hydroxide solution, then treated while hot with excess of hydrochloric acid. If a fugitive rose-red colour is obtained, which turns green on adding excess of ammonia, the wax is artificially coloured.   Another piece of the wax is melted in a capsule with saturated boric acid soution; on evaporating to dryness the residue acquires a reddish colour with wax containing added colouring matter.

Dieterich (*Chem. Zeit.*, 1907, 31, 987) has shown that the analytical values of *beeswax from combs five years old* differ very little from those of new beeswax; the chief differences were in the colour, and the sp. gr. and m. p. of the waxes.   Thus, the fresh wax was nearly colourless, had the highest sp. gr. (0.966) and the highest m. p. (65° to 66°).   The old wax was dark brown, had the lowest sp. gr. (0.9599) and lowest m. p. (63° to 63.5°).

Hehner's Method for the Analysis of Complex Candle-mixtures.[1]— The estimation of the percentage of beeswax in so-called wax candles

[1] From a paper by Hehner read before the Society of Public Analysts.

has assumed importance since, in 1904, the College of Rites of the Roman Catholic Church prescribed the use of candles containing definite percentages of beeswax for certain ritual and altar purposes. Such candles may contain, besides beeswax, paraffin wax (ceresin, ozokerite), stearine (commercial stearic acid), and spermaceti.

Hehner's method for the analysis of such mixtures depends primarily upon the approximate constancy of composition of normal beeswax. Thus, 24 samples of good commercial bleached wax were found by Hehner to contain free acid, calculated as cerotic acid (Brodie's formula, $C_{27}H_{54}O_2$), ranging from 15.5 to 17.6% and averaging 16.6%, or almost exactly one-sixth of the wax, and saponifiable esters, calculated as myricyl palmitate, ranging from 85.2 to 89.9% and averaging 87.7% or very nearly 5.3 times the acidity expressed as above. The free acid extracted from a small number of samples was found to have a molecular weight of 407 ($C_{27}H_{54}O_2 = 410$).

Upon the basis of these figures, the composition of a mixture containing only *beeswax* and *paraffin* wax is easily inferred from the depression in acidity and saponifiable substance, the relation between these (1 : 5.3) remaining unaltered. With a mixture of *beeswax* and *stearine* the amount of saponifiable matter gives the measure of the wax, and by difference that of the stearine, commercial stearine as used for candle manufacture having an average molecular weight of about 272. Lastly, in a mixture of *beeswax* and *spermaceti* the free acid measures the amount of wax, the spermaceti being practically free from acid. It is when the ingredients are unknown, or when the ratio is disturbed in two directions by the presence of both stearine and spermaceti that the problem becomes difficult; an estimation of one or both of the main components of beeswax then becomes essential.

Except carnaüba wax, which is not commonly used in candle manufacture, beeswax is the only candle material which contains free cerotic acid, but for the separation of this acid from the esters Hehner points out that alcohol cannot be used, since the esters themselves are much too soluble in alcohol for even an approximate estimation to be based upon the greater solubility of the free acid. He, therefore, converts the free acid into potassium salt, which is soluble in warm water and from which the insoluble esters can be separated by shaking out with ether. The difficulties of the process

are mechanical and arise chiefly from the great viscosity of the soap solution. Thus, with pure beeswax not more than 5 grm. can be dealt with in a volume of 1500 to 2000 c.c., but with mixtures the mechanical difficulties become less. The process is carried out as follows:

10–12 grm. of the material to be examined are boiled with 70–100 c.c. of alcohol and carefully and exactly neutralised by adding phenolphthalein and alcoholic potassium hydroxide solution; about 600 c.c. of hot distilled water are then added and the unsaponified matter is allowed to come to the top, where it forms an oily layer. The soapy turbid solution is siphoned from below the oily layer into a large separating funnel holding about 2 litres, the layer being washed 3 times more with hot water, so that the total volume of soapy liquor in the funnel, containing the whole of the originally free acid, measures about 1500 c.c. (The unsaponified portion can be kept for subsequent operations.) The soapy liquor is cooled to about 35°, and to it are added from 150 to 200 c.c. of ether, and the funnel very gently shaken. Violent shaking must on no account be resorted to, as an emulsion would form with which it would be almost impossible to deal. The funnel is placed in a large vessel of water at about 35° and left for an hour or two for the ether to rise. The aqueous portion is then drawn off into another funnel and shaken twice more with ether, after which it should be clear or nearly so. Alcohol must not be added at this stage to promote separation of the ether, as partial saponification of the esters would occur and lead to inaccurate results. The ethereal solution is rejected as it is separated, and *not* washed with water. To the soap solution is now added hydrochloric acid in excess, by which the soap is decomposed and a layer of ether containing the liberated fatty acid rises. This is allowed to separate thoroughly, and the lower aqueous layer is drawn off and rejected. The fatty ether, having been washed carefully with water several times, is evaporated, and the residual fatty acids dried and accurately weighed; they are then very carefully titrated with alcoholic potassium hydroxide solution, *which must not be stronger than* $N/3$, *owing to the high molecular weight of the cerotic acid.* Care must also be taken that the alcohol in which the acid is dissolved before titration is exactly neutralised, and that the alkaline solution is kept free from carbonate and accurately standardised.

The only acids which can compose the material titrated are the free acids of the wax, with a mean molecular weight of about 407, and the "stearine," with a molecular weight of 272 ± 1. The molecular weight gives, therefore, the proportion of crude cerotic acid in the mixture.

In a separate portion of the original wax mixture the total acidity is now estimated as usual, and also the ester value. The molecular weight of the free acids being known, the actual percentage of free acids in the mixture can be calculated, and as the percentage of real wax acid of molecular weight 407 in these free acids is also known, the percentage of free wax acid in the mixture can also be calculated. Multiplying this by 6, the amount of beeswax in the mixture is arrived at; and subtracting it from the total acid, the percentage of "stearine" is obtained. Multiplying the wax acid by 5.3, the ester portion of the beeswax, expressed in terms of myricin, results; this subtracted from the total saponifiable matter gives the measure of any spermaceti that may have been present. A calculation reducing this remainder from terms of myricin, with an equivalent of 676, into terms of spermaceti, with an equivalent of about 480, results in a close approximation to the actual percentage of spermaceti. This remainder, if any, is paraffin wax. The presence of paraffin wax, if more than 4 or 5%, is always seen during the saponification for the estimation of the ester value. The paraffin wax is the only material estimated by difference.

Of other acid substances which would interfere with the process there might be present traces of mineral acid or oxalic acid from the bleaching processes. These can easily be detected and, if necessary, removed by melting some of the substance with boiling water and testing the aqueous solution. Resin acids do not mix to any practicable amount with candle materials. The bee stops all crevices of the hive with various resins collected from trees and buds, called *propolis*. All honeycomb is more or less contaminated with propolis, but the latter separates from the melted wax and is not an ingredient of commercial wax. Carnaüba wax has an exceedingly small acid value, which need not be taken into consideration.

The following results of analyses of known mixtures show the degree of accuracy obtainable:

	Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found
Beeswax	48	50	80	85	20	18	69.8	65	26.5	28
Spermaceti..........	4	4	0	0	10	12	14.0	15	.....	.....
Stearine....	10	10	10	10	35	36	6.3	10	.....	.....
Paraffin wax........	10	} 36	10	5	35	34	9.9	10	.....	.....
Ceresin.............	28									

When the candle mixture is free from spermaceti the total saponifiable matter, calculated as myricin, should be 5.3 times the amount of wax acid found. How nearly this is the case is shown by the following analyses of candle material acknowledged to be free from spermaceti:

ANALYSES OF CANDLES FREE FROM SPERMACETI

Total free acid calculated as $C_{27}H_{54}O_2$	Real wax acid of molecular weight 407	Real percentage of free acid	Total saponifiable esters calculated as myricin	Paraffin wax	Wax acid × 6	% wax stamped on candle
25.7	12.5	22.4	66.0	present	75	75
22.1	11.1	19.2	55.3	present	66.6	65
55.3	3.1	39.4	16.6	present	18.6	25
25.6	12.4	22.1	64.3	present	74.4	75
22.1	10.6	19.1	56.5	present	63.6	65
55.4	3.3	39.6	17.6	present	19.8	25
23.4	10.8	20.6	55.4	present	64.8	65
50.9	3.2	36.9	16.4	present	19.2	25
25.9	12.6	22.4	64.8	present	75.6	75
23.3	11.2	19.4	55.3	present	67.2	65
51.5	4.4	37.3	22.4	present	26.4	25
23.7	9.4	19.8	47.5	present	56.4	75
50.9	1.9	36.1	9.9	present	11.4	25
73.7	nil	50.0	1.3	present	0	25
30 3	9.0	44.8	46.4	present	54.0	65
50.3	2.8	35.8	23.5	present	16.8	75
34.1	3.6	38.8	26.8	present	21.6	75
26.8	12.4	23.0	67.2	present	74.4	75
49.1	3.9	35.6	23.3	present	23.4	75

In all these cases, the free acid in column 1 multiplied by 5.3 equals or exceeds the total saponifiable matter as myricin and leaves no room for spermaceti or fatty substance, satisfactorily proving that the real wax acid had been correctly estimated, that spermaceti was absent, and that the wax used had been of normal composition and

was not Bombay or other wax of abnormal composition. Some of the stamped percentages were fully confirmed by the analysis; in other cases the stamp was obviously deceptive. From the figures in the table the real composition of the candles can be calculated, as already explained. The following are analyses of material containing spermaceti:

ANALYSES OF CANDLES CONTAINING SPERMACETI

Analytical Data.					
Total free acid calculated as $C_{27}H_{54}O_2$.....	34.8	10.9	14.8	34.9	59.1
Actual wax acid.........................	9.6	10.9	12.3	9.1	4.0
Real percentage of free acid.............	27.5	10.9	14.2	27.6	42.3
Total saponifiable esters calculated as myricin.	63.4	64.7	74.8	62.0	30.6
Calculated Composition.					
Beeswax.............................	57.6	65.4	73.8	54.6	24.0
Spermaceti...........................	8.8	4.8	8.1	9.7	6.6
Stearine.............................	17.9	none	2.5	18.5	38.3
Paraffin wax.........................	15.7	29.8	15.6	17.2	31.1
% of wax stamped on candle............	55	65	75	55	25

Hehner points out that his method is not applicable to candle mixtures containing abnormal or insect waxes (see Ghedda Wax), which he does not regard as true beeswax. For the analysis of mixtures which may contain such waxes besides the four main ingredients above mentioned, the alcoholic as well as the acid constituents need examination. No satisfactory method is at present available. Hehner has endeavoured to elaborate a method based upon the fact that oxidation by means of chromic acid in acetic acid solution converts a wax alcohol, such as cetylic alcohol, into the corresponding acid, but in practice the action is complicated by the fact that partial acetylation of the alcohol occurs, and the acetyl derivative is not attacked by the chromic acid. The appl cation of the method to a comparatively simple wax-like spermaceti and the estimation of paraffin wax in admixture with spermaceti or sperm oil is illustrated as follows:

The substance is saponified, diluted, and the paraffin wax and wax alcohols shaken out with ether. The fatty acids are liberated from

the soap solution, and their mean molecular weight and iodine value determined; from which the proportions of palmitic, stearic, and oleic acids are deducible.   The alcohols + paraffin wax are dissolved in glacial acetic acid, and solid chromic acid is ntroduced, in small quantities at a time, until a decided excess is shown by the colour of the liquid. The solution is largely diluted with hot water, whereby all reaction products and the paraffin wax separate.   These products are boiled with excess of alcoholic potassium hydroxide to hydrolyse the acetyl derivatives formed, and by addition of water and acid separation of the material from the alcohol is again effected.   Once more oxidation with chromic acid in glacial acetic acid is carried out, and practically the whole of the wax alcohol will now have been converted into its corresponding fatty acid.   By treatment with alcoholic potassium hydroxide, dilution of the soap solution and shaking out with ether, a separation of the paraffin wax is effected, and the fatty acid is then separated from the soap solution and its molecular weight ascertained.   An insight into both the acid and the wax-alcoholic portions of the substance is thus obtained, and any paraffin wax present is separated and estimated.

The same process is applicable to more complex mixtures; but there are many practical difficulties caused by the sparing solubility of myricyl alcohol in ether and the fact that the soaps of the higher acids are so little soluble in water and form such very viscid solutions.

Indian Beeswax (Ghedda Wax)

Chinese Beeswax

This wax, though of good quality and colour, yields analytical values which differ very materially from those obtained with European waxes.   It is softer and more plastic than normal beeswax.   The acid values are very low, and the ester values high, with the result that the ratio-numbers range from 7.4 to 17.9, the mean being about 12.

According to Hooper (*Indian Agric. Ledger*, 1904, 73–100; *J. Soc. Chem. Ind.*, 1904, 23, 828), Ghedda wax is derived from three species of bees, *Apis dorsata*, *A. indica*, and *A. florea*, but chiefly from *A. dorsata*.   The analytical characters of the waxes are shown in the following table:

Origin of wax		M. p., °	Acid value	Saponification value	Ester value	Iodine value
A. dorsata (23 samples)	Max.	67.0	10.2	105.0	97.8	9.9
	Min.	60.0	4.4	75.6	69.5	4.8
	Av.	63.1	7.0	96.2	89.4	6.7
A. indica (7 samples)	Max.	.64.0	8.8	102.5	95.9	9.2
	Min.	62.0	5.0	90.0	84.0	5.3
	Av.	63.25	6.8	96.2	89.6	7.4
A. florea (5 samples)	Max.	68.0	8.9	130.5	123.8	11.4
	Min.	63.0	6.1	88.5	80.8	6.0
	Av.	64.2	7.5	103.2	95.6	8.0

Buchner (*Chem. Zeit.*, 1905, **29,** 32, and 1906, **30,** 528) is of opinion that Ghedda wax is a true beeswax, differing from the European kind quantitatively but not qualitatively. Thus, he obtained by analysis of a sample: cerotic acid, 5.13; palmitic acid, 37.87; melissyl alcohol, calculated from the hydrogen evolved in Buisine's process, 65.09; hydrocarbons, 8.65%. Hooper says Indian wax is rarely adulterated, and as there is a large quantity of it produced, analysts must be on their guard against mistaking specimens of this wax for adulterated beeswax.

Buchner (*Zeit. öffentl. Chem.*, **3,** 570) obtained the following results by examination of several samples of Indian and Chinese beeswax:

Kind of wax	M. p.,°	Acid value	Saponification value	Ester value	Ratio number	Iodine value
Indian........	65	6.1	83.3	77.2	12.1	10
Indian........	66	6.01	82.12	76.11	12.6	10
Chinese.......	66	7.55	93.7	86.15	11.4	..
Chinese.......	.....	6.28	90.2	83.82	13.9	..
Chinese.......	.....	6.40	96.7	90.30	15.6	..
Chinese.......	.....	5.33	95.61	90.28	17.9	..
Chinese.......	62–63	8.72	120.17	111.45	12.78	..
Chinese.......	.....	7.51	92.14	84.63	11.26	..
Chinese.......	.....	9.74	117.40	107.66	11.06	..

Hooper (*loc. cit.* above) also describes the wax produced by the Dammar or Kota bees, *Melipona (Trigona)* species. These very small stingless insects produce a sticky, dark coloured wax, having a

m. p. of 70.5°; acid value, 20.8; saponification value, 110.4; ester value, 89.6; ratio number, 4.3; and iodine value, 42.2.   The product more nearly resembles the propolis of honey bees than true wax, from which it differs largely in chemical and physical characters.

Very similar to Indian beeswax from *A. dorsata* is *Annamese beeswax*, which has been examined by Bellier (*Ann. Chim. anal. appl.*, 1906, **11**, 366).   The commercial wax is greyish-yellow, not homogeneous, and appears to have been kneaded by hand into prismatic cakes which were in one case found to contain 5.02% water, 0.5% insoluble in benzine, and 0.08% of ash.   After melting and straining, it resembles European beeswax in general appearance, but its chemical and physical characters are similar to those of the Indian wax, as shown below.

```
Sp. gr............................................  0.964
M. p.............................................  61°
Acid value......................................  7.8
Saponification value............................  94.4
Ester value.....................................  86.6
Ratio number....................................  11
Iodine value....................................  6
Hydrogen liberated at 250° by potash-
    lime, per grm. of wax......................  60.3 c.c. at 0° and 760 mm.
Hydrocarbons...................................  10.5
```

CANDELILLA WAX

The candelilla plant, which grows abundantly in Mexico and Texas, reaches a height of about 25 inches.   Several factories have been established for extracting the wax from the shrub.   According to a U. S. Consular Rep. (Sept. 12, 1919), the wax is extracted by putting the shrubs, as gathered, into water, which is then gently heated to the boiling point.   Sulphuric acid is now added, and the separated wax is collected and put into receptacles to solidify.   It is subsequently treated with steam and sulphuric acid in another tank, and after this refining is cast into moulds.

Buchner (*Chem. Zeit.*, 1918, **42**, 373) obtained the following average results with samples of candelilla wax: acid value, 16.96; ester value, 33.86.   The wax contained from 50 to 52% of hydrocarbons.

The wax is used for phonograph records, carbon duplicating papers, varnish, linoleum, celluloid, and lubricating oils.   Its usual m. p. is from 68°–70°.

CARNAÜBA WAX. CARNAHUBA WAX

(See pp. 113, 338 and 350.)   This is a very hard, sulphur-yellow or yellowish-green substance, which coats the leaves of a palm, *Copernicia cerifera*, the carnaüba tree of Brazil.   The leaves are detached, beaten, and the dust, amounting to about 50 grm. per leaf, collected and melted into a mass.   The brittle, lustrous wax thus obtained has a sp. gr. of 0.999, melts at 84° to 85°, and dissolves in alcohol and boiling ether.   On ignition, it leaves a small quantity of ash, which often contains iron oxide.

Carnaüba wax has a very complex composition.   It has been investigated by Bérard, Story-Maskelyne, Piverling, and very thoroughly by Stürcke (*Annalen*, 223, 283), who found it to consist mainly of myricyl cerotate.   In the alcoholic extract of the wax, Bérard found free cerotic acid, since confirmed by Hehner and by Hübl; Story-Maskelyne and Stürcke, in the same solution, found free myricyl alcohol.   Stürcke obtained from carnaüba wax the following substances: a crystalline *paraffinoid hydrocarbon* melting at about 59°; *ceryl alcohol*, $C_{27}H_{55}OH$, a crystalline substance melting at 76°; these two fractions did not exceed $1\frac{1}{2}$ to 2%.   *Myricyl alcohol* was found to the extent of about 45%; a *dihydric alcohol*, $C_{23}H_{46}(CH_2OH)_2$, melting at 103.5°, and converted on heating with soda-lime into an acid melting at 102.5°, and having the composition, $C_{23}H_{46}(COOH)_2$; an *acid* of the formula $C_{23}H_{47}.COOH$, melting at 72.5°, isomeric with lignoceric acid; *cerotic acid*, the chief acid of carnaüba wax, melting at 79°, or an acid isomeric therewith; and a *hydroxy-acid* of the formula $CH_2OH.C_{19}H_{38}.COOH$, yielding on heating with soda-lime the acid $C_{19}H_{38}(COOH)_2$, melting at 90°.

Allen and Thomson (*Chem. News*, 1881, 43, 267) obtained 54.87 %, and Archbutt 52.4% of unsaponifiable matter (alcohols, etc.) from carnaüba wax.   Lewkowitsch (*Analyst*, 1899, 24, 321) found an acetyl value of 55.24, the same sample having a saponification value of 79.68.

The constants of carnaüba wax have more recently been redetermined by Radcliffe (*J. Soc. Chem. Ind.*, 1906, 25, 158).

A sample of Ceará wax melting at 84° was used for the experiments; and also a bleached sample, which melted at 61°.   The figures for the acid value range from 4 to 8, and O. Eichhorn (*Zeit.*

anal. Chem., 1900, **39**, 640) states that by dissolving 3 grm. of the wax in 120 c.c. of boiling amyl alcohol he obtained an acid value of 9.71.   A repetition of the above method gave for the Ceará wax 5, and for the bleached sample 0.56.   The saponification values stated by various observers vary from 79 to 95.   A series of experiments were made in order to ascertain which method gave the maximum value; and it was found that, by treating 5 grm. of the wax with 60 c.c. of amyl alcohol and 50 c.c. of ordinary alcoholic potassium hydroxide (60 grm. to the litre) and boiling for 6 hours, the figure 88.3 was obtained, the bleached sample giving 33 to 34.   The iodine value by Wijs' method was, after 24 hours, 13.17.   The values obtained on one and the same sample of carnaüba wax were:

M. p. (in capillary tube)	84^c
Acid value	2.9
Saponification value	88.3
Ester value	85.4
Iodine value	13.17

Carnaüba wax, when in a separate state, is readily recognised by its physical characters and the results of its saponification.   It is sometimes employed as an adulterant of beeswax, in which its presence may be recognised by the high sp. gr. and m. p. of the substance, and by the m. p. of the fatty acids produced by the saponification of the neutral esters of the sample.   The presence of carnaüba wax in soap is best recognised by mixing the sample with sand, drying thoroughly, and exhausting the mixture with petroleum spirit (boiling at about 100°) or hot toluene in a Soxhlet's tube. The residue left on distilling off the solvent is identified by a comparison of its characters with those of the unsaponifiable matter from carnaüba wax given on p. 340, or by the isolation of myricyl alcohol.   The weight of alcohols, etc., divided by 0.53 gives approximately the amount of carnaüba wax in the quantity of soap employed.

Valenta found carnaüba wax in a number of commercial ceresins and paraffin waxes which were characterised by their high m. p. and great hardness.   It is employed to impart these properties and to give a peculiar lustre to the wax.   Valenta gives the following figures showing the influence of carnaüba wax, melting at 85°, on the m. p. of mixtures containing it.

Percentage of carnaüba wax	M. p.,° of substance or mixture		
	With stearic acid	With ceresin	With paraffin wax
0	58.50	72.10	60.15
5	69.75	79.10	73.90
10	73.75	80.56	79.20
15	74.55	81.60	81.10
20	75.20	82.53	81.50
25	75.80	82.95	81.75

These results show a very marked increase in the m. p. of the substances by the addition even of 5% of carnaüba wax. Further additions increase the m. p. in a diminished ratio.

The proportion of carnaüba wax existing in admixture with the foregoing substances, or with Japan wax, can be ascertained by estimating the percentage of potassium hydroxide required for the neutralisation of the free acid and for the saponification of the esters of the sample, and by the estimation of the unsaponifiable matter.

Carnaüba wax is bleached for candle-making (*J. Soc. Chem. Ind.*, 1894, **13**, 744) by filtration through animal charcoal, or by hydrogen peroxide or potassium dichromate. Candles are seldom made of carnaüba wax alone, but of a mixture containing 20 to 30% of stearine and ozokerite. "Brilliant paraffin" is a mixture of paraffin wax, 75%; carnaüba wax, 25%. "Brilliant gelatin," used for finishing leather, is prepared by adding a liquid containing water, potassium carbonate, and carnaüba wax to a solution of gelatin. Carnaüba wax is also used in making special varnishes, in the manufacture of phonograph cylinders, and as a constituent of "carbon" duplicating papers.

MONTAN WAX

(See p. 113.) Montan wax is the commercial name of a wax of high m. p., which is extracted by means of solvents from lignites or lignite tar and from peat. It differs considerably in its characteristics according to its source and mode of preparation, but, as usually sold, it is a hard, dark brown product with a wax-like surface.

Zaloziecki and Hausmann (*Zeitsch. angew. Chem.*, 1907, **20**, 1141) separated a mixture of waxes from German peat by extraction

with hot alcohol, the yield being 1%. The product when fractionated with ether or benzine was separated into a dark green soluble portion and a brown insoluble portion, the former containing and acid, $C_{16}H_{25}O_5$, (m. p. 184°), and the latter an acid, $C_{21}H_{35}O_7$, not melting at 260°. The same alcohol, $C_{20}H_{40}O$, was obtained from both portions. It was of a yellow colour and melted between 124° and 130°.

The montan wax separated by Ryan and Dillon (*Scient. Proc. Roy. Dublin Soc.*, 1913, 12, 202) from Irish peat differed materially from that described by Zaloziecki and Hausmann. It was a yellow crystalline substance melting at 76°. It was sparingly soluble in cold alcohol, ether, chloroform and gasoline (petroleum spirit), but readily soluble in the hot solvents.

A sample consisting of 53% of acid and 47% of unsaponifiable matter gave the following results:

```
Acid value......................................  73.3
Saponification value............................  73.9
Iodine value....................................  16.0
```

It contained no resins or phytosterol. The acid, which consisted almost entirely of montanic acid, $C_{28}H_{56}O_2$, could be crystallised from alcohol in crystals of m. p. 83°. The unsaponifiable matter was crystallised from benzine in fine needles melting at 58° to 59°. It had a sp. gr. of 0.92 and contained 83.56% of carbon, 14.0% of hydrogen, and 2.44% of oxygen. It contained neither primary nor secondary alcohols.

Montanin wax, also examined by Ryan and Dillon, had m. p. 95° to 97° and differed from montan wax only in the fact that part of the montanic acid was present in the form of its sodium salt, so that the wax was harder.

Montan wax from Irish lignite gave values similar to those of montan wax.

Pschorr and Pfaff (*Ber.*, 1920, 53, 217) found crude montan wax from German lignite to contain up to 17% of montanic acid (m. p. 83.5°), not less than 53% of montanic acid esters, and 30% of substances of unknown composition.

Montan wax is used for various purposes in which a wax of high m. p. is required, such as phonograph records and "carbon" duplicating papers, and the residues which are obtained in purifying the better qualities of wax are used in shoe polishes and the like.

The partly saponified product (see *montanin wax, supra*) is also used for the manufacture of commercial articles (*e. g.*, carbon papers) in which a wax of very high m. p. is required.

CHINESE INSECT WAX

(See p. 113.)   This wax is derived from an evergreen tree, *Ligustrum lucidum*, which grows in western China (*J. Soc. Chem. Ind.*, 1892, 11, 282) not far from the Thibetan frontier.   Early in the spring, numerous brown pea-shaped scales containing the larvæ of the wax insect, *Coccus pela*, appear on its boughs and twigs.   These scales are gathered, wrapped in packages, conveyed about 200 miles to Chia-ting, the centre of the industry, made up into small packets with leaves, and suspended under the branches of a species of ash.   The insects on emerging from the packets creep up to the leaves of the ash trees, and afterward descend to the twigs and branches on which the wax is deposited by the males.   After 100 days, the deposit is complete, and the branches are then cut down, the wax scraped off, and what remains on the twigs is separated by boiling with water, which destroys the insects and necessitates a fresh supply of larvæ in the next year from outside districts. A pound of larvæ scales will produce 4 or 5 pounds of wax.

The product is a clear white, highly crystalline, brittle wax, called from its appearance "vegetable spermaceti."   It consists, principally, of ceryl cerotate.   It is chiefly used in China for coating the exteriors of candles made of animal and vegetable tallow, also as a sizing for paper and cotton goods, for imparting a gloss to silk, and as a furniture polish (*J. Soc. Chem. Ind.*, 1897, 16, 685).

SPERMACETI

(See also table on p. 113.)   Spermaceti exists in solution in the oil from the sperm whale, bottlenose whale, dolphin, and allied cetaceans, but not in the oil from the whalebone whales.   It is present most abundantly in the oil from the head cavities, and is commonly stated to be a special product thereof.   This is an error, the oil from the blubber also depositing spermaceti on cooling, and in practice the head and blubber oils are treated together.

Crude spermaceti forms crystalline scales of a yellowish or brownish colour.   It is purified by fusion, pressure, and boiling with a

solution of potash, to remove adhering oil and neutralise traces of acid. In practice, the complete removal of the oil is not aimed at, as a small proportion is found to confer desirable properties on the product. It is then remelted and cast into cakes.

As thus obtained, spermaceti is a snow-white or transparent substance of marked crystalline structure. It melts at 43° to 49°.[1] The sp. gr. at the ordinary temperature is usually between 0.942 and 0.946; but differing statements are made, probably owing to difficulty attending the determination, in consequence of the crystalline structure of the substance. Much more trustworthy determinations can be made of the sp. gr. in the melted condition, the value then ranging between 0.808 and 0.816 at a temperature of 98° to 99° (water at 15.5° = 1.0).

Spermaceti is insoluble in water, but dissolves in boiling alcohol, ether, chloroform, carbon disulphide, and fixed and volatile oils. Cold alcohol dissolves the adhering oil only. It separates in crystalline form from its solution in hot alcohol or ether and, after repeated purification in this manner, the m. p. reaches 53.5°, and the crystals consist of pure cetin.

Cetin or Cetyl Palmitate, $C_{16}H_{33}.O.C_{16}H_{31}O$, is the chief constituent of spermaceti, which, in addition, contains certain homologous esters. Thus, on saponification it yields:

Acids		Alcohols	
Lauric	$C_{12}H_{24}O_2$	Dodecyl alcohol	$C_{12}H_{26}O$
Myristic	$C_{14}H_{28}O_2$	Tetradecyl alcohol	$C_{14}H_{30}O$
Palmitic	$C_{16}H_{32}O_2$	Cetyl alcohol	$C_{16}H_{34}O_2$
Stearic	$C_{18}H_{36}O_2$	Octadecyl alcohol	$C_{18}H_{38}O_2$

Cetyl Alcohol, $C_{12}H_{33}.OH$, may be obtained in a state of approximate purity by saponifying spermaceti previously crystallised from hot alcohol. On evaporation of its ethereal solution, cetyl alcohol remains as a white or yellowish-white, tasteless, inodorous, crystalline mass, melting at 49.5°. When carefully heated it distils without decomposition at about 400°, and is volatile with the vapour of water. It is quite insoluble in water, but readily soluble in alcohol, ether, and petroleum spirit.

[1] The figure commonly stated as the m. p. of spermaceti really refers to the solidifying-point as determined by the "titer test." The spermaceti from bottlenose oil melts at a somewhat higher temperature than that from true sperm oil.

When heated with potash-lime to a temperature of $250°-280°$, cetyl alcohol is converted into potassium palmitate, with evolution of hydrogen.

Cetyl alcohol heated with glacial acetic acid forms cetyl acetate, $C_{16}H_{33}.C_2H_3O_2$, a crystalline substance melting at $22°$ to $23°$, and boiling at $200°$ under a pressure of 15 mm.

The proportion of potassium hydroxide required for the saponification of spermaceti is about 12.8%, corresponding to a saponification equivalent of 438. The molecular weight of cetyl palmitate is 480, and hence these figures point to the presence of a notable proportion of lower homologues of palmitic acid, such as have been proved by other means to exist in spermaceti.

On saponification, agitation of the aqueous solution of the resultant soap with ether, and subsequent decomposition of the soap solution with an acid, Allen found a sample of spermaceti to yield:

Higher alcohols, melting at $47.5°$...................... 51.48%
Fatty acids, mean combining weight, 231.4............. 52.96%

Pure cetyl palmitate would yield, theoretically:

Cetyl alcohol, melting at $49.5°$...................... 50.41%
Palmitic acid, combining weight, 256.................. 53.33%

Commercial Spermaceti.—Spermaceti is liable to turn yellow and rancid on exposure to air. Hehner found 2 out of 3 samples to be wholly devoid of free acid; the third had an acidity corresponding to 0.81% of free palmitic acid. 12 samples examined by Kebler (*Rev. intern. falsif.*, **10**, 208; *J. Soc. Chem. Ind.*, 1898, **17**, 383) ranged in acid value from 124.8 to 136.3. Five specimens of genuine spermaceti examined by Dunlop (*J. Soc. Chem. Ind.*, 1908, **27**, 63) gave the following results:

Sample number	1	2	3	4	5
Description	Spermaceti from "head-matter" of Cachalot; extracted in laboratory		Refined spermaceti from a reliable source		
M. p., °..................	41–41.5	41–42	44–44.5	44.5–46	45–45.5
Solidifying-point, °........	41.0	....	44.0	45.7	45.0
Iodine value (Wijs)..........	....	9.33	7.21	5.32	5.50
Saponification value........	129.0	120.0	120.6	121.8	120.6
Wax alcohols, etc., %........	54.22	53.20	53.00	51.56	....
Fatty acids, %..............	49.78	....	50.58	....	....
Free (oleic) acid, %.........	....	....	....	0.10	0.24
M. p. of fatty acids..........	32–33	....	39.5–40	....	....
M. p. of wax alcohols, etc.....	46–46.5	45.5–46	47–47.5	47.5–48	47.5–48
Iodine value of wax alcohols, etc	....	6.35	4.26	3.41	2.98

Dunlop directs attention to the iodine values found by him, which are considerably higher than those hitherto recorded. Pure spermaceti absorbs no iodine. Lewkowitsch found commercial samples of the wax absorbed from 3.52 to 4.09%, due, probably, to small amounts of sperm oil adhering to the spermaceti. In the case of Dunlop's No. 2 sample, the exceptionally high iodine value is accounted for by the presence of more sperm oil than usual, owing to the low temperature and pressure employed in its preparation.

The behaviour on saponification, low acid and iodine values, together with its physical characters, amply suffice to identify spermaceti and to detect any admixture. The most likely adulterants are stearic and palmitic acids, stearine, tallow, and paraffin wax.

Palmitic and *stearic acid* will be detected and estimated by determining the free acid of the sample by titration with standard alkali and phenolphthalein, any proportion of acid less than 1% being neglected. An admixture of beeswax would somewhat increase the acidity of the sample. Added fatty acids may also be detected by melting the sample in a test tube immersed in boiling water, agitating it with 2 volumes of ammonia of 0.960 sp. gr., and allowing the whole to cool. If the spermaceti is pure, it will rise to the surface and leave the ammonia nearly or entirely clear; but if adulterated with stearic acid, a thick white emulsion will be formed, which retains the spermaceti if the proportion of the adulterant is large, but allows it to rise and form a separate layer if the stearic acid is present only in moderate amount. 1% of the adulterant is said to be recognisable by this test. Dunlop found it reliable, down to about 3%, but with smaller quantities the test appeared somewhat uncertain.

Tallow and *stearine* are recognisable in spermaceti by the iodine value being in excess of the numbers given above; by the change in the fracture, feel, and appearance of the sample; and by the tallowy smell produced on heating. They will also be indicated by the results of the saponification of the sample. In presence of either adulterant the percentage of alkali required for saponification will be increased, the saponification equivalent correspondingly lowered, whilst the ether-extract will be diminished and the percentage of fatty acids increased almost in direct proportion to the extent of the adulteration. The saponification equivalent of spermaceti averaging about 438 and that of tallow about 288, each unit per cent. of the adulterant will reduce the saponification equivalent by 1.5. Thus, if a sample requires

14.78% of potassium hydroxide for saponification, corresponding to an equivalent of 380, the proportion of tallow may be assumed to be

$$\frac{(438 - 380) \times 2}{3} = 38.7\%$$

If free fatty acids are present, together with neutral fats, the same method of calculation will show approximately the sum of the two adulterants and, the fatty acids having been previously estimated, the proportion of fats can be ascertained; or, preferably, the fatty acids may be previously estimated in the same portion of the sample, and only the additional quantity of alkali required for the saponification of the neutral fat taken into account in the calculation. The ether-residue from genuine spermaceti being at least 50%, and from fatty acids and neutral fats practically *nil*, the percentage of such adulterants can be ascertained with accuracy. Each unit % of ether-residue obtained represents, approximately, 2% of real spermaceti in the sample.

Paraffin wax diminishes notably the sp. gr. of the sample, yields 100% of ether-residue, neutralises no alkali, and cannot, by admixture with any proportion of fatty acid or fat, be made to give results on saponification similar to those yielded by genuine spermaceti. Thus, a mixture of equal parts of paraffin wax and tallow will yield 50% of ether-residue, but the saponification equivalent will be about 576. Paraffin wax can be detected by Holde's test, as in the case of sperm oil, as little as 3.5% (according to Dunlop) being capable of detection. Smaller quantities, however, may be detected by boiling the unsaponifiable matter with acetic anhydride and observing the behaviour of the solution. If the spermaceti is genuine, the solution remains clear on cooling, but if paraffin wax is present, it becomes turbid, owing to separation of the wax. As little as 1% of paraffin wax in spermaceti can be detected in this manner (Dunlop).

BUTTER FAT

By CECIL REVIS, AND E. R. BOLTON

REVISED BY E. R. BOLTON

Butter fat is the fat of milk. When used without qualification the term means the fat from cow's milk, but the milks of other animals yield similar products.

Butter fat, as obtained from butter, has the well-known colour, taste, and smell of butter itself. The melting and solidifying-points differ considerably in different samples, being influenced by the mode of feeding and other factors. According to Meyer (*Milch Zeit.*, 1892, 21, 49) the m. p. is lowered by food consisting of easily digestible carbohydrates, but raised by straw, oil cakes, and sour fodder. Bell states that the m. p. is usually comprised between 29.5° and 33°, the maximum being 34.7°. These figures are in agreement with those of other observers. The sp. gr. and the coefficient of expansion are higher than those of most of the fats likely to be used for adulteration.

Butter (save for small quantities of unsaponifiable matter, discussed later) is composed almost exclusively of triglycerides of the fatty acids. The characteristic constituent is the radicle of butyric acid, which is present together with certain of its higher homologues.

Bell obtained the following products by saponifying 100 parts of butter fat.

Butyric acid	6.13	
Caproic, caprylic and capric acids	2.09	(mean combining weight = 136)
Myristic, palmitic, and stearic acids	49.46 ⎫	= 85.56
Oleic acid	36.10 ⎭	
Glycerol (calculated)	12.54	
	106.32	

The fatty acids soluble in water were regarded as butyric acid. Those soluble in hot water only appear in the analysis as caproic acid, etc., the combining weight being deduced from the amount of barium carbonate left on igniting the salts.

Siegfield (*Zeitsch. Nahr. Genussm.*, 1912, **24,** 45) has carried out some work on the acids present in butter fat and is of the opinion that the non-volatile acids consist of oleic, palmitic and myristic acids, a considerable quantity of the latter being sometimes present. Stearic acid was not found. The volatile acids consist chiefly of butyric, caproic and caprylic acids in very variable proportions, whilst the volatile insoluble acids contain a small quantity of caprylic acid and probably traces of palmitic and myristic acids.   According to v. Fodor (*Ibid.*, 1913, **26,** 641) caproic acid is the normal acid and not the isobutylacetic acid; this is confirmed by Smedley (*Biochem. J.*, 1912, **6,** 451), but the latter investigator finds 10 to 15% of stearic acid, a result which coincides with the analyses of Holland and Buckley (*J. Agric. Res.*, 1918, **12,** 719) who, having directly esterified butter fat, separated the esters by fractional distillation, and having obtained iodine and saponification values of the fractions deduce the composition of the fat to be as follows:

	PER CENT.
Butyric acid	3.15
Caproic	1.36
Caprylic	0.98
Capric	1.83
Lauric	6.90
Myristic	22.62
Palmitic	19.23
Stearic	11.38
Oleic	27.37

These authors had previously stated (*J. Agric. Res.*, 1916, **6,** 101) that the proportion of stearic acid in butter varied according to the nature of the animal's food, and give the percentage as 7–22, the increase resulting from feeding with beef tallow and palm oil.

This more recent work is contrary to the finding of previous observers who suggested much smaller quantities of stearic acid. Drummond and Channon in paper read before the Biochemical Society (December, 1923) expressed the opinion that the method used by Holland and Buckley is based upon a fallacious argument, and they do not confirm these authors' figures.

Examination of Butter Fat.—The examination of butter fat is undertaken for the purpose of detecting adulteration with foreign fats. Many substances have been described as being used for such purpose, but the fats used are more particularly confined to lard, oleo products, and oils of the coconut group. Cottonseed oil,

stiffened with beef stearine, and cottonseed stearine, and other vegetable oils are also used, but these latter are very easy of detection. Certain commercial cooking fats sold under the name of "compound" (and when they contain lard as "lard-compound") may be added. Such compounds may be divided into two classes: (a) a liquid oil admixed with beef stearine or hydrogenated fat, (b) a liquid oil hydrogenated only sufficiently to produce a soft solid. The adulteration may consist of the entire substitution of margarine (oleomargarine) for the butter, in which case no difficulty is experienced in detection; or one or more of the above-mentioned foreign fats may be used, when small sophistications (under 10%) are often difficult to certify, especially if a judicious mixture has been used. Coconut and palm-kernel oils probably seldom find their way into butter directly, but as a constituent of substitutes. It is therefore absolutely necessary not to rely on any one test, the use of two or three reliable methods, however, being usually quite sufficient to detect the most skilful adulteration.

During the last few years, many methods have arisen for the purpose of detecting one or other form of adulteration in butter. As, however, many of these either fail to effect the required result, or are no advance on existing methods, only such are given here as are easy of application, of real utility, and which, with one exception, are used fairly generally. In all forms of butter fat analysis, reference to limits for true butter fat is an absolute necessity; a selection of the results obtained by various observers with each method is therefore given:

The methods described are those which directly or indirectly obtain values for: (1) The refractive index of the fat; (2) the content of volatile fatty acids soluble and insoluble in water; (3) the sp. gr. of the fat; (4) the mean molecular weight of the total fatty acids; (5) the mean molecular weight of the soluble and insoluble fatty acids.

1. **The Refractive Index of the Fat.**—This test is of considerable value for quickly detecting very flagrant adulteration; it breaks down, however, in the case of the more skilful forms of scientifically made mixtures. This will be understood when one considers that coconut and palm-kernel oils give a lower figure than butter fat, while beef fat, lard, and other adulterants give higher figures. It is obvious, therefore, that mixtures can be made to give the same read-

ing as genuine butter fat. Notwithstanding this, the test is so quickly and easily performed, and so often affords immediate indication as to the direction of the adulteration, that it should not be neglected.

Several different forms of instrument are made for measuring the refractive index of fats.

The Zeiss scale *butter refractometer* is by far the most convenient, requiring only about 5 drops of the fat; and reading with extreme delicacy. The scale is an arbitrary one, and may be converted to refractive index (N_D) if required. It should be noted that free fatty acids tend to reduce the reading, but the amount usually contained in butter fat is too small to produce any effect. Much confusion has arisen owing to there not being any fixed temperature at which to make the observation, and various workers have unfortunately chosen different temperatures. The most used temperature is 40°, and it is hoped that as this temperature is the one recommended by a sub-committee of the London Section of the Society of Chemical Industry it will become universal for fatty oils. Readings taken at other temperatures may be converted with sufficient accuracy by subtracting or adding 0.55 of a scale division for every degree rise or fall in temperature—the refraction being reduced as the temperature rises. In order that the reading may be taken at any temperature and quickly converted to the equivalent at the standard temperature, Leach and Lythgoe have devised a special slide rule to perform the calculation, and also to convert the Zeiss scale to N_D or *vice versa* if required. They take account of the fact that the correction is not the same for all fats. Richmond (*Analyst*, 1907, 32, 44) criticises this rule adversely and points out sources of error. To avoid chance of error it is therefore better to take the reading at the temperature required, in which case the Zeiss water-heating apparatus should be used, by the use of which the prisms of the instrument may be brought to the required temperature in a few minutes, and maintained within a few tenths of a degree for a considerable time. Richmond (*ibid.*) gives the following method for the preparation of a correction chart:

"In the centre of a sheet of squared paper, at least 20 units by 12, lay out vertically the 35° line, dividing it into 100 parts. At the 100 line draw a line perpendicular to this on both sides and lay out temperatures 1° = 0.7 unit; at the 24 line draw a similar line, laying out

temperatures $1° = 0.5$ unit. Join the corresponding temperatures extending them to zero. These will be the temperatures lines. On the 109 line find a point 8.5 units to the right; join this and 100 on the 35° line, extending it across the sheet; draw through each 5 on the 35 line lines of refraction parallel to this. To correct readings, find corresponding temperature and refraction lines. The correction is the number of units between lines corresponding to the temperature read and the temperature to which it is to be corrected, measured horizontally."

The following figures have been recorded:

Norwegian (Rifle), 38.7 (December) to 43.7 (June) at 45°; mean 39.5 to 41.95.

Russian (Lewin), 38.4 to 42.0 at 45°.

British (Thorpe) 371 samples from various farms and colleges. 37.3 to 43.0 at 45°.

Dutch (Bemelmanns), stall-fed cows 41.9 (November) to 43.2 (September), and for cows kept in the open field 43.3 to 47.6.

Dutch (Fritzsche), 42.0 to 45.4 at 40°.

Ludwig, for 110 samples of pure butter (1906) 40.0 to 43.6 at 40°.

Observation of the refractive index of the fatty acids themselves has been suggested. Reference should be made to Ludwig (*Zeitsch. Nahr.-Genussm.*, 1907, **14,** 208); Sprinkmeyer and Fürstenberg (*ibid.,* 213); Sudendorf (*ibid.,* 217), and Dons (1906, **13,** 257).

2. **The Content of Volatile Fatty Acids, Soluble and Insoluble, in Water.**—(The words "soluble" and "insoluble" are relative. Soluble or insoluble in the quantity of water employed is meant.) Butter itself is distinguished by the large percentage of volatile water-soluble acids which it contains as compared with practically every other fat. The volatile water-soluble acids of butter are almost entirely butyric acid and caproic acid. The volatile water-insoluble acids are comparatively small in amount and consist practically of caprylic acid, with traces of capric and lauric acids. Lard and oleo-products contain practically no volatile water-soluble acids, whilst in coconut oil and palm-kernel oil the volatile acids, though larger in quantity than in most fats other than butter fat, consist for the greater part of water-insoluble acids. These facts enable the following general deductions to be made:

1. Lard and oleo-products will reduce the percentage of volatile water-soluble acids.

2. Oils of the coconut group will increase the percentage of volatile water-insoluble acids.

To ascertain the actual percentages of these acids is a difficult process, but the Reichert-Meissl-Polenske-Kirschner method allows of the estimation of such a quantity of these acids as shall give sufficient information.   As the Reichert-Meissl value is practically a measure of the butyric and caproic acids present, the Kirschner of the butyric, while the Polenske value indicates the proportion of the glycerides of caprylic, capric and lauric acids, it will readily be understood that genuine butter will have a small Polenske value relative to the Reichert-Meissl, and a high Kirschner value, whilst the addition of oils of the coconut group will depress the Reichert-Meissl and raise the Polenske figure.   The process for ascertaining these values, which is described below, is a standard method.   The result of a large amount of criticism is to show that the process must be carried out under standard conditions, and with the greatest attention to details, if comparative results are to be obtained by different observers.   The details of procedure here given are of a standard nature and include Polenske's original dimensions for the apparatus.

A short table of limits is appended, but to avoid complication, no other figures are given here, as the Polenske figure depends on the type of apparatus, etc., used.   As, however, the Reichert-Meissl figure, apart from the Polenske figure, is in itself a standard value in butter analysis, a large number of references to this figure are given. It must, however, be borne in mind that this figure also depends slightly on the form of apparatus, etc.

It is necessary to draw attention to the fact that the Reichert-Meissl figure is not lowered proportionately to the amount of added lard or margarine, and also that the addition of these produces a slight but distinct increase in the Polenske figure in many cases, which might be taken as indicating coconut oil.

Many methods for the detection of coconut oil have been published from time to time during the last few years.   Few of them, however, give such reliable information as the original standard Reichert-Meissl determination, but the most important are here referred to.

Amongst the earlier papers more or less of historical interest may be menioned:

Hanus, *Zeitsch. Nahr.-Genussm.*, 1907, **13**, 18–24.

Robin, *Compt. rend.*, 1906, **143**, 512–514.

Dons, *Zeitsch. Nahr.-Genussm.*, 1907, **14**, 333–342.

Wijsman and Reijst, *Zeitsch. Nahr.-Genussm.*, 1906, **11**, 267–271.

More recently, Shrewsbury and Knapp (*Analyst*, 1910, **35**, 385) devised a process which has the advantage of taking less time than the Reichert-Meissl-Polenske, and proved satisfactory in the hands of the authors, although other workers (*vide* Elsdon and Bagshawe, *infra*) have experienced some difficulty in obtaining concordant results and suggested various modifications (Elsdon and Bagshawe: *Analyst*, 1917, **42**, 72; 1917, **42**, 95). The authors themselves also put forward modifications (*Analyst*, 1912, **37**, 3).

Blichfeldt (*J. Soc. Chem. Ind.*, 1910, **29**, 792; 1919, **38**, 150T) described a method which is really a modification of the Polenske process, carried out in an apparatus specially designed by him, and Van Gilmour (*Analyst*, 1920, **45**, 2) gives a further modification of Blichfeldt's method of separating the volatile acids into three groups depending on their solubility in saturated brine. This method of Blichfeldt gives practically the same information as the original Reichert-Meissl-Polenske process, and had it been devised before the latter, would doubtless have fulfilled the purpose just as well, but in view of the vast accumulation of data obtained not only with butter fats of various types and sources, but also with other fats, it is hardly to be expected that the practical analyst will disregard such a store of figures and commence to accumulate others by another process which can hardly claim to give any additional information to that obtained by the existing and proved methods.

The following table showing the Reichert-Meissl figures for Danish State Control butter for one year is exceedingly interesting. The rise and fall in the minimum figure is clearly marked, and the period of the year when low figures may also be expected.

R. M. No.	1906		1907									
	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.
30 and above	279	202	468	636	1005	1063	831	566	303	57	33	135
29–30	456	474	421	415	445	561	651	696	699	293	180	382
28–29	385	405	365	334	250	220	268	381	686	593	394	393
27–28	203	309	295	254	124	89	93	148	251	499	457	278
26–27	155	176	227	107	38	37	24	62	115	256	377	264
25–26	147	94	81	37	12	16	9	15	27	103	219	273
24–25	129	30	32	3	1	1	2	2	4	36	54	213
under 24	98	13	11	0	0	0	0	0	1	9	18	99

For low Danish R. M. values see Swaving (*Zeitsch. Nahr.-Genussm.*, 1906, **11**, 505).

British butters (1901) (Thorpe) from a large number of farms and agricultural colleges had the following R. M. values. The table does not include Irish butters.

	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.
Min.	26.5	26.0	22.5	23.4	22.4	22.3[1]	23.3	23.9	25.6	22.0	27.1	25.3
Max.	32 8	32.8	31.4	30.5	29.5	29.6	32.9	30.4	31 0	31.6	34.3	33.1

[1] One farm gave 19.4.

Norwegian butters (Rifle) 1898–1901.

    Min.,   21.1 June.
    Max.,   34.8 November.
    Means, 28.5 (July)–31.0 (Jan. and Feb.).

German butters (Ludwig), 26.0–32.6 for 110 samples, 1906.

Dutch butters (Bemelmanns), 1905.

    Stall-fed,   29.6 (Sept.) – 33.4 (March).
    In open fields, 20.11 (Oct.) – 32.6 (March).

Note the low figure for the exposed cattle.
Australian and New Zealand (Theodor), 1903–04.

    26.5–30.4.   These butters are usually distinguished by high values.

Canadian (Theodor), 27.7 – 30.7.

The Reichert-Meissl figure is undoubtedly depressed in butter derived from cows that have been poorly fed and badly housed, especially in low temperatures. This is borne out by Cranfield and Taylor (*Analyst*, 1915, **40**, 433). It is undoubtedly these causes which led to the low figures so common in Siberian butter, and which brought them under grave suspicion. The figure also shows a regular fall during the lactation period in individual cows, so that, when calving takes place almost entirely at one period, as for instance in Ireland, periods of low Reichert-Meissl values will be found. To obviate this, calving should be spread over the whole year. This is well seen in the following table (Handby Ball, *Analyst*, 1907, **32**, 202).

Dairy	Reichert-Meissl value	Polenske's new butter value	Zeiss butyro-refractometer 45°	Saponification value
Limerick..............	22.7	1.5	42.1	222.6
Bruree................	21.5	1.5	42.2	221.5
Mallow...............	23.3	1.55	41.4	224.8
Clonmel..............	23.5	1.5	41.8	224.8
Tipperary............	22.1	1.5	42.0	221.5

A long and searching investigation of the variations in the Reichert-Meissl and Polenske figures for the butter fat of single cows over the whole period of lactation has been carried out by Beerbohm (*Milch. Zentr.*, 1913, **42**, 513). It appears that, in general, the Reichert-Meissl figure falls during lactation, whilst the Polenske figure rises. The curves and tables given are very interesting, but are too lengthy for reproduction here.

The Reichert-Meissl-Polenske method has been extended by the writers to work in connection with the method of Kirschner, and a description of the method of procedure will be found following that of the Reichert-Meissl-Polenske process. As was pointed out by Kirschner and confirmed by the writers, this latter value is practically a measure of the butyric acid present and consequently gives a more sensitive indication for the detection of coconut oil than the Polenske value alone. The writers have suggested the following comparative values:

KIRSCHNER VALUE	POLENSKE VALUE
20	1.6
22	2.1
24	2.6
26	3.2

These figures have been confirmed by Cranfield (*Analyst*, 1915, **40**, 439; 1916, **41**, 336) who has determined the R. M., Pol. & K. values for a large number of butters after making detailed examinations of butters obtained from cows differently fed on pasture, groundnut, linseed, hempseed and decorticated cottonseed cakes; and further, Cranfield and Taylor (*Analyst*, 1916, **41**, 240) found that feeding on dried yeast caused a raising of the Polenske value.

A variation of 1.0 must be allowed either way in the Polenske value corresponding to any particular Kirschner value, the addi-

tion of less than 5% of coconut oil causing the Polenske value to fall outside this limit.

Richmond (*Analyst*, 1919, 44, 166) has studied the relation between the Kirschner and Reichert-Meissl figures with a view to estimating the percentage of coconut oil indicated by these figures.

Kirkham (*Analyst*, 1920, 45, 293), working in British East Africa, found that butter fats analysed there invariably gave low Polenske values, and experimentally arrived at the conclusion that the Polenske and Reichert-Meissl values are functions of the pressure, and that it is necessary to correct all values to normal temperature and pressure, a refinement which seems hardly necessary in this country.

According to Sunberg, (*Zeitsch. Nahr. Genussm.* 1913, 26, 422) the percentage of coconut oil may be calculated from the tables given by Polenske (*Arbeit kaiserlich Gesundheitesamte* 1904, 5, 45) by taking the percentage there given, as percentages referred to the actual butter fat concurrently present and then calculating the percentage on the mixed fat. For instance, if the Polenske figure obtained gives from Polenske's tables 27%, then the actual percentage present in the mixture would be given by $\dfrac{27 \times 100}{100 + 27} = 21.5\%$.

The question of the likelihood of obtaining butter fat apparently adulterated with coconut oil, from cows fed on coconut-oil cake, has been investigated by Ledent (*Bull. Soc. Chim. Belge.*, 1913, 27, 325) whose results appear to show that the butter fat in such cases does give indications of the presence of coconut oil. This opinion has been confirmed by Barthel and Soden[4] (*Zeitsch. Nahr. Genussm* 1914, 27, 439) who show that it is not only the case with coconut-oil cake, but also with that of beet-root leaves. The writers are of the opinion that whilst this may occur occasionally in practice, it has not come under their notice in samples of butter representing the chief supplies of the English market. Should this adulteration with coconut oil be suspected, it could be confirmed by the phytosteryl acetate test, which would give positive results for the presence of phytosterol if the recrystallisation is carried out sufficiently often.

3. **Specific Gravity of Butter Fat.**—This was suggested by James Bell, who showed that melted butter fat is of sensibly higher sp. gr. than lard or margarine. Bell took the sp. gr. of the fat at 100° F. (37.8°) by means of a sp. gr. bottle furnished with a thermometer,

and his figures express the sp. gr. at 100° F., as compared with that of water at the same temperature. Some chemists take the sp. gr. at 100° C. and thereby greatly diminish the sensitiveness of the test, in that the difference between butter fat and most fats likely to be used as adulterants is not so great at the high temperature, owing to the greater coefficient of expansion of butter fat. Unfortunately many figures are recorded at $\frac{100}{15}$ where the coefficient of expansion of glass has not been corrected for.

Skalweit (*J. Soc. Chem. Ind.*, 1894, **13**, 54) finds that the differences between butter fat and the fats likely to be used as adulterants are greatest at 35°, and this he shows in the following table:

Temperature	Lard	Margarine	"Butterine"	Butter fat
35	0.9019	0.9017	0.9019	0.9121
50	0.8923	0.8921	0.8923	0.9017
60	0.8859	0.8857	0.8858	0.8948
70	0.8795	0.8793	0.8793	0.8879
80	0.8731	0.8729	0.8728	0.8810
90	0.8668	0.8665	0.8663	0.8741
100	0.8605	0.8601	0.8598	0.8672

Bell gave 0.911–0.913 (133 samples) at $\frac{37.8°}{37.8°}$ as limits. They are, however, too narrow.

Thorpe for 361 samples of British made butter gave 0.90935–0.9135.

Lewin for Russian butters 0.911–0.91238, and for Siberian butters 0.91058–0.91204.

4. The Mean Molecular Weight of the Total Fatty Acids.—On account of the large percentage of esters of the lower fatty acids in butter fat, the mean molecular weight of the total acids will be lower than that of most fats, with the exception of coconut and palm-kernel oils. It therefore constitutes a valuable figure in the examination of butter fat. In practice it is usual not to estimate actually the mean molecular weight, but the number of mgrm. of potassium hydroxide necessary to saponify 1 gm. of the fat. This value is called the Köttstorfer or Saponification Value. If the weight of fatty acids used is known, the mean molecular weight is easily obtained.

Lard and oleo-products and most other fats have a lower saponification value than butter fat, whilst oils of the coconut and palm-kernel group have a higher value.   It is therefore possible to adjust the admixture of these in butter in such a way that the saponification value is practically unaltered.

Köttstorfer gave 221.5 to 223.0 as limits for genuine butter.

Fritzsche for Danish butters 221.1 to 231.9, but for one department 217.7 to 218.9.

Bemelmanns for Dutch butters 226.5 to 235.1 (lowest in June and highest in March) for stall-fed cattle; and 213.0 to 232.9 (lowest in October and highest in March) for cattle kept in the open field.

Avé Lallemant for German butters, 220.3 to 241.1 (mean 227.4).

Thorpe for 347 samples of British butters, 215.8 to 239.8.

Arnold gives for margarine, 195.5 to 197.1; for oleomargarine, 196.4 to 198.0; for lard, 195.3 to 199.7; for coconut oil the value is 255 to 259; for palm-kernel oil the value is 243 to 250.

5. **Mean Molecular Weights of Soluble and Insoluble Fatty Acids and the Relation Between these Values.**—The data derived from methods involving directly or indirectly these estimations are of more value than any for the detection of adulteration.   At the same time the available methods are long and laborious.   The mean molecular weight of the insoluble fatty acids can be ascertained by the method of Hehner and Angell, *i. e.*, saponification of the fat, liberation of the fatty acids and the washing out of the soluble acids with large quantities of water, drying, weighing, and saponifying the insoluble acids.   According to Juckenack and Pasternack (*Zeitsch. Nahr. Genussm.*, 1904, **7**, 193), the mean molecular weights of both classes of fatty acids may be estimated by steam distillation of the mixed fatty acids after acidification of the soaps.   The acids being thus separated, their weights and saponification values are found, and so the mean molecular weights.   The following are limits obtained in this way by the latter authors:

Mean mol. wt. of water-soluble acids in pure butter, 95.0 to 99.0.
Mean mol. wt. of non-volatile acids in pure butter, 259.5 to 261.0
Mean mol. wt. of water-soluble acids in coconut oil, 130.0 to 145.0.
Mean mol. wt. of non-volatile acids in coconut oil, 208.5 to 210.5.
Mean mol. wt. of non-volatile acids in lard, 271.5 to 273.5.

Olig and Tillmans (*Zeitsch. Nahr. Genussm.* 1905, **10**, 728) give, however, for Danish butters (autumn) much higher values, *viz.*,

255.4 to 271.6 for the non-volatile acids. Siegfeld (*Milch Zentralblatt*, 1905, 1, 155) confirms these figures for autumn and winter Danish butters:

Mean mol. wt. of volatile acids, 97.2 to 104.4.

Mean mol. wt. of non-volatile acids, 255.0 to 269.1.

Arnold gives the following figures for lard compounds:

Mean mol. wt. of non-volatile acids, margarine, 272.6 to 275.0.

Mean mol. wt. of non-volatile acids, oleomargarine, 271.6 to 272.8

Mean mol. wt. of non-volatile acids, lard, 272.4 to 275.8.

The writers, using Juckenack and Pasternack's method, have obtained rather variable results. The difficulty appears to consist in the fact that a variable quantity of the non-volatile acids is carried over mechanically during steam distillation, and no sharp dividing line is possible.

The following table showing the relation of soluble acids (calculated as butyric acid) to insoluble acids for a number of British butters is taken from values published by Thorpe.

	Minimum		Maximum	
	Soluble	Insoluble	Soluble	Insoluble
May...............	5.13	88.11	6.27	87.00
June......	4.92	89.32	6.79	86.91
July...............	4.21	89.45	5.62	88.54
Aug...............	4.31	89.76	5.73	87.99
Sept...............	4.15	90.01	5.90	88.42
Oct....	3.77	90.73	5.61	88.49
Nov........	4.15	89.91	6.48	.....
Dec...............	4.09	90.44	6.73	.....
Jan............	4.54	89.39	6.03	87.20
Feb............... .	4.09	89.71	6.04	87.60
March.......	5.00	88.73	6.67	87.36
April...............	4.86	89.00	6.44	.....

The method of Avé Lallemant (*Zeitsch. Nahr. Genussm.*, 1907, 14, 317) is directed to a very similar end, but in this case the barium saponification numbers of the acids forming water soluble and insoluble barium salts are estimated. The method, has been criticised most favourably by Fritzsche (*Zeitsch. Nahr. Genussm.*, 1907, 14, 329) and has, in the writers' hands, given such excellent results that it is here detailed in full as giving the most useful information.

It is simple and easy of manipulation, and has the exceptional advantage that, while giving evidence of the presence of either oils of the coconut group or lard compounds, the effect of the presence of these together is additive and not mutually destructive as in many other forms of investigation.   The actual mean molecular weights are easily estimated by the use of the following formulæ:

B = Insoluble Baryta value (see below).
C = Soluble Baryta value (see below).
K = Saponification value.
U = Unsaponifiable matter.
M_0 = Mean mol. wt. of fatty acids forming insoluble barium salts.
M_1 = Mean mol. wt. of fatty acids forming soluble barium salts.
$\left.\begin{array}{l} S \\ S_0 \\ S_1 \end{array}\right\}$ weight of $\left\{\begin{array}{l} \text{total fatty acids.} \\ \text{acids forming insoluble barium salts.} \\ \text{acids forming soluble barium salts.} \end{array}\right.$

$$S_0 = \frac{M_0 \times B}{76.7} \div 1000.$$
$$S = 1 - (K \times 0.0002258 + U).$$
$$S_1 = S - S_0.$$
$$M_1 = \frac{S_1 \times 76.7}{C} \times 1000.$$

S_0 is directly estimated by drying and weighing the insoluble barium soaps and igniting.

As values for M_1 Avé Lallemant gives:

For butter fat.. 110.3
For lard... 281.1
For coconut oil...................................... 145.8

The following figures are given by him:

Fat		R. M. fig.	a	b	c	b− (200+c)
Butter German	Maximum[1]...........	32.3	329.9	254.8	76.7	− 23.8
	Minimum[1]...........	24.6	300.9	247.4	50.8	− 0.7
	Mean...............	28.7	310.7	250.7	60.3	− 9.6
Butter.......		29.9	313.0	253.0	60.0	− 7.0
Butter + 10% lard..............		26.3	306.7	254.6	52.1	+ 2.5
Butter.......		27.5	308.0	249.0	59.0	−10.0
Butter + 10% coconut oil........		28.8	318.2	259.2	59.0	+ 0.2
Butter + 10% lard..............		26.0	311.7	258.2	53.5	+ 4.7

[1] The figures a, b and c do not correspond, as they do not belong to the same sample.

Avé Lallemant states that butter has always a negative value for $b - (200 + c)$, whilst for a number of other fats it is always positive and not less than $+39.0$.

The writers are of the opinion that this formula must not be adhered to too strictly, as in certain cases with mixtures of butter fat and coconut oil negative values are obtained for $b - (200 + c)$, but in such mixtures they have always found the value for b to exceed 260.00, whilst in cases of butter fat which give only a very small negative value for $b - (200 + c)$ the value for c is always well below 260.00.

The following are a selection of figures obtained by the writers with different butters:

Butter	Total Ba	Insoluble Ba	Soluble Ba	Difference	R.M. No.	Polenske No.	Kirschner No.
Danish....................	315.90	252.95	62.95	−10.00	29.7	2.7	24.2
	308 59	251.18	57.41	− 6 23	30 6	2.7	23.8
	310.38	253.31	57.07	− 3.76	30.2	1.9	23.8
	3'4 38	254.19	60 19	− 6.00	31.8	2 9	22.8
	312 03	254.30	57.73	− 3.43	30.1	1.8	21.4
	312.18	252.98	59.20	− 6.22	30.4	2.4	21.4
	317.66	256.04	61.62	− 5.58	31.8	3 0	20 9
	316 19	254.95	61.24	− 6.29	30.9	2 9	......
	317.52	255.90	61.62	− 5.72	29.1	3 0	......
	312.78	252.24	60.54	− 8.30	31.4	2.3	......
English....................	313.16	253.18	59.98	− 6.80	30.1	2.3	24.6
	312.71	252.98	59 73	− 6.75	29.8	2.4	21 9
	312.04	253.57	58.47	− 4.90	30.1	2 5	21.9
	314.38	255.35	59.03	− 3 68	28.3	2.1	20.1
	312.26	251 61	60.65	− 9.04	31.4	2.4	22.9
	312 88	255.42	57 46	− 2.04	29.8	2.4	......
	313.46	254.44	59.02	− 4.58	28.5	2.4	......
New Zealand...............	309.78	251.40	58 38	− 6.98	30.5	2.2	23.1
	316.90	251.86	65.04	−13.18	32.7	2.7	24.7
	311.11	252.03	59.08	− 7.05	31.8	2.2	22.0
	317.59	253.87	63.72	− 9.85	29 6	3.3	......
	313 41	252.91	60.50	− 7.59	32.4	2 7	......
	318 70	254 50	64.20	− 9.70	32.2	3.0	......
	316.25	254.15	62.10	− 7.95	32 4	2.6	......
Irish.....................	315.83	256.23	59.60	− 3.37	32 2	2 8	......
	314.68	254.03	60.65	− 6.62	31 4	2.5	. . ..
	311 41	254.24	57.17	− 2.93	28.1	2 1	......
	309.05	251.55	57.50	− 5.95	27.4	2.3	19.2
Normandy..................	316.43	253 90	62.53	− 8.63	32.4	3 2	.. ...
	316.26	252.52	63 74	−11 22	31.9	3 0	......
	311.94	254 95	56.99	− 2.04	28 8	2.1	......
	316.96	256.73	60.23	− 3.50	31.4	2 9	......
Probably adulterated..	312.75	258.17	54.58	+ 3.59	28.5	2 3	......
	307.22	256.30	50 92	+ 5 38	26.6	1 8	......
	300.13	257.89	51.24	+ 6 65	27.1	2.1	
	303.06	255.48	47.58	+ 7.90	24.6	1.7	.... .

The above figures illustrate the type of result obtained. There is a great similarity in butters from different sources, and in the case of butters arriving from a known source, the method is of the great-

est value.   In many cases in which a positive result was obtained indirect evidence was forth-coming to support the analytical data.

The following table gives a few results obtained by the writers using the above methods:

	Val.	Iod. No.	R. M. Val.	Pol. Val.	Sap. Val.	Total Ba (a)	Insol. Ba (b)	Sol. Ba (c)	b—(200+c)
Butter A.........	28.8	33.9	28.7	3.2	228.4	312.2	255.4	56.8	— 1.4
Butter A +10% coconut oil	25.2	31.4	26.6	4.1	231.1	315.9	262.8	53.1	+ 9.7
Butter B.........	30.3	36.5	28.1	2.5	227.8	311.4	254.8	56.6	— 1.8
Butter B +10% coconut oil	26.4	33.7	25.8	3.9	230.3	314.8	260.5	54.3	+ 6.2
Butter C.........	27.0	35.7	30.5	3.5	227.0	310.3	255.1	55.2	— 0.1
Butter C +10% coconut oil	24.0	32.8	28.0	4.3	230.5	315.1	263.6	51.5	+12.1
Butter D.........	30.2	38.7	30.8	2.9	224.8	307.3	252.8	54.5	— 1.7
Butter D +10% lard	35.2	40.6	27.7	2.4	221.8	303.2	254.6	48.6	+ 6.0

It must be borne carefully in mind that the values obtained in the methods given above have a distinct connection one with another. This is perhaps best illustrated by a study of the following table due to Thorpe.

357 samples of butter fat by Thorpe (*J. Chem. Soc.*, 1904, **73**, 254):

No. of samples	Reichert-Wollny number	Sp. gr. $\frac{37.8°}{37.8°}$	Saponification value[1]	Zeiss buty-ro-refrac-tometer number at 45°	Soluble[2] acids % on fat	Insoluble acids % on fat	Mean molecular weight of insoluble acids
7	22.5	0.9101	219.65	42.0	4 3	90.1	266.9
17	23.5	0.9104	221.39	41.5	4.5	89.7	265.5
15	24.5	0.9108	223.24	41.5	4.7	89.4	265.0
27	25.5	0.9110	223.41	41.3	4.8	89.3	264.2
37	26.5	0.9113	225.39	41.0	4.9	88.9	261.9
51	27.5	0.9114	226.75	40.6	5.2	88.7	261.7
78	28.8	0.9118	228.32	40.1	5.4	88.4	260.9
56	29.5	0.9120	229.91	40.1	5.6	88.3	259.6
41	30.5	0.9123	231.43	39.9	5 8	87.9	260.1
18	31.3	0.9125	232.30	39.7	5.7	87.9	258.0
10	32.6	0.9130	232.58	39.4	6.0	87.7	257.8
357							

[1] Calculated by Lewkowitsch from the saponification equivalents given by Thorpe.
[2] Calculated as butyric acid.

ESTIMATIONS

Butter fat is conveniently prepared from butter. The required quantity is melted in a beaker by standing in water at 50° to 60°. As soon as the water and the bulk of the curd have settled, the fat is poured on to a dry, warm, thick, plaited filter, keeping the filter warm during filtration. The fat so obtained should be clear and bright; if not so, it should be warmed and refiltered. The fat must at no time be heated above 60°.

The following method due to Stokes is excellent, especially when only a small quantity of the fat is wanted quickly. A strong tube about 6 in. long and 0.75 in diameter, tapered at one end, is used. Both ends are open, and can be closed with corks. The tube is warmed and pushed through the butter till the tube is full. The corks are inserted and the tube placed in water at about 55° to 60° until the contents are liquid, rotated while warm, and then a good plug of dry absorbent cotton wool is pushed down through the fat by means of a perforated metal plunger fitting the tube. The fat passing the cotton is obtained clear and bright and ready for use. By having the small end of the tube graduated, a rough idea of the water content is also obtained.

1. *Construction and Mode of Action of Butter Refractometer.*—The instrument was orginally introduced by Zeiss, but since the war other makers have constructed similar instruments. Complete working instructions and descriptions are issued by the manufacturers, and it is therefore only necessary to describe briefly one instrument, and the following description applies to the refractometer made by Bellingham and Stanley, Ltd. This instrument is of similar construction to the original and well known Zeiss butter refractometer comprising a heatable double prism of the Abbe type viewed by a fixed telescope with a sliding objective, operated by means of a micrometer screw, enabling fractions of a scale division to be estimated. The instrument may be used in daylight or by sodium light. In the case of the former illuminant a compensating arrangement is provided whereby the border line may be achromatised. A water jacket surrounds the prisms, and this may be fed by a variety of more or less complicated water heating arrangements. The following is the general principle of an efficient yet simple type of heater. A water tank (a) is placed 3 or 4 feet above the

instrument, provided with an overflow so as to maintain a constant head, and a supply tap which can be accurately adjusted to deliver the desired flow of water, and connected to the heating coil (b) below the level of the instrument.   This may conveniently be constructed of coiled metallic pipe, (e. g. ¼ in. compo) contained in a bath of hot water, 6 in. diameter by 6 in. deep.   The water from the coil is led up to the bottom prism of the instrument and flows out at the T piece bearing the thermometer into a back pressure vessel (c) 1 in. above the level of the instrument, and so arranged as to maintain a constant back pressure of 5 or 6 in. of water.   The temperature of the water flowing to the instrument may be accurately adjusted by varying the flow of water through the coil rather than by altering the temperature of the water bath.

Method of Using the Instrument.—As soon as uniform heating of the prisms has been established the instrument is opened as shown in
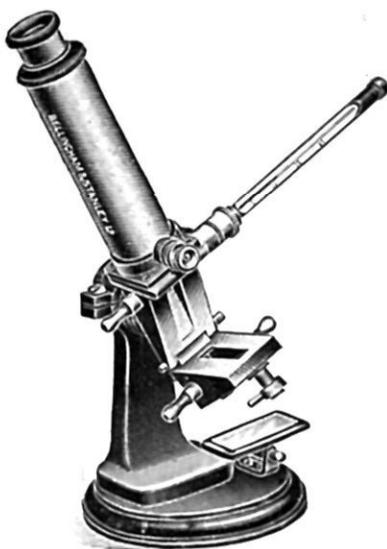
FIG. 8.—Bellingham and Stanley's Butter Refractometer.

the illustration, and tilted in such a way as to make the lower ground surface horizontal.   Three to five drops of the clear melted fat are placed on the ground surface and care taken that no bubbles are present which would detract from the sharpness of the border line. The instrument is then closed, preferably by so tilting it as to bring the top prism down to the lower one rather than by closing the lower prism.   The beam of light is directed through

the prism by means of the mirror, and the border line and scale focused by moving the ocular. If the border line does not exactly coincide with a given scale division it is made to do so by turning the milled head of the micrometer screw in an anti-clockwise direction. If the fat has reached the temperature of the prisms the border line will not move. The scale division is then read, to which is added the fraction estimated by the micrometer, and the temperature is noted at the moment of reading. The temperature of 40° is recommended at which to make the reading (see p. 61) and readings made at temperatures near to 40° may be adjusted to 40° by adding 0.55 Zeiss degree per degree above, or subtracting 0.55 per degree below 40°.

The arbitrary scale of this instrument, which is equivalent to refractive indices from 1.42 to 1.49, provides a range which covers, with very few exceptions, practically all the oils and fats likely to be examined, but for those who wish to increase the range of the scale Messrs. Bellingham and Stanley provide an additional prism which gives an increase from 1.34 to 1.43 on the one side, and if this prism be reversed a similarly increased range may be obtained in the opposite direction.

2. *The Reichert-Meissl-Polenske-Kirschner Method.*—In this process the saponification is conducted according to the method devised by Leffmann and Beam. 5 grm. of the fat and 20 grm. of glycerol are weighed into a 300 c.c. flask and 2 c.c. of 50% sodium hydroxide solution added (made by dissolving good sodium hydroxide in an equal weight of water and allowing to stand till clear). The flask is heated over a flame with constant shaking, till the contents clears suddenly. When the soap has cooled below 100°, 100 c.c. of recently boiled hot water are added, and should solution of the soap not be brought about thereby, the flask is warmed until solution is effected. 0.1 grm. of powdered pumice sifted through muslin (the grade and quantity are important) is added and then 40 c.c. of sulphuric acid solution. (20 c.c. of sulphuric acid diluted to 1000 c.c., and the solution adjusted so that 35 c.c. neutralise 2 c.c. of the sodium hydroxide solution.) The flask is at once connected to the condenser, and heated with a small flame till the insoluble acids are completely melted,[1] the flame is then increased and 110 c.c. distilled in 19 to 21 minutes. Condenser water should be from 18° to 20°, and dimen-

[1] The heating must not be intermittent, and if not evenly maintained violent bumping may result on subsequent boiling.

sions of apparatus exactly as shown in Fig. 9.   When 110 c.c. have distilled, the flame is removed and a 25 c.c. cylinder placed under the condenser to catch any drops.   The flask containing the 110 c.c. of distillate is placed in water at approximately 15° for 15 minutes,[1] and after mixing the contents, filtered, and 100 c.c. titrated with
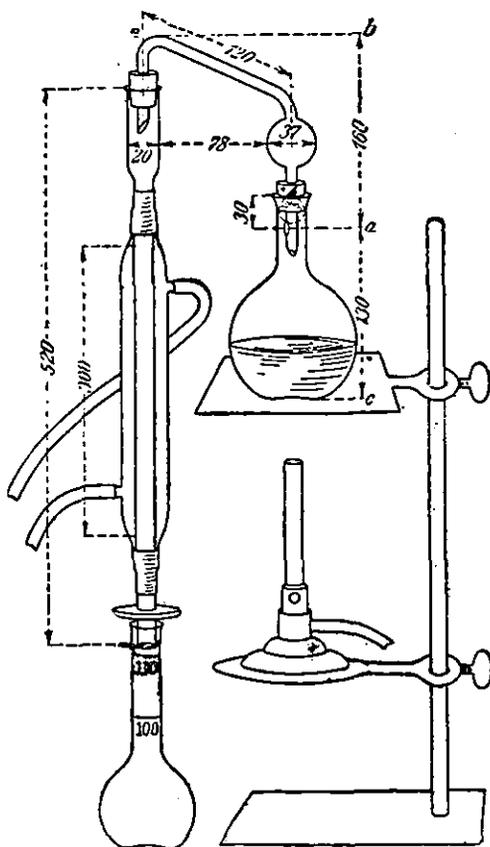
FIG. 9.

N/10 alkali (baryta if the Kirschner value is to be subsequently estimated, 0.5 c.c. of a 1% alcoholic solution of phenolphthalein being used as indicator.   This number of c.c. increased by $\frac{1}{10}$, after subtraction of the blank (which must be estimated in an exactly similar way by using all the reagents except the fat) is the Reichert-Meissl value.   The condenser, cylinder, and 110 c.c. receiver are washed with three successive portions of 6 c.c. of cold

[1] Polenske originally prescribed a water temperature of 10°, but Richmond (*J. Soc. Chem. Ind.*, 1920, 39, 80T) has shown that in the case of butter (but not coconut oil) the temperature of cooling does not greatly affect the result.

water, which are then poured over the filter used to filter the distillate and rejected. The condenser is washed out with four successive portions of 10 c.c. of hot neutral alcohol, which are received in the cylinder and poured successively over the filter and into the 110 c.c. flask, the mixed alcohol solutions being then titrated with N/10 barium hydroxide, using phenolphthalein as indicator. A blank value is obtained in a similar way. The number of c.c. of N/10 barium hydroxide used less the number used for the blank is the Polenske figure or New Butter Value.

Rather varying results have been obtained by various observers, but the following table will be found a very fair guide:

REICHERT-MEISSL VALUES	POLENSKE VALUES
32	3.5
31	3.2
30	3.0
29	2.9
28	2.7
27	2.4
26	2.0
25	1.8
24	1.7
23	1.6

A Polenske value exceeding by 0.5 c.c. the figure corresponding with the Reichert-Meissl value found indicates the presence of coconut or palm-kernel oil or coconut "stearine."

As before explained, a still more definite idea of the amount of any oils of the coconut group present can be obtained by extending the Reichert-Meissl-Polenske method in the following way in order to obtain the Kirschner value.

Kirschner's Extension.—To the 100 c.c. of the 110 c.c. distilled and titrated with baryta for the Reichert-Meissl value (care having been taken not to exceed the neutral point) is added 0.5 grm. of finely powdered silver sulphate, and the whole allowed to stand for an hour, with occasional shaking. The liquid is then filtered, 100 c.c. measured off, 35 c.c. of water and 10 c.c. of sulphuric acid (as previously employed) added, together with a coil of aluminium wire, and 110 c.c. again distilled off in the standard Reichert-Polenske apparatus in 20 minutes; 100 c.c. of the mixed distillate are titrated, and the number of c.c. so obtained, corrected for the

blank, is calculated to the Kirschner value by the following formula:

$$K = x \times \frac{121 \times (100 + y)}{10,000},$$

where x = the corrected Kirschner titration;

y = the number of c.c. of baryta used to neutralise 100 c.c. of the Reichert-Meissl distillate.

If an approximate idea of the amount of coconut oil present is desired, Polenske's original table (*Arbeit aus dem Kaiserl. Gesund.*, 1904, **20**, 543) should be consulted (reproduced in Lewkowitsch: Oils, Fats and Waxes, Vol. ii, p. 850, 6th Ed.).

These processes, together with the Reichert-Wollny method, are further dealt with under "Margarine" see (p. 416).

3. *Specific Gravity of the Fat.*—This is best determined in a 25-grm. bottle. The dry melted fat is run into the bottle a few degrees below the temperature at which the gravity is to be observed, great care being taken that no air bubbles are introduced at the same time. The stopper is screwed gently home and the bottle immediately immersed in water of the desired temperature for 45 minutes. The test is then finished in the usual manner. For convenience, especially if many determinations are made, a bath regulated to the temperature by means of a thermostat may be used.

4. *Saponification Value* (Köttstorfer Value).—The saponification value is defined as "the number of mg. of potassium hydroxide, which is necessary to completely saponify 1 grm. of fat."

(Saponification equivalent is the number of grm. of butter fat saponified by 56.1 (*i. e.*, one equivalent) of potassium hydroxide. It is obvious that this is merely another mode of expressing the same result, and the one figure can easily be calculated from the other. Köttstorfer's original mode of expression is now more generally used.)

Solutions required: 1. N/2 hydrochloric acid accurately prepared. 2. Alcoholic potassium hydroxide approximately N/2 strength. 3. 1% alcoholic solution of phenolphthalein.

The potassium hydroxide solution is prepared by dissolving 17 to 20 grm. of stick potassium hydroxide (purified by alcohol) in the smallest possible quantity of water, and then making up to 500 c.c. with alcohol of not less than 94% (by weight). The solution is allowed to stand over-night, and the clear liquid syphoned off for use. If the alcohol is pure, the solution will be colourless, or nearly

so (it is advisable to test the alcohol before making up the solution and rejecting any which gives more than a very pale colour when boiled with a strong solution of sodium hydroxide).

The test is carried out as follows:

About 2 grm. of the clear melted and filtered fat are weighed into a 200 c.c. flask, which should be of high quality glass, and an accurately measured quantity of the alcoholic potassium hydroxide solution run in from a 25 c.c. pipette. A like quantity of the same solution is run from the same pipette in exactly the same way into a clean 200 c.c. flask. The flasks are connected to reflux condensers and heated in a water-bath so that the alcohol boils gently; this is continued for 30 minutes. The flask containing the butter fat should be shaken occasionally, particularly at the commencement. The flasks are removed from the bath, 20 drops of phenolphthalein solution added to each, and the contents titrated while hot with the $N/2$ acid.

If F = grm. of fat taken.
  X = c.c. of acid required in the control experiment.
  Y = c.c. of acid required to neutralise the excess of alkali in the test.

Then sap. value $(S) = \dfrac{(X - Y) \times 0.02805 \times 1000}{F}$,

and saponification equivalent $= \dfrac{56,100}{S}$.

5. *The Barium Method of Avé Lallemant.*—Saponify 1.9 to 2.0 grm. of the filtered butter fat with 25 c.c. of approx. $N/2$ alcoholic sodium hydroxide solution (carefully standardised), boiling for 30 minutes; while still warm, titrate with $N/2$ hydrochloric acid to phenolphthalein. Remove the alcohol as completely as possible by boiling and blowing air into the flask, and dissolve the soap in 150 to 180 c.c. of hot recently boiled distilled water, in a 250 c.c. flask. Stand on the water-bath 5 minutes, and add 50 c.c. of approximately $N/5$ barium chloride solution (25 grm. crystallised barium chloride in 1000 c.c.). Allow to remain 15 minutes on the water-bath to cause the insoluble barium salts to coalesce. Cool, fill to the mark with water and filter off 200 c.c. into a beaker, heat this to nearly boiling on a sand-bath, add 1 c.c. hydrochloric acid and 10 c.c. of approx. $N/1$ sulphuric acid. Filter the barium sulphate on a gooch crucible, wash till free from chlorides, and finally with two quantities of 10 c.c. of warm alcohol. Dry to constant weight. Increase the weight of barium sulphate found by 25%, and calculate

to BaO (BaSO$_4$ × 0.6571 = barium oxide).   Subtract this last from the barium oxide value of the barium chloride solution (which must be standardised in an exactly similar way).   This gives the barium oxide value of the acids forming insoluble barium salts.   Calculate this to 1 grm. of fat = insol. barium oxide value (b).   The saponification value is also calculated as barium oxide (KHO × 1.367 = barium oxide) for 1 grm. of fat = total barium oxide value (a), then a − b = sol. barium oxide value (C), and so find b − (200 + C).

After much experience with this method and owing to the necessity for extreme accuracy in estimating the saponification value, the writers advise the use of 5 grm. of fat for the test.   After saponification and removal of the alcohol, the soaps are made up to 250 c.c. with water at 38°, and 100 c.c. pipetted off at that temperature for the estimation of the barium oxide, the test being finished as above.   By this means a more accurate figure is obtained for "a."

Qualitative Tests.

The above quantitative examinations may be supplemented when desirable by one or more qualitative tests.   These are useful more especially as confirmation of the presence or nature of some adulterant indicated by the quantitative figures.   Some of them are sometimes used as "sorting" tests.

1. *Microscopical Appearance.*—When genuine butter is examined in a thin film, under a low power (× 25 to 50 diam.) between crossed nicols, it appears as a homogeneous mass, but if it has been melted, bright specks or patches, or sometimes even crystals, giving a play of colours with a selenite plate, may be noticed.   Margarine (oleomargarine) has a similar appearance to butter which has been melted and reset.

This test may be used for rough sorting out purposes, setting aside for further examination all samples showing crystalline structure.   It is advisable to place a cardboard tube around the objective and enclosing the preparation, so as to exclude adventitious rays.

2. *The Foam Test.*—(*Farmers' Bulletin, U. S. Dept. Agric.,* No. 131.)   This is a rough and ready method of distinguishing butter substitutes and renovated butter from genuine butter.   In fact, it is especially valuable in the case of renovated butter, the chemical composition of which is the same as that of true butter.

A lump of about 5 grm. of butter is melted in a spoon over a very small bunsen flame; genuine butter boils quietly, producing consider-

able foam, whilst butter substitutes and renovated butter crackle loudly and splutter, but do not produce any appreciable quantity of foam.

It will further be noticed that on melting genuine butter, the curd separates in a very finely divided state, whilst in the case of margarine and renovated butter the curd is lumpy.

A few trials of this test will enable the operator to see differences which are difficult to describe in words.

This test has, however, lost much of its value on account of the additions now made to margarine in order to bring about "browning" and "foaming" which are considered so essential in ordinary culinary operations. These substances generally consist of some compound of casein together with sugar, and egg yolk is also used for the same purpose, as well as certain vegetable proteins.

3. *Wanklyn's Test.*—The production of ethyl butyrate, when butter fat is heated with alcoholic solution of alkali, may be used as a sorting test for distinguishing "straight" oleos (that is, butter-substitutes containing no appreciable amount of butter fat). The test is most satisfactorily applied by the method described in Leffmann and Beam's "Select Method of Food Analysis" 2d Ed., 236. A few grm. of the sample (which need not be filtered) is placed in a test-tube, about 10 c.c. of strong solution of sodium hydroxide in alcohol added, the mixture heated until it foams actively, and then promptly poured into about 100 c.c. of cold water. The pineapple odour of ethyl butyrate is at once noticeable if appreciable amounts of butter are present. Care must be taken not to mistake the somewhat aromatic odour of the alcoholic solution for that of true ester. The nature of the reaction is not known.

4. *The Valenta Test.*—The glycerides of the saturated fatty acids present in butter have varying solubilities in pure acetic acid. The temperature at which a solution of the fat in acetic acid begins to deposit solid glycerides varies with the constitution of the mixture. Butter itself shows a turbidity within reasonably close limits under strict conditions of experiment. The addition of the glycerides of the higher fatty acids, as by the use of lard and similar products, causes the turbidity temperature to rise, while the addition of the glycerides of the lower members of the series, such as is brought about by the use of coconut and palm-kernel oils, will lower the temperature. The test, therefore, if carefully performed, is of real value,

especially as confirmatory or diagnostic of adulteration by lard products.

Many methods of carrying out the test have been proposed, but the following is simple and easy and quite sufficient.   A long thin test-tube, perferably of high quality glass, about 0.5 in. in diameter, and sufficiently long to take in the scale of a thermometer up to 60°, is marked accurately at 3 and 6 c.c. with lines all round the tube.   A thermometer with very small bulb is fixed in the tube by means of a cork, so that the bulb is opposite the 3 c.c. line.   The carefully dried butter fat (filter-paper pellets should be shaken up with it beforehand) is measured in at 27 to 29° till the bottom of the meniscus coincides with the 3 c.c. line.   Absolute acetic acid is then run in until the 6 c.c. line is reached (the acid, should be measured at a definite temperature, say 15 to 16°).   The thermometer is inserted and the fat dissolved by shaking in water at about 50°.   The tube is then withdrawn, and the contents allowed to cool in the air, shaking gently, and holding the tube in a good light.   Immediately ,the faintest turbidity is noticed the temperature is read.   The tube is then slightly warmed and a fresh reading obtained.   The end point is quite sharp, and consecutive readings should scarcely differ.

It must be carefully borne in mind that every operator should obtain figures for himself for pure butters, as the least change, especially in the acid, produces a change in the results.   Operating in the above manner, the writers have found butter to vary between 35° and 44.4°, mostly between 37° and 42°.   The greatest variations were found in Danish State Control butters.   10% of lard produces a rise of about 7°.

Fryer and Weston have very fully investigated this test especially in its applicability to other fats and oils, and further details will be found under Margarine, p. 424.

5. *Halphen's test for cottonseed oil and cottonseed "stearine"* may be carried out as follows: 2 to 3 c.c. of the melted fat are dissolved in an equal volume of amyl alcohol in a test-tube, 2 to 3 c.c. of a 1% solution of sulphur in carbon disulphide added, and the tube is placed in a boiling water-bath for 20 minutes, more satisfactory results being obtained if the tube is tightly stoppered.   In the presence of cottonseed oil, or cottonseed "stearine" a characteristic crimson colour is produced.   This test is capable of detecting less than 5% of cottonseed oil and if the heating be done in closed test-tubes, 1%

may be detected. It is possible to treat cottonseed oil so as to evade this test, but this is not usually done. The test is applicable to the acids from cottonseed oil.

Gastaldi (Abs. *J. Chem. Soc. Ind.*, 1912, **31,** 934) has introduced an improvement by substituting pyridine for the amyl alcohol employed.

The modified test is carried out as follows: To 5 c.c. of the oil add 1 drop of pyridine, shake well and after adding 4 c.c. of carbon disulphide, containing 1% sulphur, heat for 20 minutes in the water-bath, the tubes being closely stoppered. The writers can confirm the value and greater sensitiveness of the test; they find it possible to detect at least 0.2% of ordinary cottonseed oil products. It must be remembered that hydrogenation (see pages 48 and 426) partly destroys the chromogenetic substance responsible for the reaction, and for this reason the greatest possible sensitiveness that can be obtained for this test is desirable.

Utz (*Chem. Rev. Fett. Ind.*, 1913, **20,** 291–295) has suggested the use of pentachlorethane (b. p. 159°) as solvent for the sulphur. The tubes can then be heated at a temperature nearly that of the boiling point of the solvent. It is stated that the test is rendered more delicate, but the writers have not had experience of the method. (See Cottonseed Oil, p. 177.) Gastaldi (*Analyst,* 1915, **40,** 15) further points out that when the temperature exceeds 160° the reaction is also given by fatty acids such as oleic, palmitic and stearic. It should also be noted that a positive reaction is given by Kapok, Baobab and Sterculia oils (*Analyst,* 1915, **40, 3**).

6. *Baudouin's Test for Sesame Oil.*—Take 10 c.c. of the melted fat in a test-tube, add 2 drops of a 2% alcoholic solution of furfural, and 10 c.c. of concentrated hydrochloric acid. Shake for a minute. In the presence of sesame oil the aqueous layer will be a crimson colour. The test is sensitive to 1%, but certain azo dyes interfere with the delicacy, and if their presence is suspected a blank test should be carried out, omitting the furfural.

Sprinkmeyer (*Zeitsch. Nahr. Genussm.*, 1908, **15,** 20–21) states that rancid cottonseed oil prevents the red coloration unless 17% of sesame oil is present, and Weehuizen (*Pharm. Weekbad,* 1918, **55,** 77–79; *Analyst.,* 1918, **43,** 273) goes back to the use of laevulose or cane sugar, since Van Ekenstein and Blanksma showed that β-hydroxy-d-methylfurfural or ω-hydroxymethylfurfural and

not furfural is formed by the action of hydrochloric acid on hexoses.

7. *Phytosterol and Phytosteryl Acetate Test for Vegetable Fats and Oils, Including Coconut Oil.*—Boil 50 grm. of the clear fat with 75 c.c. of 95% alcohol.   Cool and pour off the alcohol and repeat the extraction with a further 75 c.c.   The combined extracts, which will contain the bulk of the cholesterol and phytosterol and some fat, are transferred to a porcelain basin, and an excess of solid sodium hydroxide having been added, evaporated, with occasional stirring. After the bulk of the alcohol has gone, more than sufficient sodium hydrogen carbonate is added to convert the sodium hydroxide to carbonate, followed by sand, and the evaporation carried to dryness.   The dry residue in the dish is ground and extracted with petroleum spirit.   The residue from the spirit is treated with 5 c.c. of approx. N/2 alcoholic sodium hydroxide solution and again evaporated to dryness with sand.   It is then re-extracted with petroleum spirit, evaporated, and taken up with the smallest possible quantity of absolute alcohol.   (If much coloured, the residue is first boiled with a small quantity of 95% alcohol and a little finely divided animal charcoal, filtered, and evaporated to dryness.)   The alcoholic extract is allowed to crystallise and the crystals examined microscopically.   The residual crystals are converted into acetate and recrystallised in the usual manner.

Juckenack and Pasternack (*Zeitsch. Nahr. Genussm.*, 1904, 7, 193–214) give from 113.2° to 114.6° (corr.) as the m. p. of the cholesteryl acetate of pure butter (after 5 crystallisations), and from 117.2° to 122.6° (corr.) for that obtained from butters adulterated with varying quantities of coconut oil.

It has been proved that animals fed on oil cakes sometimes produce a butter fat giving indications of the oil present in the cakes, notably by Halphen's test, but phytosterol has not been found in butter fat from animals so fed.

The use of hardened vegetable fats has necessarily brought this test into greater prominence and utility, as it may be, in certain cases, the only method by which a hardened vegetable fat can be detected in admixture with animal fats.

The method of separating the sterols has been simplified by the use of digitonin which with these substances forms compounds almost insoluble in alcohol, and from which the original sterols are easily regenerated.

The method of applying the digitonin test first devised by Marcusson and Schilling (*Chem. Zeit.*, 1913, 37, 1001) is g.ven on page 768.

The method as thus devised gives difficulty sometimes, as the *digitonides form emulsions with the fat*, and in any case it is only applicable if the sterols are present in the free state. It has been objected to by Klostermann (*Zeitsch. Nahr. Genussm.*, 1913, 26, 443) on the ground that esters of the sterols may be present and these are not precipitated by digitonin. He proposes to saponify the fat (100 grm.) with alcoholic potash in the ordinary way, and to dilute the saponified mass with water, acidify, and extract the fatty acids and sterols with 250 c.c. of ether. The ether is washed with water and 250 c.c. of petroleum spirit and 25 grm. sodium chloride are added. The water which separates is run off and the ether filtered through cotton wool. The filtrate is heated with 1 grm. of digitonin dissolved in 20 c.c. of 90% alcohol, and the crystalline precipitate which forms filtered after 15 minutes and washed free of oil with ether. This fat-free residue is then boiled with 20–30 c.c. of acetic anhydride, evaporated to dryness, dissolved in 50 c.c. of alcohol, and 25 c.c. of water gradually added. The precipitate is filtered off, washed with 70 c.c. alcohol, and recrystallised from 90% alcohol, in the usual way.

It is easier (*particularly if more than 100 grm. of fat are used*) to employ the method given above, in which the fat is boiled out first with alcohol. The alcoholic extract is saponified once only, the fatty acids liberated, dissolved in ether, washed and treated direct with alcoholic digitonin solution (0.2 grm. digitonin per 100 grm. of fat). The digitonides are filtered and washed with ether to remove any traces of oil, dried and treated with acetic anhydride in the usual way, in an evaporating basin or stoppered tube (5 c.c. of acetic anhydride for 50 grm. of fat). The acetic anhydride is evaporated off and the residue taken up with absolute alcohol, and boiled, if necessary, with recently ignited animal charcoal (fine powder), filtered, evaporated to dryness and the residue recrystallised from 90% alcohol. The precipitation of the acetates from alcoholic solution by water, previous to final crystallisation, as suggested by Klostermann (see *supra*), is not to be recommended, as the resultant liquid filters in some cases with great slowness. As it is generally necessary to crystallise the acetates 4 to 5 times, very small quantities of alcohol must be used for the recrystallisa-

tions and very small test-tubes should be employed.   The crystals are filtered off in a very small funnel, having a glass bead fitting the neck.   As each crop is thus filtered it is washed with 2 to 3 drops of 70% alcohol, and the bead lifted and the crystals washed into a fresh tube with 1 to 2 c.c. of boiling 90% alcohol.   The crystals are dissolved by heating and again allowed to separate.   By thus avoiding filter paper, etc., no difficulty will be found in carrying even small quantities to 4 to 5 crystallisations.

A very small quantity of the crystals is placed on a porous tile and the m.p. determined.   Cholesteryl acetate melts at 113° C. (corr.), and phytosteryl acetate at from 125°–133° C.   If the m. p. of the fourth crystallisation is above 116° C., phytosterol may be assumed to be present in the original mixture.

8. *Hinks' Test* (*Analyst*, 1907, **32**, 160).—This is a valuable qualitative test for coconut and palm-kernel oils.   It is based on the fact that the latter contain a fat which crystallises from alcohol in a characteristic form.   To one who has once become familiar with the shape of the crystals, the test is valuable, but without this experience, and if not carried out exactly as recommended, it may prove misleading.   The writers have been able to detect 2.5% of coconut oil in this way. .

The test is carried out as follows:

5 c.c. of the clear fat are dissolved in twice their volume of ether, in a wide test-tube, and packed in ice.   After 30 minutes (much solid fat will have separated) the whole mass is thrown on a pleated filter. The filtrate is evaporated in a basin and heated on a boiling water-bath.   The residual fat is poured into a test-tube, and 3 to 4 times its volume of alcohol (96 to 97% by volume) added.   After boiling to effect solution the tube is kept in water at 5° for 15 minutes, and the alcoholic layer is then rapidly filtered into another tube, which is then kept at 0° for 2 or 3 hours.

After this time a portion is withdrawn by a glass tube, dropped on a slide, covered without pressure, and immediately examined at a *magnification of 200 to 300 diameters.*   (*The examination must be quickly carried out, as the crystals are soon redissolved as the liquid warms.   In hot weather a cooled stage is necessary, conveniently made by placing a flat piece of ice contained in a petri dish under the slip.*)

Butter crystallises in round granular masses, but if coconut or palm-kernel oil is present, numerous fine feathery crystals will be seen as well. Lard, however, produces crystals which are not unlike those from coconut and palm-kernel oils.

BUTTER

The examination of butter itself, apart from the special examination of the butter fat, usually consists of the estimation of water, fat, curd, and salt. By "curd" is usually meant the solids-not-fat, without the mineral constituents, which are usually included under the general term "salt." For special purposes, the actual percentage of proteins is estimated, and also the actual percentage of salt as sodium chloride. Besides these, an investigation into the nature of the colouring matter and preservative present (if any) is often necessary.

Such an examination is of value for the purpose of ascertaining whether a butter is properly made, whether it has been properly worked so as not to include an excess of moisture, and also whether any addition of milk (whole or condensed), casein, dried milk, or of other similar substances has been made, such additions having been rather frequently made of late years. For an excellent paper on the "Physical Constitution of Butter" see Bean (*Rev. Gén. de Lait.*, 1904, **10**, 224).

Before pass ng to consider the various constituents, it may be well to quote br efly the regulations enforced in various countries (1906).

Canada.—Maximum imit for water 16%. No renovated or process butter to be made or imported.

New Zealand.—Butter to be made only from milk or cream and to contain only salt, and certain preservatives and colouring matters. Grading is by government officials and butter is officially marked.

Queensland.—Maximum limit or water 16%. Minimum limit for fat 80%.

No extraneous ingredients, except harmless colours or preservatives, such as boric acid and borax (not more than 0.5% as boric acid). Butter is officially marked.

Victoria.—Maximum limit for water 15%. Minimum limit for fat 80%.

Denmark.—Butter control official since May, 1904. The creameries form associations and must not be connected, directly or

indirectly, with the manufacture of margarine or edible oils. The chemical analyses of butter from every creamery are known and recorded.

Belgium.—Maximum limit for water 18%, unless declared. Butter is regarded as abnormal and prohibited for sale if, (1) The Reichert-Meissl figure is below 28, and if (2), in addition, the fat gives one of the following values:

(a) Refraction (Abbé-Zeiss) above 44 at 40°.

(b) Sp. gr. below 0.865 at 100°.

(c) Saponification value below 222.

(d) Hehner value above 88.5.

Germany.—(1902) Minimum limit for fat 80%. Maximum limit for water 18% (unsalted butter). Maximum limit for water 16% (salted butter).

Italy.—Minimum limit for fat 82%.

Butters with R.-M. value 26 or above are pure.

Butters with R.-M. value 20 to 26 are suspicious.

Butters with R.-M. value below 20 are adulterated.

Refraction (Zeiss) not to be above 48 at 35°.

Sp. gr. not to be below 0.865 at $\dfrac{100°}{15°}$.

No preservatives, except common salt and boron mixtures, which shall not be present in greater quantity than 0.3% reckoned as boric acid.

United States of America.—Minimum limit for fat 82.5%, and in renovated and process butter, not more than 16% of water.

Reichert-Meissl value not less than 24.

Sp. gr. at 40°/40° not less than 0.905, but there are different regulations in different States.

England.—Maximum limit for water 16%, and in milk-blended butters 24%.

1. **Water.**—Apart from the examination of the fat, this estimation is the most important. The percentage of water in butter varies naturally for many reasons. The method of churning, and especially the temperature of churning, is a most important factor in determining the quantity of water left in the worked butter. Taking 60° F. as roughly the correct churning temperature, temperatures decidedly above, or decidedly below this, will result in the inclusion of too much water. At elevated temperatures a very

large quantity of water can be worked into and retained by the butter, as is found in the case of Irish "pickled" butters, and butters so made are often quite firm, and do not even appear moist. The addition of salt tends to produce a drier butter, though the appearance of a salt butter would lead to an opposite conclusion, seeing that moisture exudes from "salt butters" in small drops when cut. There is no difficulty, in properly managed churning operations, in keeping to a fairly constant water content, and for this reason, in most countries, a maximum percentage for water is either legally or tacitly enforced.

It seems to be generally agreed that butters containing 13 to 14% of water have the best flavour.

Canadian Butters.—The Dept. of Argiculture gives 12.3% as the average of a large number. Theodor, in 1903–04, gives 9.2 to 15.5%.

New Zealand.—(1905) Average 10.59. Theodor gives 9.9 to 11.7 (1903–04).

Australian.—10.0 to 13.6% (Theodor).

Danish.—From 1897 to 1900, 95.2% of butter contained between 12.0 and 16.0% of water.

From 1897 to 1904, in butters supplied to Canada by Denmark, a steady increase from 13.79 to 14.25 was found by the Dept. of Agriculture, Ottawa.

Irish Firkin Butter.—Twooney (Report of Dept. Committee, 1906, England) gives the following percentages of butters containing more than 16% of water.

Season 1902–3	(53,166 samples)	7.49%.
Season 1903–4	(49,197 samples)	5.06%.
Season 1904–5	(40,464 samples)	7.7%.
Season 1905–6	(35,859 samples)	3.87%.

There has been a marked tendency of late years for the water content of butter to approximate to 16%. This is shown by the following successive figures obtained for various butters:

Danish.
15.8, 14.9, 16.2, 15.6, 15.8, 15.9, 15.7, 15.7, 15.7, 15.9, 15.1, 15.8, 15.5, 14.6, 15.0, 15.3, 15.4.
Blend 1.
15.0, 14.0, 15.3, 15.2, 14.7, 15.3, 15.9, 15.3, 14.7, 15.7, 15.3, 15.9, 15.6, 15.4, 15.7.
Blend 2.
15.0, 15.7, 15.2, 16.1, 15.8, 16.4, 15.9, 15.4, 16.7, 15.9, 16.5, 15.9, 14.6, 15 9, 15.8, 14.9, 15.9.
English (country made).
14.6, 14.9, 14.1, 14.2, 14.4, 14.5, 13.5, 14.7, 14.3, 15.4, 15.3, 15.4, 14.2, 13.8, 14.0, 14.2.
Irish.
14.0, 14.0, 13.7, 14.4, 13.8, 13.6, 13.9, 13.6.

The difference between the last two which do not compete on so keen a market, and the first three which do so compete, is very noticeable.

2. **Curd.**—Under this term is usually included the total solids-not-fat, less the ash. It is rather a variable figure, and depends very much on the method of and care in making. The curd is likely to be much higher in the case of butters made from whole milk than from cream, but as the former is scarcely made to-day, certainly not for the market, it does not much concern the analyst. In properly made butters the curd varies from very small amounts to 2.5%. The higher limit is rare, and 1.0 to 1.5% is most usual. As this estimation is chiefly of value for the detection of the addition of condensed milk, casein, etc., it is far preferable actually to estimate the protein. When this estimation gives more than 1.0% of casein, it may be taken as almost certain that addition of milk products has been made. In such cases there is usually an excess of water, and if whole or dried milk has been worked in, an amount of lactose capable of estimation will probably be found.

3. **Ash.**—This term usually includes salt and preservative, as well as mineral constituents of the original cream. It is sometimes necessary to estimate the actual sodium chloride present. In fresh butters only a trace of chlorides will be found, whilst in salt butters even 12% may occur, the quantity of salt present being almost entirely controlled by the taste of the consumer.

The careful estimation of the various constituents of curd and ash is only necessary when forms of adulteration are suspected which are not easily apparent. The question of preservatives and colouring matters is now practically determined by the law of the country concerned.

The following table gives a number of values for water, curd, salt. etc., for various butters:

Butter	Water		Casein $N_2 \times 6.39$	Sugar	Salt	Ash
German, 364 samples (Hesse)	Summer max.	12.80.....	0.60	0.52	1.32	0.12
	Summer min.	11.67.....	0.51	0.45	1.02	0.10
	Summer mean	12.31.....	0.57	0.50	1.17	0.11
	Winter max.	12.70.....	0.74	0.64	1.62	0.12
	Winter min.	12.29.....	0.66	0.55	1.34	0.09
	Winter mean	12.50.....	0.68	0.59	1.40	0.11

Vieth gives the following analyses:

Butter	Fat	Curd	Salt	Water
English...........................	86.85	0.59	1.02	11.54
French....................... ...	84.77	1.38	0.09	13.76
French (salted)................	84.34	1.60	2.01	12.05
Kiel...........................	85.24	1.17	1.35	12.24
Danish....	83.41	1.30	1.87	13.42
Swedish.....	83.89	1.33	2.03	13.75

Estimations

For exact analysis, care must be taken to get a representative sample. From a small sample a piece may be cut from opposite corners and from the middle. From a large bulk, a suitable piece is cut from within the bulk by means of a fine wire. In either case, the sample is then placed in a 4-ounce stoppered bottle, the fat melted by standing in water at about 50°, shaken to the consistence of cream, and weighed out while in this state.

1. Water.

2–3 grm. of the sample are weighed out into a large weighing bottle, 2 inches deep and 1.5 inches wide, and having parallel sides, and dried in the water oven at 100° (shaking every 10 minutes), to constant weight (2 to 3 hours). As soon as the curd has stuck to the bottom, the bottle should be tilted on its side, drying being thus much facilitated.

A few methods for the rapid estimation of water in butter have beem devised for factory work, but it is probable that the ordinary direct drying method is really the simplest, though for obvious reasons the time required is not possible in factories where blending is going on, and the percentage of water is required whilst the butter is passing the blenders.

The following method, due to Patrick (*J. Amer. Chem. Soc.*, 1906, 27, 1613) is exceedingly useful for control purposes or for sorting samples. About 10 grm. of butter are weighed into an aluminium beaker (a wide glass test-tube may be used), and the water gently boiled off over a naked flame, until the hissing sound which accompanies the evaporation of the water ceases. Care must be taken to avoid overheating and consequent discoloration of the butter.

Foaming may be reduced by heating the upper part of the beaker or tube. Patrick gives −0.10 to +0.17 as the limits of deviation from results obtained by the official A. O. A. C. method.

Another rapid method of estimating the water is to heat the sample in a platinum basin over a small flame. The addition of 0.03 grm. of sodium bicarbonate for 10 grm. of fat will prevent spurting (Monhaupt, *Chem. Zeit.*, 1919, 43, 385–386; *Analyst*, 1919, 44, 320).

These last two methods are satisfactory and probably the most expeditious, but require some little skill and attention to hit the exact point when all the water has gone and decomposition of the curd has not commenced.

For this reason distillation methods have been introduced which are rapid and quite accurate enough for the purpose.

Gray's Method (*U. S. Dept. of Agric., Bureau of Animal Industry,* Circ. 100).

Apparatus.—The apparatus required for the test is as follows:

Balance.—Sensitive to 0.025 grm.

Pipette.—For measuring 6 c.c.

Paper.—Parchment, 5 by 5 in.; must be perfectly dry.

Special Apparatus.—As shown in Fig. 10. *A* is a flask of capacity of a little over 70 c.c. *C* is a graduated tube, which is connected with flask *A* by means of a rubber stopper. *F* is a glass stopper ground into the tube *C*. The tube *C* is graduated after this glass stopper *F* has been ground in, the zero mark being the end of the stopper. Each mark of the graduation represents 0.02 c.c., or, when a 10-grm. sample of butter is used, each mark represents 0.2% of water. *E* is a glass condensing jacket connected with the graduated tube *C* by rubber stopper *D*, as shown in the figure.

Amyl Reagent.—A mixture of amyl acetate (5 parts) and amyl valerate (1 part). Must be free from water-soluble impurities in order to give accurate results.

Preparing the Sample.—The sample of butter is placed in a suitable container (1 pint jar or metal cup will be satisfactory), and the latter immersed in water at about 100° F. The butter is stirred with a spatula or spoon until it has the consistence of thick cream and no free water can be seen. Samples of butter should not be left standing in open containers any considerable length of time before making the water estimation, as some of the water will evaporate and the percentage of water found finally will be too low.
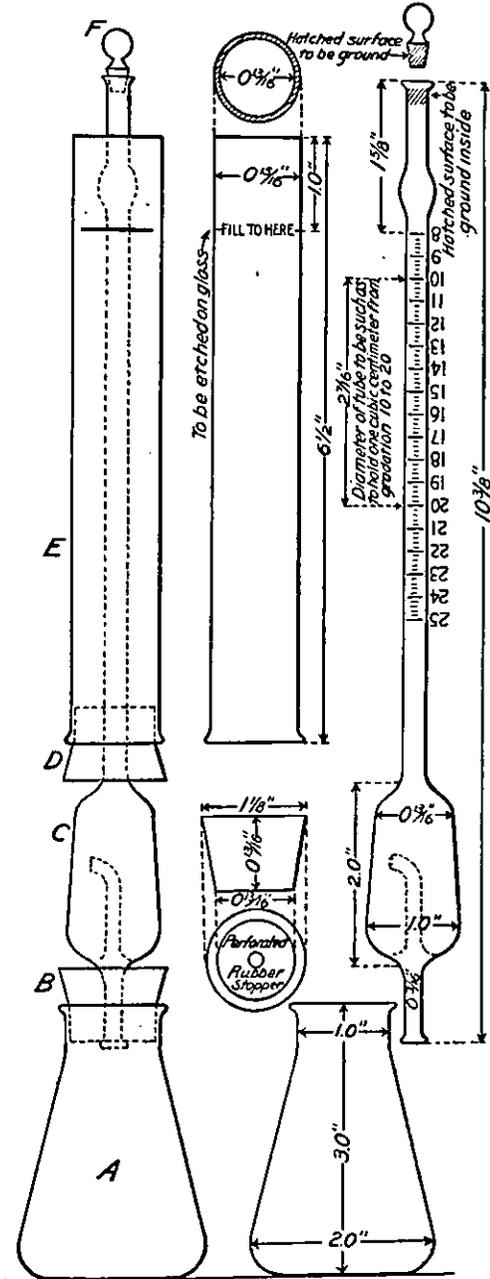
FIG. 10.

Weighing the Sample.—Place on each pan of the balance one sheet of parchment paper and balance accurately. Place the 10 grm. weight on one pan and balance again by placing butter on the parchment paper on the opposite pan, placing the sample as near the centre of the paper as possible.

When exactly 10 grm. are weighed out remove the sample from the pan, and fold it in the parchment paper in such a way that the paper and butter may be slipped into flask *A*. Add 6 c.c. of the amyl reagent to the butter in the flask, connect the apparatus as shown in the figure, and fill the condensing jacket *E* with cool water to within 1 in. of the top. Remove the stopper *F*.

Place the apparatus over the flame of the burner, applying heat to the bottom of the flask *A*. In a short time the butter will melt, running from the parchment paper into the amyl reagent. The water in the sample then boils and passes as steam into the tube *C*, where it is condensed and trapped. Watch the condensation in the graduated part of the tube *C*, and do not let the steam get higher than the 15% mark. If it goes higher than this, remove the flame, as there is danger of water being lost. If there is any indication of the mixture in the flask *A* foaming over, remove the flame. Foaming is usually prevented by 6 c.c. of amyl reagent, but some samples of butter, especially those with high moisture, require a trifle more than 6 c.c. In case of continued foaming, allow the mixture in the flask to cool, and add about 2 c.c. of the amyl reagent, and continue heating. After the water in the sample has boiled out, the temperature rises and the amyl reagent boils, driving the last traces of water and water-vapour from the flask and bottom of the stopper. Some of the amyl reagent is carried into the tube *C* with the steam, and some is boiled over after the water has been driven off. This amyl reagent in the tube is no disadvantage. The time required to expel all the water from the sample is not less than 5 minutes, and with most samples need not be more than 8 minutes. When the mixture in the flask becomes brown and all the crackling in boiling ceases, it is safe to conclude that all water has been driven from the flask. *Disconnect the flask A from the stopper B, place the glass stopper F in the tube C,* giving it a slight turn to ensure its being held firmly, invert the tube *C*, first being sure that the mouth of the small tube inside the bulb is held upwards; pour the water from the condensing jacket *E*, after which the jacket may be removed. When the tube

C is inverted, the water and amyl reagent flow into the graduated part of the tube. To separate these and to get the last traces of water into the graduated part, the tube C is held with the bulb in the palm of the hand and the stoppered end away from the body, raised to a horizontal position, and swung at arm's length sharply down to the side. This is repeated a number of times until the dividing line between the water and the amyl reagent is very distinct and no amyl reagent can be seen with the water, and *vice versa*. The tube should then be held a short time with the stoppered end downwards, and the amyl reagent in the bulb of the tube agitated, in order to rinse down any water that may be adhering to the sides of the bulb. The reading should not be taken until the tube and its contents have cooled so that very little warmth is felt. The water is in the bottom of the tube, and when a 10 grm. sample is taken the percentage may be read directly. Read the lower part of the meniscus.

2. Fat.

(*a*) This is usually estimated by extracting the dried residue from the water determination with five successive quantities of ether, allowing as long as possible for the ether to act at the fourth extraction. The ether is poured off carefully each time, and no loss need occur. The residue is dried and weighed, the difference between the weights before and after extraction giving the fat.

For accurate estimations of the fat, the Gottlieb method is to be preferred. The method as given by Hesse (*Zeitsch. Nahr. Genussm.*, 1904, 8, 673) is as follows: 1.5 to 2 grm. of the sample are weighed into a long graduated tube with 8 c.c. of warm water and the fat completely melted by placing the tube in hot water. 1 c.c. of 10% ammonia and 10 c.c. of strong alcohol are added with mixing between and after each addition, and the mixture well cooled. 25 c.c. of methylated ether are added; the liquids mixed by inversion; 25 c.c. of petroleum spirit (distilled below 60°) added, and again mixed three times by inversion. The mixture is allowed to separate; the ethers pipetted off; 50 c.c. of ether again added and pipetted off without shaking; then the mass is shaken out finally with 25 c.c. of ether and 25 c.c. petroleum spirit and pipetted off as before. The mixed ethereal solutions are evaporated and the fat weighed. The last addition of ethers may be omitted without serious error.

(b) Combined Method for Estimating Fat and Salt.

1. *Estimation of Fat: Apparatus Required.*—A centrifuge.

A special separating funnel.

A balance which is sensitive to 0.01 grm. (A torsion balance, such as is used in the moisture test, is satisfactory, if it is in good condition.)

An accurate set of metric weights.

A 10 c.c. graduated glass cylinder.

A 100 c.c. glass beaker.

SPECIAL SEPARATING FUNNEL.—This is essentially a separating funnel with a capillary stem. The capacity of the funnel should be about 75 c.c. and its weight, when empty, should not exceed 70 grm. The stopper may be dispensed with if desired. It is a convenience in the final weighing, but not a necessity. Fig. 11 shows the form and dimensions of the funnel.

SPECIAL SOCKET.—This is a double socket for holding the above funnel while centrifuging, and is made of heavy sheet copper with hangers of steel. Each socket will hold 2 funnels. The cut shows the construction and dimensions. It differs in no material way from the socket ordinarily used on the Babcock centrifuge, except for the opening in the side. If the dimensions given fail to fit the centrifuge at hand, they may be changed to suit, so long as the dimensions of the barrels are not altered. Care must be taken that the capillary stem of the funnel does not project far enough through the hole in the socket to strike against the side of the centrifuge when being whirled. It is best to fit a disc of rubber to the bottom of the socket.

Sampling the Butter.—In estimating fat in butter great care must be taken in securing a representative sample and in preparing this for the test. Errors introduced by improper sampling are far greater than those in the actual test.

Samples are best taken with a butter trier, and one should always take several plugs from different parts of the tub or churn. These are placed in a suitable container, such as a 1-pint preserve jar or a cup, which is placed in water at about 100° F. The sample is then mixed with a spatula or spoon until of about the consistence of thick cream. The sample must not be left any length of time in open containers, since some of the moisture will evaporate. Should the sample be kept for any reason for a day or two before it is mixed,

it should be placed in warm water (with the cover on the container) until melted, and then cooled, after previous shaking, until it solidifies. The reason for this is that, on standing, some of the water will ooze out and cannot be reincorporated except by emulsi-
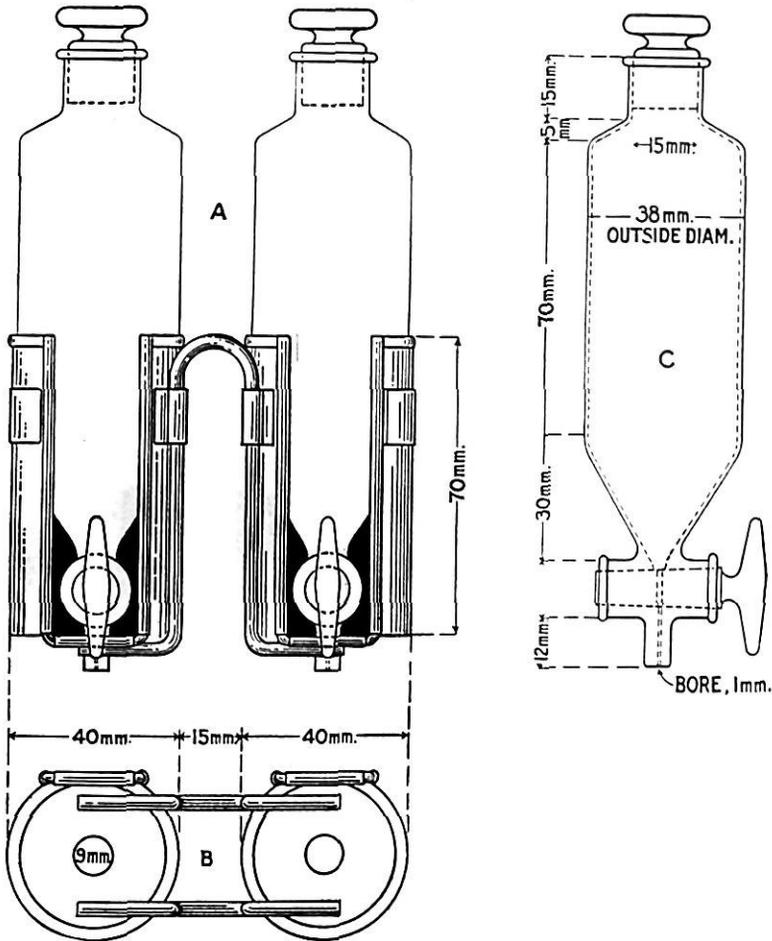
FIG. 11.—The special apparatus for estimating fat and salt in butter. A, the socket with funnels in position; B, view of socket from below; C, the separating funnel with capillary stem. (Reduced one-half.)

fying and cooling while in this condition. Too much stress cannot be laid on careful sampling and mixing the sample, for upon this the accuracy very largely rests.

Estimating the Fat.—It will be found more economical in some cases if 4 or multiples of 4 estimations are made at once. In this

case the 2 double sockets will balance when placed opposite in the centrifuge. If only 1 or 2 estimations are made it will be necessary to balance the centrifuge by putting weights in the opposite socket. The weight of the clean, dry separating funnel must first be ascertained. This weight, once found, will suffice for all estimations made with that particular funnel.

I. WEIGHING THE CHARGE.—Counterpoise the small beaker on the balance and carefully weigh out 20 grm. of the sample mixed as directed.

II. TRANSFERRING THE CHARGE TO THE SEPARATING FUNNEL.— Place the beaker containing the charge on a radiator or steam pipe until the butter is melted. (This may also be accomplished by adding a small quantity of boiling water.) Next pour the charge into the funnel, which must be maintained in an upright position, and no part of the charge lost in transferring. With a fine stream of hot water rinse down the sides of the beaker and pour the rinsings into the funnel. Repeat this, using not more than a teaspoonful of water at a time until the funnel is full to within $\frac{1}{4}$ in. of the shoulder. The rinsing can be done very conveniently with the arrangement on many steam centrifuges for filling the Babcock test-bottles, i. e., the rubber tube ending in a glass or metal point and connected with a water tank heated by steam. The point must be fine, however. Should it be larger than $\frac{3}{16}$ in., it can be replaced with the tip of a small oil can. Should this arrangement not be at hand, one can easily be improvised from a tin can, a rubber tube and an oil-can tip. In transferring the melted butter and rinsings the last drop may be prevented from running down the outside of the beaker by touching the lip of the beaker on the neck of the separating funnel.

III. CENTRIFUGING.—Insert the separating funnel in the special socket, allowing the stem to project through the hole in the bottom and the handle of the stopcock through the open side. (Caution: The socket must always be placed in the centrifuge with the open side facing the direction in which the wheel revolves. This is very important, for, if the opening faces the reverse direction, the stopcock will be thrown out and broken.) Whirl 1 minute at the same speed used in testing milk on the Babcock method. The centrifuge must be kept warm.

IV. REMOVING THE WATER.—Remove the separating funnel from the socket and allow the water to flow through the stopcock until

the fat (or curd) is within ⅛ in. of the stopcock. In this and subsequent operations care must be taken that the stopcock does not stick. It must always be under control, and it is best to give it frequent slight movements when the water or acid is running through it, to be sure that this control is maintained, otherwise it may stick at the critical moment and the estimation be lost. Most of the salt and part of the curd are taken out by the water. The remainder of the curd and all of the fat stay in the funnel.

V. DISSOLVING THE CURD.—Measure out with the glass measure 9 c.c. of cold water (preferably distilled) into the beaker. Add to this 11 c.c. of sulphuric acid (sp. gr. 1.82–1.83) and mix by gently shaking. While still very hot add the mixture to the contents of the separating funnel. Now dissolve the curd by giving the funnel a circular motion with the hand grasping the neck. Centrifuge 1 minute, as before. Draw off the acid solution until the fat layer is within ¼ in. from the stopcock and repeat the operations in this paragraph.

VI. FREEING THE FAT FROM THE ACID SOLUTION.—The fat will now be in a clear transparent layer free from curd, and the solution below it will be practically colourless. To separate these, draw off the latter until the fat nearly reaches the stopcock, and centrifuge another minute. Allow the fat to descend through the stopcock until it just reaches the end of the capillary stem. This last step offers no difficulties, provided the stopcock is kept in control, but it requires care.

VII. ESTIMATING THE PERCENTAGE OF FAT.—Carefully dry the separating funnel on the outside with a clean soft towel and weigh it. The weight thus obtained, minus the weight of the empty funnel, represents the weight of butter fat in 20 grm. of the sample. The percentage is obtained by dividing this weight by 2 and multiplying by 10.

Sometimes it is possible to obtain a clear layer of fat with but one addition of acid, but in the majority of cases it will be found necessary to add it a second time, as directed. The proportion of acid and water selected is the outcome of a number of experiments, and is the one which gives the best results. The test for fat alone involves 4 centrifugings of 1 minute each. The centrifuge should be kept warm and the contents of the funnel in a melted state when the acid is added. The time consumed should not be much longer than in testing cream

by the Babcock test, and the operations involved are simple.   No difficulty has been experienced in obtaining a clear fat.   Occasionally a slight emulsion appears at the bottom of the fat layer when the latter is drawn into the stem.   This is so small in amount that it does not seem to affect the accuracy of the test to any considerable extent.   The emulsion should be weighed as fat and considered as such.

Cleaning the Separating Funnels.—The separating funnels should be washed after each estimation, but it is not necessary to dry them before use, providing their weight, when clean and dry, has been found.   The cleaning is easily done with hot water and either soap or cleansing powder.   They should be well rinsed with clean water and drained.

2. *Estimation of Salt—Additional Apparatus Required.*—A 50 c.c. burette graduated to 0.1 c.c.

A 250 c.c. volumetric flask.

A 25 c.c. pipette.

A 250 c.c. beaker or white cup.

CHEMICALS REQUIRED.—An aqueous silver nitrate solution containing 14.525 grm. of pure silver nitrate per litre and a 10% aqueous solution of potassium chromate.

METHOD.—To estimate the percentage of salt the wash water, obtained as previously directed in paragraph IV, is allowed to run into the 250 c.c. flask, and the operations in Paragraph IV conducted 3 times instead of but once, the water each time being allowed to run into the flask.

After the washings have become cool the flask is filled to the mark with cold water and the contents mixed.   25 c.c., which represent 2 grm. of the original sample, are then measured with the pipette into the beaker or cup and titrated with the silver nitrate solution from the burette, 2 or 3 drops of the potassium chromate solution being used as the indicator.   The first appearance of a permanent red is the end point.   The silver nitrate solution is of such strength that 2 c.c. represent 1% of salt if a 1 grm. charge is used.   In the above test where 2 grm. are represented $\left(\frac{25}{250} \times 20 \right)$ the number of c.c. divided by 4 gives the percentage of salt in the original sample.   As an example, if the burette reading showed that 10.6 c.c. of the silver nitrate solution were consumed in reaching the end point,

then 10.6 divided by 4, or 2.65, would be the percentage of salt in that particular sample.

3. Curd.

This may be estimated in the residue from the fat estimation in the first method by breaking the mass up carefully and extracting it with water, the insoluble residue being finally washed on to a tared filter, which is then dried at 100° and weighed. The filter should then be incinerated and the ash deducted from the weight of curd. While this method is useful, when only an approximate idea of the curd is required, if a proper estimation of the protein is desired, especially when the milk-sugar is to be ascertained by difference, the nitrogen should be estimated by the Kjeldahl process (*q. v.*), 6.39 being used as the factor.

In this estimation about 12 grm. of butter are weighed into the digestion flask, and rapidly dried by placing the flask in boiling water and exhausting the interior. About 20 c.c. of ether are added and the curd allowed to settle. The ether is poured off (if turbid, through a small filter), the curd washed once again with a little ether, and after evaporation of all traces of ether from the flask, the sulphuric acid digestion is proceeded with. If a filter has been used, this is dropped in before digestion. If the fat is not thus removed, serious frothing will take place when the distillation is carried out.

If the moisture is determined in a separate charge by one of the reliable methods, the percentage of curd may be found with sufficient accuracy by subtracting the sum of fat, salt, and moisture from 100.

4. Lactose.

This is not usually estimated directly, but is found by difference, unless adulteration with sugar is suspected, when the aqueous extract of the curd may be examined polarimetrically or with Fehling's solution, to confirm the result by difference.

5. Total Ash.

The solid-not-fat is gently ignited in a crucible, at as low a temperature as possible, or chlorides will be appreciably volatilised.

6. Salt.

This is best estimated in another sample of butter. 10 grm. of the butter are weighed into a cylinder, 5 c.c. of chloroform added and

sufficient water to make with the water in the butter 50 c.c., mixed well, without vigorous shaking, and allowed to settle, or, better, separated by rotation.   10 c.c. of the aqueous layer (= 2 grm. of butter) are pipetted into a white porcelain dish, 20 c.c. of water added, the whole roughly neutralised to neutral litmus paper, and titrated with N/10 silver nitrate, with the use of a potassium chromate indicator.   The exact strength of the silver solution should be ascertained against a known weight of sodium chloride.

If the solution is carefully neutralised before titration, the following preservatives, up to the strengths given, do not interfere:

Boric acid, 0.5%; sodium fluoride, 0.5%; salicylic acid, and β-naphthol, sufficient to saturate the aqueous layer.

Colouring Matters.—Colouring matters likely to be found in butter or margarine fall under two main headings:

(1) Vegetable or animal colours, e. g., annatto, turmeric, saffron and cochineal.

(2) Azo dyes such as Methyl Orange, Aniline Yellow.

The following method proposed by Stebbins (*J. Amer. Chem. Soc.*, 1887, 41) is satisfactory for effecting a separation of the dye. Into the melted fat is stirred about a tenth of its weight of finely powdered fuller's earth and the whole allowed to settle while still warm.   The bulk of the fat is then drained off, petroleum spirit added, the whole stirred, allowed to settle and the solution decanted through a filter. The process is repeated until the fat is completely removed, and the precipitate on the filter is washed with petroleum spirit and dissolved in alcohol.   The separation may be made quantitative by boiling out the precipitate three times with 94% alcohol, evaporating the alcohol and weighing the residue.

Coal Tar Dyes.—G. Van. B. Gilmour (*Analyst*, 1920, 45, 173) notes that on heating the filtered fat (separated below 100°) from butter or margarine to a temperature of 180–190° for 10 minutes natural and vegetable colours are destroyed, whilst coal tar dyes are not.   According to Robin, coal tar dyes may be distinguished by adding excess of calcined magnesia to the extract of the colouring matter (see above), then a little *20% mercuric acetate solution, boiling and filtering.*   If the filtrate is coloured, or if colour develops on adding acetic acid, a coal tar dye is indicated.

For distinguishing *coal tar dyes* and *annatto* Doolittle's method is recommended as being a simple one (*U. S. Dept. Agric. Bur. of*

Chem. Bul. 65, 152). About 2 c.c. of the melted and filtered fat are dissolved in a little ether, in each of 2 test-tubes. Into one is poured an equal volume of dilute (1:3) hydrochloric acid, and into the other an equal volume of dilute (1:10) potassium hydroxide. The mixtures are shaken well and allowed to stand.

A yellow aqueous layer in alkali tube indicates annatto.

A reddish aqueous layer in acid tube indicates azo-dyes, and a little practice with this method will enable the operator to find both dyes when present together, as is often the case.

Colour	Sulphuric acid	Nitric acid	Nitric and sulphuric acids	Hydrochloric acid
Annatto..........	Indigo blue to violet	Blue becoming colourless	Same	No change or brownish.
Turmeric.........	Pure violet	Violet	Violet	Violet to original colour on evaporation.
Saffron..........	Violet to cobalt blue changing to red-brown	Light blue to light red-brown	Same	Yellow to dirty yellow.
Carrot..........	Amber-brown	Decolorised	Same with NO₂ fumes and odour of burnt sugar	No change.
Marigold........	Dark olive-green	Blue, changing at once to dirty yellow-green	Green	Green to yellowish green.
Safflower......	Light brown	Partly decolorised	Decolourised	No change.
Aniline yellow...	Yellow	Yellow	Yellow	Yellow.
Martius yellow..	Pale yellow	Yellow, reddish ppt. Magenta at margin	Yellow	Yellow ppt. treated with NH₃ and ignited deflagrates.
Victoria yellow..	Partly decolourised	Same	Same	Same. Colour returns on neutralisation with NH₃.
Methyl orange[1]..	Pink to brickred, yellow at edges	Pink and decolorised.	Pink rapidly decolourised with NO₂ fumes finally yellow	Pink, the well-known colour with acids.

[1] Added by writers.

For the *systematic examination* for colouring matters, the following method of Leeds (*Analyst*, 1887, 22, 150) should be used:

100 grm. of butter are dissolved in 300 c.c. petroleum spirit (0.638 sp. gr.) in a separating funnel, the curd and water drawn off, and the

petroleum spirit washed several times with water. The ethereal solution is kept at o° over-night; it is then poured off from separated glycerides and shaken with 50 c.c. N/10 alkali. The aqueous layer is separated and titrated with hydrochloric acid till just acid to litmus. The precipitate is filtered, dried, and weighed. If only the identification of the colour is required, less quantities than the above may be taken. To identify the colour, dissolve the precipitate in a few drops of alcohol and test by allowing 1 drop to fall into watch-glasses containing the concentrated acids.

As slight differences of opinion as to the colours may occur, it is advisable, where possible, to check them with the actual dye.

A mixture of two dyes is not differentiated, the predominating dye alone giving results as a rule, but Witt (*Zeitsch. anal. Chem.*, 1887, **26,** 100) describes a simple test to determine if a mixture of dyes is present, and for this purpose he dusts the powdered dye over concentrated sulphuric acid and watches the behaviour of the particles as they dissolve.

Geissler's method (A. O. A. C.) for azo-colours: Spread a few drops of the clarified fat upon a porcelain surface and add a pinch of fuller's earth. In the presence of various azo-dyes, a pink to red colouration will be produced in a few minutes. Some samples of fuller's earth act more readily than others.

Special oil-soluble, azo-colours (Sudans) are now much used. See A. O. A. C. methods, 1908, p. 195.

The following points may be noted with regard to individual colouring matters:

(*a*) *Carotin.*—This substance is the natural yellow pigment of butter and animal fats, but the detection of *added* carotin is rendered necessary by the oleomargarine laws of many States. This is a matter of considerable difficulty, and Palmer and Thrum (*J. Ind. Eng. Chem.*, 1916, **8,** 614) have criticised Cornelison's test for carotin (*J. Amer. Chem. Soc.*, 1908, **30,** 1478) and have pointed out that, as stated by Leach, the test detects carotin, but does not distinguish between the carotin of genuine butter and carotin prepared from carrots.

(*b*) *Highly coloured oils,* such as palm oil and fixed oil of mustard, are occasionally used. Leffmann and Beam (Select Methods in Food Analysis, 2nd Ed., 238), describe methods for their identification.

(c) *Cochineal.*—Robin's test is reliable and may be carried out as follows: The aqueous colour solution is acidified with hydrochloric acid and shaken in a separating funnel with amyl alcohol. In the presence of cochineal the solvent is yellow, the depth of colour depending on the amount present. The amyl alcohol solution is then washed with water until neutral, and to one portion is added a little water, and then, drop by drop, a solution of uranium acetate, with shaking between each addition. In the presence of cochineal the water is coloured emerald green. To another portion ammonia is added, and a violet colour develops if cochineal is present.

(d) *Turmeric.*—The alcoholic solution is yellow. On drying a filter paper immersed in the alcoholic solution, dipping it into a dilute boric acid or borax solution slightly acidified with hydrochloric acid, and again drying it, a cherry red colour develops, turning dark green on moistening with dilute alkali. It may be noted that legislation as to the colouring of butter and margarine is in force in many countries. For example, in the U. S. A. some 8 shades of yellow and red are permitted; Denmark and Australia allow certain colours, whilst France and New Zealand allow no colouring matters.

Neutralising Agents.—It should be noted that butter made from neutralised cream will differ in its salts from that made from normal cream. Ferris (*J. Ind. Eng. Chem.*, 1920, 12, 757; *Analyst*, 1920, 45, 369) gives a method which is based upon the ratio between the alkalinity of the salts present and the phosphoric acid, which ratio increases with the amount of alkali which has been used. Details of the method and a formula for calculating the acidity neutralised will be found in the original paper.

Preservatives Systematic Examination.—About 50 grm. of butter are placed in a long tube, 25 c.c. of chloroform added and mixed with the butter. 100 c.c. of 0.1% sodium hydrogen carbonate are added and the whole gently mixed. Vigorous shaking must be avoided. The tube is stood upright until the aqueous layer has separated, or it may be rotated. The aqueous layer is used as follows:

Boron Compounds.—1 c.c. is mixed with 1 drop hydrochloric acid and 8 drops of a saturated alcoholic solution of turmeric, and evaporated to dryness in a porcelain crucible lid. In the presence of 0.02% of *boric acid* the residue is a purple-red, changed to indigo

by a drop of strong ammonia (o.880). When boron compounds are not present, the residue is a dirty yellow, and changed by ammonia to a salmon colour.

β-naphthol.—A few c.c. of the aqueous solution are mixed with an emulsion of diazotised naphthionic acid. An *immediate* crimson colour indicates *β-naphthol*, a similar colour being given by *abrastol*.

Pure butter *gradually* develops a rather similar colour.

The reagent is prepared as follows: About o.2 grm. of 1–4 naphthylaminesulphonic acid is boiled with 10 c.c. of 50% alcohol, cooled (in ice if possible), 1 c.c. of 1:3 sulphuric acid added, and then, gradually, about 1 grm. of potassium nitrite dissolved in about 10 c.c. of water. The suspension gradually becomes yellow. (If the liquid is red, the nitrite has been added too fast.) The mixture is allowed to stand for 5 minutes, and the precipitate filtered off and washed with a few c.c. of water. The filter is pierced and the precipitate washed into a test-tube with about 5 c.c. of water. The emulsion so obtained is used as above; o.02% of β-naphthol is easily detected.

Salicylic Acid.—10 to 15 c.c. of the aqueous solution are strongly acidified in a separating funnel with dilute sulphuric acid, and 20 c.c. of ether added and mixed with gentle shaking. The ether is allowed to separate, the aqueous layer run off, the ether washed with 1 to 2 c.c. of water, and then about 10 c.c. of water added with 1 drop of phenolphthalein indicator. N/10 sodium hydroxide is run in until, on shaking, the lower layer remains permanently pink. The aqueous layer is run off, N/10 sulphuric acid added equal to alkali used, and the liquid tested ·with ferric alum solution. A violet colour indicates salicylic acid. Minute quantities (1:200,000, can be detected.

Benzoic Acid.—The tube containing the butter-chloroform-water mixture is vigorously shaken and again allowed to settle out (this may be hastened with a centrifuge). The aqueous layer is separated and treated exactly as for salicylic acid, except that neutralisation is effected by a saturated solution of barium hydroxide. The pink aqueous layer obtained is filtered into a small procelain dish, evaporated to 1 to 2 c.c., poured into a test-tube, the colour discharged by a drop or two of very dilute acetic acid, and then a drop or two of neutral ferric chloride solution added. A flesh-coloured precipitate indicates benzoic acid. o.1% can be detected in this manner, but owing to the solubility of benzoic acid in fat, the

following alternative method is recommended for detecting smaller quantities:

About 10 grm. of the butter are boiled for 30 minutes with 10 c.c. of alcohol and 1 to 2 drops of dilute sulphuric acid, the mixture well cooled, and after pouring off the alcohol into a separator, diluted with water and a few drops of dilute suphuric acid added, extracted with ether, and finished as above.

Fluorides.—10 c.c. of the aqueous solution are evaporated to dryness in a platinum crucible and ignited gently. The ash is moistened with a few drops of sulphuric acid, and the crucible closed with a watch-glass, coated with paraffin wax, having some scratches made through the wax. Cold water or ice is placed in the watch-glass and the crucible stood on a hot plate for 2 hours. In the presence of fluorides the scratches will be found to be etched on the glass.

Detection and Estimation of Individual Preservatives.—(1) *Boric acid* may be detected as described above, the water which separates from the butter on melting being used. It may be estimated in the following way (Richmond and Harrison, *Analyst*, 1902, **27**, 179, and Richmond and Miller, *Analyst*, 1907, **32**, 144):

25 grm. of butter and 10 to 15 c.c. of chloroform or petroleum spirit are placed in a stoppered cylinder and sufficient water added to make the total quantity of water present 25 c.c. (the butter as an average may be taken to contain 3.5 c.c. of water). The substances are gently mixed and allowed to stand until separation occurs, or are centrifuged. 20 c.c. of the aqueous layer (containing the boric acid of 20 grm. of butter) are pipetted into a 300 c.c. flask, and 10 c.c. of a 0.5% solution of phenolphthalein in 50% alcohol added. The mixture is boiled, and titrated while boiling with N/10 sulphuric acid until colourless, and then with N/10 sodium hydroxide until faintly pink. 25 c.c. of glycerol or 2 grm. of mannitol are added and the liquid again titrated until pink. Then, if x = c.c. of alkali used for the final titration, and y = c.c. required by the glycerol or mannitol used:

$(x - y) \times 0.0062 \times 5$ = boric acid in %. The factor 0.0062 is given here, but it is advisable to ascertain this against the alkali used.

Hawley (*Analyst*, 1915, **40**, 150) describes a satisfactory routine method for (a) detection and (b) rough estimation of boric acid in large numbers of samples.

(2) *Benzoic Acid*.—Hinks[1] has devised the following method of detecting and estimating benzoic acid (and incidentally salicylic acid) in milk products.

10-20 grm. of cream are heated with an equal volume of concentrated hydrochloric acid until the curd is completely dissolved, and the mixture is cooled and shaken with 25 c.c. of normal methylated ether and petroleum spirit (1 : 2). The ethereal layer is separated, and 1 drop of ammonia (0.880) added and then 5 c.c. of water. The mixture is shaken, the aqueous layer separated, heated for a few minutes on a water-bath to expel ammonia and then tested for benzoic acid, in the usual manner, with ferric chloride. It is probably advisable to add a trace of acetic acid before the ferric chloride, in order to ensure against alkalinity in the test solution, and in order to be certain that the ferric chloride solution is neutral, ammonia should be added to the freshly prepared solution till the iron precipitates, the solution filtered and the filtrate used for the test.

Hinks has shown that on adding ammonia to the ethereal extract (before the addition of water) a precipitate of ammonium benzoate appears, whilst, in the case of pure milk, no effect or only a slight opalescence is produced, and that the test is very delicate for benzoic acid. It is probable that it is in no way characteristic of benzoic acid, but that other organic acids, probably lactic acid, would show a similar percipitate, for which reason, whilst note should be taken of this precipitate the result should be substantiated by the ferric chloride test.

The method is made quantitative by dissolving the cream as before, using a reflux condenser, and extracting the cooled solution 3 times with 20 c.c. of a mixture of equal parts of methylated ether and petroleum spirit. The mixed ethereal extracts are made alkaline with ammonia, 10 c.c. of water added and the mixture shaken, and the aqueous layer separated. This process is repeated twice more, adding more ammonia if necessary. The mixed aqueous extracts are made acid with hydrochloric acid and again extracted 3 times with 20 c.c. of mixed ethers. The combined ethereal extracts are allowed to evaporate spontaneously, and the residue dried in a desiccator till constant in weight (about 24 hours). The residue is then heated at 100° for 1-2 hours and again weighed. The difference gives the benzoic acid in the original quantity of cream taken.

[1] *Analyst*, 1913, 38, 555.

The method gives excellent results.

Butter should be shaken out violently with sufficient of a 1% solution of sodium bicarbonate, and the aqueous layer, after separation, boiled with hydrochloric acid and extracted with ether.

(3) *Cinnamic Acid.*—This substance appears to be used occasionally as a preservative. In order to detect its presence, the preservative is extracted, either as described under benzoic and salicylic acids (Vol. VIII, p. 190) up to the point of extracting the ether with barium hydroxide, or by Hinks' method (see above). In either case the ether is extracted with ammonia, the aqueous layer evaporated to dryness, and the residue heated to boiling with 5 c.c. of dilute chromic acid solution (1 part dilute sulphuric acid (1 : 3) saturated with potassium dichromate and 7 parts water), in a covered crucible. The crucible is then cooled without opening and, when cold, the odour of benzaldehyde is at once noticed on removing the lid, if so small a quantity as 0.2% of cinnamic acid is present in the original cream.

(4) *Salicylic acid*, if present to the extent of 0.1%, may be detected by shaking the melted butter with ferric chloride solution.

In addition to the colorimetric method given above, the following procedure based on the method of the Paris Laboratory is recommended for estimations.

25 grm. of butter are gently shaken in a separating funnel or tube with repeated quantities of a 0.5% solution of sodium bicarbonate. The aqueous extract containing the salicylic acid in the form of sodium salicylate is rendered just acid by means of dilute sulphuric acid and extracted three times with ether. The ethereal extract is evaporated, and to the residue is added a little mercuric nitrate solution; a precipitate results which is practically insoluble in water. The precipitate is filtered off, washed with water and decomposed with dilute sulphuric acid. Solution in ether is again effected, the ether evaporated and the residue dried at 80–100°. The residue is then extracted with petroleum spirit, and the extract diluted with an equal volume of neutral 95% alcohol and titrated with $N/10$ alkali with the use of a liberal quantity of phenolphthalein as indicator. Then 1 c.c. $N/10$ alkali = 0.183 grm. salicylic acid.

The method of Revis and Payne (*Analyst*, 1907, **32**, 286) may be modified to apply to butter.

(5) *β-naphthol*, if present to the extent of 0.1%, may be detected by mixing the butter, rendered alkaline by a few drops of sodium carbonate solution, with the diazo-emulsion.

Rancidity.

The question of rancidity of butter as a whole is the one which chiefly concerns the analyst. The causes of this change cannot, in the present state of our knowledge, be set forth in any definite pronouncement. It has been attributed largely to the growth of micro-organisms and moulds, but light and oxygen play a considerable part in the chain of factors tending to this end.

In the case of butter fat, Laxa (*Arch. f. Hyg.*, 1902, 41, 119) has certainly shown that species of *Oidium*, *Penicillium*, and *Mucor*, also *Bacillus fluorescens liquefaciens*, effect hydrolysis of the fat, thus forming fatty acids. The volatile fatty acids are in their turn further attacked. It seems that the method of attack is enzymic in its nature.

While in certain forms of rancidity free fatty acids make their appearance and can be estimated in the usual way (page 10), it must not be supposed that rancidity is correctly measured in all cases by the free fatty acidity.

Soltsien (*Chem. Rev. Fett Ind.*, 1905, 12, 177) has shown that the products causing the characteristic effect of rancidity can be distilled in a current of steam, and finds that the products from rancid lard give strong aldehydic indications, but that aldehydes hardly occur in the case of rancid butter. For the detection of rancidity he recommends the application of Welman's phosphoric reagent to the distillate.

In conclusion, it may be said that taste and smell are, so far, the best indicators of rancidity.

Recent investigations have added little to the knowledge of the causes of rancidity.

In the case of butter, it is necessary to distinguish two different types of rancidity which occur in practice. (1) The rapid change which takes place in butter after it has been placed on the market, particularly after it has been removed from cold storage; this is probably due entirely to the effect of light, possibly aided by the action of moulds. The change is confined to the outer layers of

the butter. (2) The slow deterioration and loss of flavour which takes place when butter is kept in cold storage.

Investigation has shown that sweet cream butter deteriorates much more rapidly than butter made from properly ripened cream; the lactic acid would appear to act as a preservative.

In spite of the fact that any lipolytic action on the fat appears to be negatived by the work of Rahn, Brown and Smith, it is difficult to say that the deterioration in taste and rancid flavour may not be due to traces of free fatty acids such as cannot be actually estimated.

A most interesting investigation into the deterioration of storage butter has been made by Rogers and others (*U. S. Dept. of Agric., Bureau of Animal Industry, Bulletin* 162, April, 1913) in which, amongst other possible factors, the action of small quantities of metals (particularly iron and copper) in producing deterioration has been investigated. As both these metals can easily be introduced into butter in minute quantities during making, and it is shown that they do produce decided deterioration, there appear to be grounds for attributing some, at least, of the loss of flavour to this cause. It is not improbable that the more rapid development of rancidity after removal from cold storage may be due to the preliminary stages having been so induced during storage.

The original bulletin should be consulted by those who are interested in the subject. Clayton in his monograph on Margarine discusses rancidity and deterioration of butter at considerable length, attaching great importance to the various micro-organisms present.

In connection with the general subject of faults in butter the following may be of interest and guidance to the analyst:

(1) A yeasty taste in butter may arise from repeated oversouring of the starter, when yeasts develop which impart this flavour. Careless washing also intensifies this (Rosengren, *Milch Zentr.*, 1912, 41, 221).

(2) Lipolytic action may take place if starters are carelessly prepared, or not used at all. Under these circumstances, according to Sohngen (Abs. *Cent. f. Bakt.*, Abt. II, 1912, 35, 331), certain organisms may become sufficiently numerous to produce action on the fat, and in contradistinction to plant lipases, these microbic enzymes are distinctly thermostable. These organisms can be

largely kept in abeyance by properly aërating the starter or cream and by the rapid development of acidity under proper conditions.

(3) Certain micro-organisms may cause fat splitting or may decompose the protein matter present.

Tests for indicating rancidity are not very satisfactory. They all depend upon the recognition of certain products of rancidity such as oxidised acids, labile oxygen, water-soluble oxidisable products and so on, but amongst the least unsatisfactory may be mentioned Kreis' reaction as modified by Kerr (*J. Ind. Eng. Chem.*, 1918, 10, 471). The test is carried out as follows: 10 c.c. of melted fat are vigorously shaken with 10 c.c. of strong (1.19) hydrochloric acid, and 10 c.c. of a 0.1% solution of phloro-glucinol in ether added, and the mixture shaken. If no red or pink colour develops in the acid layer, the fat is passed as satisfactory, and if such a colour does develop two further tests are made in which the original fat is diluted to 1 in 10 and 1 in 20 with kerosene. A reaction in the greatest dilution indicates rancidity so far advanced that it may be evident to taste and smell, whilst a fat giving a colour only when undiluted would probably not keep for long.

Issoglio's method (*Ann. Chim. Applic.*, 1916, 6, 1) depends on the proportion of aldehydes and ketones liberated by steam distillation under constant conditions, and is measured with permanganate solution (*cf.* p. 189).

R. H. Kerr and D. G. Sorber (*J. Ind. Eng. Chem.*, 1923, 15, 383) have investigated most of the known tests for rancidity, and come to the conclusion that by far the most valuable is the modified Kreis test referred to above.

MARGARINE

During the last few years the composition of margarine has under-gone profound changes. These changes, which are still in progress, have rendered the analysis of modern margarine mixtures one of the most complicated problems with which the analyst can be con-fronted.

They may be two main varieties of margarine:

(*a*) Containing animal fat, with or without vegetable oil.

(b) Containing vegetable oil only.

Either of these two classes may contain a proportion of butter fat, added for flavouring purposes, but in many countries the amount

of butter fat allowed in such products is limited by law, 10% being commonly the maximum allowed.

(*a*) **Oleo-margarines** containing as their base "oleo-oil," a product of beef fat.

The best portions of the fat are taken from the newly killed animal, chilled quickly, and rendered at a low temperature. The product, which is called "Premier Jus," is allowed to set slowly to a granular condition, and then, after being placed in bags, submitted to hydraulic pressure. The soft portion of the oil is expressed, producing "oleo-oil." The m. p. of the "oleo-oil" can be adjusted to the time of year, by regulating the pressure employed.

This "oleo-oil" is worked up either by itself or with lard, cottonseed oil, coconut, and other oils, according to the grade of margarine desired. The fat is then churned with milk, which has been "soured," after pasteurisation, with a proper butter "starter," a butter colour (annatto in cottonseed oil, or a mixture of annatto and azo-dye) being added to the charge in the churn. The churn mass is cooled with a stream of ice-water, in order to set it, and prevent crystallisation as far as possible. The mass is then thrown on the "worker," salt and a preservative being usually added.

When margarine first came into use as a butter substitute all the better class varieties were oleo-margarines, but of late years the use of animal fat has been rapidly decreasing.

(*b*) **Vegetable margarines,** in which the place of animal fat has been taken by coconut and palm-kernel products, which often reach 70% in the fatty mixture. As a certain percentage of butter fat is often present, which may either arise from the milk used in manufacture, or be purposely added to improve flavour, a recasting of the methods of analysis was imperative. A very large number of methods of dealing with these mixtures have been published, but the writers are of the opinion that the original Reichert-Meissl method, with the additions of Polenske and Kirschner, is quite sufficient for the resolution of mixtures containing coconut and palm-kernel products in the presence of butter fat and indifferent oils. It is only necessary to carry out the process in a standard manner, when the tables and curves proposed by the writers are applicable. *It must, however, be understood that unless the conditions of experiment are carefully adhered to, the tables, etc., will not apply.*

Exact details for carrying out these processes are given under "Butter Fat."

As the Reichert-Wollny method for estimating butter fat is still in use in a few laboratories, and must be carried out in a standard manner, a description is here given.

The following details were laid down by the Government Laboratory and a Committee of the Society of Public Analysts (England): (For details of the A. O. A. C. methods generally used in the United States see pages 25–27. The alkali-glycerol method is quite satisfactory for general inspection work.)
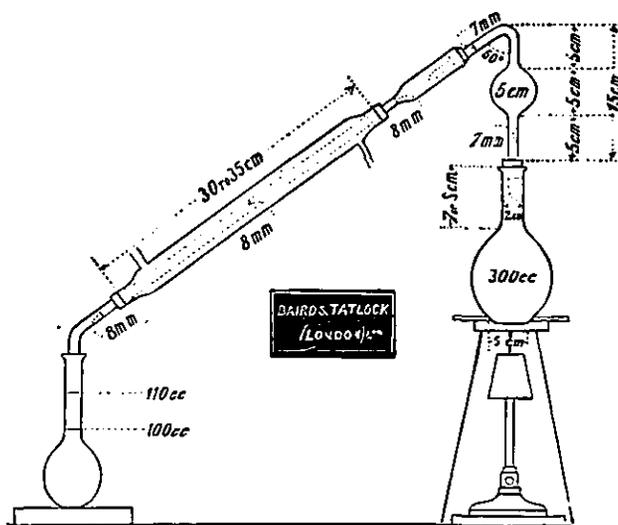
FIG. 12.

5 grm. of the fat are introduced into a 300 c.c. flask (of the form seen in Fig. 12). 2 c.c. of a sodium hydroxide solution (prepared by dissolving 98% sodium hydroxide in an equal weight of water and protected from absorption of carbon dioxide) and 10 c.c. of alcohol (about 92%) are added, and the mixture heated for 15 minutes under a reflux condenser, connected with the flask by a T-piece, in a bath of boiling water. The alcohol is evaporated by heating the flask on the water-bath for about $\frac{1}{2}$ hour, until the soap is dry. 100 c.c. of hot water which has been boiling at least 10 minutes are added, and the flask heated till the soap is dissolved. 40 c.c. of N/1 sulphuric acid, and 3 to 4 fragments of pumice are added, and the flask at once connected with the condenser as shown. The flask is first heated with a very small flame until the insoluble fatty acids

are melted completely without boiling the liquid. The heat is then increased and 110 c.c. are distilled into the graduated flask (within 28 to 32 minutes). The distillate is shaken, 100 c.c. are filtered off, transferred to a beaker, 0.5 c.c. of 1% alcoholic phenolphthalein solution added, and the liquid titrated with N/10 sodium hydroxide or barium hydroxide. A blank test of the reagents is carried out in an identical manner. It should not exceed 0.3 c.c. of N/10 alkali. The volume of N/10 alkali, less the blank, and multiplied by 1.1 is the Reichert-Wollny figure. Operating in this way, the following relations hold fairly well:

R.-W. figure of margarine	Percentage of butter fat present
4.0	10
4.3	11
4.6	12
4.9	13
5.2	14
5.5	15
5.9	16
6.2	17
6.5	18
6.8	19
7.1	20

Discussion of values obtained in the Reichert-Meissl-Polenske Kirschner process.

From a number of experiments made by the writers the following general deductions are made:

(1) That for the Kirschner values for *both coconut and palm-kernel oils* (with or without admixture of butter fat up to 10%), a straight line can be plotted which will represent, with very great closeness, the values experimentally obtained (see curves).

Further, for any percentage of coconut or palm-kernel oils the difference in the Kirschner values for "no butter fat" and for any percentage of butter fat (up to 10%) will be proportional, within very small limits, to the percentage of butter fat; the closeness of the agreement indicates that the relation will also hold for higher percentages of butter fat.

(2) On examining the values obtained for coconut and palm-kernel oils, it is seen that the Polenske value is practically inde-

pendent of the amount of butter fat present, when present up to 10% in the mixture, and is practically dependent on the presence of the coconut or palm-kernel oil only.   The mean value was there-fore calculated from the four values obtained for mixtures corre-
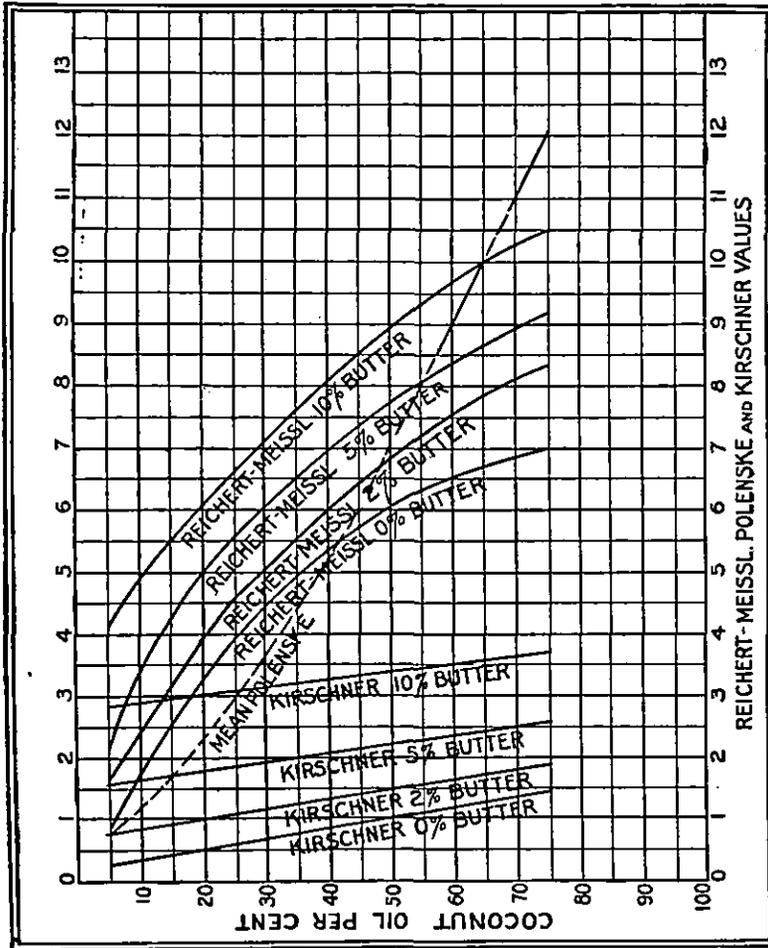
FIG. 13.

sponding to each different percentage of coconut or palm-kernel oil (see Table 1), and on plotting these mean values a regular curve was obtained.   The following equations have been worked out for these "mean value" curves:

$$x(\text{C.N.O.}) = 12.3 \ (P - 0.45)^{0.747};$$
$$x(\text{P.K.O.}) = 16.72 \ (P - 0.45)^{0.806};$$

where $x =$ the percentage of coconut or palm-kernel oil.

(3) The Polenske value acts as an "indicator," so that when a margarine containing coconut or palm-kernel oils is examined by the Reichert-Meissl-Polenske-Kirschner process, reference to the mean curve at once determines the percentage of coconut or palm-kernel
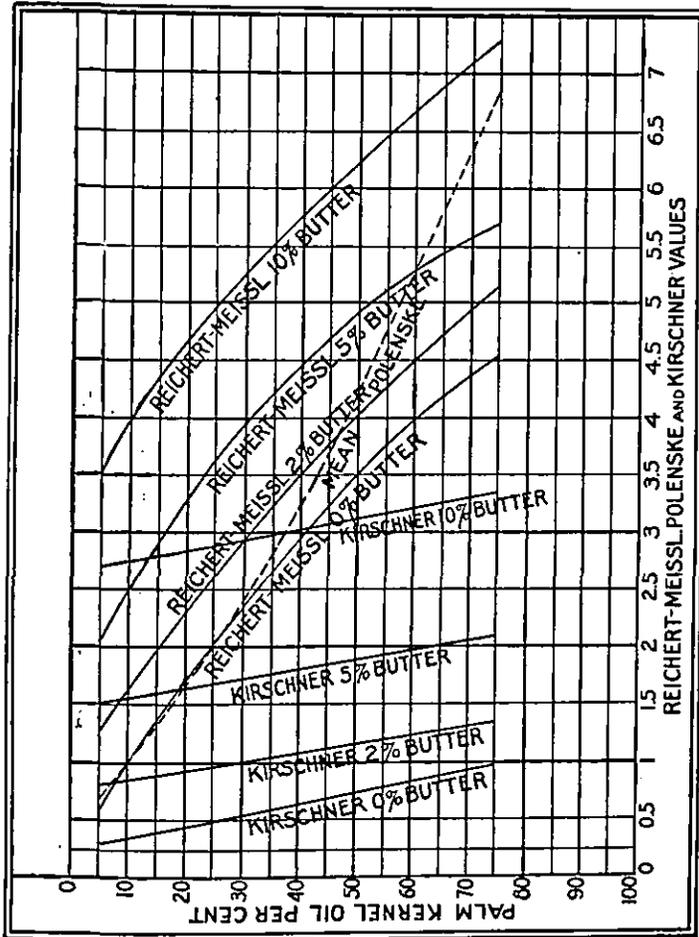
FIG. 14.

oil, apart from other values. The corresponding Kirschner value obtained from the typical curve then determines the presence or absence of butter fat, the Reichert-Meissl value acting as a confirmatory figure, and controlling the small fluctuations which may, in the Kirschner value, be occasioned by a variation in butyric acid content of different butters.

On account of the similarity of the results obtained for coconut and palm-kernel oils, the following formula will give the percentage of butter fat present with either fat for the Kirschner and Polenske values found experimentally:

$$\text{Butter fat per cent.} = \frac{K - (0.262P^{0.63} + 0.09)}{0.242};$$

or nearly as exactly by the more simple formula:

$$\text{Butter fat per cent.} = \frac{K - (0.1P + 0.24)}{0.244}.$$

The following formulæ connect the Kirschner value and percentage of butter fat when neither coconut nor palm-kernel oil is present:

$K = 0.236B + 0.33$, or, with a small increase in the probable error, $K = 0.244B + 0.28$, which is practically the formula given above.

The tables here given for coconut and palm-kernel oils, with or without the admixture of butter fat, are the typical values obtained from the curves given above, and are a reliable guide, provided the method be carried out under the standard conditions laid down, the standard apparatus being also employed (see p. 416).

TABLE I

Coco-nut oil, %	Polenske indicator value		Butter fat			
			0 %	2 %	5 %	10 %
0	0.45	Kirschner..............	0.18	0.80	1.49	2.70
		Reichert-Meissl.........	0.38	0.92	1.70	3.25
5	0.76	Kirschner..............	0.25	0.75	1.55	2.82
		Reichert-Meissl.........	0.87	1.65	2.15	4.10
10	1.22	Kirschner..............	0.34	0.84	1.60	2.90
		Reichert-Meissl.........	1.60	2.45	3.42	4.90
15	1.75	Kirschner..............	0.42	0.92	1.68	2.96
		Reichert-Meissl.........	2.52	3.15	4.35	5.55
25	2.91	Kirschner..............	0.60	1.08	1.82	3.08
		Reichert-Meissl.........	3.92	4.57	5.55	6.55
50	7.10	Kirschner..............	1.02	1.50	2.20	3.38
		Reichert-Meissl.........	6.05	6.88	7.72	8.95
75	12.19	Kirschner..............	1.45	1.92	2.55	3.70
		Reichert-Meissl.........	7.00	8.35	9.20	10.50
100	16.5	Kirschner..............	1.88	....	....	....
		Reichert-Meissl.........	8.08	....	....	....

TABLE II

Palm-kernel oil, %	Polenske indicator value		Butter fat			
			0%	2%	5%	10%
0	0.45	Kirschner...............	0.18	0.80	1.49	2.70
		Reichert-Meissl..........	0.38	0.92	1.70	3.25
5	0.68	Kirschner...............	0.30	0.80	1.51	2.70
		Reichert-Meissl..........	0.53	1.27	2.05	3.50
10	1.00	Kirschner...............	0.35	0.85	1.54	2.75
		Reichert-Meissl..........	1.00	1.62	2.50	4.00
15	1.35	Kirschner...............	0.40	0.90	1.57	2.80
		Reichert-Meissl..........	1.35	2.00	2.90	4.35
25	1.97	Kirschner...............	0.48	0.97	1.65	2.87
		Reichert-Meissl..........	1.97	2.60	3.62	4.97
50	4.22	Kirschner...............	0.72	1.16	1.87	3.12
		Reichert-Meissl..........	3.50	4.05	4.92	6.22
75	6.87	Kirschner...............	0.97	1.35	2.07	3.35
		Reichert-Meissl..........	4.55	5.15	5.70	7.30
100	9.82	Kirschner...............	1.07	....	....	....
		Reichert-Meissl..........	5.22	....	....	....

It is necessary to draw attention to an observation which the writers have made. In the standard apparatus that part of the still-head which passes through the cork and into the interior of the distillation flask is provided with a small hole in the side to prevent the collection of condensed liquid in the still-head. As originally designed by Polenske, this hole was at a fixed distance from the stopper of the flask. Insufficient attention is paid to this point by makers of the apparatus, and the writers have found that, if the hole is much more than 1 cm. from the lower surface of the cork, low Polenske values may be obtained with high percentages of coconut oil; if this method be made a standard one, particular attention should be given to this point.

These methods, whilst quite satisfactory so long as only coconut or palm-kernel oil is present, together with indifferent fats, leave a certain amount to the imagination if both coconut and palm-kernel oils are present together. The resolution of the mixture is then only possible when the percentage of the other fats or oils present is known, which is seldom the case, and it may not be possible to infer the quantity within 10 to 15%. Calculations based on the saponification values are often satisfactory, as by far the larger number of oils which are likely to be used with coconut and palm-kernel

products have a saponification value in the neighbourhood of 192 to 195, and the figures for coconut and palm-kernel oils themselves are remarkably constant.

The following addition to the Polenske determination has been made by Burnett and Revis (*Analyst*, 1913, **38**, 255). It gives information as to the relative percentages of coconut and palm-kernel oils in mixtures and may also on occasion throw light on the actual nature of the product present.

In an ordinary "straight" mixture of coconut and palm-kernel oils, the Polenske figure will determine the proportion with at least as great exactness as any other method. For instance, if the Polenske values are plotted as abscissæ, with percentage composition as ordinates, then a straight line joining the points which represent 100% coconut oil and 100% palm-kernel oil respectively will include the Polenske values for all mixtures of these two. The following process is for mixtures containing other constituents:

The ordinary Reichert-Meissl-Polenske determination is made in the *standard* apparatus and by the *standard* method. The Polenske figure is obtained with the use of N/10 *baryta*. The insoluble barium salts are then filtered off on a hardened filter-paper under pressure and the salts washed 3 times with 3 c.c. of 93% alcohol (by vol.), the funnel being kept covered during filtration and washing. The paper, after all possible alcohol has been sucked out, is dropped into a wide-mouthed CO_2 flask, 10 times the Polenske value in c.c.'s of 93% alcohol[1] (by vol.) added, and the flask boiled under a reflux condenser till the barium salts are in solution. About 5 c.c. of the hot solution are then poured rapidly into a strong test-tube (6 in. $\times$ 12 in.), which is at once closed with a stopper carrying a small bulb thermometer and aluminium wire stirrer. The liquid is rapidly stirred, with the tube held in a good light and the turbidity point noticed. The liquid is then warmed till again clear and the turbidity point again noted. This second temperature is taken as the turbidity temperature. If desired, the tube can be fixed in a wider tube so as to obtain slower cooling.

Working in this manner, coconut oil gives a turbidity temperature of 52.5° and palm-kernel oil of 68.5° and mixtures of these fats give

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[1] The alcohol used in these experiments had a sp. gr. 0.8235 at $\frac{15.5°}{15.5°}$. Alcohol of the right strength may be obtained by placing 7 c.c. of water in a 100 c.c. flask and making up to the mark at 15°5° with absolute alcohol.

temperatures between these limits proportionate to the percentage composition. The turbidity point is very sharp, is independent of the outside temperature, and the barium salts, on which the test depends, are quite insoluble after cooling in the alcohol used for the Polenske determination. The turbidity points are also quite independent of the amounts of the 2 fats present in the original sample, but determine their relative percentages, and so supply the necessary information. The strength of alcohol (93% by volume) must be strictly adhered to if the values here given are to be employed. It is the most satisfactory concentration. Other oils and fats (such as are likely to be present) do not interfere. In certain cases small quantities of insoluble volatile acids distil in the Polenske method, which give barium salts insoluble in boiling 93% alcohol. In such cases a clear solution cannot be obtained. The turbid liquid is therefore poured into a long test-tube, which is corked and kept upright in a water-bath at 70° to 71° until the solid matter has settled. The clear supernatant liquid is then poured off into the turbidity tube and the temperature of turbidity determined. This process does not affect the results. This *permanent* turbidity, due to barium salts of acids other than those derived from coconut and palm-kernel oils, must be distinguished carefully from that due to palm-kernel "stearine." The barium salts of the insoluble volatile acids of this "stearine" do not dissolve in 10 times the Polenske value in c.c. of 93% alcohol, but the liquid becomes more turbid *immediately* after the flask is removed from the water-bath.

So long as mixtures of coconut oil and palm-kernel oil are dealt with, the above method gives good confirmatory evidence of the relative percentages. It has been found that coconut oils of different Polenske values give practically identical turbidity temperatures. It is to be noted that the filtration of the barium salts and their subsequent solution must be carried out *within a few hours of the Polenske titration*, as otherwise the salts become partially insoluble and the results are inaccurate.

Mixtures of the "oleines" and "stearines" are sometimes employed in place of the whole oils, but probably rarely. In these cases, although the turbidity temperatures do not give accurate information on account of the very variable composition of these products, at the same time they give most useful information as to their presence.

The following table gives the results obtained with some of these products.

Fat	Reichert-Meissl	Polenske	Turbidity temperature, °
Coconut oil..........................	7.5	16.5	52.5
Palm-kernel oil.......................	5.2	9.6	68.5
Palm-kernel "oleine".................	7.2	12.1	59.5
Palm-kernel "stearine"...............	....	8.2	72.5
Coconut "oleine".....................	....	....	53.0 (calc.)
Coconut "stearine"...................	....	....	63.0 (calc.)
Coconut "oleine," 80%.............. } Palm-kernel "oleine," 20%.......... }	8.24	17.05	54.5
Coconut "stearine," 60%............ } Palm-kernel "stearine," 40%........ }	4.43	9.93	67.0

It is interesting to note that cohune oil, which is analytically identical with coconut oil, gives exactly the same turbidity figures.

Stokoe (*J. Soc. Chem. Ind.*, 1921, 40, 57T) proposes a method for estimating the proportions of palm-kernel and coconut oils where both may be present in a mixture, depending on the same principles as the above, but obviating the expense of using a large quantity of strong alcohol, and also free from the drawback that the solution of the barium salts in alcohol is seldom perfectly clear. His method has the advantage of being readily carried out as an extension of the standard Reichert-Meissl-Polenske-Kirschner process without in any way affecting the original process. He takes the "seeding point" of the insoluble fatty acids, in capillary tubes which he afterwards returns to the Polenske titration flask.

He gives the following tables of figures:

(1) *Mixtures containing only coconut and palm-kernel oils.*

Coconut, %	Palm-kernel, %	Temperature of turbidity. Average
85	15	11.8
75	25	13.4
60	40	15.5
50	50	16.9
40	60	17.9
25	75	19.5
10	90	21.8

(2) *Mixed fats containing* 30% *oleo,* 10% *cottonseed oil,* 60% *coconut or palm-kernel oil or mixtures of them.*

Relative proportions of coconut and palm-kernel oils	Mean, °
Coconut 100%...	11.4
Palm-kernel 100%......................................	23.6
Coconut 75%, palm-kernel 25%..........................	14.3
Coconut 50%, palm-kernel 50%..........................	17.55
Coconut 25%, palm-kernel 75%..........................	20.6

(3) *Mixed fats containing* 50% *oleo,* 20% *cottonseed oil,* 30% *coconut or palm-kernel oil or mixtures of them.*

Relative proportions of coconut and palm-kernel oils	Mean, °
Coconut 100%...	12.0
Palm-kernel 100%......................................	24.0
Coconut 33⅓%, palm-kernel 66⅔%.......................	19.8
Coconut 50%, palm-kernel 50%..........................	17.7
Coconut 66⅔%, palm-kernel 33⅓%.......................	16.3

It may be noted that in mixtures of oils of the coconut group and fats not containing volatile fatty acids, the Reichert-Meissl-Polenske values do not increase at quite the same rate as the proportion of coconut oil, perhaps because where more than 40% of coconut oil is present the distillate would become saturated with the only partly soluble caprylic acid, and any additional quantity distilling would cause an increase in the Polenske and not the Reichert-Meissl value. When butter fat requires to be determined in such a mixture F. H. Van der Laan (*Rec. Trav. Chim.*, 1922, 41, 724–739) proposes to determine what he calls the "new Kirschner" value. For this purpose the mixed neutralised liquids obtained from the Reichert-Meissl-Polenske determinations are mixed, and made up to 200 c.c. with distilled water; 100 c.c. are used for determining the mean molecular weight by evaporating the sodium salts to dryness, sub-tracting the weight of phenolphthalein present, and multiplying the weight of residue by 10, and dividing by the number of c.c. of N/10 sodium hydroxide used. The quotient, less 22, gives the mean molecular weight. To the other 100 c.c. N/10 silver nitrate

is added to 1.1 times half the sum of the volumes employed in the Reichert-Meissl-Polenske titrations. The solution is filtered and the silver in 50 c.c. determined by Mohr's method. From this the "titer" of the volatile fatty acids forming the soluble silver salt can be calculated and is called the "new Kirschner" value.

Hardened Fats

The resolution of margarine mixtures has, however, been still further complicated by the introduction up to some 30% of "hardened" or "semi-hardened" fats (compare page 49). The process of hydrogenation completely destroys the identity of the original fat or oil, except in the case of the saponification value, and if the process is carried to any great extent the liquid vegetable oils begin to assume the properties of the solid fats.

The detection of hardened fats thus has become practically dependent on the detection of traces of the catalyst, which is commonly nickel. The most delicate test for nickel is the following due to Atack (*Analyst*, 1913, **36**, 316) who uses α-benzildioxime as the reagent, which has been found to be much more delicate than diacetyldioxime which had been previously employed. Further, the activity of the former reagent is more circumscribed than of the latter (compare page 51).

50–100 grm. of the carefully filtered fat are ignited in a platinum or silica basin, or else shaken out with a 5% solution of hydrochloric acid (sp. gr. 1.14 to 1.16) and the acid aqueous extract concentrated on a water-bath and gently ignited. The residue in either case is taken up with very dilute hydrochloric acid (and if a platinum basin has been used transferred to porcelain), a drop of nitric acid added and the solution evaporated till *almost* dry; a large excess of ammonia (sp. gr. 0.925) is added and then a 0.2% solution of the reagent in ammoniacal solution. A rose-red colour or precipitate indicates nickel.

The relative proportion of ammonia in the reagent used in the above test has been found by the writers to be of importance, but as the personal equation is a factor, it is best for the investigator to make a few tests with known amounts of nickel, in order to determine the most delicate combination.

It may be pointed out that a large number of carefully prepared hardened fats have been washed free of nickel by means of hydro-

chloric acid or other means; these are therefore not detectable by the above process.

It may also be remembered that the process of hardening, if carried to a certain point, results theoretically in the production of a large proportion of triglycerides containing at least 1 molecule of stearic acid. From the observation of hardened fats there is a likelihood that molecules of considerable complexity are actually formed, but, as this point has not yet been sufficiently investigated, it will be accepted for the moment that stearic acid is the final product.

The presence of this acid in the triglycerides leads to the result that the usual microscopical test for stearin, after crystallisation of the fat from ether, may give misleading indications. For instance, the same fat hardened in the same manner may give crystals of different appearance, when crystallised in an identical manner on two different occasions. The crystals as a rule approximate to those of beef fat, but, in general, the crystalline conglomerates tend to radiate in all directions from a common centre, whilst the true beef fat conglomerate has usually the well-known fan-like appearance, though in some instances the crystals of hardened fats are practically identical with those of true beef fat.

The estimation of "iso-oleic" acid can be used as a guide not only to the presence of partially hydrogenated fats, but also as an indication of the amount present. Iso-oleic acid, a solid isomer or mixture of isomers of ordinary liquid oleic acid, is formed during the course of hydrogenation. It occurs in marked quantities in hydrogenated fats, and may be estimated with comparative ease by the ordinary lead salt and ether separation of the fatty acids. The lead salt of iso-oleic acid is nearly insoluble in methylated ether and almost completely insoluble in petroleum spirit, so that the separation is preferably made with petroleum spirit b. p. 40°–60° in place of the more usual methylated ether, and at as low a temperature as possible, say 5°. In carrying out this test it should be borne in mind that oxidised acids are insoluble in petroleum spirit and, if present in the sample under examination, their presence should be taken into account (Lewkowitsch, 6th Ed., Vol. I, 593). Practically the whole of the iso-oleic acid will then be found in the solid acids obtained by the separation, and an idea of the proportion may be obtained by calculation from the iodine value.

It has been shown (C. T. Moore, *J. Soc. Chem. Ind.*, 1919, 38, 320T) that the proportion of iso-oleic acid to oleic acid rapidly tends to approach a fixed ratio of 10 : 15 during hydrogenation, and it will have reached this ratio in most commercial hydrogenated oils used for margarine.   Such oils, which usually have iodine values lying between 50 and 60, contain approximately 30% of iso-oleic acid.   However, the presence of iso-oleic acid, and even more its amount, is likely to be a less reliable guide in the future, since it has recently been found (E. J. Lush, *J. Soc. Chem. Ind.*, 1923, 42, 219T) that there are processes of hydrogenation giving very much less iso-oleic acid than normal.

For these reasons no infallible rules for guidance can be laid down, and it is absolutely necessary for the investigator to familiarise himself with the various appearances by the actual examination of many hardened fats, which will enable him to recognise these fats in many circumstances in a way which no verbal description can impart.

Considerations of Analytical Data

The writers very tentatively venture to suggest the following considerations as a guide to those who have to analyse margarine mixtures.

The disappearance of coconut and palm-kernel oils from the margarine industry is, in view of their extreme utility, very doubtful, and it is to be assumed that they will constitute the major part of the fatty mixture.   Nothing as yet has arisen to invalidate the Reichert-Meissl-Polenske-Kirschner process, and its findings may be taken as reliable, the further extension of Burnett and Revis being employed in doubtful cases.

The percentage of coconut and palm-kernel products being obtained, it is easy, after determinating the ordinary analytical constants of the fat, to arrive by calculation at the saponification value, iodine value, etc., of the remaining base.

This remainder may be a hardened or a partially hardened fat, or a mixture of hardened fat and some liquid vegetable oil or liquid vegetable oil only.

If the various tests of Baudouin, Halphen, etc., give negative results, there is at least a probabilty that the base is all of a hardened variety.   The nickel test is then applied, but the absence of nickel will not disprove the presence of hardened fat, though a positive result is of indicative value.

The microscopical appearance of the crystals (if any) obtained from a 25% solution of the fat in methylated ether (more or less according to the rapidity with which the crystals separate) will also point to the presence or absence of hardened fat.

Beyond the above indications analytical methods at the present moment avail but little, and, in any case, the nature of the hardened fat if diagnosed is distinctly problematical.

It has been assumed in the above outline that animal fats are absent.

Most countries have regulations governing the manufacture and sale of margarine, and amongst them the following may be noted:

The amount of water must not exceed 16% in Australia or 14% in New Zealand. Preservatives (excepting salt) are not allowed in France, Denmark or Canada. In France and New Zealand no additional colouring matter may be added, and the colour is regulated in Denmark.

Where the presence of boric acid is permitted the amount is usually limited, in Australia and New Zealand to not exceeding 0.3%. 10% of Sesame oil is compulsorily present in many continental countries including Denmark, whilst Australia enforces the addition of 1 part per thousand of potato starch. As a rule not more than 10% of butter fat may be present.

VITAMINS

Of late years a very voluminous literature has grown up round these accessory food factors, of which three distinct types are at present known:

1. Fat-soluble A.
2. Water-soluble B.
3. Antiscorbutic C.

Recent work appears to indicate the existence of a fourth and possibly a fifth.

We are here only really concerned with vitamins as they affect butter and margarine, that is to say, the so-called fat-soluble vitamin A.

It is now well known that all three vitamins, and possibly the fourth and fifth suggested above, are essential to normal growth and development. They are, however, present in the various food stuffs in such minute quantities that their isolation provides almost unsurmountable difficulties, and although their chemical compo-

sition is gradually being elucidated, our knowledge is still very far from complete.

Fat-soluble A is found to a marked extent in butter, to a lesser extent in practically all animal fats, except lard, in which it is entirely absent, while vegetable fats contain as a rule small quantities. In fact, in many cases it appears to be practically absent from vegetable fats. It may also be noted that the fish liver oils are valuable sources of this vitamin.

This introduces an important consideration when comparing the nutritive values of butter and margarines. Oleo-margarines, from the vitamin point of view, are distinctly more valuable substitutes for butter than purely vegetable margarines since oleo oil contains more vitamin than vegetable fat. It must be remembered, however, that vitamins have been shown to be very unstable substances in the presence of air at high temperatures, so that generally speaking the process of refining and deodorising fats has the effect of destroying any vitamins present. If the processes are carried out with the absolute exclusion of oxygen this does not, however, appear to be the case. (See F. G. Hopkins *Biochem. J.*, 1920, 14, 725–33.) Butter fat itself, which is probably the richest source of vitamin A, excluding the fish liver oils, has been shown to undergo a gradual loss of nutritive value on oxidation (Drummond and Coward, *Biochem. J.* 1920, 14, 73 4–8).

A considerable amount of work has been and is being carried out with a view to isolating the fat-soluble A vitamin, so that in time it may be possible to add it to the refined oils. If this becomes practicable there is no reason why vegetable margarine should not equal butter in nutritive value.

Drummond and Zilva have been able to show (*J. Soc. Chem. Ind.*, 1922, 41, 125–127T) that processes of extraction of vegetable oils with exclusion of oxygen caused most of the seed vitamin to be extracted with the oil. They found that linseed oil and crude palm oil contained by far the greatest proportion of vitamin, but did not have much success in preparing a fraction containing the unsaponifiable constituents (in which it has been shown that the vitamin is mainly contained) in such a way that its addition to margarine caused a raising of the vitamin content.

The Detection and Estimation Fat-soluble of Vitamin A.—This is not an easy problem. No chemical tests have as yet been perfected,

and the only satisfactory method that can be employed is the physiological feeding test method. Extreme care is here necessary in the preparation of a basal diet free from the vitamin under investigation, and in experiments on fat-soluble vitamin A the rat is probably the most satisfactory animal to use. These points are fully dealt with in a paper by J. C. Drummond and A. F. Watson (*Analyst*, 1923, 47, 235). Zilva and Miura (*Biochem. J.*, 1921, 15, 654) by measuring and administering the supplements to be tested were able to obtain definite qualitative results.

Some very interesting work has recently been carried out on chemical tests for detecting and estimating vitamin A in the fish liver oils. Such work is at present in its infancy, and fresh advances are continually being made. It seems highly probable that the substance present in liver oils responsible for the purple coloration obtained with sulphuric acid bears a close relationship to vitamin A and may even be identical to it (Drummond, *Analyst*, 1922, 47, 341–348), and if this is so we may shortly look to see the development of colourimetric methods for the estimation of these substances. Chemical methods for these investigations are greatly to be desired, as physiological methods, although reliable, are costly and lengthy (see also Vol. VIII.)

Ghee

Ghee, in the strict sense of the word, is the pure clarified milk-fat of the buffalo, sheep, cow or the goat, but as has been shown by the writers (*Analyst*, 1910, 35, 343; 1911, 36, 392) it is nearly always adulterated.

In the table below their figures are given for some 16 samples of ghee obtained from different parts of India.

The preparation of ghee is carried out in the following manner: the milk is boiled, immediately after milking, for 1 to 3 hours in earthen pots and when cold is inoculated with some sour milk. When curdled the whole of the milk is churned with a split bamboo for about half an hour, hot water added and the churning continued until the butter "comes." The butter is then skimmed off and kept for a short time when it becomes somewhat rancid.

The butter so produced is heated in an earthen pot until practically all the water present has been boiled away. It is then allowed to clarify and the clear fat, which constitutes ghee, is run into jars while warm.

ANALYSES OF GHEE

Source	Rangoon 75s.	Rangoon 71s.	Rangoon 57s.	Rangoon 53s.	Rangoon[1] 40s.	?	Ambala	Ambala	Ceylon
Price per cwt.									
Reichert-Meissl value	30.58	30.42	18.04	11.88	0.44	23.34	29.3	31.5	21.9
Polenske value	1.62	2.42	1.33	0.60	0.47	1.45	2.6	1.66	1 32
Saponification value	228.8	228.7	213.9	206.7	193.4	219.1	223.8	229.1	215.9
Iodine value (Wijs)	30.63	30.75	40.85	45 65	55.73	36.25	30.92	29.60	47.00
Refractometer index at 40° C. (Zeiss scale)	41 4	41.4	44.6	46.3	49.3	42.9	42.3	41.5	45.4
Valenta No. (° C.)	24 0	24.5	47.5	63.0	95.0	....	33.25	23.5	38.25
Sp. gr., 99°/15° C.	0.8632	0.8637	0.8612	0.8603	0.8577	0.8609	0.8624	0.8631	0.8625
Baryta value:									
(a) Total	312.8	312.6	292.4	282.5	264.4	299.5	305.8	313.5	294.0
(b) Insoluble	251.7	253.3	255.7	257.4	263.3	282.5	254.9	248.7	255.0
(c) Soluble	61 1	59.3	36.7	25.1	1.1	17.0	50.9	64.8	39.0
$b - (200 + c)$ value	−9 4	−6.0	+19.0	+32.3	+62.2	+65.5	+4.0	−16.1	+16.0
Free fatty acids (as oleic), %	3.68	2.60	1.80	1.44	0.59	....	1.52	2.59	2.56
Solidifying-point, ° C	....	24.5	28.0	....	4 0	31.0	....	....	....
Unsaponifiable matter, %	....	....	....	....	30 43	....	....	....	....
Inferences	Pure	Pure	Adulterated	Adulterated	Milk fat entirely absent	Adulterated	Slightly adulterated	Pure	Adulterated

[1] Marked "Mixed with grease."

ANALYSES OF GHEE

Source	Malabar coast	Bombay City					
		A	B	C	D	E	F
Reichert-Meissl value	24 4	19.00	25.70	26.20	28.40	29.80	25.60
Polenske value	1 8	0.90	0.90	1.50	1.60	1.40	1.20
Saponification value	228.2	219.90	213.80	223.60	224.90	225.40	221.40
Iodine value (Wijs)	....	32.37	37.28	29.24	28.11	29.55	31.83
Refractometer index at 40° C. (Zeiss scale)	42.7	43.10	44.30	44.80	42.00	42.00	42.60
Valenta number (° C.)		48.50	43.50	42.50	36.00	33.50	50.00
Sp. gr., 99°/15° C.	....	0.8635	0.8627	0.8619	0.8656	0.8656	0.8618
Baryta values (Avé Lallemant):							
(a) Total	312.0	300.50	292.30	305.60	307.50	308.10	302.70
(b) Insoluble	256.7	252.20	256.80	256.20	252.40	251.50	256 40
(c) Soluble	55.3	48.30	35.50	49.40	55.10	56.60	46.30
b − (200 + c)	+1.4	+3.90	+21.30	+6.80	−2.70	−5.10	+10.10
Free fatty acids (as oleic)	....	0.37 %	2.23 %	2.39 %	1.83 %	1.84 %	0.92 %
M. p. (° C.)	....	42 50	45.00	43.00	43.00	41.00	43.70
Inferences	Doubtful purity	Adulterated	Highly adulterated	Adulterated	Pure	Pure	Adulterated

The fats and oils used as adulterants are very numerous and comprise the carcass fat of various animals together with coconut, ground-nut, cottonseed, poppy-seed, sesame, safflower and niger-seed oils. Of the vegetable fats the most popular adulterant is obtained from the seeds of *Bassia butyraceæ*, a fat which is very like shea-nut oil in appearance and consistency but fortunately yields very different analytical figures (*vide* page 259). On account of this frequent substitution the fat of *B. butyraceæ* has come in some text-books to be referred to as "ghee." According to Barnes and Singh (*Analyst*, 1916, 41, 72) Poli oil, *obtained from the seeds of a species of Carthamus, one of the safflowers, is now becoming some-what extensively used as an adulterant of ghee.* These authors give a table showing the analytical and physical constants of the oil.

Kesava-Menon (*J. Soc. Chem. Ind.*, 1910, 29, 1428) publishes a Reichert-Meissl value of 18.24 for 1 sample of ghee made from buffalo milk. This figure must be regarded as most abnormal and differs entirely from figures of pure ghee published by various observers.

The Calcutta chemists have lately decided to fix standards for Ghee, and T. K. Ghose (*Analyst*, 1920, 45, 444) states that it was decided that the sample should be regarded as pure when the Reichert-Wollny value was 30 and over. This, however, was reduced to 28 in consideration of accidental admixture with cow's ghee. The following table gives a few of the actual results of analysis from which the standard was derived.

TABLE I. RESULTS OF ANALYSIS OF SAMPLES OF BUFFALO GHEE MADE IN THE LABORATORY FROM MILK OF SINGLE BUFFALOES

M. p.	Reichert-Wollny value	Saponification value
35·5	38.6	237
35·3	34·5	234
36	42	239
35	30	229
35	42	240
36	35·7	235
38	33·4	232
35	32	233
37	33	235
37	37	236
36	35·9	236
37	34·6	233

TABLE II. RESULTS OF ANALYSIS OF SAMPLES OF BUFFALO GHEE
MADE FROM BUTTER PRODUCED FROM MIXED MILK OF
SEVERAL BUFFALOES. THE SAMPLES WERE COLLECTED
FROM DAIRIES IN DIFFERENT PARTS OF INDIA

Butyro-refractometer reading at 40°	Reichert-Wollny value	Saponification value
42	30.1	228
42	36.1	236
42	36.3	235
41.5	35	233
42	33.7	230
41	35.3	235
42	35	234
42	30.1	229
40	31.3	229
41	29.2	230
42	29	227
42	32.6	231
41	32.1	230
42	29	227
40	31	229
41	32.3	230
42	32.8	230
41.5	31.8	228
42	30.7	226
41	37.6	236

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LARD

By GEORGE A. REITZ, B.Sc., Ph.C.

Lard is the fat from any and every part of the hog. This is the present definition. The original conception covered the fat rendered from the leaf of the pig, *i. e.*, the fat from the kidneys and bowels. This, however, has changed owing to the market conditions. What was originally termed lard is still being sold on a small scale as *"butcher's lard"* and "home rendered lard." Compared with the enormous quantities which are being produced in the slaughter houses of America, especially in those of the U. S., the amount of lard which is produced locally on a small scale has become an insignificant quantity. *"Bladder lard"*—so named from the package—used to be the leaf lard rendered in small establishments. The term is still used to denote the best quality of home rendered lard. *"Keg lard"* is another quality of lard sold in the retail trade. It always contains, besides leaf lard, the fat taken from other parts of the animal.

I. **Neutrals.**—The following grades of lard are recognized in the U. S.: *Neutral lard* No. 1 from the leaf of the pig, rendered between 40–50°, contains up to 0.25% free fatty acids. Sometimes divided into grade "1" and "2." Neutral lard No. 1 is prepared from the leaf. *Neutral lard* No. 2 is prepared from the back fat.

II. **Leaf lard** is rendered from the residue left from the neutral lard by steam heat and pressure.

III. **Choice kettle rendered lard,** rendered in steam jacketed open kettles from portions of leaf and back, is not used for neutral lard.

IV. **Prime steam lard** is rendered by steam from the head, heart and small intestines. It may also contain fat from other parts.

Neutral lard No. 1 and neutral lard No. 2 do not keep well owing to the fact they are not cooked, therefore cannot be used like leaf lard and steam lard for domestic purposes.

The U. S. Department of Agriculture defines lard as follows:

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(1) Lard is the rendered fresh fat from hogs in good health at the time of slaughter.   It must be clear, free from rancidity and contains, incorporated in the process of rendering, not more than 1% of substances other than fatty acids and fat.

(2) Leaf lard is lard rendered at moderately high temperature, from the internal fat of the abdomen of the hog, excluding that adherent to the intestines, and has an iodine number not greater than 60.

(3) Neutral lard is lard rendered at low temperatures.

The New York Produce Exchange defines Standard Prime Steam Lard as follows:

Rule 2, Sect. A.—Standard Prime Steam Lard shall be solely the product of the trimmings and the fat part of the hog, rendered in tanks by the direct application of steam and without subsequent change in the grain or character by the use of agitators or other machinery, except as such change may unavoidably come from the transportation.   It must have proper colour, flavour, dryness, and soundness for keeping, and no material which has been salted must be included.   All lard must be rendered in conformity with the rules and regulations of the U. S. Dept. of Agriculture.   The name and location of the renderer, the date of packing, and the grade of lard shall be plainly branded on each package at time of packing.

Sect. B.—Prime Steam Lard of superior quality as to colour, flavour and body may be inspected as "Prime Steam Lard Choice Quality" and shall be deliverable on contracts for "Prime Steam Lard."   Prime steam lard is the lowest grade of edible lard.

All those parts of the hog which have not been used for the production of edible lard—such as "guts," etc.—are worked up in autoclaves in order to obtain the last portions of the fat they contain. Such fat is known as "yellow grease."   With it is mixed all the refuse fat resulting in the course of rendering the edible qualities.   The "yellow grease" is usually worked up together with any hogs that have died in the stock yards.   This quality is of course only used for manufacturing purposes, such as production of soap, low quality lard oil, or grease stearine.   Hogs that have died in transit are rendered for fat in their entirety, after the intestines have been removed, as the fat from the latter would discolour the resulting grease. The grease so obtained is sold as white grease for manufacturing purposes.

The intestines are worked up separately and yield a grease known as "brown grease." This is used for the manufacturing of soap and lowest class of commercial lard oil.

"Pig's foot grease" is a by-product obtained in the glue department of the packing house. It is also used in the manufacturing of soap and low grade lard oil substitute.

Uses.—No. 1 grade lard is used in oleomargarine. The second quality is used by confectioners. Lard is also used in pharmacy and perfumes. The grease obtained after the edible lard is used in the manufacture of soap, lard oil, stearine, etc.

Composition of Lard.—Lard contains the glycerides of stearic, palmitic, myristic, lauric, oleic, and linolic acids, whilst Farnsteiner (*Zeit. Untersuch Nahr. Genussm.*, 1899, 2, 1) has also detected traces of linolenic acid.

Examination of Commercial Lard.—*The analytical values* ordinarily obtained in the examination of pure lard are shown in the table on page 112. There are, however, cases of frequent occurrence in which it is difficult to decide whether a sample is genuine though abnormal in its values, or whether is has been skilfully adulterated. Taking into consideration the natural variations in fat from different pigs and from different parts of the same pig, a sample giving abnormal values can only be regarded as suspicious, unless the presence of an adulterating substance be detected by special tests.

Specific Gravity.—Very little value can be obtained from this figure in determining the presence of an adulterant, as some of the other adulterants have about the same sp. gr. as lard oil. It has been noted, however, that cottonseed oil raises the sp. gr., as also does arachis oil.

Melting Point.—What has been said of the sp. gr. is also quite true of this figure, as many adulterated lards have the same m. p. as pure lard; however, this is considered a sufficiently important figure to be determined.

In case the fat is unadulterated the m. p. determination will help to show from what part of the body the fat has been rendered.

Iodine Value.—This value, as shown by various authors, has a rather wide range. In the present stage of manufacturing it is difficult to give with certainty a definite range within which the sample can be considered pure. Still a lard oil outside the range of

46–66 can be considered suspicious.   The feeding has quite an in-
fluence on this constant, as has been proved by C. L. Hare, Jr. (*Ind.
Eng. Chem.*, 1913, 5, 410).   A sample of lard oil can also be adulter-
ated with such oils as would show an iodine value well within the
limits stated; hence it is safe to conclude that the iodine value alone
is not sufficient proof of the purity of the product.   What is true
of the m. p. is also true of this value, *viz.*, provided adulteration with
foreign fats be excluded, the part of the body from which the fat is
rendered can be determined.   This figure should never be omitted
as it will assist the analyst greatly to determine if the sample should
be looked upon with suspicion or not.   Both the iodine value of
the fat and that of the liquid fatty acids have some value but should
never be considered final.   The range of iodine value for liquid
fatty acids is as follows: minimum, 90; maximum, 110.   A sample
either above or below this range may be looked upon with suspicion.

The Bromine Thermal Value.—This corresponds closely with the
iodine value in the case of lards, and the method described in page
28 affords a very rapid means of determining the halogen absorp-
tion of a sample.

Refractometer Reading.—The part of the body from which the fat
is obtained has an influence on this figure also.   The results obtained
with the butyro-refractometer or oleo-refractometer approximate
roughly to the iodine value.   The difference between the European
and American lards is not very distinct in this reading, as is usually
the case with the iodine value.

Solidification Point of Fatty Acids.—This differs with the origin of
the fat.   Thus fatty acids from the ham and head fat, solidified at
34.8° and 34.6° respectively, whilst those from the flare of the same
pig solidified at 40° (Hehner and Mitchell).   This value, however,
when used in conjunction with the others determined, will assist
greatly in deciding upon adulteration.

Acidity.—The free acid in lard calculated to oleic acid is usually
below 0.5%.   Freshly rendered lard is practically neutral.   Twelve
samples of American lard examined by Wiley gave the following
results: 0.35 to 1.00%.   24 samples examined by Spaeth gave
0.098–0.564%.   This figure is greatly increased on exposure to air.

Water.—The percentage of this adulterant is very low in American
lards; Wiley reports from a trace to 0.7%.   Samples examined by
Fischer and Schellens; none contained more than 0.3% moisture.

In case of lards adulterated with water, which in some countries is demanded by the buyer, the water may be estimated by heating 10 grm. of the sample at 110° until no more globules of water are seen, and determining the percentage loss in weight.

Detection of Vegetable Oils.—When a consideration of the analytical values (notably the iodine value) of a sample of lard indicates the probable presence of a vegetable oil, further evidence may be obtained from the iodine value of the liquid fatty acids, as mentioned above.

The *phytosteryl acetate test* (see page 386) may then be used for further proof, and special tests may be applied for the detection of the vegetable oils most likely to be present. These are *cottonseed oil* and *cottonseed "stearin," sesame oil, maize oil, arachis oil* and *coconut oil.*

Cottonseed oil and stearine may be detected by the silver nitrate test, Halphen's test and the nitric acid test (see *Cottonseed Oil,* page 177).

Sesame oil may be detected by the furfural test, Soltsien's test and Tocher's test (see *Sesame Oil,* page 186).

Maize Oil.—No distinctive colour test for this oil has been discovered. Its presence in lard will be indicated by the phytosteryl acetate test, the high iodine value of the liquid fatty acids, a high yield of linolic tetrabromide on brominating the liquid fatty acids, and the negative results of characteristic tests for the other oils. The Reichert-Meissl value may also afford confirmatory evidence (see *Maize Oil,* page 185).

Arachis oil is best detected by a determination of the arachidic acid by Renard's method (see *Arachis Oil,* page 118).

Coconut oil will be indicated by the increased saponification value and the Reichert-Meissl value (see also *Coconut Oil,* page 261, and *Butter,* page 389).

In drawing conclusions as to the adulteration of a lard with cottonseed or sesame oil, it should be remembered that indications given by the special colour tests may possibly be due to the pigs having been fed upon cottonseed or sesame oil-cake. Thus, Soltsien (*Chem. Zentralbl.,* 1901, 1, 539) found that many American lards gave a faint coloration in Halphen's test for cottonseed oil similar to that which would have been produced by an addition of about 1% of that oil; whilst Dunlop (*J. Soc. Chem. Ind.,* 1906, 25, 459) found

that fat from the back and shoulder of a pig fed upon cottonseed cake gave indications in the test corresponding to no less than 10%. The iodine value of the fat, however, was quite normal. (See p. 177.)

Beef Fat and Other Animal Fats.—Some indications of the presence of beef or mutton stearin in lard may be afforded by the determination of the m. p. of the fatty acids and of the proportion of stearic acid which they contain. These tests, however, must be considered in conjunction with the iodine value and the results of special tests for *vegetable oils*. The detection of tallow or beef stearin in lard is a very difficult problem and should in all cases be compared to results on samples of pure lard, as well as this lard mixed with known amounts of the suspected adulterant.

Crystallisation of the Fat.—Belfield directed the dissolving of the fat in ether, allowing the solution to evaporate spontaneously in a test-tube, closed with a little cotton-wool. Crystals are obtained which, when examined under the microscope, appear broad with chisel-shaped ends in case of lard, but needle-shaped and grouped in fan-like bunches when derived from beef or mutton fat. When a mixture of lard and beef fat is crystallised in this way, the form of crystals is intermediate between those from the respective ingredients, though approximating more toward the form of the lard crystals.

Dunlop (*ibid.*, 1906, 458) carried out experiments with beef and mutton fat, showing that on recrystallisation they very often show flat, chisel-ended crystals closely resembling those obtained in the first crystallisation from lard.

Stock (*Analyst*, 1894, **19**, 2) combined the method of Belfield and Delafontaine and worked out a quantitative determination of the stearin. He takes the deposits obtained under definite conditions (*viz.*, washing with a definite quantity of ether at a definite temperature) and weighs same. This is compared with results obtained under the same conditions from standard mixtures of lards of different m. p. with different proportions of beef stearin.

In the light of the experiments of Hehner and Mitchell (*Analyst*, 1896, **21**, 328) and of Dunlop (*loc. cit.*), further investigation of the nature and behaviour of the deposits from mixed fat appears necessary before trust can be placed in the results of this test.

With regard to the original qualitative test, Dunlop has shown that it is necessary to examine the crystals under a magnification of 300 or 400 diameters to see the form of individual crystals, and not to

rely solely on the fan-like grouping of the bunches of crystals, as seen under a magnification of 100 diameters, as a proof of the presence of beef stearin.

At its best, the test can, as yet, only be regarded as affording confirmatory evidence of adulteration; and, as was pointed out by Hehner (*Analyst*, 1902, 27, 24), the occurrence of the "beef-form" of crystals should only be regarded as a proof of the presence of beef or mutton fat when the presence of a vegetable oil has been detected and the lard has a high iodine value.

For the detection of beef fat in lard Vitoux and C. F. Muttelet (*Ann. Falsif.*, 1920, 13, 593–601) propose the following method which was proposed originally by Bömer, and depends on the presence of α-palmitodistearin, m. p. 68.5°, in lard and of β-palmitodistearin, m. p. 63.3°, in beef fat. The fatty acids separated from these two glycerides melt at 63.2°. 50 grm. of the fat are dissolved in 50 c.c. of pure acetone, the solution is cooled to 15°, and after 1 hour the separated crystals are collected on a filter, dried over concentrated sulphuric acid, then dissolved in 50 c.c. of ether and again allowed to crystallise. These crystals are collected, the m. p. determined, a portion is then saponified, the fatty acids separated, and their m. p. determined.

The crystals of glycerides obtained from pure lard melt above 62°, those from beef fat at about 58.5°. In the case of pure lard the value $(2G - A)$ is never less than 68°; $G =$ the m. p. of the crystals, and $A =$ that of the fatty acids.

Investigations of the Bömer Method for Detecting Tallow in Lard (J. Prescher Z. *Nahr.Genussm.*, 1915 29, 433–7).—58 fats of known character were examined, by both the Bömer (*C. A.* 8, 1174) and the Polenske (*C. A.* 2, 716) methods in order to ascertain their relative efficiency in detecting foreign fats in lard. In the case of 25 samples of adulterated lard, only three, containing respectively 10, 20 and 30% of beef tallow, could be detected by the Polenske method, the others, some containing as much as 15% of beef tallow, giving negative results. The Bömer method failed in only two cases, in which 5 and 10% of beef tallow were present. Eighteen samples of pure lard gave negative tests by the Bömer method, the Polenske procedure giving false indications of adulteration in two cases. Hydrogenated vegetable oils give a positive Bömer test and can be distinguished from beef tallow by the

phytosteryl acetate test. The Bömer method is to be preferred for simplicity and accuracy.

Lewkowitsch was of the opinion that further research is required to solve the problem of detecting with certainty in every case 5% or 10% of beef stearin in lard. If by the examination of the mixed fatty acids the statement should be confirmed that lard differs essentially from tallow, in that it contains notable amounts of myristic acid (which is practically absent from tallow), the fractional distillation of the methyl esters might lead to a decision. He did not however, test the value of this suggestion by experiments. In the case of lard that has been adulterated with both beef stearin and a vegetable oil, the phytosteryl acetate test alone furnishes the best information. If it then should be desired to estimate the amount of tallow or beef stearin resort should be had to the Wessons's cooling test (*J. Soc. Chem. Ind.*, 1905, 714).

Detection of Fats Containing Tristearin.—R. H. Kerr (*J. Assoc. Off. Agric. Chem.*, 1920, 4, 195–201) proposes the following method: 5 grm. of the lard are diluted to 25 c.c. with warm acetone in a stoppered cylinder, and the mixture is kept at 30° for 18 hours, the liquid is then decanted and the mass of crystals at the bottom of the cylinder is washed twice with warm acetone, using 5 c.c. each time, and taking care not to break up the deposit. The latter is shaken with a further 5 c.c. of warm acetone, transferred rapidly to a small filter, again washed with acetone, and the excess of the latter removed, as far as possible, by suction. The crystalline deposit is spread on paper, dried, and the m. p. determined. A m. p. below 63° indicates adulteration. The fatty acids are then obtained from the crystals in the usual way and their m. p. determined. If the m. p. of the glycerides (crystalline deposit) plus twice the difference between the m. p. of the glycerides and the m. p. of the fatty acids is less than 73° the lard is considered adulterated.

Hydrogenated arachis and sesame oils gave glycerides of high melting point (70.6° to 71.5°), whilst the corresponding fatty acids melted at 68.6 and 68.5° respectively hence these glycerides apparently consisted of tristearin.

Hydrogenated cottonseed oil, however, gave a mixture of glycerides melting at 61.3° and containing fatty acids melting at 38°.

The melting point differences ranged from 0° to 0.8° for hardened arachis and sesame oils and reached 2.8° in the case of the cottonseed oil.

These hardened fats lowered the difference in the melting point of lard to a greater extent than beef fat, from which, however, they could be distinguished by the phytosteryl acetate test.

The least soluble glycerides of the fat of sucking pigs and of pigs fed abnormally upon coconut, maize, sesame and cottonseed-oil cakes differed from those of normal lard in containing a smaller proportion of α-palmitodistearin and more stearo-dipalmitin; but such abnormal feeding did not interfere with the detection of beef fat by this method.

A modification of Bömer's method will detect the presence of a small proportion of lard in coconut oil.

Sprinkmeyer and Diedrichs (*Zeit. Untersuch. Nahr. Genussm.*, 1914, **27,** 571) find that the method will usually detect 5% of beef or mutton fat in lard.   In the case of lards rendered in the laboratory the difference between the melting point of the least soluble glycerides and their fatty acids ranged from 4.4° to 7.4°, whilst Bömer's value (melting point of glycerides plus twice the difference between the melting point) varied from 73.1 to 76.5.

With beef and mutton fats the difference was 0.8° to 1.2° and the Bömer figure 65.2 to 67.3.   Lard containing 5 to 10% of either foreign fat always gave a value below 72 and frequently below 70.

Hydrogenated oils depressed the Bömer value of the lard to the same extent as beef or mutton fat.

LINSEED OIL

BY GLENN H. PICKARD[1]

Linseed oil is obtained from the flax plant (*Linum usitatissimum L.*). The plant is widely distributed. Temperature, associated with rainfall, humidity and soil type, govern its distribution. Generally speaking, the plant may be said to grow best on the cold side of the temperate zones.

Cultivation.—The flax plant forms the basis of two industries, for from the stalk linen is made, whilst the seed yields linseed oil and linseed meal—a valuable feeding stuff. The cultivation of flax for fibre and the cultivation of flax for seed or oil are, with one exception, two distinct industries. Fibre flax is a variety distinct from seed flax. The yield of seed from fibre flax usually is considerably lower than that from flax grown primarily for seed, yet the quantity of seed produced is sufficient to constitute a by-product, valuable to producers of fibre. Fibre flax can best be grown in regions where moderately cold, damp weather prevails during the summer. The countries which, previous to 1914, provided the world with flax fibre were: Russia, Austria-Hungary, France, Italy, Ireland, Belgium, some of the Balkan States, the Netherlands, Sweden and Japan. With the exception of Russia and Austria, these countries produced insignificant amounts of flaxseed for oil manufacture. In Russia, the country which produced fibre in the largest amount, there were two vast areas over which flax was grown, and in these two areas the culture was widely different and pursued for different purposes. In certain provinces it was grown for seed only, whilst in the others the cultivation was for fibre, but a large part of the seed from these districts was sold to manufacturers of linseed oil. Russia today is exporting very little flaxseed or fibre.

[1] In the following material the writer has extracted freely from a series of articles written by him and published in the *American Paint Journal*, St. Louis, Vols. 5-6, 1921.

It has been observed that, other conditions being equal, the flaxseed which matures where the lowest average temperature obtains during the life of the plant will yield an oil of the best quality, that is, capable of absorbing the maximum of oxygen during the drying process.

Previous to 1914, the cultivation of flax for seed was carried on in four great areas. They are the "black soil" districts of Russia, in North America, the northwestern portion of the United States, and the districts just north of it in Canada, in South America, the Argentine Republic and in certain portions of British India. With the exception of Russia, these countries are now producing flaxseed in normal quantities. Manchuria produces small amounts . of flaxseed annually. Siberia is producing a little. These areas, together with those various localities which produce a little excess seed from flax grown for fibre, comprise the world's source of flax-seed for the manufacture of linseed oil.

It has been supposed that flax culture impoverishes the soil, but Bolley (*Farmers' Bulletin, Dept.* of *Agri., U. S. A.,* 274) has proved, by experiments carried out at the North Dakota Agricultural College and elsewhere, that the cause of poor yields from flaxseed is an infection of soil, or seed or both simultaneously by a fungus, "fusarium lini." His first work resulted in overcoming the trouble by disinfecting both soil and seed at time of sowing with form-aldehyde. Later, Bolley developed, through plant breeding, several strains of wilt-resisting flaxseed.

In conjunction with Bolley, the author has shown that this breeding for wilt resistance has affected neither yield of seed, yield of oil from the seed, nor oil quality.

In this connection, Bolley said: "There never was any truth in the thought that flax is hard on land or soil exhausting. This statement has many times been disproved by carefully conducted investigations by chemical and physical experiments. It has been found that flax removes less water and less plant foods than wheat, oats, barley, corn or potatoes. Crop rotation experiments here and elsewhere and the work of numerous farmers prove that flax does not in any way reduce the yields of other crops which immedi-ately follow it. The reverse is the fact. When properly handled, such flax-cropped lands yield better crops of cereals than lands previously cropped to cereals."

Oil Content.—The oil content of flaxseed grown for seed purposes is a decided variable. It varies from country to country, it varies from season to season in the same country, and it varies from point to point in a given locality during any one season.

The most important factor in determining, during the growth of the flax plant, how much oil it will contain seems to be the weather, for from season to season, on the same general type of soil, the percentage of oil will vary. Generally, also, the whole crop will be high or low, as the case may be, thus eliminating the soil as a predominant factor, although undoubtedly a better seed—that is, one with higher oil content—will be obtained from good ground than when sown on poor soil, other conditions being equal. Again, when seed high in oil from a certain locality is sown in a different district where the oil content is generally low, the formerly high oil seed will produce one low in oil. It seems, therefore, as though the atmospheric condition controlled this property of flaxseed to a greater extent than any other influencing force. The general observation is that an excessively dry season will yield flaxseed low in oil.

Eyre and Fisher (*J. Agric. Sci.*, 7, 120–34) confirmed the work of Ivanov (*Belhefte Botan. Centr.*, 28, 159–91), who proved that there is little difference in oil content of seed from fibre crop and that from linseed crop grown in the same locality. The oil content of seeds reaches nearly the maximum value several weeks before the seed ripens. A comparison of the oil content of several varieties of imported seed with that of seed produced from them in different parts of England showed close agreement. The larger seeds contained a higher percentage of oil than the smaller ones. Repeated growth from the same stock of seed showed no diminution in the oil content whilst artificial fertilizers had no effect on it.

The determination of the amount of oil in flaxseed must be carefully done if accurate results are to be obtained. The solvent, as well as the procedure, influences the result. Extraction with spirit ether yields larger quantities of crude oil than is obtained by using petroleum ether.

Leather (*J. Soc. Chem. Ind. (Abstract)*, 26, 622) used a double extraction, consisting in first extracting the bulk of the oil, then drying and crushing the residue before a second extraction. This method gave values 3% higher than by single extraction.

A simpler method is to first grind the flaxseed in a laboratory mill or by means of of a mortar and pestle, then weigh the ground material, transfer it to a smooth mortar and grind again with an equal part of clean, washed and ignited sand.   This separates the compact masses, making penetration by the solvent and consequent extraction more rapid and sure.

Schindler and Washata (Benedikt and Ulzer *Analyse der Fette*, etc., 1908) found in 43 samples of linseed oil from 35.74 to 43.26% of oil, an average of 39.48.   The following table, showing the oil contents of seed from different sources, is due to them.

Kind	Oil in %	Average
Calcutta....................	38.55–43.26	40.16
Bombay.........	36.96–42.90	41.03
Russia.........................	36.53–39.06	37.96
Mamara........................	....	41.27
Constanza........................	38.00–38.94	38.47
Levant.......................	36.95–42.04	40.04
Hungary.......................	36.63–37.86	37.13
Morocco........................	35.74–39.75	37.74
North America................................	....	36.41
La Plata................................	36.45–39.18	37.59

During each of 5 years the average analyses of North American seed received by one mill in the United States for the several seasons were as follows:

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1st................................................ 40.2%
2nd................................ ........................ 38.5%
3rd.............................. ........................ 39.4%
4th............................................... 39.8%
5th............................................ .. .. 38.7%
6th.............................................. . . .. 38.9%
7th................................ ........:...... ...... 35.8%
Average...... .... ..... ........................ 38.8%
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South American seed for five seasons ran as follows:

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1st.......... ............ ........................... 37.1%
2nd... ..... ...     ........................ 36.9%
3rd......... . ........................... .. 39.5%
4th........ . ........................... 39.5%
5th........................................... 39.6%
Average.............................................. 38.5 %
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When flax is harvested there is more or less foreign matter, comprising seeds of other plants, some of which are oleaginous, bits of stalks, leaves and dirt.   The amount of extraneous material

depends upon the carefulness of the farmer and the extent to which the seed is cleaned before it reaches the mill.

The linseed crushing mills of North America are all equipped with seed cleaning machinery which enables them to clean the seed to an extent that renders the extraneous material remaining of no appreciable effect upon the quality of the oil.

Sheppard (*J. Ind. Eng. Chem.*, 1912, 4, 14) gives the following data obtained by the examination of linseed from different localities. The oil was obtained by pressing both the picked and original seed:

	Oil, %	Sp. gr., 15°	Av. weight per seed, mg.	Oleaginous impurities, %	Non-oleaginous impurities, %	Oil in total impurities, %
1. American...............	39.67	1.1413	4.61	1.5	1.69	10.1
2. American...............	39.40	....	4.53	1.01	1 05	....
3. La Plata...............	36 98	1.1415	5.56	0.58	5.64	14 1
4. Calcutta...............	40.82	1.1326	5.41	4.85	5.03	14.9
5. Bombay.................	41.23	1.1182	7.88	0.81	2.80	....
6. S. Russia (Keitch).......	39.11	1.1375	5.74	5.05	1.71	....
7. N. Russia..,...........	36.95	1.1458	4.19	3.31	1.97	....

The oil content was determined by extraction. The average of 11 more recent samples of Calcutta seed was 6.90% of impurities, containing 15.1% oil. The average oil content of the cleaned seed was 41.01%.

Sheppard has made analyses of the oils expressed from the seed when new and after 2 years, and from his results concludes:

(1) Oil pressed from clean linseed does not differ materially from commercially pure linseed oil.

(2) The dark colour of La Plata oil is due to non-oleaginous impurities.

(3) A high percentage of oleaginous impurities does not affect the colour appreciably, but does affect the iodine value slightly.

(4) The technical manufacture of oil by the extraction process does not lower the iodine value.

(5) The constants of the oil pressed from the seed which had been kept 2½ years in a closed container do not appear to be affected by the ageing of the seed.

Hydrocyanic Acid from Flaxseed.—Flaxseed contains a cyanogenetic glucoside, together with an enzyme which occurs naturally in the seed.

Kohn-Abrest (*Ann. fals.*, 13-482-7) gives a method for determining the hydrocyanic acid content of material containing cyanogenetic

glucosides. The original article should be consulted for details. He found that twelve samples of linseed from different sources gave 0.0107 to 0.0310% total HCN. Collins (*Proc. Univ. Durham Phil. Soc.*, 4, 99) says that under usual conditions hydrocyanic acid is not likely to be liberated in dangerous quantity in the stomach of animals fed upon linseed, because the normal acidity of the alimentary canal inhibits its formation.

Manufacture of Linseed Oil.—Linseed oil is manufactured from flaxseed by the application of pressure or by extraction with a volatile solvent. By far the greater portion of the world's supply of linseed oil is made by hydraulic pressure, though the plants employing volatile solvents are steadily increasing in number, especially in Europe.

Ennis[1] describes the methods employed, particularly those adopted in the United States. This work should be consulted for the mechanical features. Pickard (*Trans. Amer. Inst. Chem. Eng.*, 1917, 10, 115–133) gives detailed description of the manufacture, by hydraulic pressure, including machinery and processes, together with discussions of their relationship to oil yield and quality.

When solvent extraction is employed, the seed is crushed but not pulverised and then subjected to a flow, either continuous or intermittent, of the solvent until the oil is removed. It is commercially possible to leave as little as 1% or even less of oil in the residue. When extraction is complete the meal is drained as free as possible from solvent and then live steam admitted until all trace of volatile liquid is removed. The oil and solvent mixture is placed in a still and first heated to distil the solvent. When a large portion has been removed live steam is admitted until all is distilled. The column still, with continuous downward flow of solvent-oil mixture and continuous upward flow of steam, is now being used in some installations.

The cost of operation of the solvent extraction may be a little higher than that of a well equipped hydraulic press plant, but the increased yield of the more valuable product, the oil, leaves a balance in favour of solvent extraction.

Linseed Cake and Meal.—The cake or meal resulting from the removal of the oil is a high protein material used as a foodstuff. The percentages of the important ingredients of it vary with the

[1] Linseed and Other Seed Oils, D. Van Nostrand & Co., N. Y., 1909.

natural variation in the seed from which it results and with the efficiency of the crushing operation.

The methods of analysis are those employed for stock foods.

The presence of hydrocyanic acid has been proved in linseed cake as well as in the seed itself. It generally occurs in less amount in the meal because the heating operation previous to crushing or the steaming subsequent to extraction greatly inhibit, if they do not prevent entirely, the action of the enzyme. Cold pressure of the seed is thought to increase any danger there may be from this source. Mixing the meal with boiling water in the preparation of the mash also prevents the formation of HCN, whilst soaking with cold water increases the amount present. The velocity of the formation of HCN by the cyanogenetic enzyme is influenced by numerous factors.

The rate of evolution of hydrocyanic acid under digestive conditions has been determined by Collins (*Proc. Durham Phil. Soc.*, 1912, 4, 99). The amount of hydrocyanic acid yielded by linseed, and the rate at which it is formed, depend on the quantity of cyanogenetic glucosides, on the proportion of enzymes, on the temperature and on the degree of acidity. Normal digestive conditions were obtained as far as possible, and it was shown that, since the acidity of the stomach contents and also that of green grass is approximately $N/20$, linseed cannot under normal conditions produce hydrocyanic acid when fed to carnivorous or herbivorous animals, but abnormal conditions causing reduction of acidity would result in the liberation of hydrocyanic acid. For details the original paper should be consulted.

English and German investigators have concluded that the resultant feeding stuff from solvent extraction is a light, rather fluffy meal, unsuitable for feeding in the open, but capable of being used for making compound cakes, or for indoor feeding in the form of meal or mash. Reports of the investigations of an English Committee on Edible and Oil Producing Nuts and Seeds (*Documents Cd.*, 8247–8248) state that it will not be more difficult to establish a market in that country for meal obtained by extraction than for cake.

In the United States large amounts of extracted meal have been sold for consumption in mixed feed and also to consumers direct in competition with linseed meal produced by grinding the press cakes.

Oil Quality.—The quality of raw linseed oil, apart from that dependent upon the seed from which the oil was made, is dependent, to a considerable extent, upon press room practice. If the seed is not freed from foreign oil-bearing seeds and from chaff, the oil will suffer both in its ability to absorb oxygen and in its colour. The oils yielded by the oleaginous foreign seeds are of a semi-drying nature and thus their effect, if any, is disadvantageous.

The presence of the chaff affects the colour only, for when this material is in the cooker and the presses, it yields colouring matter to the oil, rendering it of a greenish shade.

The cooking operation is of importance because of its relation to quality. A cold-pressed oil is of a pale golden yellow and will not "break," that is, separate a gelatinous matter when heated to between 200° and 260°. As the temperature of the meal in the cooker rises, particularly if the moisture content rises simultaneously, the colour of the oil darkens and the amount of dissolved matter increases. The colour difference is measured by an increase of red units.

The colour of the oil, therefore, is an indication of the manner of its manufacture, although there are differences in the colour of the oil yielded by different seeds when the same press room practice obtains in each instance.

The Inter-Departmental Committee, Standard Specifications Board, of the Government of the United States has drawn up colour standards for raw linseed oil which are a part of their specification. Use is made of a mixture of sulphuric acid and potassium dichromate of varying concentrations as a basis for colour comparisons. The range of colours, which are impossible to control, and those colour changes which result from controllable variables are so closely related that it is impossible to devise a system of colour measurement which will clearly differentiate between that colour range which is unavoidable, and that which could be prevented in the factory.

The Break.—When raw linseed oil is heated with sufficient rapidity in any container to a temperature between 200° and 260° there separates from it a gelatinous mass of a reddish brown colour. Simultaneously the oil bleaches to a greater or lesser extent, depending upon its quality.

This phenomenon is called "breaking" and the material separated out is termed the "break" of linseed oil. The ability to break is not

confined to linseed oil, for soya bean, sunflower seed and other oils employed in the paint and varnish industry do the same thing.

The "break" is composed of materials dissolved by the oil, during the crushing process, from the tissues of the seed. If separated and washed free from oil, it is found to consist of approximately equal parts of organic and inorganic matter. Among the inorganic substances present are those salts usually found in plant ash, such as the phosphates and sulphates of iron, calcium and magnesium. The identification of the organic portions is not very well worked out. It is variously described as albuminous and mucilaginous matter. The opinion is held by some that it is a vegetable lecithin, because a small amount of nitrogen is present.

The amount of the "break" varies. There is little data on this subject. Thompson (*J. Soc: Chem. Ind.*, 1903, 22, 1005) reported 0.27% on one sample of linseed oil analysed.

The "break" seems, in part at least, to be held in unstable, colloidal solution. Heat coagulates and precipitates it. Also, when raw oil stands this material separates out very gradually and falls to the bottom as one of the constituents of foots or settlings. An analysis of the settlings checks closely with one made upon the "break" separated by heat.

Years, however, are required to cause an oil to settle sufficiently to remove all of the "break" when the oil is stored in a large mass in the tanks usually employed for this purpose, when little oxidation occurs.

Attempts have been made to connect the temperature at which an oil breaks with the quality of that oil, and especially as an indicator of the age of the raw oil. After doing considerable work on this point the writer abandoned it because the results did not conform with the known facts. For instance, old, well-settled oil of excellent quality broke at lower temperatures than fresh samples, and this with the conditions under which the breaking test was made held rigidly to an outlined procedure in each case.

The mass of the oil and the rate of heating influence the breaking temperature, but with these held constant, concordant results cannot be obtained on the same sample, nor can reliance be placed upon the breaking temperature found for different oils.

In using the test, the writer judges quality by the appearance of the oil and of the separated material. Some oils, particularly

fresh ones, will give a clear supernatant oil of bright green colour, whilst others will be straw colour, with or without a greenish tinge. If the oil is dark after heating to the breaking point, a poor quality is indicated.

When the break is in apparently normal amount and of a light reddish colour an average quality of not very old oil is indicated. When reddish brown in colour and of small amount a well settled, old oil is shown, whilst a heavy, reddish brown break indicates one containing an excess of the break and one which will fail in service in too short a time.

This test should be applied only as a confirmatory test and one which would indicate the necessity of further examination to account for erratic behaviour. For instance, a perfectly clear, fine looking raw linseed oil was examined because of slow "bodying" and slow drying. The break test showed an excessive amount of very red material, thus indicating that the oil came from near the bottom of a storage tank, but above the level at which the foots lay. An analysis for foots failed to indicate this condition. A survey of the situation showed the indications of the break test to be correct, for the oil was from near the bottom of a storage tank which had held oil for a long time.

Because the break test may furnish information of sufficient importance to justify the expenditure of the small amount of time it requires, the writer includes it, with other tests, in the evaluation of raw linseed oil.

Foots Test.—The term foots is used to define the composite matter which separates from linseed oil during storage. The formation is gradual, proceeding at rates varying with the nature and composition of the mass and with the conditions obtaining during the period of separation. Temperature has a greater effect than any other variable, because the solubility of the matter in the oil increases with a rise in temperature.

The presence of foots in raw linseed oil does not necessarily imply improper filtration or clarification. There is practically no linseed oil received by consumers which was not, at one time, perfectly clear and bright. This state of affairs is explained by the fact that the substances which, taken together, compose the foots of raw linseed oil are present in an unstable solution, probably to a large extent colloidal, in the oil proper. As time passes the components

become insoluble and separate out. Obviously, therefore, only that portion which has separated previous to filtration is removed by that process. Consequently, the lapse of time between crushing and filtration and the temperature of the oil during passage through the filtering medium have a direct bearing upon the amount of foots that will later separate out.

Exclusive of solid particles of seed and other foreign matter, which never ought to be, and seldom are, present in the linseed oil of commerce, the foots of raw oil comprise three main elements which vary in amount. They are, first, the high melting-point, saturated fats which are solids at normal temperatures; second, the "break" and, third, water.

Obviously, the amount of high melting-point fats will vary with the composition of the oil, which, in turn, depends upon natural conditions prevailing during the growth of the flax plant. Inasmuch as these bodies are liquid above a certain temperature and solid below it, the amount present will vary also with the temperature at which filtration took place; if below the point of solidification, removal will be accomplished—otherwise they will remain in solution.

The solubility of the materials forming the "break" is affected to a less extent by temperature, though a portion of the amount originally present is undoubtedly removed by filtration when comparatively cold. Time is an important factor in the removal of this material, since a gradual precipitation occurs. The amount of the "break" also depends upon press room practice.

Moisture is dissolved by the oil during the operations of crushing. Flaxseed contains a varying amount of it, and more or less is added during the cooking or tempering operation. Generally speaking, the more moisture there is in the ground seed as it goes to the hydraulic press, the more water there will be dissolved by the oil. The amount will, of course, be dependent upon the ability of the oil to dissolve it. Within certain limits, the higher the temperature of the oil the more water there can be present in it while still remaining clear and bright.

To measure the amount of foots-forming materials in raw linseed oil has been a problem upon which much thought has been expended.

The first test devised was one which allowed a measured amount of the oil to deposit foots in a graduated vessel for a definite period

of time.   This method was impracticable because of the time required, the varying density of the deposit, and the incompleteness of the precipitation.

Later, precipitation from a solution of the oil in petroleum spirit was tried.   This failed for the reasons just given and also because of variations in solvent power.

Acetone was next employed.   It gave only fair satisfaction when used alone.   Walker and Wertz (*Proc. Amer. Soc. Test. Mat.*, 18, Part 1, 615) evolved a method employing acetone and an acid solution of calcium chloride, which is more satisfactory than any other.

A method devised by C. D. Holley (Drugs, Oils and Paints, 1916,51) is carried out as follows: "It depends on the precipitation of the foots by shaking 100 c.c. of syrupy phosphoric acid and 100 c.c. of the oil, thinning with 150 c.c. of naphtha and allowing the foots to collect in the calibrated neck of a suitable flask, keeping the temperature at approximately 30° during the operation."   This method is not very generally employed.

The Walker-Wertz method has given greater satisfaction than any other, but is still open to criticism.   Different operators applying the test to the same sample of oil do not check as closely as they will when using the other tests usually applied to linseed oil.   Committee D-1 of the American Society for Testing Materials (*Proc. Amer. Soc Test Mat.*, *Vol.* 18, 24) has reported much work done upon this test.   These reports show the test to be quite inaccurate and, therefore, capable of limited application.   In the writer's opinion, these differences are, in part, brought about by the effect of temperature changes on the oil previous to the determination of the percentage of foots present, and also to the temperature prevailing during the settling period.

When the oil has been chilled and then brought to room temperature before the estimation is made the percentage of foots will be higher than it would have been if the temperature of the oil had not been lowered.   The effect of a low temperature is somewhat reduced by heating the well-shaken sample to 65°, keeping it there for an hour or more, and then allowing it to cool to room temperature immediately before making the estimation.   When this is done more concordant results are obtained.

M. Y. Seaton (Private communication) and the writer have both observed cases in which this foots test has failed to show poor quality

caused by the presence of an excessive amount of the "break." Each observed that oils, which had shown a normal amount of foots, behaved badly in use. When the break test was applied an unusually large amount of a deep red "break" separated. Evidently, the "break"-forming substances are soluble in acetone.

The effect of the foots upon the action of the oil or service of those products of which it is a part is not well defined. Some users have noted no appreciable difference caused by the usual variations—others state that the rate of drying of a paint, for instance, is slowed up, that the gloss is dimmed and the service shortened. The presence of an excess of foots is thought by Gardner and others to produce a greater tendency on the part of the paint to "wash" when applied during humid and rainy periods. Gardner noted that the surface of a panel, upon which a paint made with an oil containing an excessive amount of foots was applied, was soapy after an exposure of two years. This is probably due to the presence of the solid, non-drying fats in excessive amount.

Undoubtedly, the composition of the foots has a bearing upon this subject, for the components would each affect the paint film in a different way. Moisture, in moderate amount, would probably produce the least trouble, because it would evaporate during the drying of the oil. The saturated fats would tend to soften the film and retard the drying, whilst the "break" materials, being somewhat water-soluble, would tend to form nuclei about which decay and disintegration could start.

The great danger from the presence of foots in raw oil is that it will be allowed to settle, and then the oil from the bottom or just above it, containing a large excess of foots, may be used as if it were good oil.

To prevent loss and trouble, agitate the oil in its container just previous to each withdrawal. In this manner, the foots are evenly distributed in all portions of the oil used and their effect thereby minimised.

The writer believes that a thorough investigation of the components of the foots of linseed oil, together with the effect of each one and the effect of the foots as a whole, would add greatly to our knowledge of raw linseed oil.

Chemical Composition.—The chemical composition of linseed oil is not definitely determined. The following figures are quoted,

but the reader is referred to Lewkowitsch (Chem. Tech. and Anal. Oils, Fats and Waxes, 1922, 2, 61) for a resumé of present views together with the references to original papers.

Linseed oil contains: 10%–15% glycerides of solid fatty acids; i. e., stearic, palmitic and myristic; 85%–90% liquid glycerides.

Hazura and Grüssner (Zeit. angew. Chem., 1888, 1, 312) state that the fatty acids from the liquid glycerides consist of:

Oleic acid... 5%
Linolic acid.. 15%
Linolenic acid... 15%
Isolinolenic acid...................................... 65%

Fahrion (Z. angew. Chem., 1910, 23, 722 and 1106):

Unsaponifiable matter................................ 0.6%
Saturated fatty acids................................. 8.6%
Oleic acid... 15–20%
Linolic acid... 30%
Linolenic acids....................................... 38%

Friend[1] says that the evidence, though admittedly conflicting, would appear to suggest that the composition of linseed oil of iodine value ranging from 170 to 180 lies between the following approximations:

Iodine number	180	170
Saturated acids	10%	10%
Linolic acid	48.3%	59.1%
Oleic acid	5.0%	5.0%
Linolenic acids	32.1%	21.3%
Glyceryl radicle (C_3H_6)	4.6%	4.6%

Coffey (J. Chem. Soc., 119, 1408) says that, from the results of the study of the mechanism of the oxidation of linseed oil, he estimates the proportions of its constituents. Linolenic acid is calculated from the amount of carbon dioxide in the volatile products, linolic acid is calculated from the total oxygen absorption, minus the absorption due to linolenic acid. From the iodine number the total unsaturation is estimated. Since the amounts of linolenic and linolic are known, oleic is obtained by difference and glycerol is determined directly. This method gives the following composition:

[1] Chemistry of Linseed Oil, D. Van Nostrand, p. 64.

Saturated acids and unsaponifiable matter............. 8.1%
Oleic acid.. 5.0%
Linolic acid...................................... 48.5%
Linolenic acid.................................... 34.1%
Glycerol.. 4.3%

These results are almost identical with those of Friend for an oil with an iodine number of 180.

Seidenberg (*J. Amer. Chem. Soc.*, 43, 1323) gives a modified method for the quantitative separation of the lead salts of the saturated from the less saturated fatty acids. This method may be of assistance in determining the percentage composition of various vegetable oils. (See p. 533.)

Morell (*J. Soc. Chem. Ind.*, 1913, 32, 1091) has examined the saturated acids of linseed oil. A yield of lead salts equal to 6% of saturated acids on the oil taken was obtained, and investigation of these salts showed that the composition of the mixed acids may be summarised as follows:

Stearic acid actually separated......................... 51.7%
Stearic acid present in eutectic mixture................. 12.7
Palmitic acid present in eutectic mixture................ 20.0
Residual eutectic mixture............................ 8.0
Oleic acid.. 4.0
                                                     _____
                                                     96.4

It is to be observed that no daturic, myristic or arachidic acids were detected, but the methods of separation of the saturated acids are very tedious, and new methods are wanted. By careful working, satisfactory results as to stearic acid are obtainable, but for palmitic, arachidic and myristic acids further investigation of their derivatives is necessary.

de Waele (*Analyst*, 1914, 39, 389) elaborates and improves upon the Fachini-Dorta method of separating liquid from solid fatty acids in oils and fats as follows: 10 grm. of the dry fatty acids are dissolved in 90 c.c. of anhydrous acetone and 10 c.c. of N/1 potassium hydroxide are added in a thin stream, constantly stirring. The vessel containing the mixture is then immersed in ice-water for 3-4 hours. The precipitated soaps of the solid acids are filtered off under suction and washed with acetone until the filtrate is colourless. The cake of soap is then removed, dissolved in water with the aid of a little alkali, and the acids separated in the usual manner. The liquid acids in the filtrate can be separated by diluting with water, adding ether,

and acidifying.   The author claims that a higher iodine value for the liquid acids is obtained than that given by Tortelli and Ruggieri's method, and in addition the process gives quantitative results.   The following figures are given for the amounts of saturated acids in various oils:

Linseed oil, Calcutta seed.....................   9.1% of iodine value 16.4
Linseed oil, Baltic seed........................   6.6% of iodine value 20.0
Linseed oil, Northwestern......................   6.0% of iodine value ....
Soyabean oil.................................   13.8% of iodine value 12.1
Para rubber seed oil...........................   16.3% of iodine value 10.7
China wood oil (varies considerably)...........   54.1% of iodine value ....
Crude menhaden oil...........................   23.5% of iodine value 20.2

The determination of the purity of linseed oil is made by an analytical procedure which involves the measurement of certain different properties of the oil, which vary within determinable ranges.   These figures are frequently called "constants" but, in view of the range between allowable extremes, the word "constants" is misapplied. The results of these various determinations also indicate the quality of pure oils.

Iodine Value.—Many of the earliest recorded iodine values are far too low.   This is due to the fact that the proper conditions for the estimation had not been ascertained.   With the development and adoption of standardised analytical methods perfectly satisfactory results are obtained.   The iodine value is one of the most characteristic tests for identification purposes, although discretion must be used in interpreting low figures.

The first reasonably accurate method was the Hübl which, whilst still used by some, has been determined comparatively inaccurate, particularly when applied to oils of high iodine value.   Concordant results on linseed oil, for instance, cannot be had when the Hübl method is employed.   There are two other methods, namely, the Hanus and Wijs, which are both satisfactory.   The Wijs method is quite generally used in Europe, whilst the Hanus is more popular in the United States.   The Association of Official Agricultural Chemists of the U. S. and the American Society for Testing Materials have adopted the Hanus method as standard.   The Committee on the Analysis of Commercial Fats and Oils of the American Chemical Society, (*J. Ind. Eng. Chem.*, 10, 315), issued tentative standards in 1918, in which they recommend the use of the Wijs method.   The reasons given are that absorption of iodine from the Wijs solution

appeared to take place with greater promptness and certainty than from the Hanus and was complete in a shorter time. Results by the Wijs method were also in closer agreement in the case of oils showing high iodine absorption than with the Hanus solution and showed a slightly higher iodine absorption for the same length of time. However, the difference was not great. (See p. 37, *Iodine Value.*)

Committee D-1 of the American Society for Testing Materials (*Proc. Amer. Soc. Test. Mat.*, 21, 3348) made comparisons of the two methods. Their conclusions are that there is little difference in the accuracy of the two and that the Wijs method gives an iodine absorption 4 to 5% higher than the Hanus method when applied to linseed oil.

Smith and Tuttle (*U. S. Bur. of Stan., Technologic Paper No.* 37; *J. Frank. Instit.*, 1914, 177, 687) have investigated the Hanus method, and found that concordant figures are obtained for raw linseed oil when the quantity of oil taken for a determination does not exceed 0.25 grm. When, however, a greater quantity of oil is used the iodine value was decreased. With burnt oils it was found that the limit of agreement diminishes, with an increased degree of burning. Variation of temperature was found to have more influence on the values obtained for burnt oils than was the case with raw or boiled oils.

The American Society for Testing Materials gives the low limit for Hanus iodine values of oil from North American seed as 180, and that from South American seed as 170.

The iodine value of any oil varies not only with the source of the seed from which it was made, but also from season to season with oils from seed from the same locality.

The iodine value affecting users of linseed oil is that of the oils of commerce. This means that it is an average of oils from seed from various localities, because the method of handling the seed mixes it, and consequently, the oil produced is average.

The writer examined a large number of samples of linseed oil produced in a laboratory hydraulic press from selected samples of seed, all of which were grown during one season within an area of a radius of a few hundred miles. The iodine values determined by the Hanus method ranged from 193 to 170.

The iodine numbers of the oils from flaxseed from the four great sources of the world differ from each other, and also between them-

selves.   Consequently a statement of the iodine number of these oils must contain limits for each, the extremes of which are rather far apart.

Such figures are given below.   They were made by the Hanus method.

	MAXIMUM	MINIMUM
Oil from North American flaxseed....................	194	180
Oil from South American flaxseed....................	184	170
Oil from North Russian (Baltic) flaxseed.............	200	188
Oil from South Russian flaxseed....................	182	172
Oil from Indian flaxseed...........................	185	176

Since the iodine absorption measures the ability of a linseed oil to dry, these figures show very appreciable differences of quality when measured by this standard.   The North Russia or Baltic oil is shown to be of the highest quality.   This coincides with the expressed opinion of European users of linseed oil who always secure Baltic oil whenever it is available in preference to that from other sources. North American oil is next, followed in turn by Indian, South Russian and South American.

Ingle (*J. Soc. Chem. Ind.*, 1911, 30, 344) gives the following limits for samples of established purity:

Baltic oil...............................	190–204 iodine value
Indian oils..............................	180–189 iodine value
La Plata................................	175–186 iodine value
Black Sea...............................	176–182 iodine value
North American.........................	177–188 iodine value
Morocco, Dutch and Turkish oils..........	185–192 iodine value

Ingle remarks that in all the foregoing values the exact method of determination is the important factor, and emphasises the necessity of using pure reagents for this purpose.   The method he used was that of Wijs.

The iodine value measures the total of the unsaturated linkages in an oil, not distinguishing between them.   In other words, it is an average number.   Thus one oil could contain a relatively large amount of the highly unsaturated linolenin and a correspondingly large amount of the slightly unsaturated olein and yet have an iodine value equal to that of an oil composed of less of the two extremes, but with more linolin present.   The latter oil would be the better of the two, because there would be less of the soft materials dispersed throughout the film.

The writer examined many samples of linseed oil representative of the commerce of the United States during years from 1916 to 1920. The range from the highest to the lowest iodine value for each year was as follows:

```
1916–1917........................................ 22%
1917–1918........................................ 26%
1918–1919........................................ 20%
1919–1920........................................ 14%
```

All of the oil examined was from either North or South American seed, or possibly mixtures of these seeds and of the oils from them.

The practical significance of these ranges in iodine value of oil shipments is the effect they would have upon uniformity of products made from them. If a factory receives a car of oil one day having an iodine value of from 188 to 190, and on another occasion one as low as 170, there are bound to be variations of no inconsiderable degree in the properties of paints, varnishes or other coatings made from the two oils. These great variations could be eliminated by mixing either the seed or the oil in such a manner that the average would reduce the range. The effect of such a procedure, were it practicable, is apparent from a glance at the average iodine value of all of the shipments tested during those years. These averages are:

```
1916–1917.......................................... 185.0
1917–1918.......................................... 180.5
1918–1919.......................................... 181.6
1919–1920.......................................... 180.0
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The differences here shown are of no great significance.

Wilhelm and Meister find that glacial acetic acid is the best solvent for oxidised linseed oil (linoxyn or scrim oil), and advise its use in determining the iodine values of such products.

The extent of oxidation to which the oil has been submitted determines its solubility, highly oxidised oils being only partially soluble, even in hot acid. In spite of these drawbacks, the authors prefer this solvent in the place of chloroform or the solvents usually used. In the case of highly oxidised oils, the end point is not so distinct as with the ordinary mixture.

de Waele finds that the use of a solvent is unnecessary in the examination of linoxyn, if the sample be comminuted by grinding in a mortar. An hour's soaking in chloroform or carbon tetrachlo-

ride previous to the addition of the Wijs (or other) solution will also serve to swell the substance and ensure its thorough interaction with the iodine reagent.

Insoluble Bromides—Qualitatiue.—Eisenchiml and Copthorne (*J. Ind. Eng. Chem.*, 1910, **2**, 28) have devised a qualitative test for fish oils in vegetable oils, based on the insolubility of the fish oil bromides in chloroform, in contradistinction to the bromides of linseed oil, which are soluble. The method is described as follows: 100 drops of oil are dissolved in 6 c.c. of a mixture of equal volumes of chloroform and glacial acetic acid. Bromine is added drop by drop until the brown colour remains. After 10 minutes the test-tubes are placed in a beaker containing boiling water. Linseed oil and other vegetable oils will clear up completely within a few seconds, whilst fish oils will remain cloudy and give a sandy precipitate at the bottom of the tube within a short time. Fish oils that have been heated to 260°, or more, for some time will not respond to this test.

Trials made by the authors cited show that it is not possible to use this method for quantitative analysis unless a minimum of fish oil present is all that would be desired, because the amount of insoluble bromides in oils of the same kind, but from different sources, varies to a considerable extent.

The fact, however, that the precipitate formed can be weighed and is, indeed, in direct proportion to the amount of fish oil present in a given sample raises this process above the level of an ordinary qualitative test; therein lies an advantage over other methods now in use. The short time required for the test and its applicability to both raw and boiled linseed oil are other factors of importance.

Hexabromide Value Quantitative.—Because of the inaccuracies of the methods employed for the quantitative determination of the insoluble hexabromides in linseed oil the results obtained prior to about 1912 are not dependable.

Eibner and Muggenthaler (*Farb. Zeit.*, 1912–18, **131**, *et seq.*, and see *Abstract Chem. Zentr.*, 1913, **1**, 567; *Analyst*, 1913) prepare the fatty acids with all precautions against oxidation, then brominate at a temperature of $-10°$, subsequently filtering on asbestos. The original communication should be consulted for details of the method, which, although lengthy, was probably the most exact recorded up to date of publication.

The authors made a large number of determinations on raw linseed oil of different origin, and obtained yields of hexabromide as follows:

Dutch oils.................................... 51.73%
La Plata oils................................. 51.66%
Indian oils.................................. 50.50%
Baltic oils.................................. 57.96%

The hexabromide value is not appreciably affected by the refining processes. The following values were obtained on applying the method to other oils:

Poppy oil.................................... 0.0%
China wood oil.............................. 0.0%
Perilla oil.................................. 64.12%
Ocumi oil.................................... 60.98%
Rape oil.................................... 6.34%
Soya bean oil.............................. 7.17%

The authors show how rape oil can be quantitatively estimated in linseed oil. When the presence of rape oil has been proved by the erucic acid test, the approximate proportion of the adulterant can be calculated from the hexabromide value, 10% of rape oil reducing the hexabromide value of linseed oil by about 4.4%. 4% should be deducted from the value of rape oil found to allow for the permissible contamination of linseed oil by *Cruciferæ*.

Committee D-1 of the American Society for Testing Materials has investigated the Eibner as well as other methods for the determination of the percentage of insoluble hexabromides in linseed oil. The Committee's records (*Proc. Amer. Soc. Test. Mat.*, 1915, Part 1, 224; 1916, Part 1, 283; 1920, Part 3, 395; 1921, Part 1, 334) show that lack of concordance existed when the Eibner method was employed. The average of the apparently correct results on North American linseed oil is 50.2%. The highest was 51.94% and the lowest 48.07%.

Steele and Washburn (*J. Ind. Eng. Chem.*, 12, 52) give in detail the following new method for the determination of insoluble hexabromide.

(*a*) **Preparation of Reagents.**[1]

The following reagents are necessary:

1. *Chloroform.*—Shake ordinary U. S. P. chloroform with several portions of water to wash out all the alcohol. Dry the product with granulated anhydrous chloride over night in order to remove all traces of water. Decant from the calcium chloride and distill.

[1] Bureau of Standards.

Add to the distillate 3 c.c. of absolute ethyl alcohol for every 100 c.c. of chloroform.   Keep in a stoppered brown bottle.

2. *Bromide Solution.*—Mix one part by volume of C. P. bromine[1] with two parts by volume of chloroform, prepared as above.   This solution must be made up fresh each day because it deteriorates upon standing.

3. *Wash Ether.*—Shake ordinary ethyl ether with 10% of its volume of ice-cold distilled water.   Separate and repeat the washing three times.   Dry the washed ether with fused calcium chloride over night.   Decant the ether through a folded filter into another flask and add thin slices of sodium.   Warm gently on a steam bath under a reflux condenser until the evolution of gas by action of the sodium has practically ceased and bits of freshly cut sodium remain bright in the ether.   Distill the ether into a dry bottle and add an excess (at least 3 grm. per liter) of finely powdered hexabromide of the fatty acids of linseed oil previously prepared.   If no hexabromide is on hand from previous estimations it may be easily prepared as follows: In a centrifuge tube dissolve about 5 grm. of the fatty acids of linseed oil in 15 to 20 c.c. of chloroform.   Place the tube in a freezing mixture and add slowly, with shaking, bromine solution until a slight red color is permanent.   Add a few drops of amylene to take up excess of bromine.   Whirl in a centrifuge until the precipitate has settled and then pour off the chloroform.   Rub up the precipitate with 20 c.c. of cold absolute ether, whirl in a centrifuge and pour off the wash ether.   Repeat the washing with three more 20 c.c. portions of ether.   After drying, the hexabromide is pure enough for the preparation of wash ether.   Shake at intervals for 2 or 3 hours or allow the mixture to stand over night.   Then place the bottle in ice water so that the ether solution will be at zero or not above 2° for three hours.   Decant the ether solution rapidly through a folded filter into a dry bottle and keep tightly corked in order to prevent loss of ether by evaporation.

4. *Amylene.*—This material may be purchased from the Eastman Kodak Co.   It is one of the organic chemicals prepared in the laboratory of the University of Illinois.   It may be prepared in small quantities from amyl alcohol by the method of Adams.[2]

(*b*) **Preparation of the Fatty Acids.**

Weigh approximately 50 grm. of linseed oil into a 1.5-liter Flor-

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[1] The authors have observed that samples of bromine marked "C. P." often contain considerable amounts of non-volatile material. All bromine which is used must be redistilled unless it is found that 5 grm. leave no weighable residue upon evaporation.

[2] *J. Am. Chem. Soc.*, 1918, 1950.

ence flask, and add 40 c.c. NaOH solution (sp. gr. 1.4) and 40 c.c. of alcohol. Place the mixture on a steam bath and heat for about ½ hour. Add 1 liter of hot distilled water and insert into the neck of the flask a 2-hole rubber stopper carrying a tube which projects into the flask so that its end is slightly above the liquid, and pass a stream of CO_2 through the tube into the flask. The soap mixture may then be heated, to remove the alcohol, either over a free flame or on the steam bath. If the free flame is used, a capillary "boiler" must be placed in the liquid, since otherwise the soap solution will bump badly. If excessive foaming takes place, the current of CO_2 should be increased until it is strong enough to break up the foam. If the solution is heated on the steam bath, usually about 2 to 3 hours are required to remove the alcohol, whilst if it is boiled over a free flame, ½ hour is usually sufficient. After the alcohol has been removed, cool the soap solution and acidify with dilute HCl (1:1). Insert a 3-hole rubber stopper, carrying two glass tubes arranged as for a wash bottle, leaving the third hole in the stopper open for an outlet for the CO_2. The inlet tube should extend to just above the layer of fatty acids, and the outlet tube should extend to the bottom of the flask. It is essential that the outlet tube should not extend down more than an inch or two inside of the flask, as otherwise siphoning would take place, causing the liquid to boil inside the tube.

Pass a stream of CO_2 through the system and boil gently, using a capillary boiler to prevent bumping, until the layer of fatty acids is clear. Plug the hole in the stopper which acts as an outlet for the CO_2. The lower layer will be forced out through the outlet tube by the pressure of the CO_2. In this manner remove as much water as possible without losing any of the fatty acids, then remove the stopper and add about 500 c.c. of hot distilled water, shake thoroughly so that the fatty acids are well washed, allow the fatty acids to separate and siphon off the wash water as before. Repeat the washing until the wash water does not give an acid reaction with methyl orange. Before removing the last washing, insert a capillary boiler and boil gently until the fatty acid layer is clear. After the last washing, remove the stopper and suck up with a pipette the last few globules of water. Filter the hot fatty acids through a folded filter under an evacuated bell jar and keep in a well stoppered bottle.

(*c*) **Preparation of Hexabromides.**

Weigh accurately in a weighed centrifuge tube (approximately 6½ in. long by 1 in. in diameter) 1.00 grm. (plus or minus 0.05 grm.) of linseed fatty acids, prepared as given above. Dissolve in 10 c.c. of chloroform and place the tube in a freezing mixture kept as near —5° as possible, made by adding a little dilute HCl to finely cracked ice. Add bromine solution from a burette at the rate of one or two drops per second, shaking the tube well during the addition. At first the bromine colour will be rapidly discharged, but later the mixture will assume a permanent orange colour indicating a slight excess of bromine. For most fatty acids of linseed oil about 1 c.c. of the bromine solution will be found necessary to give the orange colour. At this point run in rapidly 0.5 c.c. more of the bromine solution, shake well, and allow the tube to stand in the ice mixture for 10 minutes. Remove the tube from the freezing bath and add amylene drop by drop with shaking until the bromine colour has entirely disappeared. Usually five to six drops of amylene are sufficient, but a slight excess does no harm. The addition of bromine solution must never be done in direct sunlight.

Results are given on light linseed oils with iodine numbers ranging from 181 to 191. The percentages of insoluble hexabromide lie between 46.9 and 45.8.

Committee D-1 of the American Society for Testing Materials (*loc. cit.*) found the results of different operators by this method more concordant than with other methods, but still far enough apart to make adoption of specification limits unadvisable.

Bailey and Baldsiefen (*J. Ind. Eng. Chem.*, **12**, 1189) outline another method for the estimation of insoluble hexabromide.

References.

The literature on the estimation of hexabromide numbers is not very extensive. The following are the recent references of value:

> "*Chem. Tech. and Anal.* of Oils, Fats & Waxes," by Lewkowitsch, 5th Ed., Vol. I, p. 568.
>
> *Farben Zeitung* (1912) No. 3 ff.
>
> Muggenthaler, Inaug. Dissert. 1912, Augsburg.
>
> Bailey and Johnson, 5, Ind. Eng. Chem. **10**, 999.

Principle.

The unsaturated fatty acids when treated under proper conditions with bromine absorb at each unsaturated linkage two or more atoms of

bromine depending on the degree of unsaturation. Thus at a double bond $-C = C-$ there is obtained a saturated bromo product $-\underset{\underset{Br}{|}}{C}-\underset{\underset{Br}{|}}{C}-$ and at a triple bond $-C = C-$ four bromine atoms are

absorbed to give a saturated compound $-\underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{C}}-\underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{C}}-$. The solu-

bility in ether of the brom derivatives decreases rapidly with increase of bromine content. Thus the di and tetra brom compounds are easily soluble, whereas the hexa (and octo) compounds are only very sparingly soluble. This fact is made use of to separate the hexa (and octo) brom derivatives in carrying out the analytical estimation.
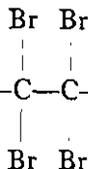
Status.

The following method is applicable to the estimation of the hexabromide number of saponifiable oils. It must be remembered that the hexabromide number depends upon the method employed in making the estimation. It is, therefore, important that in reporting results, the particular method must be specified.

Reagents and Apparatus.

(a) *Reagents:*
1. C. P. sodium hydroxide solution of 1.4 sp. gr.
2. 95% alcohol.
3. Distilled water.
4. C. P. hydrochloric acid.
5. CO_2 or nitrogen.
6. C. P. bromine containing *no non-volatile matter.*
7. Glacial acetic acid *showing no reduction with dichromate or permanganate in the usual test.*
8. Wash ether:

Shake ordinary ethyl ether with 10% of its volume of ice-cold distilled water. Separate the water and repeat the washing three times. Dry the washed ether with fused calcium chloride over night. Decant the ether through a folded filter into another flask and add thin slices of sodium. Warm gently on a steam bath under

a reflux condenser until the evolution of gas by action of the sodium has practically ceased and bits of freshly cut sodium remain bright in the ether. Distill the ether into a dry bottle and add an excess (at least 3 grm. per liter) of finely powdered hexabromide of the fatty acids of linseed oil previously prepared. (If no hexabromide is on hand from previous estimations, it may be prepared as follows: In a centrifuge tube dissolve about 5 grm. of the fatty acids of linseed oil in 25 c.c. of ether. Place the tube in a freezing mixture and add slowly with shaking bromine solution until a red colour is permanent. Let stand for at least 15 minutes and then whirl the tube in a centrifuge until the precipitate has settled and then pour off the ether. Rub up the precipitate with 20 c.c. of cold absolute ether, whirl in a centrifuge and pour off the wash ether. Repeat the washing with 3 more 20-c.c. portions of ether. After drying, the hexabromide so obtained is pure enough for the preparation of the wash ether.) Shake at intervals for 2 or 3 hours or allow the mixture to stand over night. Then place the bottle in ice water so that the ether solution will be at zero or not above 2° for at least 3 hours. Decant the ether solution rapidly through a folded filter into a dry bottle and keep tightly corked in order to prevent the loss of ether by evaporation.

(b) *Apparatus:*

1. Steam bath.
2. Gas burner.
3. Iron tripod, ring stand and wire gauze.
4. Round bottom flask of 2 liters capacity.
5. Separatory funnel, 500 c.c.
6. Bell jar.
7. Well annealed test tubes 5 by 1 in.
8. 50-c.c. burette.
9. Glass stirring rods 6 by $\frac{3}{16}$ in.
10. Glass battery jars.
11. Graduated cylinders 10 and 50 c.c. capacity.
12. Small pipettes about 3 cc. capacity for weighing out samples.
13. Centrifuge giving about 3000 r.p.m.
14. A vacuum showing no higher than 40 mm. pressure.

Estimation. .

(a) *Preparation of Fatty Acids.*—Weigh approximately 50 grm. of oil into a 2-litre round-bottom flask and add 40 c.c. of NaOH solu-

tion (sp. gr. 1.4 = 36.50% sol.) and 40 c.c. of alcohol. Place the mixture on a steam bath and insert a 2-hole rubber stopper into the neck of the flask carrying a tube which projects into the flask so that its end is just above the liquid. Heat for about one-half hour, passing a stream of CO_2 through the apparatus all the while. Add 1 litre of hot distilled water and boil the soap solution to remove the alcohol, either over a free flame or on a steam bath. If a free flame is used about one-half hour's boiling will be sufficient, but it may be necessary to insert capillary tubes to prevent bumping of the liquid. If the solution is heated on the steam bath, usually 2 to 3 hours are required. After removing the alcohol, the solution is cooled somewhat and then acidified with dilute HCl (1 : 1). Warm the mixture until the fatty acids form a clear layer, continuing to pass CO_2 through the system all the time. The fatty acids are separated from the aqueous layer by means of a 500-c.c. separatory funnel. The funnel is filled with the mixture, and the fatty acids will float on top, and the aqueous portion is run off. The remainder of the mixture in the flask is added to the funnel and the aqueous portion again run off. A brisk stream of CO_2 is passed into the funnel to replace the air; 300 c.c. of hot distilled water is added and the mixture is vigorously shaken. After the fatty acids collect on top the aqueous portion is run off. This washing is repeated until the water is neutral to methyl orange, three washings usually being sufficient. The warm fatty acids are run into a centrifuge tube (1 by 5 in.) and whirled for about 1 minute to collect any remaining water at the bottom. They are then filtered by decantation on to a folded filter under an evacuated bell jar and kept in a well-stoppered bottle.

(b) *Preparation of the Hexabromides.*—Weigh accurately in a weighed centrifuge tube (1 in. diameter by 5 in. long) as nearly as possible 1 grm. of fatty acids. It was found that in the case of linseed oil better results are obtained by keeping the weight of the sample as near to 1 grm. as possible, so the deviations from this should not be more than ±0.02 grm. Dissolve the fatty acids in 25 c.c. of the specially prepared ether and place the tube in a freezing mixture kept at about −5° made by adding a little HCl to finely cracked ice. Add bromine solution[1] from a burette at the rate of about one or two drops per second, shaking the tube well during the addition until a deep red colour is produced. This should not be done

[1] 5 c.c. bromine, 25 c.c. glacial acteic acidm ade up just before use.

in direct sunlight.   The tube is then allowed to stand in an ice chest over night (about 14 hours), the proper precautions being taken to prevent the loss of solvent by evaporation by inserting a stopper.

It is necessary to let the tube stand for this period of time because in the case of oils which contain only a small amount of linolenic acid (soya bean oil is a good example) the precipitation of the hexa-bromide proceeds more slowly than in the case of an oil with a larger content of linolenic acid (linseed for example).

Next morning cool the tube by immersion in a bath of cracked ice and rub up the precipitate by means of a weighed glass rod, being sure to loosen any material adhering to the side of the tube.   Whirl the tube in a centrifuge till the precipitate forms a hard cake on the bottom, cool in the ice bath, and decant the ether.   Add 20 c.c. of the wash ether previously prepared and cooled to 0° C. and rub up the precipitate with the glass rod.   Return the tube to the ice bath and when cold whirl it in the centrifuge.   Return the tube to the ice bath and then remove the ether by decantation.   Repeat this washing twice more.   After the last washing incline the tube and carefully tap it to spread the hexabromide precipitate part of the way up the sides.   Warm the tube in water at 60° until most of the ether has evaporated, then attach it for 15 minutes to a vacuum line showing a pressure of 30–40 mm. keeping the temperature around 60°.   Wipe the tube dry and allow it to stand in the balance at least 15 minutes before weighing.   To the weight of the precipitate in the tube add the weight of the slight amount adhering to the glass rod.   This total weight of precipitate multiplied by 100 and divided by the weight of fatty acids taken, gives the hexa-bromide percentage.

Notes.

1. The fatty acids are used instead of the glyceryl esters because the latter give inconcordant results.

2. In the case of linseed oil, the weight of the sample should be kept as near 1 grm. as possible.

3. Care should be exercised in preparing the wash ether for if it is unsaturated with hexabromides according to directions, the results will be low.

The results obtained by this method are lower than those by the Steele-Washburn estimation, which method yields lower percentages than the Eibner method.   Bailey and Baldsiefen say that their

method is less complicated than some of those previously proposed, and gives more concordant results, and that the hexabromide value of pure extracted and expressed linseed oils varies between comparatively narrow limits, and is, on the average, about 42.

The writer obtained a maximum of 49.4% and a minimum of 45.9% of hexabromide from commercial linseed oils, analysed in his laboratory, by the Steele-Washburn method. In doing work on samples of linseed oil made in a laboratory hydraulic press from samples of flaxseed grown in North Dakota the determination of the hexabromide value was made. The history of each sample of seed is known. An oil with an iodine number (Hanus) of 193.2 gave 52% of hexabromide, whilst one with an iodine number of 179 gave but 41.7%. These results are of interest because they show a wide difference in quality of oil from seed grown in the same locality.

An example of how the hexabromide value can be used to show differences in composition, and consequently quality, when the iodine value fails to do so, is afforded by the results of the analysis of two linseed oils made by the writer. One, a commercial sample with an iodine number of 178.5, gave a hexabromide value of 47.1, whilst an oil from a small sample of seed which had an iodine number of 179 yielded but 41.7% of insoluble hexabromide. These figures show an appreciable difference in the amount of linolenic acid present in two oils which would be pronounced of equal value by their iodine values.

In determining adulteration of linseed oil by semi-drying oils, use is made of the great difference in the hexabromide values of these oils. Soya bean oil, for instance, yields about 6% of insoluble hexabromide.

Assuming linseed oil to have a hexabromide value of 52% and an iodine number of 192, and soya bean oil to have a hexabromide value of 6% and an iodine value of 140, the following calculation shows how the hexabromide value would detect adulteration of linseed oil with 20% soya bean oil when the iodine number would not.

$$80 \times 52 = 41.6$$
$$20 \times 6 = 1.2$$

Hexabromide value of mixture.................. 42.8

$$80 \times 192 = 153.6$$
$$20 \times 140 = 28.0$$

Iodine value of mixture........................ 181.6

A hexabromide number of 42.8 would show the oil to be an adulterated linseed oil, whilst an iodine number of 181.6 would show it to be a linseed oil of fair quality. A similar adulteration with a lower iodine and hexabromide value would make the difference still greater.

Tschudy (*J. Ind. Eng. Chem.*, 1921, **13**, 941), by assuming maximum and minimum iodine value and hexabromide results by the Bailey-Baldsiefen method, works out an equation by which the amount of linseed oil and soya bean oil in unknown mixtures can be calculated.

Insoluble Bromoglycerides.—The original method of Hehner and Mitchell (*Analyst*, 1898, **23**, 315) has been largely replaced by an estimation of the insoluble linolenic hexabromide in the mixed fatty acids, as described above. This is due to the fact that it has not been found possible, hitherto, to purify the insoluble bromides of the mixed glycerides in such a way as to obtain concordant results. Davidson (*J. Ind. Eng. Chem.*, 1921, **13**, 801) has devised a method in which this drawback has been, to some extent, obviated. He used a solvent previously saturated with the insoluble brominated glycerides.

H. Toms (*Analyst*, 1924, **49**, Feb.) has now shown the true cause of these discrepancies. It is that the so-called "insoluble bromide" obtained from the glycerides is really a mixture of two crystalline bromides, which are probably (*a*) linolic-dilinolenic bromoglyceride, and (*b*) either trilinolic bromoglyceride or oleic-linolic-linolenic bromoglyceride. Both of these bromoglycerides have been prepared in crystalline form by crystallisation from ethyl acetate. The "insoluble bromide" hitherto obtained has consisted of mixtures in varying proportions of these two compounds.

Toms has devised the following method of estimating the more insoluble bromoglyceride (*i. e.* that of linolic-dilinolenic, m. p. 153° (corr.). About 1 c.c. of the linseed oil is weighed and dissolved in 10 c.c. of ethyl acetate. Liquid bromine (1 c.c.) is run in slowly, care being taken to prevent rise of temperature. After a short time the precipitate is collected in a weighed Gooch crucible, washed with 20 c.c. of ethyl acetate, and dried at 80°. Duplicate estimations give concordant results.

Four different samples of pure linseed oil yielded from 15.8 to 19.26% of this bromglyceride, and some relation was established between the amount of precipitate and the iodine value of the original oil.

Acid Value.—The acid value, that is, mg. of KOH required to neutralise the free fatty acids in 1 grm. of oil, can be estimated on limpid linseed oils by boiling the sample under a reflux condenser with neutral 95% ethyl alcohol and then titrating with standard alkali, or by shaking the sample in the cold with a neutral mixture of equal parts of 95% ethyl alcohol and pure 90° benzol. If polymerised or oxidised oils of a viscous nature are to be analysed, from 1 to 2 grm. only of the oil should be weighed into a 200 c.c. Erlenmeyer flask, 40 c.c. of the neutral alcohol-benzene mixture added and the whole boiled for 30 minutes under a reflux condenser, cooled and titrated with N/10 alkali, with phenolphthalein as the indicator.

The rate of hydrolysis in linseed oil depends upon conditions obtaining both before and after crushing.

The action also takes place in the seed or other material of which the oil is a part. It is quite rapid when any oil-bearing material—flaxseed, for instance,—is damaged or becomes wet and consequently moulds or ferments. The oil yielded from such material will always be high in free fatty acid. Sometimes sound, sweet seed will yield an oil high in acid. When this happens, the degree of acidity increases with the length of time the seed is stored before being crushed. The reaction is probably due to an enzyme in the flaxseed. The acid number of an oil also increases gradually on standing. The rate of increase is much greater if the oil is moist.

The acid number of raw linseed oil will generally fall under 6. Usually the acidity will be between 1.5 and 4 mg. Generally speaking, the lower the acid number the better the quality of the oil as yielded by the seed and the more carefully it has been handled after manufacture. There will be comparatively little difference noted in the use of oils with acid numbers up to about 4, but when this number is exceeded, differences such as the thickening of paints in which basic pigments are used, or the rather slow bodying of the oil under heat treatments, will exist.

Saponification Value.—The saponification value of linseed oil will lie between 189 and 195. The ageing or oxidising of the oil raises this figure. Oxidation is indicated by a red colour of the alcoholic soap solution.

Specific Gravity.—Bearse (*Proc. Amer. Soc. Test Mat.*, 1911, **11**, 211) has determined the density and thermal expansion of linseed oil with great precision. From this work it appears that if the density

of any sample of pure linseed oil be determined at 25° its density at any other temperature between 10° and 40° may be calculated within the limits of ordinary experimental error by the use of the general equation

$$D_t = D_{25} + a(t - 25) + B\ (t - 25)^2$$

in which "A" is taken as -0.0006847 and "B" as $+0.00000012 0$. Or the density may be measured at any other convenient temperature, and for short temperature intervals the corresponding value of "a" used.

The sp. gr. of pure raw linseed oil will vary with the source of the seed from a minimum of 0.931 at $\frac{15.5°}{15.5°}$ for oil from South American seed to 0.938 at $\frac{15.5°}{15.5°}$ for oil from Baltic seed.

The sp. gr. of an oil rises with oxidation or polymerisation. The iodine number is simultaneously lowered. Therefore, when a low iodine number is noted the sp. gr. should be determined simultaneously to permit of proper interpretation.

Unsaponifiable Matter.—The percentage of unsaponifiable matter of linseed oil wil vary from about 0.75% to a little over 1%, but should never be higher than 1.5%.

Either the extraction of the soap solution or of the dried soap will give satisfactory results.

Refractive Index.—Owing to the fact that the refractive index of linseed oil does not differ greatly from that of other oils, its value as a means of determining purity is somewhat limited. Ageing, blowing, polymerising, oxidising and treating with driers, all raise the index of refraction.

The temperature coefficient, $\frac{\delta n}{\delta t} = 0.00037$ · at temperatures between 25° and 40° applies to linseed as well as to many other vegetable oils. The refractive index varies with the source of the oil and on pure, untreated raw oils will raise as the iodine number and sp. gr. go up.

The limits at 25° for raw oil will be between 1.4789 for South American up to 1.4818 for Baltic.

Thompson and Dunlop (*Analyst*, 1906, 31, 281) give the following results:

Oil	Index of refraction, 25°
Argentine.....................	1.4789
Calcutta..	1.4793
North American........	1.4802
Russian (Petrograd)...........	1.4807
Russian (Riga)...........	1.4815

Ash.—The ash of raw linseed oil is very low. Because of the slight difference between the amount of ash in oils of poor and of good quality, the estimation cannot be used to advantage.

Thompson (*J. Soc. Chem. Ind.*, 1903, **22**, 1005) has estimation the ash in samples of oil, and obtained the following results:

1. Fresh, double filtered, raw, American linseed oil............. 0.1429% ash
2. Fresh, double filtered, raw, American linseed oil............. 0.1967% ash
3. Good well settled oil....................................... 0.0609% ash
4. Best American linseed varnish oil.......................... traces

Lewkowitsch has examined linseed oils containing 0.2% of ash and states that such oils deposit considerable quantities of mucilage. Brannt[1] gives the following analyses of ash:

	From linseed	From linseed cake
Potash............................	28.80	25.24
Soda..............................	1.66	1.64
Magnesia..........................	13.63	14.40
Lime..............................	8.59	8 45
Ferric oxide...................... ..	2.03	3.52
Chlorine..........................	0.06	1.31
Sulphuric acid....................	0.10	1.68
Silica............................	0.40	1.81
Phosphoric acid...................	44.73	41.98

The paralellism between the percentages of the various constituents of the ash of linseed oil and cake show clearly that the material of the oil which yields the ash has the seed as its source. That is, the matter is dissolved by the oil from seed in the crushing operation.

Extracted oil has a lower ash than expressed.

The American Society for Testing Materials (*loc. cit.*) has reported percentages of ash varying from 0.02% to 0.21%.

Moisture and Volatile Matter.—When used, this estimation should

[1] Animal and Vegetable Fats and Oils. 1896.

be made carefully, on account of the rapidity with which linseed oil oxidises causing gain in weight, or decomposes, causing loss if high temperatures be used.   An oil of good quality should, only contain from traces to 0.2% of material volatile at 105° to 110°.

Drying Time.—The drying time, that is, the period elapsing between the time the oil is exposed until it has set so that it will not wet an object placed in contact with it, is an important criterion of oil quality.   The drying time or rate of linseed oil is modified by several factors which obtain during exposure, chief among which are:

1. Character of surface on which exposure is made.
2. Thickness of film.
3. Temperature.
4. Degree and character of incident light.
5. Relative humidity.
6. Access of air.

In order to reduce to a minimum these variables the surfaces over which samples of linseed oil are made to flow should be absolutely free of grease, moisture, and other matter.   The writer has found that a slightly etched surface of glass gives more concordant results than a polished surface.   The thickness of film is determined by spreading a definite amount of oil over a predetermined area.   The other variables can be controlled by making the exposure in a room or a box provided with temperature, humidity and air circulation controls.

Because of these varying influences no reliable data are existent which can be cited to show the relation of the variations in the composition of linseed oil to the drying rate.

Gardner (*Circ. No.* 167, *Educ. Bur. Paint Mfgrs. Assn., U. S. A.*) describes an apparatus consisting of an alarm clock device fastened on an upright base.   Attached to the hour hand of the clock is a very lightly constructed wire wheel covered with a circular drum formed of light tin plate or of aluminum.   The drum is slotted to receive the test piece upon which the coating is applied.   This winds under the mandrel rod at the top of the drum and is pressed in contact at that juncture with a sheet of soft, light tissue paper of the same width as the test piece.   Both of these are automatically pulled from an adjoining double shelf stand, by the action of the clock.   Just so long as the coating is wet, it will stain the tissue paper at the joint of junction, the paper adhering quite tenaciously to the tacky film.   Just at the point of firm setting of the coating, the paper will no

longer be stained when it comes in contact with the test piece and will not adhere thereto during its subsequent journey around the drum.

The test piece, developed for this work after a trial of many materials, consists of a roll of celluloid moving picture film (waste short ends of undeveloped raw stock) that has been light struck but not developed. This material was selected because of its opacity (white silver coated surface) upon which, applied clear coatings are quite evident. Because of its great smoothness of surface, paint and varnish coatings do not penetrate it, but dry upon the surface somewhat as they would upon glass. Moreover, the solvents usually present in paint and varnish apparently do not affect the film, and they seem to evaporate in the same time as they would from tin or glass. Solvents of the ester type, or acetone-containing solvents, such as may be used in lacquers, could not be used. Moreover, such film is of a standard size and character of finish and is obtainable in practically any part of the country at a low cost from moving picture firms.

Eibner (*Chem. Umschau Fette, Oele, Wachse u. Harze*, 29, 269–274 and *C. A.*, 16, 4082) has worked out three short methods for the evaluation of drying oils, by means of certain film properties of the oxidised material.

(1) *The Oil Film Thermal Test.*—The thin oil film on the glass plate is cut into strips which are then tested for their melting power in the ordinary way. Films of the linseed oil group are infusible and carbonise at 240 to 260°, with evolution of gas. Small impurities of other oils or rosin cause the linseed oil film to melt at a lower temperature.

(2) *Colour Film Test.*—Red lead is rubbed with the oil and is spread on the glass plate. When dry without being sticky, the film is cut into strips shaken in cold ether. Linseed oil films are nearly insoluble and no red pigment enters the ether; poppy seed films dissolve largely and red lead falls to the bottom.

(3) *Colour-coat Test.*—The oil to be tested is rubbed with red lead and spread on a glass plate as in the No. 2 test. When dry without being sticky, the film is covered with squares of other colours also rubbed up with the same oil, and colours are selected which both aid and prevent cracking. Films of the linseed oil group show no cracking of the second coat, poppyseed oils do.

These three tests give concordant results among each other and permit of a classification of oils according to their technical applicability. This classification brings the linseed oil group into first place, then poppy oils, fish oils, olive oils and castor oil. A detailed discussion is given of this new classification, as compared with the customary one according to content of unsaturated fatty acids.

Specifications for Raw Linseed Oil.—The American Society for Testing Materials has issued specifications covering raw oil from North and South American seed. The two specifications were issued because it was thought that, if one was made to cover oils from the two sources, the wide limits necessary would permit of adulteration of an oil from North American seed and still have a product that would pass a specification for oil from South American flaxseed.

The A. S. T. M., specifications (*A. S. T. M. Standards*, 1921) for oil from North American seed follow:

Raw linseed oil from North American seed shall conform to the following requirements:

	MAXIMUM	MINIMUM
Sp. gr. at $\frac{15°.5}{15°.5}$	0.936	0.932
or		
Sp. gr. at $\frac{25°}{25°}$	0.931	0.927
Acid value	6.00	.....
Saponification value	195	189
Unsaponifiable matter	1.50	......
Refractive index at 25°	1.4805	1.4790
Iodine value (Hanus)	......	180

There is also in tentative position an item calling for a maximum of 2% foots by volume, when determined by the Walker-Wertz method.

The specifications (*Proc. A. S. T. M.*, 21, 613) for raw oil form South American seed follow:

Properly clarified, raw linseed oil from South American seed shall conform to the following requirements:

	MAXIMUM	MINIMUM
Sp. gr. at 15.°5/5.5°	0.9360	0.9310
Acid value	6.00	......
Saponification value	195	189
Unsaponifiable matter, %	1.50	......
Refractive index at 25°	1.4805	1.4780
Iodine value (Hanus)	......	170

The Interdepartmental Committee, Standard Specifications Board United States Government, has issued the following specifications:

RAW LINSEED OIL

	Maximum	Minimum
Loss on heating at 105 to 110° (%)............	0.2	....
Foots by volume (%).................	2.0	... ...
Sp. gr. 15.5°/15.5°.................	0.936	0.932
Acid value...................	6.0	. ...
Saponification value..........................	195.0	189.0
Unsaponifiable matter (%)...................	1.5	....
Iodine value (Hanus)[1].........................	....	170.0
Colour.....................................	Not darker than a freshly prepared solution of 1.0 grm. potassium dichromate in 100 c.c. pure strong (1.84 sp. gr.) sulphuric acid.	

[1] When raw linseed oil from North American seed is specified by the purchaser, the iodine value must be not less than 180 and the oil shall conform to all the other requirements as above.

The following is a table of some of the chemical characteristics of linseed oil:

CHARACTERISTICS OF LINSEED OIL

Sp. gr.......................................	0.931–0.937 at 15°
Solidification point.........................	−27°, stearine deposits at −25°
M. p.......................................	−16 to −20°
Flash-point...............................	450–500° F. (close), 258° open
Ash..	from traces to 0.2% (limit)
Free fatty acids............................	0.5%–3%
Unsaponifiable matter......................	up to 2.0%, average 1.5%
Saponification value.......................	189–195 mgrm. KOH, average
Reichert-Meissl value......................	0.50
Iodine value...............................	170–190, sometimes higher
Bromine values { absorbed......	105–115
addition...................	100–110
substitution............ ..	less than 7
Insoluble bromides........................	45 to 52%
Mauméne test............................	90–145
Bromine thermal value...........	29.8–33
Refractive index...............	1.4800–1.4825 at 15°
Optical rotation.....	Practically nil.
Acetyl value........	4 to 8.5

OXYGEN ABSORPTION

The drying of linseed oil is essentially an oxidation process, the final oxidation product being as yet unknown. During the drying

process considerable quantities of volatile products are formed, the quantity depending on several factors. The so-called oxygen absorption figure obtained by ascertaining the increase in weight of a film of oil on exposure to air does not represent the total quantity of oxygen actually taking part in the drying process, as no account is taken of that contained in the volatile products: thus Olsen and Ratner (*Eighth Int. Cong. Appl. Chem.*, 1912, *Sect. Ve, Orig. Commun.*, 12, 165) found that after 74 days drying, linseed oil had increased in weight 18.05%, whilst the volatile products collected by potash and calcium chloride amounted to 5.21% and 14.55% respectively— the total oxygen absorbed (assuming the increase in weight of the KOH and $CaCl_2$ to be CO_2 and water) amounted to 37.80%, the linseed oil having lost 1.87% of its carbon and 14.73% of its hydrogen in the process of drying. Friend (*Proc. Paint and Varnish Soc.*, London, 1914, 6, 145), after 65 days, found an increase in weight of oil of 9.35%, whilst volatile products amounted to 14.94%, giving a total oxygen consumed of 24.29%. The divergence in these figures illustrates the variable results obtained in investigations of this kind.

Sabin (*J. Ind. Eng. Chem.*, 1911, 3, 2) has shown that films of linseed oil or paint containing linseed oil increase in weight to a maximum in less than a week, after which these films begin to lose weight, though not so rapidly as they had gained.

With raw linseed oil the decrease in weight after 8 months was about $\frac{9}{10}$ of the increase, and even at this stage the decrease was continuing. It therefore appears that the oxidation of linseed oil has no definite end point, solid linoxyn apparently still losing volatile matters and becoming transformed into the fluid superoxidised linseed oil described by Reid. For analytical purposes the limitations of present experimental methods must be taken into account when considering the results obtained by the various methods proposed. The volatile products evolved during the drying of linseed oil have been shown to have definite germicidal value and the hygienic value of paint has been demonstrated in this connection. These products have been shown to contain the lower fatty acids and aldehydes. There is distinct evidence that the chemical constitution of the oxidised product and the volatile product evolved by drying oils varies with the temperature of oxidation.

Fahrion (*Zeit. angew. Chem.*, 1910, 23, 722), from a study of the drying processes of linseed oil, is of the opinion that the chemistry of the drying of the oil is essentially the same as that of the drying of the fatty acids and further that the addition of siccatives does not alter the process, except in so far as auto-oxidation is accelerated. Fahrion (*Farb. Zeit.*, 1912, 17, 2530 *et seq.*), gives the following characteristics of a linoxyn film obtained by drying a film of linseed oil on glass plate for 10 days:

```
Fatty acids........................................ 25.3%
M. p. of acids..................................... 38.0°
Iodine value of acids.............................. 42.9
Hydroxy acids, soluble in ether.................... 40.2%
Hydroxy acids, soluble in alcohol.................. 20.2%
Iodine value....................................... 28.3
Hehner value....................................... 85.7
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Ingle (*J. Soc. Chem. Ind.*, 1913, 32, 639) is of the opinion that he has established the following points:

(1) In the oxidation of a drying oil in air, the amount of oxygen absorbed in dry air is in the ratio of 2I to 2O, but, if the air be moist, the peroxides thus formed are decomposed with the production of volatile compounds—aldehydes and acids.

(2) That the free acids of linseed and other oils absorb only half the amount of that absorbed by their glycerides. The same remarks apply to their ethyl salts, these only absorbing 1 atom of oxygen for every 2 atoms of iodine absorbed.

Fritz and Zymandi (*Chem. Rev. Fett Ind.*, 1914, 21, 43) give the following values for oxidised linseed oil:

	Walton oil, 4 samples	Rapid oxidation oil, 2 samples	Runnings, 1 sample
Consistency...................	Hard	Very soft	Very soft
Sp. gr. water at 4°............	1.0862 at 15° to 1.0734 at 21°	....	1.0693 at 20°
Iodine value (Wijs)............	61.8 to 65.5	96.2(I)	98.4
Ash, %.........................	1.16 to 1.41	0.15(I)	4.36
Unoxidised fatty acids, %......	26.2 to 31.2	43.5 to 49.4	50.7
Oxidised fatty acids, %........	46.4 to 56.4	42.1 to 42.5	20.0
Water soluble fatty acids, %...	5.5 to 8.6	2.7 to 5.7	8.3

Fokin (*J. Russ. Phys. Chem. Soc.*, 39, 607; 40, 276) states that the rate of setting of a linseed oil film follows Spring's rule, in that it is doubled for every 10 degrees rise in temperature; moisture retards the time of setting.

Genthe (*Zeit. angew. Chemie*, 1906, **19,** 2087) showed that the rate of oxidation of linseed oil exposed to ultra-violet light was greatly accelerated. In the dark the maximum absorption was reached in 50 days, whereas when exposed to light from a mercury lamp the maximum was attained in 25 hours. Under these conditions linseed oil was found to absorb 34% of its weight from the atmosphere.

Coffey (*J. Chem. Soc.,* **119,** 1152, C. A. **15,** 3559) says that curves representing the gain in weight of linseed oil films on exposure to air show only the apparent oxygen absorption, because of a simultaneous loss of volatile products. Absorption of oxygen at 100° was measured by exposing a film of the oil within a flask filled with oxygen and noting changes in pressure within the flask at frequent intervals. With widely varying amounts of oil results concordant within 1% show that linseed oil absorbs a mean of 28.7% oxygen: and linseed oil fatty acids 30.09%. Volatile products from oil oxidised in air at 100° showed strong positive reaction, of H_2O_2. Oxidising the oil in oxygen at 100° and absorbing the volatile products in $Ba(OH)_2$ showed CO_2 equal to 5.4% of the original oil, equivalent to 3.9% O; and volatile carboxylic acids, present chiefly as acetic acid, also equivalent to 3.9% O. The total true oxygen absorption is greater than that called for by the theory of molecular autoxidation (*i. e.,* addition of oxygen at the double linkages) by an amount approximately equivalent to the oxygen found in the volatile products. This indicates that, whilst the primary reaction in the oxidation of linseed oil is molecular autoxidation, there is a further excess oxidation. The glyceryl radical appears to have no effect on the mechanism of the oxidation reaction, but the free fatty acids oxidise more rapidly. Coffey thinks that linolic and alpha-linolenic acids, the drying constituents of linseed oil, probably oxidise differently. The true oxygen absorption of pure beta-linolenic acid was found to be 38.5% and from the oxygen absorption of mixed acids the true oxygen absorption of the alpha-linolenic acid was calculated as 51.4%, corresponding to 9 atoms of oxygen per molecule of alpha-linolenic acid $(C_8H_{30}O_2)$. This is 3 atoms of O more than is required for simple molecular oxidation. Coffey suggests an oxidation process whereby one molecule of CO_2 and one of acetic acid per molecule of alpha-linolenic acid are formed. Such a process agrees with the amounts of CO_2 and acetic acid actually found in the volatile products given off during oxidation, and

indicates that all volatile oxidation products from linseed oil come from the linolenic acid only. The true oxygen absorption of linolic acid was found to be 24.4%, which means that it simply oxidises by addition of O_2 to each unsaturated linkage to form linolic acid diperoxide.

From these data Coffey calculated the percentage composition of linseed oil as noted on page 460.

The property which linseed oil possesses of absorbing oxygen is the fundamental one which is the basis of all of its applications, except that of making soap. In other words, in practically all places where linseed oil is used the reason of its employment is its ability to absorb oxygen. The rate varies with the conditions obtaining during exposure, particularly temperature, moisture, degree of light and quality of the oil.

Oxidation causes a lowering of the iodine value and of the hexabromide percentage. It simultaneously raises the sp. gr., the saponification value, the acid value, the refractive index, acetyl value and viscosity. The rate of drying is also increased when the oil is partially oxidised. There is no effect produced upon the unsaponifiable matter and very little change is made in the molecular weight. There are produced, however, insoluble oxidised acids which separate out when the partially oxidised oil is mixed with petroleum spirit. The amount of these insoluble acids depends upon the extent of the oxidation and also upon the composition of the oil, for the larger the amount of linolenic acid present, the greater will be the percentage of insoluble acids. During oxidation there is a gain in weight proportional to the amount of oxygen absorbed and there is, also, a simultaneous contraction in volume.

When raw linseed oil is spread in a thin film upon glass, it will dry to the touch when there has been a net increase in weight of from 16% to 18%.

Polymerised Oil.—Another very important property of linseed oil is its ability to polymerise, which process results in an increase in the viscosity or consistence of the oil, proportional to the degree of polymerisation.

These polymerised oils are known as litho oils or lithographic varnishes.

Friend (The Chemistry of Linseed Oil, 1917.) says that, when heated in the absence of air, linseed oil gradually thickens and its iodine value falls, as does also its yield of hexabromide. This is well

illustrated by the following figures given by Ingle (*J. Soc. Chem. Ind.*, 1911, **30**, 344), who examined samples of oil that had been kept for varying lengths of time at 195°–200°:

Duration of heating, hours	Density	Iodine value	% Hexabromide
0	0.9315	179.5	35.3
2	0.9350	175.5	30.7
4	0.9383	170	27.4
6	0.9148	165	26.2
11	0.9501	154	16.0
15.5	0.9583	145	10.5
43	0.9800	121	0.9

Closely similar results are obtained by heating the oil for shorter periods at higher temperatures. A particularly interesting series of experiments was carried out along these lines by Krumbhaar, (*Chem. Zeit.*, 1916, **40**, 937). Other useful data are given by Kitt, (*Chem. Rev.*, 1901, **8**, 40; Leeds, *J. Soc. Chem. Ind.*, 1894, **13**, 203), from which the following data are taken. The oil was heated in a current of carbon dioxide, so that the effects of oxidation were entirely excluded from the results.

Temp., °	Duration, hours	Acid value	Saponification value	Viscosity (relative)	Iodine value	Refractive index 25°	Sp. gr. 25°
....	....	1.1	194.5	1.00	175.0	1.479	0.924
200	20	2.6	193.9	1.13	168.7	1.480	0.926
200	40	3.4	194.8	1.35	160.1	1.482	0.929
260	15	5.8	192.0	2.35	145.6	1.486	0.933
260	30	7.4	191.1	7.96	108.0	1.489	0.946
300	10	17.8	193.1	115.0	120.4	1.492	0.961
300	20	40.0	191.2	(no flow)	76.3	1.496	0.970

The acid value showed a remarkable rise, whilst the saponification value remained fairly constant. Of particular interest are the relative viscosities, the final 40° rise in temperature causing a thickening out of all proportion to the effect produced at 260° and below. After 20 hours at 300° the oil was so thick that it ceased to run, and its viscosity could not be determined. The refractive index and density rose with the viscosity.

The fall in the iodine value led Fahrion (*Zeit. angew. Chem.*, 1892, **5**, 171), in 1892, to suggest that polymerisation had taken place, and this was confirmed by Fokin (*Ref. Augsb. Seifens-Ztg.*, **34**, 821) who found that by heating linseed oil in a sealed tube to 250°–

300° a substance of molecular weight approximating to 2000 was obtained. Other investigators have obtained analogous results, *e.g.* Morrel, (*J. Soc. Chem. Ind.*, 1915, **36**, 105). The figures in the accompanying table show that polymerisation may be observed at temperatures as low as 200°, and that it rapidly increases in extent with rise of temperature and with the duration of the heating. (Friend, *Trans. Chem. Soc.*, 1917, **111**, 162.

Duration of heating, hours	Temperature,°	Molecular weight	Coefficient of expansion with rise of temperature
0	...	740	0.000760
30	200	760	0.000743
36	300	1000	0.000741
42	300	1420	0.000717

It is interesting to note that the coefficient of expansion with rise of temperature shows a steady decrease as the molecular weight rises.

Morrell (*loc. cit.*) found that linseed oil, thickened at 260°–280° C., contained two modifications (C.f. Kronstein, *Ber.*, 1916, **49**, 722; 1902, **35**, 4150) both of which were soluble in petroleum spirit but one only in acetone. The properties of these are given in the following table:

		Thickened oil	
	Original linseed oil	A Part insoluble in acetone	B Part soluble in acetone
Sp. gr. (15°).............	0.933	0.9763	0.9527
Refractive index..........	1.4831	1.4964	1.4846
Molecular weight.......	805	1788–2517	904–975
Saponification number....	197	190–204	193
Iodine value..........	185	97–121	92–143
Acid value............	0.4	0.2	7.5–8.0

Approximately equal quantities of the two components A and B were present in the oil thickened at 260°. Part A exhibits every evidence of polymerisation, its density and refractive index being

considerably higher than that of the original oil, whilst its molecular weight is twice or three times as great. The lead and barium salts of these oils were prepared, and from them the free organic acids. It was found that all traces of linolic and linolenic acids had disappeared, and Morrell concludes that linkage changes must have occurred during thickening and anterior to the polymerisation. The probability is that linolenin, or if mixed glycerides are present, those containing linolenic acid, are the first to undergo polymerisation on account of the higher condition of unsaturation of linolenic acid, and are hence the main source of component A. The remainder, B, will thus be derived largely from the glyceride containing linolic and other more saturated acids. This receives substantial support from the fact that thickened poppy-seed oil closely resembles component B. Now raw poppy-seed oil contains linolic acid but practically no linolenic acid. The inference is clear.

From the foregoing it is evident that the thickening of linseed oil in the absence of oxidation is due to polymerisation, the first stage being the formation of a product insoluble in acetone consisting of polymerised glycerides. The precise constitution of these complexes is at present unknown.

The rate of polymerisation is closely related to several variables, the most important of which are the temperature maintained, the mass of the oil, the quality of it, and, to a slight extent, the length of time the oil has been aged previous to being heated. The higher the temperature, the more rapidly the oil will polymerise and, consequently, increase in viscosity. Very slow polymerisation is effected at temperatures under 280°. Quite rapid action takes place at 300°. A large proportion of the oils treated are carried at 315°, whilst 330° is the maximum of general practice.

The higher the iodine value of the oil, the more rapidly it will polymerise. This is due, of course, to the greater number of unsaturated linkages.

Generally speaking, the older the oil, the more rapidly it will body.

The loss in weight is an important consideration in the polymerisation of linseed oil because it is of economic value. The loss is, to a very large extent, dependent upon the mass. That is, when the same oil, in varying amounts, is heated under predetermined conditions to a definite viscosity, the loss will be

less when the largest amount of oil is used. Laboratory determinations, for instance, will show a loss of 10% to 15%, whilst the same operation in the factory in the usual 100 gallon batch will sustain a loss as low as 1% and not greater than 5% in obtaining the viscosity. The oil which loses the least in a required heat treatment is the most economical to employ.

The rate of formation of free acids is also dependent upon the temperature. Generally speading the higher the temperature, the greater will be the amount of free acid present in the finished oil.

REFINING

In order to fit linseed oil for certain special requirements for which the raw product is not applicable, it is refined, There are two general methods for accomplishing this. They are, by treating with sulphuric acid and with alkali solutions.

The acid refining is employed because of its ability to bleach the oil, thus producing a product which will change to the minimum extent the colours of white and delicately tinted paints of which it is the vehicle. The operation essentially consists in adding sulphuric acid of varying dilutions and in amounts up to 2% to the raw oil while under agitation. After a thorough mixing, the oil is allowed to rest, when the sulphuric acid and matter which it has coagulated, separate out as a black, sticky mass. The supernatant oil is decanted from the surface and the acid removed by washing or by fuller's earth. The colour will vary from a pale straw shade to a golden yellow depending upon the efficiency of the operation.

This procedure also causes hydrolysis to a varying extent. Bleached oils are sought with acid values from 4 to 15. If a good raw oil is employed this minimum can be obtained. The acid bleached oils are used for grinding pigments and reducing pastes to a brushing consistency. As a rule, the high acid oils are employed for mixing and grinding with white lead, particularly in pulp mixing, and to some extent, with mixed paints when an increased consistency of the paint is desired. The low acid oils are generally used with zinc oxide and with paints high in this pigment. Extracted oil bleaches to a paler shade than can be obtained with expressed oil. The amount of acid required is considerably lower with solvent extracted linseed oil.

When linseed oil is to be used in the varnish kettle, it must not "break," and must bleach to as pale a shade as possible and must darken to the minimum extent during polymerisation. An oil possessing these qualities to the greatest extent is one refined by an aqueous solution of sodium hydroxide. The details of the process vary with different operators. When properly carried out, the oil resulting will be of a pale, golden yellow or straw colour, will bleach almost "water white" when heated to 300° and will yield a viscous oil of pale straw colour. There is little change made in the constants of the raw oil except that of acid number. If the operation is skillfully performed, the oil will be practically neutral when used. Extracted oil gives more satisfactory colours when polymerised after refining with caustic alkali solution.

The Interdepartmental Committee, Standard Specifications Board, United States Government (*loc. cit.*), give the following as specifications covering refined oil:

REFINED LINSEED OIL

Contract shall state whether acid refined or alkali refined is desired.

	Maximum	Minimum
Loss on heating at 105–110° (%)	0.2	....
Foots by volume (%)	0.2	....
Sp. gr. at 15.5/15.5°	0.936	0.932
Acid number (acid refined oil)	9.0	3.0
Acid number (alkali refined oil)	3.0	....
Saponification number	195.0	189.0
Unsaponifiable matter (%)	1.5	....
Iodine number (Hanus)[1]	....	170.0
Colour	Not darker than a freshly prepared solution of 0.1 grm. potassium dichromate in 100 c.c. pure strong (1.84 sp. gr.) sulphuric acid.	

[1] When refined linseed oil from North American seed is specified by the purchaser, the odine number must be not less than 180 and the oil shall conform to all the other requirements as above.

AIR TREATED OILS

For certain purposes where the colour of the polymerised product is not important, as in patent leather, dark varnishes, black enamels and certain grades of linoleum, the raw oil is treated with air to a moderate extent. This prevents the "breaking" of the

oil when heated to high temperatures. Also, because of the partial oxidation, the rate of increase in viscosity at any given temperature is increased and the loss sustained reduced somewhat. Oil for this purpose is usually oxidised by the passage of a relatively large volume of air through it at high temperatures. The operation is continued until the oil has a sp. gr. of approximately .950 at 15.5°. If the operation is carried a shorter time, the sp. gr. will be lower and the bodying rate slower, whilst the kettle activity will be moderate. As the operation is continued, the bodying rate and kettle activity increase. The operation reduces the iodine value and content of hexabromide and raises the acid value, the saponification value, the index of refraction and the sp. gr.

BOILED LINSEED OIL

The rate of drying or oxidation of raw linseed oil is comparatively slow in that it requires from 48 to 72 or more hours to complete the reaction, when the oil is flowed in a thin film over glass or other non-absorbent surface. This rate is too slow for many of the purposes for which linseed oil is employed. It is necessary, therefore, to accelerate the drying of the oil. This is done by adding substances which cause a more rapid absorption of oxygen under the normal conditions of exposure. These substances are termed driers. They are metals which can form more than one oxide, provided that the salts of the lower oxides are more stable than the salts of the higher oxides. Such small quantities of these metals in active state are required that they fall into the class of catalysts. Mackey and Ingle (*Jour. Soc. Chem. Ind.*, 1917, 36, 319) classify metals in the following order of descending powers of drying: Co, Mn, Ce, Pb, Cr, Fe, U, Na, Ag, Zn, Hg, and Al. By far the most common of the driers are manganese, lead, and cobalt, though iron, in the form of Prussian blue, is used in the patent leather industry. Manganese is considered by Ingle to be less satisfactory than lead, although its oxidising power is greater and in his opinion has much to recommend it from general practice. It is necessary that the metal be in a form in which it is soluble in linseed oil when added to that liquid, or that can be slowly dissolved by the oil during the period of contact previous to, and during, the drying operation.

Action of Driers.—Morrell and Weale (Rubber, Resins, Paints, Varnishes, 1920, 70) say that the metallic driers are catalysts and

that, the term catalysis as defined by Henderson (Catalysis in Industrial Chemistry, 1919) is more generally used to designate those chemical changes of which the progress is modified by the presence of a foreign substance: the agent which produces the effect is called a catalyst. The theories advanced to explain the mechanism of catalysts fall into two classes: (*a*) chemical and (*b*) physical.

The chemical theories of drying depending on the formation and decomposition of unstable intermediate products are the most favoured, although the importance of the physical aspect is growing. On Engler's hypothesis of catalytic oxidation (*Ber.*, 1897, **30**, 1669) oxygen (actor) oxidises the metal of the drier (inductor), which in turn oxidises the oil (acceptor). In the description of the general properties of linseed oil it was pointed out that molecular oxygen was absorbed at the double linkages, with the formation of peroxides. The peroxides are components of "linoxyn," the oxidised skin of the oil. It was pointed out that these peroxides may undergo transformation into oxides or yield ketones or hydroxyketones.

It is possible that cobalt and manganese may produce superoxidised oil in which all the double linkages are attacked, and such a condition would not favour durability, because of the possibility of degradation into simpler molecules.

The metallic elements act as oxygen carriers or as pseudocatalysers serving to stabilise or assist in the formation of the autocatalytic peroxide, and very small amounts are able to effect the drying of large quantities of oil. Many theories have been put forward to explain the action of the metal and much work has been done by many investigators, but none are entirely satisfactory, owing to the difficulty of investigating the products of the reaction.

The physical theory of catalysis seeks to explain the phenomena as due to the condensation or increase in concentration of the reacting substances at the surface of the catalyst, such increase in concentration being due to the action of capillary forces (Henderson, Industrial Catalysis, 1919). This aspect has been neglected in the consideration of paint and varnish drying problems (British Association Reports, 1920). The influence of surface phenomena is of great importance, and the activity of the metallic driers is due partly to chemical and physical causes. It must be remembered that substances of a colloid nature are under consideration in

paints, varnishes and oils, and the activity of metals in solutions containing colloids is more active than in aqueous solutions. If the surface tension to air of a lead drying oil is lower than that of the oil (there is reason to believe that this is so) the surface concentration of the lead would be increased. A more careful study of Livache's method by drying in the presence of finely divided lead would establish a connection with the phenomena observed when unsaturated oils are reduced with hydrogen in the presence of metallic catalysts. It is for the chemist to decide from the examination of the products of oxidation the chemical changes which have occurred. It would appear that the activity of driers is to be attributed to causes put forward by both theories taken together.

Coffey (*J. Chem. Soc.*, 121, 17) says that the determination of the true oxygen absorption values shows that the addition of a drier modifies the course of the oxidation, and does not act as a catalyst in the strictest sense. The presence of driers lowers the final oxygen absorption and shortens only the induction period of the oxidation, whilst the rate of the main oxidation remains unaltered. The oxidation curves do not run parallel to the curve for the oil alone and deviate considerably from the logarithmic curve suggested by Fokin. The amount of carbon dioxide evolved is approximately the same whether driers are present or not, but an accurate estimation of other volatile products is impossible on account of the basic properties of the driers. No trace of the formation of hydrogen peroxide in the presence of driers could be detected.

In the use of these metals the lead, manganese, and cobalt compounds are combined with oil, with resins or, perhaps, with other substances by the aid of heat or by precipitation methods. This operation converts the metals into compounds which are soluble in linseed oil and, therefore, active during the drying process. When the compounds are used in the manufacture of boiled oil, they are not thinned, and are termed crushers' driers, but when employed by being added to raw oil, the compounds are thinned with volatile liquids such as turpentine or petroleum distillates. They are then termed liquid driers, or siccatives. Generally, crushers' driers will contain from 2 to 8% of ash, a large proportion of which is lead and manganese, in the form of oxides. Such a drier as this cannot be too concentrated, because it would then become a paste and be hard to handle, instead of a liquid which can be pumped from point to point. In the manu-

facture of boiled oil, these driers are added, in amounts proportional to their strength, to raw oil under agitation.   Heat is applied until the oil reaches a certain maximum temperature which is set by the manufacturer.   It varies in the United States from about $105°$ to $150°$.

The analyses of several samples of boiled linseed oil show lead and manganese in all of them.   The maximum amount of manganese obtained by an analysis of these oils was 0.09% by weight of the oil, expressed as metallic manganese.   The minimum was 0.04%, whilst the average was 0.06%.   With lead the maximum was 0.37%, expressed as metallic lead, the minimum was 0.05%, whilst the average was 0.16%.   Davidson has shown that with manganese the maximum drying efficiency, when used with linseed oil, is reached at a concentration of 0.08% of metallic manganese, but that at about 0.04% a very satisfactory rate of drying is established, nearly as rapid, in fact, as at 0.08%.   When used in amounts above about 0.1% of manganese the drying rate is retarded.   With lead he shows that the effect is slight below 0.5% of metallic lead, and that it reaches its maximum effect at 1.4%.   It nears its maximum activity, however, at about 0.9%.   From this we can see that only a small amount of drier is necessary.

There is a tendency to add too much drier.   This is particularly harmful in the use of manganese, because it retards the drying and makes the film rather sticky and tacky.   An excess of lead does not seem to slow up the drying rate, but does cause a softening of the film.   Because the oxidation of drying oils is a continuous process, resulting in the decay of the film of which they form the binder, and because driers hasten this reaction and are otherwise detrimental, it is good policy to use the minimum amount of drier possible, consistent with the drying rate required, in all coatings of which drying oils are an integral part.   When manganese and lead are employed together, the result is better than if either one is the only drying agent.   The drying rate is more sure, and less influenced by climatic conditions and temperature than when a single drying agent is adopted.   Particularly is this true of manganese, which, when used alone, is quite erratic.   Under certain conditions, an exceedingly small amount of manganese will cause linseed oil to set in a sufficiently short time, but when those conditions are changed, as, for instance, a lower average temperature and a higher degree of humidity,

the drying is slowed up materially. This does not happen to nearly so great an extent when lead and manganese are employed together. When manganese is used with lead the total amount of drier necessary is considerably less than when lead alone is employed.

To obtain the greatest efficiency, considered from the rate of drying obtained and from the service rendered by the coating, it is necessary to have the driers in perfect solution in the oil, and to use the lowest possible amount necessary to produce a satisfactory drying rate.

The American Society for Testing Materials (*loc. cit.*) have issued the following standard specifications for the purity of boiled linseed oil from North American seed and tentative specifications for that from South American seed.

Boiled linseed oil from North American seed shall conform to the following requirements:

	Maximum	Minimum
Sp. gr. at $\frac{15.5^\circ}{15.5^\circ}$	0.945	0.937
Acid value	8	.....
Saponification value	195	189
Unsaponifiable matter, %	1.5	.....
Refractive index at 25°	1.484	1.479
Iodine value (Hanus)	.....	178
Ash, %	0.7	0.2
Manganese, %	.....	0.03
Calcium, %	0.3	.....
Lead, %	.....	0.1

Boiled linseed oil from South American seed shall conform to the following requirements:

	Maximum	Minimum
Sp. gr. at 15.5°/15.5°	0.945	0.936
Acid value	8.00	.....
Saponification value	195	189
Unsaponifiable matter, %	1.50	.....
Refractive index at 25°	1.4840	1.4780
Iodine value (Hanus)	.....	168
Ash, %	0.7	0.2
Manganese, %	.....	0.03
Calcium, %	0.3	.....
Lead, %	.....	0.1

The Interdepartmental Committee, Standard Specification Board, United States Government (*loc. cit.*), issued these specifications for boiled linseed oil:

BOILED LINSEED OIL

Boiled oil shall be pure, well-settled linseed oil that has been boiled with oxides of manganese and lead. It shall conform to the following requirements:

	Maximum	Minimum
Loss on heating at 105 to 110° (%)............	0.2	....
Sp. gr. at 15.5°/15.5°......................	0.945	0.937
Acid value......	8.0	. .....
Saponification value........................	195.0	189.0
Unsaponifiable matter (%)....................	1.50	....
Iodine value (Hanus)[1]......................	....	168.0
Ash (%).............................	0.7	0.2
Manganese (%).............................	....	0.03
Lead (%).............................	....	0.1
Time of drying on glass (hours)........... . ..	20.0	....

[1] When boiled linseed oil from North American seed is specified by the purchaser, the iodine number must be not less than 178 and the oil shall conform to all the other requirements as above.

EFFECT OF STORAGE

The effect of the storage of linseed oil in closed vessels is illustrated by the following analysis made by Klein: Storage in closed vessels does not appear to effect any considerable change. The following values were obtained by the writer from a sample of genuine Baltic linseed oil, which had been stored in a closed vessel for 40 years:

Sp. gr. 15°/15°.....................................	0.9348
Saponification value................................	190.3
Acid number..	4.32
Iodine value..	166.6
Unsaponifiable matter..............................	0.67%
Yield of hexabromide..............................	22.4%
M. p. of fatty acid, hexabromide....................	177.0°

These figures appear to confirm the opinion of Fahrion that during storage the unsaturated acids polymerise, but the effect is not very marked in a period of 40 years.

The effect is further illustrated by the following table which is taken from the results of Committee D-1 of the American Society for Testing Materials:

Property considered	Year	Samples			
		1	2	3	4
Sp. gr. $\frac{15.5°}{15.5°}$	1909	0.9347	0.9331	0.9331	0.9344
	1911	0.9342	0.9329	0.9331	0.9344
	1915	0.9348	0.9334	0.9334	0.9345
Acid value	1909	1.15	3.50	1.94	1.58
	1911	1.39	4.38	2.79	1.86
	1915	1.61	5.09	3.64	2.10
Saponification value	1909	190.6	190.1	190.1	190.2
	1911	190.7	190.8	190.2	190.4
	1915	191.5	191.8	191.9	191.5
Unsaponifiable matter	1909	0.99	0.96	0.99	0.98
	1911	0.96	0.95	0.99	1.04
	1915	1.12	1.13	1.04	1.22
Refractive index at 25°	1909	1.4800	1.4794	1.4797	1.4797
	1911	1.4799	1.4792	1.4793	1.4794
	1915	1.4807	1.4797	1.4801	1.4800
Iodine value (Hanus)	1909	187.9	184.5	186.1	186.0
	1911	186.9	183.0	186.0	184.1
	1915	188.2	185.2	187.4	186.0

This oil was stored either in brown glass bottles or in sealed 5 gallon tin cans. It will be seen from these results that, under the conditions described, the changes in the oil over a period of 5 years are not material.

If the same oil were stored in factory tanks of ordinary dimensions, the changes would be no greater. If, however, the oil is stored in small amounts as, for instance, in thin layers in the bottom of tanks where the ratio of surface to volume is high, material changes will result owning to oxidation.

The reactions that take place during storage are the elimination by precipitation of a large proportion of the moisture and the dissolved material which forms the "break," together with a separation of a certain amount of the saturated fats which are present. The temperature at which the oil is stored influences particularly the last item, for some of these substances do not separate out at the higher temperatures. In other words, if the oil is stored in-doors

in heated rooms the amount of fats which will separate out will be less than if storage takes place out-of-doors.

DETECTION OF ADULTERANTS IN LINSEED OIL

Linseed oil may be adulterated in a variety of ways. The particular adulterant used is largely dependent upon the prevailing prices of linseed oil and of the possible adulterants. The likely adulterants are hydrocarbon oils, the semi-drying oils, such as cottonseed, soya bean, and rape oil (when cheaper), fish oil, and rosin oil.

Numerous colour tests have, at times, been described and used but in most cases they lack accuracy and, therefore, no authoritative statement can be based upon them.

The hydrocarbon oils are qualitatively detected by saponifying a few drops of the oil with alcoholic potassium hydroxide and then diluting with an equal volume of distilled water. The presence of mineral and rosin oils is indicated by a cloudiness caused by an emulsion due to the presence of unsaponified matter. The accuracy of this test is dependent upon the complete saponification of the oil and the use of distilled water, for if there are salts in the water insoluble soaps will precipitate which might be mistaken for an emulsion due to unsaponified oil. The mineral and rosin oils can be estimated approximately by the determination of the saponification value. The percentage can be estimated by using a saponification value of 190 as a basis for the calculation. The determination of the amount and the character of the hydrocarbon adulterant can be made by an estimation of the unsaponifiable matter.

Fish oil can be qualitatively estimated by the test of Eisenshiml and Copthorne (*loc. cit.*). In experienced hands, the odour may also be used as a means of identification. An increase in the percentage of hexabromide and the action of the hexabromide precipitate on heating would also indicate the presence of fish oil. The insoluble bromides of fish oil will not melt but blacken, whereas those from linseed oil will melt.

The semi-drying oils are harder to detect. When adulteration in large amount has been carried on, the reduction in sp. gr. and iodine value will indicate the presence of the foreign oils. However, due to the range of these figures which applies to pure raw linseed oil, the results are not certain. When accurately made, the estima-

tion of the percentage of insoluble hexabromide is the best test, for the range of the per cent. of this compound is lower for linseed oil than is the case with most of the other estimations. Experience, however, in the handling of this estimation is a prerequisite of accurate results as the matter stands today. An examination of the oxidised film will indicate the presence of semi-drying oils. The suggestion of Eibner (*loc. cit.*) may be employed in this connection. Lewkowitsch (Chem. Tech. Anal. Oils, Fats, Waxes, 6 Ed., Vol. 2, 70) writes on this subject: The presence of considerable quantities of drying oils, such as candlenut oil, safflower oil, sunflower oil, and expecially soya bean oil, is indicated by an iodine value lower than 175. Their presence would also be indicated by the bromide test, if the yield of the ether-insoluble bromides of the mixed acids falls below 45%. Since tung oil and poppyseed oil yield no ether-insoluble bromides, safflower, soya bean, and walnut oils a very small quantity only, and candlenut oil less than half of the quantity to be expected from linseed oil, the bromide test will be found of greater help than the iodine test.

An inducement to adulterate linseed oil with cottonseed oil will only present itself whenever the latter is cheaper than linseed oil. The presence of cottonseed oil would be detected by a low iodine value of the sample. The Halphen colour test should be applied as a confirmatory test; the melting-point of the fatty acids should also be determined. In the presence of considerable quantities of cottonseed oil, the "titer test" number will be considerably above $20°$.

Rape oil is indicated by a lower saponification value than the normal one (of course, in the absence of unsaponifiable oils). A few per cent. of rape oil, such as are frequently present in commercial linseed oil, will not be detected thereby. The saponification value will, however, in many cases afford some guidance as to the excess of foreign seeds in the linseed from which the sample has been obtained. In important cases the estimation of erucic acid must be carried out.

Fish Oils—Blubber Oils.—Since fish oils absorb fully as much iodine as linseed oil does, and yield as much and even more ether-insoluble bromides, the quantitative tests alone will not give a satisfactory answer, and it is imperative to take the m. p. of the bromides. From linseed oil, a white or only slightly yellowish hexabromide is obtained, melting sharply without decomposition at $175°–180°$, whereas the octobromides from fish and blubber oils become dark or

almost black at 200°, and do not melt.   Even 10% of fish oil can thus be detected.   In doubtful cases the phytosteryl acetate test will furnish a reliable means for the detection of fish (liver) and blubber oils.   Crystallised phytosteryl acetate from pure linseed oil melts at 128°–129° (Bömer and Winter).   In the presence of cholesterol the m. p. of the acetate is much lower.

Rosin (colophony) is best detected qualitatively by applying the Liebermann-Storch reaction.   If the colour of the sample be very dark, it is best to warm it with alcohol, so as to extract the bulk of the colophony, and test the alcoholic extract.   The amount of rosin can be estimated quantitatively by titrating the sample with aqueous standardised alkali, using phenolphthalein as an indicator. From the amount so found, there must be subtracted the amount of alkali used for neutralising the free fatty acid in linseed oil, which rarely exceeds about 3%.   Test experiments made in the revisor's laboratory with mixtures of linseed oil and rosin proved the reliability of this method.   If, however, a large amount of linseed oil fatty acids is present, as in linseed oil soap stock (see Vol. III), the amount of rosin in the alcoholic extract must be determined quantitatively by Twitchell's method.

Another important phase of the analysis of linseed oil is that of determining the purity of the vehicles from mixed paints and other protective coatings.   The oil must first be separated from the other material by extraction.   If nothing but volatile thinners and driers have been used in the manufacture of the paint, this operation can be carried out with fairly good results.   But, when treated oils or varnishes have been employed as constituents of the vehicle, the problem becomes one that is impossible of correct solution.   Great care must be taken in the extraction operation to prevent oxidation of the oil and contamination with solvents.   After the liquid has been separated, the volatile material can be removed best by a steam distillation followed by drying of the residual liquid in a current of hydrogen or carbon dioxide.   Then an analysis can be made by the usual procedure, upon the results of which dependence can be placed.

It must be remembered that oils extracted from paints containing reactive pigments such as white lead and zinc oxide frequently carry appreciable amounts of these metals in solution.   Amounts are encountered sufficient to vitiate the results of an analysis, because

ORIGINAL OIL

Pigment used	Sp. gr.			Ash, %			Iodine value			Acid value		
	G	B		G	B		G	B		G	B	
	0.932	0.934		0.19	0.13		181.0	179.6		2.5	1.7	
	2 years	1 year	2 years	2 years	1 year	2 years	2 years	1 year	2 years	2 years	1 year	2 years
White												
Zinc oxide................	0.9237	0.935	0 934	0.360	0.25	0.13	161.0	181.3	179.7	3.5	......	......
Basic carbonate white lead..........	0.9372	0.940	0.938	1.149	0.35	0.40	157.5	175.0	177.3	8.6	......	......
"Leaded zinc"................	0.9389	......	......	0.922	......	......	157.4	......	......	5.7	......	......
Basic carbonate white lead 50%...... / Zinc oxide 40%................ / Barytes 10%................	......	......	......	0.674	......	......	154.1	......	......	6.7	......	......
Basic sulphate white lead 60%....... / Zinc oxide 40%................	0.9334	......	......	0.626	......	......	157.8	......	......	5.6	......	......
Barytes................	0.9325	......	......	0.212	......	......	169.6	......	......	3.5	......	......
Silica................	0.9465	......	......	0.204	......	......	149.2	......	......	8.7	......	......
Black												
Kaolin containing CaSO₄............	......	0.939	0.936	......	0.12	0.14	......	173.0	171.6	......	..	..
Carbon black................	0.9356	......	......	0.195	......	......	163.0	......	......	10.5	......	..
Graphite......	......	0.934	0.933	0.201	0.21	0.15	158.5	......	......	13.3	......	......
Artificial graphite................	......	0.935	0.939	......	......	0.15	......	181.0	180.0	......	..	..
Lamp black. (See carbon black.)												
Black magnetic oxide...........	......	0.937	0.935	......	0.17	0.13	......	174.6	173.2	......	..	
Yellow Red												
Red lead...............	......	......	......	15.56	......	......	135.4	......	......	19.2	......	......
Iron oxide...........	0.9457	0.941	0.939	0.456	0.15	0.14	156 3	173.8	172.5	8.6	......	......
Basic chromate of lead.	0.9390	......	......	1.271	......	......	156.7	......	......	8.3	......	......
Zinc chromate........	......	0.934	0.934	......	0.20	0.18	......	180 2	179.5	......	......	......
Chrome yellow..	......	0.937	0.935	..	0.14	0.14		176.3	175.7	......	..	..
Chromium oxide.	......	0.937	0.937	..	0.01	0 05		178 0	180.2	..	....	..

of the increased sp. gr. of the oil. Such difficulty can be obviated by saponification of the liquid and liberation of the free fatty acids. When properly carried out, an analysis of these acids will be of more value than an analysis of the oil containing the metals in solution.

The effect of the storage of oils in contact with pigments is shown by Gardner (*J. Frank. Inst.*, 1912, **174**, 415) and Boughton (*J. Ind. Eng., Chem.*, 1913), whose results are tabulated on preceding page.

HIGHER FATTY ACIDS

REVISED BY H. E. COX, M.Sc., Ph. D., F. I. C.

The term "fatty acids," used in its widest sense, includes the whole series of homologous acids of which formic acid is the lowest member, together with the unsaturated acids of the acrylic or oleic series, the peculiar acids obtained on hydrolysis of castor and drying oils and many others.

The lower members of the saturated series (formic, acetic, etc.) have been considered in Vol. 1.

The following tables give some particulars of fatty acids of interest or importance as constituents of fixed oils or fats. With one or two possible exceptions, fatty acids containing an uneven number of carbon atoms do not occur in nature; where such have been described it has generally been shown on subsequent investigation that the acid so described was a mixture of acids having an even number of carbon atoms. Usually the naturally occurring fatty acids have a normal constitution. True monobasic fatty acids having an uneven number of carbon atoms, $C_{13}H_{26}O_2$, $C_{15}H_{30}O_2$, $C_{17}H_{34}O_2$, and $C_{19}H_{38}O_2$, have been obtained by Fischer and Schneider (*Ber.*, 1920, 53, B. 922) by the catalytic oxidation of paraffins; these acids have m. p. respectively 38°, 50°, 58° and 65°. The process appears likely to be of industrial importance in the near future. Information regarding the analytical characteristics of caprylic, pelargonic, and capric acids will be found in Vol. 1. Palmitic, stearic, and oleic acids are described at length in subsequent sections, as they are of frequent occurrence. Further information regarding arachidic, erucic, linoleic, and ricinoleic acids will be found in the sections treating of the oils of which they are especially characteristic—namely, arachis oil, rape oil, linseed oil, and castor oil.

Methods for the detection and estimation of the lower members of the acetic series are described in Vol. 1.

A. HIGHER ACIDS OF THE ACETIC OR STEARIC SERIES, $C_nH_{2n}O_2$, or $C_nH_{2n+1}CO_2H$

Name	Formula	Chief sources	M. p.	B. p.	Sp. gr.	Other characteristics
Caprylic (octoic)....	$C_8H_{16}O_2$	Coconut oil and butter fat.	16.5°	236°/760 mm. 123.5–124.3°/10 mm.	0.910 20°/4°	Crystallises in needles or plates. Soluble in 400 parts of boiling water, mostly deposited on cooling, readily soluble in alcohol, ether, and benzene. Barium salt moderately soluble.
Pelargonic (nonoic)	$C_9H_{18}O_2$	....	12.5°	186°/100 mm.	0.911 12°/4°	
Capric...........	$C_{10}H_{20}O_2$	Butter fat, codliver and coconut oils.	31.3–31.4°	268–270°/760 mm. 199.5–200°/100 mm. 153–154°/13 mm.	0.930 (37°) 0.8858 40°/4°	Crystallises in plates, slightly soluble in water; easily in alcohol and ether. Barium salt dissolves in boiling water.
Lauric...........	$C_{12}H_{24}O_2$	Coconut, palmnut, croton, laurel oils.	43.6°	225°/100 mm. 176°/15 mm.	0.883	Crystallises in scales from fused state. Lead salt insoluble in ether and sparingly soluble in alcohol.
Ficocerylic........	$C_{13}H_{26}O_2$	Wax of wild fig tree.....	57°	....	....	
Myristic..........	$C_{14}H_{28}O_2$	Coconut and dika oils, nutmeg butter and spermaceti.	53.8°	250.5/100 121° vacuo	0.8584 60°/4°	Insoluble in water, lead salt insoluble in ether, soluble in alcohol.
Palmitic.........	$C_{16}H_{32}O_2$	Palm oil and most fats...	62.6°	339–356°/760 mm. (decomp.) 215°/15 mm. 138–139° vacuo	0.8527 62.6°	See " Palmitic Acid."
Daturic..........	$C_{17}H_{34}O_2$	Datura oil............	59.5°	227°/100 mm.	0.8532 60°/4°	Probably identical with synthetic margaric[1] acid.
Stearic...........	$C_{18}H_{36}O_2$	Most fats.............	69.32°	359–380°/760 mm. 291°/100 mm. 232°/15 mm.	0.845° (m. p.)	See "Stearic Acid."
Arachidic........	$C_{20}H_{40}O_2$	Arachis oil............	77°	....	....	Sparingly soluble in cold, easily soluble in hot alcohol. Lead salt insoluble in ether.
Behenic..........	$C_{22}H_{44}O_2$	Oil of ben............	83–84°	306°/60 mm.	....	
Lignoceric........	$C_{24}H_{48}O_2$	Arachis oil, beech-wood tar.	80.5°			
Pisangcerylic......	$C_{24}H_{48}O_2$	Pisang wax	71°			
Cerotic..........	$C_{26}H_{52}O_2$	Beeswax and carnaüba wax.	78 5°			
Melissic.........	$C_{30}H_{60}O_2$	Beeswax............	90°			

[1] The margaric acid described in earlier literature is probably a eutectic mixture of palmitic and stearic acids.

B. HIGHER ACIDS OF THE ACRYLIC OR OLEIC SERIES, $C_nH_{2n-2}O_2$ *or* $C_nH_{2n-1}CO_2H$

Name	Formula	Chief sources	M. p.	Other characters	Isomeric (or polymeric) acids produced by the action of nitrous acids on natural acids
Hypogeic... ...	$C_{16}H_{30}O_2$	Arachis oil.........	33°	Forms colourless crystals, readily soluble in alcohol and ether. Combines with Br_2. Yields gaïdic acid with nitrous acid and sebacic acid on distillation. Lead salt soluble in ether.	*Gaïdic acid* forms a crystalline mass m. p., 39°. Volatilises almost unchanged. Readily soluble in alcohol. Combines with Br_2.
Physetoleic... ...		Said to exist in sperm oil.	30°	Differs from hypogeic acid in not yielding sebacic acid on distillation	
Oleic...		The majority of fatty oils form the oleine of commerce.	14°	See "Oleic Acid,"....................	*Elaïdic acid*, produced by action of nitrous acid on oleic acid. Pearly plates m. p., 51–52°, and distilling almost unchanged.
Isoöleic.......	$C_{18}H_{34}O_2$	By distillation of hydroxystearic acid.	45°	Soluble in alcohol and ether. Unites with Br_2. Behaves like oleic acid, when fused with alkali. Lead salts less soluble in ether than lead oleate.	
Rapic.............		Rape oil.	Liquid	Forms a crystalline zinc salt soluble in alcohol or ether, m. p. 78°.	Does not yield a solid isomeride with nitrous acid.
Gadoleic.........	$C_{20}H_{38}O_2$	Cod liver oil, herring and whale oils.	24.5°	Potassium salts very sparingly soluble in cold alcohol. Resembles oleic and erucic acids.	
Erucic or Brassic...	$C_{22}H_{42}O_2$	Said to exist in cod-liver oil. Rape oil, black and white mustard oils.	33–34°	Crystallises from alcohol in long laminæ or needles. Combines with Br_2. Lead salt less soluble in ether than is lead oleate. Yields acetate and arachidate when fused with potassium hydroxide.	*Erucaïdic* or *Brassaïdic acid*, produced by action of nitrous acid on erucic acid; m. p., 65°. Lead salt nearly insoluble in warm ether.

C. HIGHER ACIDS OF THE PROPIOLIC OR LINOLEIC SERIES, $C_nH_{2n-4}O_2$

Name	Formula	Chief sources	M. p.	Other characters	Isomeric acids
Elæomargaric	$C_{18}H_{32}O_2$	Japanese wood oil. ...	48	On exposure to light the solution in alcohol or ether deposits isomeric elæostearic acid.	*Elæostearic acid;* m. p. 71°.
Linolic..........	$C_{18}H_{32}O_2$	Linseed and other drying oils.	below −18°	Liquid at low temperature. Not solidified by nitrous acid. Yields stearic acid by hydrogenation and *sativic acid* when oxidised in alkaline solution. Combines with Br₄. Lead salt soluble in ether. Absorbs oxygen rapidly from air. Sp. gr. 0.9206 (14°).	*Tariric acid* found in fat of seeds of Guatemalan *Picraminia.* M. p., 50.5°. Combines with Br₄.

D. HIGHER ACIDS OF THE LINOLENIC SERIES, $C_nH_{2n-6}O_2$

Name	Formula	Chief sources	Other characters
Linolenic..............	\} $C_{18}H_{30}O_2$	Linseed and other drying oils.	Liquid; very oxidisable. Combines with Br₆. Forms linusic acid, m. p., 203°, when oxidised in alkaline solution. Lead salt soluble in ether.
Isolinolenic...........		Said to exist in linseed oil, but has not been isolated from it.	Resembles linolenic acid, but forms isolinusic acid, m. p., 173°–175° when oxidised in alkaline solution.

E. HIGHER ACIDS OF THE HYDROXYOLEIC, OR RICINOLEIC CSERIES, $C_nH_{2n-2}O_3$

Name	Formula	Chief sources	Other characters	Isomeric acid
Ricinoleic..............	\} $C_{18}H_{34}O_3$	Castor and curcas oils..	Thick oily liquid, sp. gr. 0.940 (15°). M. p. 4–5°, optically active.	*Ricinelaïdic acid,* produced by action of nitrous acid on ricinoleic acid. M. p., 50°. Crystallises from alcohol in silky needles. Combines with Br₂. Lead salt, m. p. 100°, is soluble in ether.
Isoricinoleic............		Castor oil.............	Resembles ricinoleic acid...........	

F. ACIDS OF THE CLUPANODONIC SERIES, $C_nH_{2n-10}O_2$

Name	Formula	Chief sources	Other characters	
Clupanodonic...........	$C_{22}H_{34}O_2$	Japanese sardine oil; present in all kinds of fish and many animal oils.	Pale yellow liquid; sp. gr. 0.9398 15°/4° N_D^{15} 1.5040, iodine val. (Wijs) 390.	This acid very readily absorbs oxygen, forming a varnish-like mass.

The m. p. and b. p. of acids of the stearic series rise with increase in the number of carbon atoms. The viscosity also increases with the rise in number of carbon atoms, but with diminishing increment for each CH_2 group above C_9. The higher members cannot be distilled under the ordinary atmospheric pressure without suffering more or less decomposition, but may be distilled unaltered under diminished pressure. The table shows the b. p. of some of the stearic series under diminished pressure.

Similarly, oleic acid may be distilled in a vacuum or in a current of superheated steam at 250°, without material alteration; but if distilled in contact with air it is partially decomposed, with formation of carbon dioxide, paraffinoid hydrocarbons, and acetic, caproic, caprylic, capric, sebacic, and other acids.

In the following tables the chief acids of the different series are arranged together. Their relationship is evident from the following list of the acids containing 18 carbon atoms in the molecule:

$C_{18}H_{36}O_2$, stearic acid.	$C_{18}H_{30}O_2$, linolenic acid; isolinolenic acid.
$C_{18}H_{34}O_2$, oleic acid; elaidic acid.	$C_{18}H_{34}O_3$, ricinoleic acid; isoricinoleic acid.
$C_{18}N_{32}O_2$, linolic acid; stearolic acid.	$C_{18}H_{34}O_2$, ricinelaidic acid, rapic acid.

General Properties of the Fatty Acids.—The lower members of the fatty acid series are soluble in water, capric and lauric acids are slightly soluble in boiling water, the higher acids are insoluble. They are all, however, soluble in hot alcohol, ether, and petroleum spirit. The alcoholic solutions all give more or less marked acid indications, and both in solution and in the melted state decompose the carbonates of the alkali metals. The interaction between an alkali hydroxide and a fatty acid in water is not a complete one, free acid and free alkali existing as well as the resultant "soap." The fatty acids of the different series formulated in the foregoing tables present certain marked points of difference and general characters of interest of which the following are the chief:

A. The higher acids of the *stearic series* are solid at the ordinary temperature. They do not give additive compounds with bromine, nor do they react with Hübl's reagent; in other words, they are saturated compounds. They do not undergo change when heated with potassium hydroxide at 300° or with phosphorus and hydriodic acid. The lead salts are insoluble in ether.

B. The higher members of the *oleic* or *acrylic* (from acrylic acid, the lowest member) series have lower m. p. than the corresponding acids of the stearic series, and are unsaturated compounds absorbing two atoms of the halogens or hydrogen. They interact with Hübl's reagent to give analogous compounds. The higher acids when in contact with sodium amalgam do not take up hydrogen to form saturated acids (Lewkowitsch, *J. Soc. Chem. Ind.*, 1897, **16**, 390), but colloidal palladium or platinum-black reduces oleic acid or unsaturated glycerides at the ordinary temperature (Fokin, *J. Russ. Phys. Chem. Soc.*, 1907, **39,** 607–609; Paal and Roth, *Ber.*, 1908, **41,** 2282–2291). The reduction may also be carried out with phosphorus and fuming hydriodic acid at 200 to 220°.

The unsaturated fatty acids may be converted into the corresponding saturated acids by the action of hydrogen at high temperatures in the presence of a catalyst such as finely divided nickel, platinum or palladium: *e. g.*, $C_{17}H_{33}CO_2H + H_2 \rightarrow C_{17}H_{35}CO_2H.$
oleic acid   stearic acid

These reactions are of much importance in connection with the hardening of fats for the margarine and other industries (see p. 426).

When heated carefully with potassium hydroxide at 300°, potassium acetate and the potassium· salt of an acid of the stearic series containing 2 carbon atoms less than the original unsaturated acid employed are obtained; when heated rapidly with this alkali, sebacic acid, $C_{10}H_{18}O_4$, is also obtained from certain of these acids. Oleic acid and some of its homologues, when treated with nitrous acid at ordinary temperatures, are transformed into isomerides of higher m. p. Oxidation with potassium permanganate in alkaline solution leads to the formation of acids of the dihydroxystearic series. The lead salts are soluble in ether; lead elaidate is, however, only very slightly soluble, like lead stearate, and this property, when utilised in separating lead salts of the unsaturated from those of the saturated series, requires to be used with caution.

C. The acids of the *linolic series* form additive compounds with 4 atoms of bromine and interact with a larger proportion of Hübl's reagent than do acids of the oleic series. They absorb oxygen from the air, and oxidation of linolic acid in the cold with dilute potassium permanganate leads to the formation of sativic or tetrahydroxystearic acid. They are not affected by nitrous acid. The lead salts are soluble in ether.

D. *Linolenic acid* combines with 6 atoms of bromine or iodine and readily absorbs oxygen. Nitrous acid does not produce solid iso-merides. Lead linolenate is easily soluble in ether.

E. *Ricinoleic acid* combines with 2 atoms of bromine, does not absorb oxygen on exposure to the air, and is gradually converted by nitrous acid into a solid stereoisomeride. Its lead salt is soluble in ether. Oxidation with potassium permanganate gives two trihy-droxystearic acids.

F. Acids of the *clupanodonic* series are highly unsaturated; they absorb oxygen very readily, and hence are isolated in the pure state with difficulty. Clupanodonic acid, the formula of which is $C_{22}H_{34}O_2$, not $C_{18}H_{28}O_2$ as hitherto supposed, is one of the most widely distributed compounds in nature; it occurs in the oils from fresh and salt water fish, reptiles and amphibian (see Tsujimoto, *Chem. Umschau*, 1922, 29, 261).[*] Other acids of the series are isanic and arachidonic acids, but their formulæ are uncertain.

Recognition and Estimation of Fatty Acids.—The methods available for the detection and, to some extent, for the estimation of the higher fatty acids may be based on the characters just described. When it is impossible to identify the acid by its physical properties, it may frequently be recognised by preparation of one of its esters which will have characteristic m. p. or b. p. The methyl or ethyl esters are easily prepared by boiling the acid with about five times its weight of the appropriate alcohol and passing in dry hydrogen chloride, after which the excess of alcohol is distilled off and the ester separated by pouring the residue into water; it is then washed and dried (see also Holland and Buckley's method described on p. 519). The m. p. of a number of phenacyl esters are given by Rather and Reid (*J. Amer. Chem. Soc.*, 1919, 41, 75); these are readily prepared by boiling under a reflux condenser the acid with rather less sodium carbonate than required for neutralisation and an equivalent quantity of phenacyl bromide in alcoholic solution. on cooling the crystalline phenacrl bromide separates out. In many cases it is unnecessary to effect actual separation of the fatty acids in a mixture, it being sufficient to ascertain the joint amount, or to ascertain indirectly and approximately the proportion of the acids of different origin known to be present.

Methods not Involving Separation.—*a.* Free fatty acids can be accurately estimated by titration in alcoholic solution with standard

alkali, with the use of using phenolphthalein to indicate the point of neutrality. The mode of operating is fully described on page 10. A mixture of 1 part of alcohol to 2 of amyl alcohol as solvent is recommended by Swoboda (*Chem. Zeit.*, 1900, 24, 285), as it avoids the formation of two layers. Neutral substances—*e. g.*, fats and hydrocarbons—do not interfere. Mineral acids and acid salts must first be removed by agitation with water, or estimated by titration in alcoholic solution, with methyl-orange as indicator, and resin acids must be separated or duly allowed for. In the case of a mixture of several fatty acids the result is best expressed in terms of the principal or most characteristic acid present, and in most cases such a mode of statement gives a close approximation to the total of the free fatty acids present.

Conversely, when the substance under examination consists wholly of a mixture of fatty acids, titration with standard alkali suffices to ascertain the mean combining weight of the mixed acids. This is found by dividing the number of mg. of fatty acids employed for the titration by the number of c.c. of normal alkali required for neutralisation.

In cases of a mixture of two homologous acids, the nature of which is known or can be ascertained by other means, the result of the titration gives the means of ascertaining the proportions in which the two constituent acids exist in the mixture. An example of the application of the method to this purpose is given on page 521.

b. The Polenske method is also applicable for the analysis of mixed fatty acids, as for example those from soaps and commercial mixtures in which the original oils are not available. Although volatile fatty acids will distil over on simply boiling with water, it is desirable to use the standard Polenske method given on page 417. Fryer (*J. Soc. Chem. Ind.*, 1918, 37, 262T) obtains the value 17.3% for the insoluble volatile fatty acids from coconut oil and 10.5% for those from palm-kernel oil. The proportion of these fatty acids in oils or mixtures may also be estimated by this method (*cf.* Burnette and Revis, *Analyst*, 1913, 38, 255).

c. Köttstorfer's method (page 16) may be regarded as a process for approximately ascertaining the mean combining weight of the fatty acids of an oil, fat or wax without actually isolating them. 3 c.c. of a 2% alcoholic solution of Alkali Blue 6B (Meister, Lucius and Bürning) can be substituted with advantage for phenolphthalein

when the oils give dark-coloured solutions. This solution is red with alkali, blue with acid. The saponification values obtained are fairly constant, and are important in determining the nature of an oil or fat; but, as a means of ascertaining the mean combining weight of the acids, the method is only applicable to oils which yield 95% of fatty acids on hydrolysis.

Tortelli and Pergami (*Chem. Rev., Fett. Harz Ind.*, 1902, 182) have stated that the acids from oils and fats contain quantities of anhydrides or lactones which are not attacked by dilute alkali in the cold, and therefore too high a molecular weight is found. The true molecular weight is found by heating with excess of N/2 alkali, and titrating back with hydrochloric acid. The further statement is made that in the case of fresh samples the number obtained is only a few units greater than the neutralisation value, but that in old samples the anhydride is quite important. A few of their results are tabulated.

MEAN MOLECULAR WEIGHT OF FATTY ACIDS

	Insoluble fatty acid		Differ-ence	Mean molecular weight calculated from		Differ-ence
	Neutral-isation value	Saponi-fication value		Neutral-isation value	Saponi-fication value	
Oleic acid fresh from olive oil...	199.5	201.4	1.9	281.2	278.5	2.7
Oleic acid, 2 years old, from beef fat...................	191.0	202.8	11.8	293.8	276.6	17.2
Oleic acid, 5 years old, commercial	181.6	189.3	7.7	308.2	296.5	11.7
Almond oil, fresh..	195.8	203.0	7.2	286.5	278.5	8.2
Almond oil, 2½ years old.....	196.0	202.2	6.2	286.2	277.5	8.7
Linseed oil, fresh..............	194.6	201.8	7.2	288.2	277.9	10.3
Linseed oil, 3 years old........	191.5	205.4	13.9	292.8	273.2	19.6
Cottonseed oil, fresh...........	200.9	203.1	2.2	279.2	276.2	3.0
Cottonseed oil, 2½ years old...	194.3	204.5	10.2	288.7	274.3	14.4
Rape oil, fresh................	176.6	181.2	4.6	317.7	309.6	8.1
Rape oil, 2 years old..........	178.3	182.5	4.2	314.6	307.4	7.2
Rape oil, 5 years old..........	176.1	181.4	5.3	318.8	309.1	9.1
Arachis oil, fresh...........	195.8	203.0	7.2	286.5	278.3	8.2

Lewkowitsch (*Jahrb. Chem.*, 1901, 11, 359) carefully repeated this work, and the results obtained were sometimes in agreement with those of Tortelli and Pergami; in other cases, however, the differences were within the limits of experimental error, and even negative differences were found. The differences are probably due to the forma-

tion of lactones from hydroxy-fatty acids, specially γ-hydroxy acids, but may also result from the formation of anhydrides from the acids by the action of heat. When lactones are present in the mixed fatty acids, as shown by a difference between the neutralisation and saponification values, the mean molecular weight of the lactone-free acids is given by the formula $m = \dfrac{56,108 + 18.016(s - a)}{s}$, where s and a are the saponification and neutralisation values respectively. (For the influence of lactones on the acetyl value of the acids see Brown, *J. Ind. Eng. Chem.*, 1915, **7**, 30).

d. The determination of the iodine value of a mixture of oleic acid with acids of the stearic series by means of Hübl's or Wijs's solution (page 33) allows the former constituent to be estimated with considerable accuracy. As 282 parts of oleic acid, $C_{18}H_{34}O_2$, absorb 254 parts of iodine, the iodine value divided by 0.9 gives the percentage of *oleic acid* present. It is even possible to ascertain the percentage of oleic acid when another unsaturated, such as linolic acid, is present. That acid absorbs four atoms of iodine, and as the molecular weights of the two unsaturated acids are very nearly the same (282 : 280), linolic acid may be regarded as absorbing twice as much iodine as oleic acid. Hence, if 90 be subtracted from the observed iodine value of the mixed acids, and the difference divided by 0.9, the dividend will be the percentage of linolic acid in the mixture. If acids of the stearic series are also present, they must be separated or duly allowed for in making the calculation. If the percentages of stearic, oleic and linolic acids are represented, respectively, by s, o, and l and the iodine value by A, then, the value of s being known, the liquid acid percentages are:

$$o = 200 - 1.11A - 2s; \text{ and } l = 100 - s - o.$$

e. Useful information respecting the fatty acids present can be obtained from the m. p. or solidifying-point of the substance. When the mixture consists merely of two acids of the stearic series, the result affords means of approximately ascertaining their relative proportions. The m. p. of some mixtures of the acids of the stearic series, as found by Heintz, are given in a tabular form on page 506 *et seq.* The m. p. and solidifying-points of the fatty acids from

different fixed oils are more or less characteristic of their origin, as also are the sp. gr. and mean combining weights.

The following table gives data obtained in Allen's laboratory. The fatty acids were prepared as follows: The oil was saponified with alcoholic potassium hydroxide, the alcohol evaporated, the residual soap dissolved in hot water and decomposed by dilute sulphuric acid. The liquid having been well boiled, the separated fatty acids were filtered through paper. With sperm and bottlenose oils the higher alcohols were removed by agitating the solution of the soap with ether, the ethereal layer separated, and the ether that remained in the soap solution removed by warming before liberating the fatty acids. In the case of the other oils the trifling proportion of unsaponifiable matter was ignored.

Kind of oil	Characters of separated insoluble fatty acids				
	Sp. gr.		M. p.	Solidifying point	Combining weight
	At 15.5°	At 98–99°			
Olive oil.................	solid	0.8430	26.6°	21.0°	279.4
Arachis oil..............	solid	0.8460	29.5°	28.0°	281.8
Rape oil................	solid	0.8438	19.5°	18.5°	321.2
Cottonseed oil (pressed)..	solid	0.8467	35.0°	32.0°	287.2
Sesame oil..............	solid	......	23.0°	18.5°	286.5
Linseed oil..............	0.9233	0.8612	24.0°	17.5°	307.2
Castor oil...............	0.9509	0.8960	.....	.....	306.6
Palm oil................	solid	0.8369	50.0°	45.5°	269.6
Coconut oil.............	solid	......	24.0°	20.5°	.....
Japan wax..............	solid	0.8482	56.0°	53.0°	265.3
Myrtle wax.............	solid	0.8370	47.5°	46.0°	243.0
Lard...................	solid	......	44.0°	39.0°	278.0
Northern whale oil......	0.9076	0.8595	.....	.....	298.7
Sperm oil...............	0.8990	......	.....	.....	289.4
Bottlenose oil...........	0.8965	......	.....	.....	294.6

The following table gives the m. p., solidifying-points and combining weights of the fatty acids ascertained by several observers:

Source of fatty acids	M. p.	Solidifying-point		Combining weight
		Various methods	Titer test) (Lewkowitsch)	
Olive oil.............	21–30°	17–26.4°	16.9–26.4°	270–285
Almond oil.......... ...	13–14°	5–12° (t)	9.5–11.8°	
Arachis oil.......... .	27–30°	24–31°	28.1–29.2°	
Rape oil.............	16–21°	12–18°	11.7–13.6°	
Cottonseed oil.........	34–40°	32–40°	32.2–37.6°	275
Sesame oil............	24–32°	18–28°	21.2–23.8°	286
Nigerseed oil..........	25–27°	....	....	....
Poppyseed oil.........	20–21°	15.5–17°	....	....
Linseed oil............	17–24°	13–20°	19.0–20.6°	....
Hempseed oil..........	17–28°	14–16°	15.6–16.6°	....
Walnut oil............	15–20°	16–17°	....	....
Castor oil............	13°	2–3°	....	290–295
Palm oil..............	48–50°	36–45.5°	35.8–45.4°	273
Palmnut oil...........	21–28°	....	20 –25.5°	211
Cacao butter..........	48–53°	46–51°	48 –48.27°	....
Nutmeg butter........	42.5°	36–40°	35.5–35.95°	....
Shea butter...........	40–56°	38–54°	53.75–53.8°	....
Coconut oil...........	24–25°	16–25°	21.2–25.2°	196–204
Japan wax............	56–62°	53–59°	58.8–59.4°	....
Myrtle wax...........	47.5°	46°	....	....
Lard oil..............	33–38.5°	....	....	....
Lard.................	37–47°	32–43°	41.45–42°	270–285
Compounded lard......	39–43°	....	....	....
Tallow, mutton........	41–49°	....	40.15–48.3°	270–285
Tallow, beef..........	41–47.5°	....	37.9–46.25°	270–285
Margarine............	42°	40°	....	....
Butter fat (insoluble acids)...............	38–42°	37–38°	....	....
Sperm oil............	13°	11–12°	11.1–11.9°	....
Whale oil............	14–18°	23–24°	22.9–23.9°	....

The differences in the m. p. and solidifying-points are in great measure due to different methods of observation.

The figures have, in some instances, considerable practical value. Thus, the high m. p. of the fatty acids obtained on saponification distinguishes cottonseed oil from nearly all other liquid fixed oils of vegetable origin, and enables its presence to be inferred in admixture with other oils; the m. p. of the acids from cacao butter is remarkably constant, and is sometimes useful as a test of the purity of the fat; whilst the solidifying-point of the acids from palm oil affords a practical indication of the value of the sample to the candle manufacturer. The same remark applies to the fatty acids of tallow, and a table has been constructed by Dalican (page 289) by which the

proportion of oleic and solid fatty acids which a sample of tallow will yield can be deduced from the solidifying-point of the mixed acids.

It must be remembered, however, that hydrogenation raises the m. p. of fatty acids, so that the observed m. p. cannot be relied upon for the identification of the fat or fatty acids, unless it is known or proved that no hardened fatty acids are present. For the methods of detecting hydrogenated fats see page 50. The following table shows the effect of hydrogenation on the m. p. of some of the commoner fatty acids (*cf.* Mellana, *Ann. Chim. Appl.*, 1914, **1**, 381 and Sandelin, *Teknikern*, 1913, 359).

Source of fatty acids	M. p.	Solidifying point	Approximate rise in m. p.
Hardened:			
Cottonseed oil............	57°	50.3	20°
Soya bean oil............	66°	61.2	38°
Kapok seed oil...........	53°	48°	21°
Whale oil................	49°	44°	33°
Sperm oil................	48°	39°	35°
Arachis oil..............	53°	39°	25°
Sesame oil..............	62°	45°	34°
Coconut oil.............	44°	28°	20°

A method for the estimation of fatty acids in mixtures based upon the depression of the m. p. has been devised by Twitchell (*J. Ind. Eng. Chem.*, 1914, **6**, 564) in which use is made of the well known freezing-point method for determining molecular weights.

Since the molecular weights of the commoner fatty acids are nearly the same, the depression of m. p. caused by the addition of a fatty acid or mixture to a pure acid is approximately independent of the kind of fatty acid added. Thus 10% of stearic acid added to oleic or palmitic acid reduces its m. p. by 2.05°, or 20% of stearic, palmitic or oleic acid added to behenic acid (m. p. 79.99°) depresses the m. p. by 4.33°.

To apply this method, 20 parts of the acid mixture are added to 80 parts of pure stearic, palmitic, behenic or other known acid and the depression of the m. p. is noted. If, for example, the depression on adding 20% of cottonseed oil fatty acids to 80% of palmitic acid is only 3.18° it would show that the mixture contained 84.6% of palmitic acid and 15.4% of other acids, *i. e.*, the fatty acid mix-

ture added contained 23% of palmitic acid. If the acid be first hydrogenated the method may be extended. Suppose, for instance, that the stearic acid in a mixture is estimated from the depression of m. p. of pure stearic acid and the depression also determined after hydrogenation of the mixture, the increase in the amount of stearic acid indicated is the measure of the unsaturated acids containing 18 carbon atoms in the original mixture.

Separation of Mixed Fatty Acids.—The actual *separation* of mixed fatty acids is often a problem of extreme difficulty, and indeed cannot in all cases be satisfactorily solved in the present condition of chemistry. Methods for effecting the recognition and separation of the lower members of the stearic series will be found in Vol. 1. The principles which have been applied to the fatty acids enumerated in the tables on page 506 *et seq.* include the following:

1. The mixed fatty acids are well washed by agitation with hot water, when those containing 10 atoms or fewer of carbon are dissolved. This process is applied to the analysis of the fatty acids from butter-fat.

2. The mixed fatty acids obtained by treating the soaps with a moderate excess of dilute sulphuric acid are distilled with water, either with or without the aid of a current of steam. This method allows a more or less complete separation of the homologues up to lauric acid from the higher members of the stearic series. The soluble acids obtained in 1 are not necessarily the same as in 2.

3. The acids are converted into barium salts, and the precipitate treated with water or alcohol. The barium salts of lower members up to capric acid can be dissolved out by boiling water.

4. The alcoholic solution of the acids is precipitated by magnesium acetate. By operating fractionally some useful separations may be effected (see below).

5. The acids are converted into lead salts, which are then treated with ether or alcohol. An application of this principle enables oleic acid and its homologues to be separated from the higher acids of the stearic series.

6. Fractional distillation, fractional fusion and pressure, and fractional solution in or crystallisation from alcohol or other solvents are other processes employed for the separation of the fatty acids.

Under this heading may be mentioned a method which has been used by Holland and Buckley (*J. Agric. Res.*, 1918, **12**, 719) for the analysis of butter fat, and is capable of application to the separation of other fatty acid mixtures. It consists in the esterification of the fatty acids by ethyl alcohol in the presence of hydrogen chloride; the esters are salted out by means of magnesium chloride and fractionated. The following fractions are separated in the case of the acids occurring in butter:

$185°$–$225°$ ethyl butyrate, caproate and oleate,
$225°$–$270°$ ethyl caprylate, caprate and oleate,
$270°$–$300°$ ethyl caprate, laurate and oleate,
$300°$–$325°$ ethyl laurate, myristate and oleate,
$325°$–$365°$ ethyl myristate, palmitate and oleate.

The proportions of the fatty acids in the fractions can be calculated from their saponification and iodine values. Details of the method are given in the original paper.

No chemical method of separating oleic acid and its homologues from linolic acid has yet been devised, but when mixed fatty acids contain the two acids only their relative proportions can be calculated approximately from the iodine value of the mixture. For example, the proportion of oleic acid (x) and of linolic acid (y) in a mixture having iodine value I is given by solving the equations $0.90x + 1.81y = I$ and $x + y = 100$ since the iodine values of the two acids are 90 and 181 respectively. Possibly a method might be based on the conversion of the acids of the oleic series into isomers of higher m. p. and modified properties by means of nitrous acid. Methods 1, 2, and 3 have already been sufficiently described, and those under 6 do not require further notice. Methods 4 and 5, however, are described in detail below.

Separation of the Higher Fatty Acids of the Stearic Series.—The higher homologues of the stearic series can be separated from the lower members by treatment with hot water or distillation in a current of steam, and from the insoluble and non-volatile acids of other series by treatment of the lead soaps with ether. By proper application of these methods there may be obtained a mixture of solid, non-volatile homologues of stearic acid, which, according to its origin, may contain more or less lauric, myristic, palmitic, stearic,

arachidic, and other less frequently occurring acids of the series. The separation of these homologues is extremely difficult, and a quantitative estimation of several immediate homologues occurring in a mixture is especially so.   Advantage may be taken of the limited solubility of *arachidic acid* in alcohol to effect its separation, as is done in Renard's process for the detection of arachis oil (page 118); and indeed the solubility of the homologues in alcohol rapidly increases with a diminution of the number of carbon atoms in the acid.

For the actual *separation* of the higher homologues of the stearic series from each other, however, a satisfactory method is that of Heintz (*J. pr. Chem.*, 1855, **66,** 1), based on fractional precipitation of the alcoholic solution of the acids with magnesium acetate.   This salt precipitates acids of the stearic series more easily than it does oleic acid and its homologues, and, of the different homologues of the stearic series, those of the highest molecular weights are thrown down first.   In practice, 40 grm. of the mixed fatty acids should be dissolved in such a proportion of hot alcohol that nothing will separate on cooling, even at 0°, and the hot liquid treated with a boiling alcoholic solution of 1.5 grm. of magnesium acetate.   The liquid is well agitated and allowed to become cold, when the precipitate is filtered off and the filtrate treated with a fresh quantity of alcoholic magnesium acetate.   This second precipitate is similarly separated, and the treatment repeated as long as anything is thrown down.   To induce precipitation of the lower homologues it becomes necessary to render the liquid alkaline with strong ammonia before adding magnesium acetate, and to allow the solution to stand in the cold for 24 hours before filtering.   The first fractions of the precipitate contain magnesium stearate and any higher homologues, the succeeding portions will consist chiefly of magnesium palmitate, and the last will probably contain myristate; but a portion of the myristic acid, the whole or nearly the whole of the lauric acid, and any oleic acid which may be present will remain in solution, and may be precipitated by addition of lead acetate after neutralising the excess of ammonia with acetic acid.   The precipitate should be filtered off, washed with cold dilute alcohol, and, if oleate be present, treated with ether.   The purified lead precipitate and the several magnesium precipitates should be washed with cold alcohol, pressed, and decomposed by hot dilute hydro-

chloric acid, the liberated fatty acids being washed free from mineral acid by repeated agitation with hot water, and further treated as described on page 20. The details of the fractional precipitation should be modified to suit particular cases, and in some instances separation into a smaller number of fractions will suffice.

The several fractions of fatty acids thus obtained, after being weighed, if desired, should then be titrated with standard alkali in the manner described on page 10. 5 grm. of each fraction will be a suitable quantity, and this should be treated with about 30 c.c. of warm alcohol (neutral) and titrated with $N/2$ sodium hydroxide, a few drops of a solution of phenolphthalein being employed as indicator. The mean combining weight of the acids constituting a fraction is found by dividing the number of mg. of fatty acids employed by the number of c.c. of N alkali required for their neutralisation. Thus, if 5 grm. of a fraction has been found to require 37.80 c.c. of $N/2$ for its neutralisation, the mean combining weight of the acids will be 264.5, for:

$$\frac{5000 \times 2}{37.8} = 264.5$$

As a rule, if the mixed fatty acids are divided into a sufficient number of fractions by precipitation with magnesium acetate, each fraction will contain only two homologues, in which case the result of the titration not only indicates the nature of the homologues present, but in many cases allows of their relative proportion being calculated. Thus, if, in the course of a systematic fractional precipitation as magnesium salts, a fraction of fatty acids is obtained having a mean combining weight of 264.5, it will almost certainly consist essentially of a mixture of stearic and palmitic acids, the former of which has the molecular weight 284 and the latter 256, the difference being 28. Hence every 1% of stearic acid in the mixture will raise the combining weight 0.28, or for every unit above 256 found for the combining weight of the fraction 3.57 of stearic acid should be calculated. As with all indirect methods of the kind, the results obtained are fairly satisfactory when both constituents are present in considerable proportions, but are of little value for mixtures in which one constituent very largely predominates.

The titration having been completed, the alcohol may be boiled off and the fatty acids again liberated and subjected to renewed

fractional precipitation or crystallisation from alcohol.   The products so obtained can be again titrated, and thus the progress of the isolation and purification of the fatty acids checked in a simple and satisfactory manner.

Valuable information respecting the composition of the various fractions obtained by the precipitation as magnesium salts is obtainable by determining the m. p. of the fatty acids.   For this purpose they should be purified by a single crystallisation from hot alcohol and dried by pressure between blotting-paper.   Unfortunately, the m. p. of a mixture of two or more homologous fatty acids is not the mean of the m. p. of the constituent acids.   The m. p. of various mixtures of solid fatty acids have been very carefully determined by Heintz, who has also noticed that the mixtures, on solidifying, crystallise in more or less characteristic forms or remain amorphous, according to the proportions in which the constituents are present.   The following are some of the more important of the results of Heintz:

MIXTURES OF LAURIC ACID WITH ITS HIGHER HOMOLOGUES

Lauric acid, %	With myristic acid		With palmitic acid	With stearic acid
	M. p.	Solidifying-point	M. p.	M. p.
100	43.6°	....	43.6°	43.6°
90	41.3°	36.0°	41.5°	41.5°
80	38.5°	33.0°	37.1°	38.5°
70	35.1°	32.3°	38.3°	43.4°
60	36.7°	33.5°	40.1°	50.8°
50	37.4°	35.7°	47.0°	55.8°
40	43.0°	39.0°	51.2°	59.0°
30	46.7°	39.0°	54.5°	62.0°
20	49.6°	44.5°	57.4°	64.7°
10	51.8°	47.3°	49.8°	67.0°
0	53.8°	....	62.0°	69.2°

MIXTURES OF MYRISTIC ACID WITH ITS HIGHER HOMOLOGUES

Myristic acid, %	With palmitic acid		With stearic acid
	M. p.	Solidifying-point	M. p.
100	53.8°	....	53.8°
90	51.8°	45.3°	51.7°
80	49.5°	41.3°	47.8°
70	46.2°	43.7°	48.2°
60	47.0°	43.7°	50.4°
50	47.8°	45.3°	54.5°
40	51.5°	49.5°	59.8°
30	54.9°	51.3°	62.8°
20	58.0°	53.5°	65.0°
10	60.1°	53.7°	67.1°
0	62.0°	....	69.2°

MIXTURES OF PALMITIC ACID WITH STEARIC ACID

Palmitic acid, %	Stearic acid, %	M. p.	Solidifying-point	Manner of solidification
100	0	62.0°	.....	Crystalline scales.
90	10	60.1°	54.5°	Slender needles.
80	20	57.5°	53.8°	Very indistinct needles.
70	30	55.1°	54.0°	Amorphous, wavy, dull.
60	40	56.3°	54.5°	Large crystalline laminæ.
50	50	56.6°	55.0°	Large crystalline laminæ.
40	60	60.3°	56.5°	Amorphous, lumpy.
30	70	62.9°	59.3°	Slender needles.
20	80	65.3°	·60.3°	Slender needles.
10	90	67.2°	62.5°	Crystalline scales.
0	100	69.2°	....	Crystalline scales.

Heintz also noticed that the addition of a third acid, even of higher m. p., to a mixture of two homologous acids causes a lowering of the m. p. This is shown in the following table:

Parts of palmitic acid added to lauric acid, 14; myristic acid, 6 parts	M. p.	Manner of solidification	Parts of stearic acid added to myristic acid, 14; palmitic acid, 6 parts	M. p.	Manner of solidification
0	35.1°	Amorphous, frond-like.	0	46.2°	Indistinct lamellæ.
1	33.9°	Amorphous.	1	45.2°	Amorphous.
2	33.1°	Amorphous.	2	44.5°	Amorphous.
3	32.2°	Amorphous.	3	44.0°	Amorphous.
4	32.7°	Amorphous.	4	43.8°	Amorphous.
5	33.7°	Amorphous.	5	44.6°	Amorphous.
6	34.6°	Amorphous.	6	45.6°	Amorphous.
7	35.3°	Amorphous.	7	46.0°	Amorphous.
8	36.0°	Amorphous.	8	46.5°	Amorphous.
9	37.3°	Indistinct minute needles.			
10	38.8°	Minute needles.			

The importance of ascertaining the solidifying-points of mixtures of fatty acids has been latterly emphasised as the data obtained are more reliable than those derived from m. p. observations. Heintz obtained his values by the capillary method, but L. E. O. de Visser (*Rec. Trav. Chim.*, 1898, 17, 182, 346), by using larger quantities and only allowing the temperature to fall slowly, obtained the following values for the solidifying-points of mixtures of stearic and palmitic acids:

MIXTURE OF STEARIC AND PALMITIC ACIDS

Stearic acid, %	Solidifying-point	Stearic acid, %	Solidifying-point	Stearic acid, %	Solidifying-point
100	69.32°	48	56.40°	36	55.62°
90	67.02°	47	56.40°	34	55.38°
80	64.51°	46	56.39°	32	55.12°
70	61.73°	45	56.38°	30	54.85°
60	58.76°	44	56.36°	29	54.92°
55	57.20°	43	56.31°	25	55.46°
54	56.85°	42	56.25°	20	56.53°
53	56.63°	41	56.19°	15	57.80°
52	56.50°	40	56.11°	10	59.31°
51	56.44°	39	56.00°	0	62.62°
50	56.42°	38	55.88°		
49	56.41°	37	55.75°		

If these values are plotted on squared paper the curve so obtained has two points of inflection, one at 54%, the other at 47.5%, and the tangent at 47.5 is parallel to the axis of composition; thus the acids exist in "solid solution" here with only one form of crystalline aggregate. The lowest solidifying-point is 54.817° at 29.76% stearic acid, but this is a mixture of two solid modifications.

The formation of "eutectic" mixtures in fatty acids has been examined by Carlinfanti and Levi-Malvano (*Gazzetta*, 1909, 39, 353). In ascertaining the solidifying-point, they take the beginning of crystallisation as the point of most value; in some instances, they also give the temperature when crystallisation is complete. When these two values are identical, the "solid solution" is identical with the liquid phase. Their values for stearic and palmitic acid mixtures are somewhat different from those of de Visser.

Stearic acid, %	Beginning of crystallisation	End	Stearic acid, %	Beginning of crystallisation	End	Stearic acid, %	Beginning of crystallisation	End
100	68.2°	.....	60	57.65°	.....	25	54.95°	
95	67.10°	.....	55	56.60°	.....	20	55.75°	
90	65.90°	61.50	52.5	56.00°	56.00	15	57.00°	
85	64.75°	.....	50	56.25°	56.25	10	58.40°	
80	63.50°	.....	45	56.10°	.....	5	59.60°	
75	62.15°	.....	40	55.90°	.....	0	61.00°	
70	60.80°	57.00	35	55.15°	.....			
65	59.30°	.....	30	54.75°	54.75			

It will be noted that the solidifying-points for the two pure acids are different from those of de Visser.

These authors have also examined stearic-oleic and palmitic-oleic mixtures, as well as mixtures of the three acids. With regard to the last the original should be consulted, as this is a very intricate case; information as to the composition of such mixtures may be derived, however, from the initial temperature of the solidification when taken in conjunction with the iodine value.

MIXTURES OF STEARIC AND OLEIC ACIDS

Stearic acid, %	Beginning of crystallisation	End of crystallisation
100	68.2°	...
95	67.15°	...
85	65.40°	...
75	63.40°	57°
65	61.25°	...
55	58.65°	45°
46	55.95°	...
35	51.90°	34°
25	46.60°	...
15	34.25°	...
5	23.45°	...
0	9.00°	...

MIXTURES OF PALMITIC AND OLEIC ACIDS

Palmitic acid, %	Beginning of crystallisation	Palmitic acid, %	Beginning of crystallisation
100	61.00°	40	46.25°
90	59.20°	30	41.60°
80	57.30°	20	35.00°
70	55.10°	10	24.80°
60	52.60°	0	9.0°
50	49.75°		

The m. p. of a mixture of two or more fatty acids taken alone is incapable of giving definite information; but if the observation is associated with other data useful inferences can be drawn. Thus the following mixtures of homologous fatty acids melt at nearly the same temperature, but may be distinguished by their combining weights, obtained by titrating them in alcoholic solution with standard alkali and phenolphthalein (page 10).

Nature of mixed fatty acids				M. p.	Combining weight
Lauric	Myristic	Palmitic	Stearic		
30	70	..	..	46.7°	219.6
50	..	50	..	47.0°	228.0
..	70	30	..	46.2°	239.4
..	50	21	29	46.5°	250.0

This method of separation must, however, be used with care, especially if more than 2 acids are present in the mixture. Kreis and Hafner (*Ber.*, 1903, 36, 2770) isolated in this way from lard an acid, $C_{17}H_{34}O_2$, m. p. 55–56°, but Holde, Ubbelohde and Marcusson (*Ber.*, 1905, 38, 1250) have shown that not only this, but all the so-called daturic acids are mixtures of acids containing an even number of carbon atoms. Erroneous conclusions from the mixed m. p. determination may arise from the presence of an acid, *a*, of a higher m. p. than acids *b* and *c*, and fractional precipitation of such a mixture may give rise to several fractions of approximately the same m. p. and combining weight. These, however, may be resolved by repeated fractionation by means of magnesium acetate or distillation *in vacuo*.

Jacobson and Holmes (*J. Biol. Chem.*, 1916, 25, 55) take advantage of the difference in solubility between the lithium salts of lauric and myristic acids for their separation, but the method appears to offer no advantages over the magnesium separation already described.

The method of examining fatty acids, proposed by Benedikt and Ulzer, consisted in preparing the acetyl derivatives and then ascertaining the amount of alkali required for saponification.

It was at first assumed that only hydroxylated acids (*e. g.*, ricinoleic acid) form acetyl derivatives when treated in this way, but Lewkowitsch (*J. Soc. Chem. Ind.*, 1890, 9, 660) showed that saturated acids, like capric, palmitic, and stearic acids give considerable acetyl values. This is due to the formation of anhydrides of these acids, thus, $2C_{15}H_{21}CO_2H + (CH_3CO)_2O = (C_{15}H_{21}CO)_2O + 2CH_3H CO_2H$, the anhydride so formed not being hydrolysed by hot water, and even only partially hydrolysed when titrated in *cold* alcohol with alkali. Lewkowitsch recommended (*J. Soc. Chem. Ind.*, 1890, 9, 846) that the acetyl groups actually combined with the hydroxylated fatty acid be estimated by hydrolysing with alcoholic potassium hydroxide, boiling off the alcohol and after liberation of the acid with sulphuric acid, distilling off the acetic acid and estimating its amount in the distillate. The value so obtained he called the "true acetyl value." The method devised by Lewkowitsch in 1897 (*J. Soc. Chem. Ind.*, 1897, 16, 503) is now in general use; it is described on p. 39.

Separation of Acids of the Stearic Series from Fatty Acids of Other Series.—The higher homologues of the stearic series of fatty acids being solid at ordinary temperatures, whilst the fatty acids of other series (*e. g.*, oleic, linolic, ricinoleic) are liquid, a more or less complete separation can be effected by subjecting the mixture to filtration or pressure. The latter plan is employed with considerable success on a large scale. Crystallisation from hot alcohol also serves to free the solid fatty acids from those fluid at ordinary temperatures, but neither plan allows of the latter being obtained even moderately free from admixed solid acids, and such methods are quite useless for quantitative work.

A general method by which stearic acid and its homologues may be separated from oleic and other liquid fatty acids is based on the fact that the lead salts of the acids of the stearic series are almost insoluble in ether, whilst the corresponding compounds of the other fatty acids are soluble. Since the lead salts of the solid acids are not wholly insoluble in ether, and those of the drying fatty acids are not completely dissolved, the results are not strictly accurate. The best known method of operating is probably that of Muter and De Koningh. 3 grm. of the fat should be treated, in a flask furnished with a long tube, with 50 c.c. of alcohol and a fragment of potassium hydroxide. The contents of the flask are boiled till hydrolysis is complete, when a drop of phenolphthalein solution is added and acetic acid until the solution is slightly acid. An alcoholic solution of potassium hydroxide is then added drop by drop until a faint permanent pink tint is obtained, when the liquid is slowly poured, with constant stirring, into a beaker containing a boiling solution of 3 grm. of neutral lead acetate in 200 c.c. of water. The solution is rapidly cooled and stirred at the same time, to induce agglomeration of the precipitate, and the clear liquid is poured off. The precipitate is well washed, by decantation, with boiling water and transferred to a stoppered bottle, in which it is treated with 120 c.c. of ether and allowed to remain 12 hours. (Wallenstein and Finck use a Drechsel gas-washing flask having the tube shortened about two-thirds to contain the ethereal solution, and pass a current of hydrogen through it for about a minute. In the case of colourless fats the liquid is said to remain practically colourless at the end of 12 hours, but if free access of air is permitted, a dark yellow solution is produced by oxidation.) Lead oleate, hypogeate, linolate or ricinoleate will be

dissolved by the ether, leaving lead laurate, myristate, palmitate, stearate, and arachidate undissolved. Lead erucate is sparingly soluble in cold, but readily in hot ether. The contents of the bottle are filtered through a covered filter into a Muter separating-tube (Fig. 15), 40 c.c. of dilute hydrochloric acid (1 : 4) added and the tube shaken till the clearing of the ethereal solution shows that the decomposition of the lead soaps is complete. The aqueous liquid, containing lead chloride and excess of hydrochloric acid, is run off through the bottom tap, water added, and agitated with the ether, and the process of washing by agitation repeated until the removal of the acid is complete. Water is then added to the zero mark and sufficient ether to bring the ether to a definite volume (e. g., 200 c.c.). An aliquot portion of this (e. g., 50 c.c.) is then removed through the side tap and the residual fatty acid weighed after evaporation of the ether in a current of coal-gas or carbon dioxide. Another aliquot portion of the ethereal solution should be distilled to a small bulk (avoiding complete evaporation of the ether), alcohol added and the solution titrated with N/10 potassium hydroxide and phenolphthalein, from which the fatty acids may be calculated from the result, or their mean combining weight deduced therefrom. A third aliquot part of the ethereal solution should be evaporated at about 60° in a flask traversed by a rapid stream of dry carbon dioxide. When every trace of ether is removed, 50 c.c. of Hübl's iodine solution should be added, the stopper inserted and the liquid kept in absolute darkness for 12 hours, after which an excess of potassium iodide

FIG. 15.

solution is added and 250 c.c. of water, and the excess of iodine ascertained with thiosulphate solution in the usual way. From the result the iodine value of the liquid fatty acids is calculated, and an opinion may be formed respecting the proportions of oleic, linolic, and other unsaturated acids present.

The following table shows the results obtained with various fats and oils:
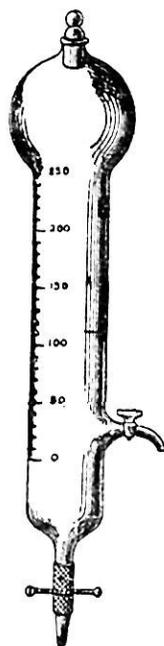
	Iodine number of		Observer
	Fat	Liquid fatty acids	
Lard, American..	66.0	104.0 (highest)	v. Raumer.
Lard, American..	65.4	104.5	Wallenstein and Finck.
Lard, Berlin.....	52.7	96.6	Wallenstein and Finck.
Lard, German.....	....	96.2 (highest)	v. Raumer.
Lard, Vienna......................	60.9	95.2	Wallenstein and Finck.
Lard, Hungarian..................	60.4	96.2	Wallenstein and Finck.
Lard, Roumanian.	59.5	96.0	Wallenstein and Finck.
Lard...........................	....	93.0 (highest)	Muter and DeKoningh.
Lard...........................	....	94.0 (highest)	v. Asboth.
Beef tallow......................	....	90.0	Muter and DeKoningh.
Beef tallow, Australian..	38.3	92.2	Wallenstein and Finck.
Beef tallow, Berlin................	45.2	92.4	Wallenstein and Finck.
Beef tallow, Hungarian.	38.6	92.7	Wallenstein and Finck.
Cottonseed oil....................	....	135.0	Muter and DeKoningh.
Cottonseed oil....................	....	136.0	v. Asboth.
Cottonseed oil, American, white... ..	108.0	147.5	Wallenstein and Finck.
Cottonseed oil, American, yellow......	107.8	147.3	Wallenstein and Finck.
Cottonseed oil, Egyptian.........	106.5	146.8	Wallenstein and Finck.
Cottonseed oil, Peruvian.......	106 8	147.8	Wallenstein and Finck.
Maize oil	122.0	140.7	Wallenstein and Finck.
Nigerseed oil.........	133.5	147.5	Wallenstein and Finck.
Arachis oil....	98.9	128.5	Wallenstein and Finck.
Rape oil...... ... . . - . ..	101.1	120.5	Wallenstein and Finck.
Coconut oil..........	8.0	54.0	Wallenstein and Finck.

For the estimation of solid fatty acids Twitchell (*J. Ind. Eng. Chem.*, 1921, 13, 806) recommends the following process: About 2 grm. of the fatty acid are dissolved in boiling alcohol and 1.5 gm. of lead acetate in alcohol solution are added, the total volume being made up 100 c.c. The mixture is cooled slowly and kept at 15° for 18 hours, the precipitate is collected on a filter, washed with 95% alcohol until the washing is free from fatty acids as shown by the absence of turbidity on diluting it with water. The precipitate is transferred to a beaker, boiled with 100 c.c. of alcohol and 0.5 c.c. of acetic acid, the solution is cooled again and allowed to stand, the precipitate is collected, washed, and then washed into a separating funnel with ether; nitric acid is added to decompose the lead salt, the acid ethereal solution is drawn off, washed well with water, evaporated and the fatty acids are weighed. The fatty acids so separated have iodine value less than 1.0 except in the case of hydrogenated fats or fatty acids.

If it is desired to estimate *stearic acid and its homologues*, the lead soaps insoluble in ether separated by Muter and DeKoningh's method described above should be detached from the filter and heated for some time with dilute hydrochloric acid, the liberated fatty acids being allowed to solidify, and then removed and weighed.   The prod-

uct may contain *arachidic, stearic, palmitic, myristic,* and *lauric acids,* besides the less commonly occurring acids of the same series. A modification of the method specially suited for the estimation of arachidic acid is described on page 118. If it is found impossible to remove the whole of the fatty acids from the filter, the latter should be treated with hot dilute hydrochloric acid, and then washed with a mixture of alcohol and ether, the fatty acids being recovered by evaporating the solution so obtained.

Lewkowitsch, however, recommends that the Muter tube be not used, the ethereal solution of the fatty acids being merely filtered through a folded filter into a flask. The ether is evaporated and the last traces of water are removed in a current of carbon dioxide by immersing the flask in boiling water.

The method is only approximately accurate and possesses the disadvantage that the filtration of the ethereal solution is frequently slow and consequently oxidation can hardly be avoided. Other solvents have been proposed, notably petroleum spirit of b. p. below 80°, in which lead palmitate and stearate are much less soluble than in ether (Twitchell, *J. Soc. Chem. Ind.,* 1895, 14, 516), and benzene (Fahrnsteiner, *Zeit. Unters. Nahr. Genussm.,* 1898, 390), the lead salts of the fatty acids being insoluble in this medium at 8 to 12°. This method is, however, not so exact as the lead salt and ether method, and preference should be given to the latter.

A good method for separating the lead salts of fatty acids has been proposed by Seidenberg (*J. Amer. Chem. Soc.,* 1921, 43, 1323) based on their solution in three solvents, alcohol, chloroform and ether, and evaporating the more volatile solvent until the insoluble salts are precipitated. 2 to 5 grm. of the mixed lead salts are dehydrated by exposure to the air and finally by washing with several portions of absolute alcohol, decanted into a cylinder and made up to 20 c.c. The residual salts are dissolved in 20 c.c. of hot chloroform, then evaporated to 8 c.c., 60 c.c. of ether are added and the warmed solution mixed with the alcoholic solution. The flask is rinsed with a little chloroform and ether and the total volume made up to 120 c.c. The volume is now reduced to 65 or 70 c.c. by aspirating air through the solution, and the precipitated salts are collected on a Gooch crucible. This precipitate is re-dissolved in a minimum quantity of hot chloroform, 50 c.c. of ether are added and the solution is heated to b.p. and allowed to cool. The precipitate

is filtered off and washed with three successive quantities of 10 c.c. of ether. The filtrates are united, 20 c.c. of strong alcohol are added and the more volatile solvents are evaporated by aspirating air through the solution until the volume is reduced to 30 c.c. The precipitate is collected, dried at 100° and weighed; if it is much discoloured, it is dissolved in 3 c.c. of chloroform, 20 c.c. of ether is added and the hot mixture cooled, evaporated and filtered. The total amount of precipitate gives the weight of lead salts of the saturated fatty acids. The method is not suitable for linseed oil or fatty acids containing much linolenic acid but is useful for mixtures containing oleic or linolic acids.

Separation of the saturated from the unsaturated fatty acids by means of sulphuric acid has also been proposed (Twitchell, *J. Soc. Chem. Ind.*, 1897, **16**, 1002) and by means of the greater solubility of the lithium salts of the unsaturated acids in alcohol (Partheil and Ferie; *Arch. Pharm.*, 1903, **241**, 545; Jacobson and Holmes, *J. Biol. Chem.*, 1916, **25**, 55), but these methods have been adversely criticised and appear to offer no advantages over the older method.

A new method which has given excellent results on known mixtures of saturated and unsaturated fatty acids is that of Grün and Janko (*Z. Deuts. Oel. u. Fettind.*, 1921, **41**, 553) depending on the wide difference in b. p. of the mixed esters of saturated acids and of the bromine addition products of esters of unsaturated acids. After esterification in the presence of hydrogen chloride, as usual the, esters, dissolved in carbon tetrachloride, are saturated with bromine. The brominated product is washed with water and with dilute solution of sodium bicarbonate and dried. The resultant mixture is fractionated under reduced pressure, (2–4 mm.) the ethyl esters of the saturated acids distil up to 175°, but the decomposition of the brominated esters does not begin until 190°. The residual brominated esters are removed and the bromine eliminated by boiling with alcoholic hydrochloric acid 2N to 3N and granulated zinc; the weight of zinc used should be equal to that of the esters. The alcohol, acid and salts are then removed by pouring into water and the esters are extracted with ether and distilled off. When there is present more than about 90% of unsaturated acids a known quantity of ethyl stearate may be added to the mixed esters, and subsequently allowed for, in order to effect a better separation.

Hehner and Mitchell have devised the following method of the estimation of *stearic acid:* Prepare a supply of alcohol saturated at 0° with pure stearic acid or with stearic acid which contains only traces of palmitic acid. Dissolve from 0.5 to 1 grm. of the mixture of fatty acids to be examined if these are solid, or about 5 grm. if fluid, in about 100 c.c. (exact measurement is not necessary) of the stearic acid alcohol solution. Leave this liquid in an ice-bath overnight, agitate the mixture next morning and allow it to stand in ice for a short time; filter off whilst the mixture remains in ice, wash with stearic alcohol solution at 0°, dry and weigh. Ascertain the m. p. of the product which should not be much less than 68.5°. Since the sides of the interior of the flask, as well as the residue of crystallised stearic acid, retain a small amount of the alcoholic solution, a correction experimentally found to be 0.005 grm. has to be applied, this amount being deducted from the total weight found. In their experiments the authors used methylated alcohol of sp. gr. 0.8183, but obviously the exact strength is a matter of no consequence.

For maintaining a constant temperature, Hehner and Mitchell used an ice-chest consisting of a metal box with sockets soldered to its sides to receive clamps for holding flasks, submerged to the neck in ice-water, in which the analyses were carried out. The metal box was fitted in a wooden box, and the space between the metal and wood was packed with wool and sawdust, whilst a cushion of wool and flannel was placed between the lids of the metal and wooden boxes.

For the preparation of the stearic solution about 3 grm. of pure stearic acid were dissolved in about a litre of warm alcohol of sp. gr. 0.8183, and the stoppered bottle containing the solution placed overnight in the ice-water (which contained lumps of ice) in the chest, so that the bottle was submerged up to the neck. After 12 hours a considerable portion of the stearic acid had crystallised out. The saturated mother-liquor was siphoned off without removing the bottle from the ice-water. The filtering siphon consisted of a small thistle funnel twice bent at right angles, fitting with its straight limb into a flask in connection with a suction pump. The bulb of the funnel, which was submerged in the ice-cold solution, was covered over with a piece of fine calico. On applying suction, a perfectly clear stearic solution was obtained, saturated at 0°, or rather at 0.2°, which was the temperature almost constantly shown by a standard thermometer.

A precisely similar mode of filtration was also adopted in the quantitative experiments on mixed fatty acids, the thistle funnel used being a miniature one, with a bulb not larger than about 0.25 inch in diameter.

ESTIMATION OF STEARIC ACID IN MISCELLANEOUS FATS

	Taken grm.	Iodine number	Stearic acid 0.005 grm.	Percentage in fatty acids
Beef stearine................	0.3024	2.0	0.1516	50.19
Beef stearine................	0.4174	....	0.2131	51.05
Oleomargarine...............	1.0107	46.50	0.2295	22.0
Oleomargarine...............	0.5192	....	0.1104	21.26
Oleomargarine...............	1.1100	....	0.2630	23.6
Margarine I.................	1.0035	....	0.2495	24.8
Margarine II................	0.5000	41.19	0.0586	11.72
Horse-kidney fat............	0.701	85.4	no deposit	....
Cotton oil "stearine"........	0.9945	....	0.0334	3.3
Stillingia tallow............	....	22.87	no deposit	....
Cacao butter...............	1.0168	....	0.3878	40.6
Cacao butter...............	0.9548	....	no deposit	....
Maize oil..................	5.4186	122.0	no deposit	....
Almond oil.................	5.0236	95.68	no deposit	....
Olive oil..................	5.5558	....	no deposit	....
Earthnut oil...............	1.0648	....	0.0751 (m. p. 67°)	7.0

Numerous estimations of the stearic acid in butter were made. In many cases none, or a minute quantity only, was found. In some cases phenomena of supersaturation apparently occurred. On the first examination in the morning the solution was perfectly clear, but after shaking the contents and allowing to stand some time longer in the ice, a small but increasing quantity of crystals formed.

The method appears to be inapplicable to the fatty acids from Japan wax. From mixtures of these with pure stearic acid, the latter could only be recovered partially, and in some cases not at all.

Kreis and Hafner (*Zeit. Nahr. Genussm.*, 1903, **6**, 22) state that this method gives trustworthy results provided that not less than 0.5 grm. of the mixed fatty acids is taken, as stearic acid easily forms supersaturated solutions. This is borne out by Emerson (*J. Amer. Chem. Soc.*, 1907, **29**, 1750) and is said to explain the differences in the solubility obtained. Appended are results:

Hehner and Mitchell found solubility at 0° in 94.4% methylated alcohol 0.15 grm.

Kreis and Hafner found solubility at 0° in 95% ethyl alcohol 0.1249 grm.

Emerson found solubility at 0° in 95% ethyl alcohol 0.1123 grm.

The alcohol used by Hehner and Mitchell, as already pointed out, was rectified methylated spirit.

Other methods of separating oleic from stearic acid or of estimating the former in mixtures of the two are described on page 543. A method for separating oleic from palmitic acid is also described on page 543.

Separation of Fatty Acids from Resin Acids.—As already pointed out, Twitchell's method has been found to be one of the most satisfactory (see page 94).

Separation of Fatty Acids from Soaps, Hydrocarbon Oils, etc.— The estimation of the constituents of complex mixtures of fatty acids with neutral oils, hydrocarbons, etc., has already been described (see table on page 94). Small quantities of neutral fats contained in free fatty acids may be detected by dissolving the substance in hot alcohol and adding a few drops of strong ammonia to the solution; in the presence of mere traces of neutral fat, the solution is rendered turbid.

PALMITIC ACID

$$C_{16}H_{32}O_2 = C_{15}H_{31}COOH$$

The glyceride of palmitic acid occurs largely in palm oil, Chinese tallow, the fat of coffee-beans, coconut oil, butter-fat, tallow, and lard. Palmitic esters of monatomic radicals exist in spermaceti, beeswax, and opium wax.

Palmitic acid is conveniently prepared from palm oil, which should be saponified with potassium hydroxide, the solution of the resultant soap decomposed by dilute sulphuric or hydrochloric acid, and the liberated fatty acid purified from the accompanying oleic acid by repeated crystallisation from hot alcohol, till the pressed crystals have m. p. 62°. Chittenden and Smith prepare palmitic acid from myrtle wax, which is said to contain only lauric acid in addition. By repeatedly crystallising the separated fatty acids from hot alcohol, pure palmitic acid, melting at 62°, is readily obtained. Palmitic acid is manufactured on a large scale by the action of potassium hydroxide upon oleic acid at a high temperature, or by saponifying palm oil and pressing the fatty acids obtained. The product is commonly, but improperly, called "palmitine."

Palmitic acid is a white substance, melting at 62.62° (de Visser) to a colourless oil, which solidifies, on cooling, to a white, finely crystalline mass. It has sp. gr. 0.8412 at 80° and N_D^{80} 1.42693 and has a

temperature coefficient of refractive index = −0.00035 for each 1° rise. It is insoluble in water or dilute acids, but is soluble in alcohol, ether, carbon disulphide, hydrocarbons, and fixed oils. It cannot be distilled without decomposition under ordinary pressure, even in the absence of air; but distils, practically unchanged, at 271.5°/100 mm.

Palmitic acid is but slightly soluble in cold alcohol. Hehner and Mitchell (*Analyst*, 1896, **21**, 323) have found 100 c.c. of methylated alcohol (94.4% by volume) to dissolve the following quantities after being kept at 0° for the time stated.

No. of hours	Grm. dissolved	No. of hours	Grm. dissolved
12	1.298–1.320	108	1.086
36	1.244	132	1.044
60	1.211	156	1.028
84	1.134		

Kreis and Hafner (*Ber.*, 1903, **36**, 2769) found 95% alcohol to dissolve 0.56 grm. at 0°. Absolute alcohol dissolves 1.45 grm. at 0°. The solubility increases rapidly with rise of temperature.

The hot alcoholic solution has an acid reaction, and on cooling deposits the acid in tufts of small white needles.

Crystallisation from hot alcohol may be employed to separate palmitic acid from *oleic acid*, and, if repeated sufficiently often, from its lower homologues *myristic* and *lauric acids*. Mixtures of palmitic acid with certain proportions of myristic or lauric acid are, however, said to be incapable of analysis by fractional crystallisation from alcohol or ether. Mixtures of these homologous acids in certain proportions melt at a lower temperature than either acid separately. The method of ascertaining the composition of such mixtures, including those containing *stearic acid*, is described on page 523 *et seq.*

A method of separating palmitic acid from *oleic* and *linolic acids* and their homologues is given on page 547. A method of separating palmitic and oleic acids, which is useful for analysing the product obtained by saponifying palm oil by the autoclave process, is described on page 548. Commercial palmitic acid may be examined in the same manner as stearic acid.

Chittenden and Smith (*Amer. Chem. J.*, 1885, **6**, 217) find that the presence of free acetic acid increases the solubility of barium,

magnesium, and lead palmitates in alcohol to such an extent as to render the separation of the acid in these forms incomplete. Further, the precipitates undergo partial decomposition when washed either with water or with alcohol containing acetic acid.

Metallic Palmitates.—These present the closest resemblance to the corresponding stearates (page 540 *et seq.*), and require but little separate description. Barium, magnesium, and lead palmitates are a little more soluble in alcohol, especially in presence of acetic acid, than are the corresponding stearates. 100 parts of absolute alcohol dissolve 0.0007 of lead palmitate at 20°.

Adipocere, a wax-like substance found in large quantity in corpses buried under certain conditions, is said to consist largely of palmitic acid mixed with potassium and calcium palmitates.

Aluminium palmitate may be prepared in a manner similar to the corresponding oleate. It is an elastic amorphous mass, insoluble in water, but dissolving in petroleum spirit and oil of turpentine to form very viscid solutions which have found applications as varnishes. The film of aluminium soap left on evaporation retains its elasticity, and is odourless and impervious to water (see *J. Soc. Chem. Ind.*, 1882, 1, 278). Aluminium palmitate has some practical interest as an ingredient of "oil pulp" or "thickener."

Palmitic Esters.—These present a close analogy to the corresponding stearates.

Glyceryl Palmitates or Palmitins are obtainable synthetically by means similar to those employed for the preparation of the stearins. Chittenden and Smith (*Amer. Chem. J.*, 1885, 6, 217) have given the following data:

	α-Monopalmitin	α-Dipalmitin	Palmitin
100 parts of absolute alcohol, at 20–21°, dissolve..............	4.135	0.210	0.005
Appearance of fat deposited from alcoholic solution.	Small spherules, showing no distinct crystalline form.	Long curved needles.	Groups of irregular crystals.
Appearance of fat deposited from ethereal solution.	Rhombic plates, either single or in branches.	Warty masses.	Irregular doubly curved bodies, single and crossed in groups.
M. p..........................	53.0°[1]	61.0°[2]	62–64°[3]
Solidifying-point..............	62.5°	57.0°	45.5–47°

[1] Krafft (*Ber.*, 1903, 36, 4343) gives m. p. 72°.
[2] Probably a monoglyceride; Grün (*Ber.*, 1905, 38, 2284) m. p. 70°.
[3] Scheij (*Rec. Trav. Chim.*, 186 u9(6d·6, 18,1 gives 65.1°, sp. gr. 0.8657/80°; Guth (*Zeit. Biol.*, 1902, 44, 78), m. p. 65.5°.

An isomeric modification of dipalmitin, the β-form, has been obtained, m. p. 67.2°.   There was also obtained a very stable mixture of 1 part of palmitin with 3 of dipalmitin.   This product crystallised from alcohol in bunches of needles, which melted at 68° to 69° and solidified between 64° and 67°.

STEARIC ACID

$$C_{18}H_{36}O_2 = C_{17}H_{35}COOH$$

The glyceryl ester of this acid occurs extensively in nature, especially in the harder fats of the animal kingdom, such as mutton and beef suet.

Pure stearic acid may be prepared by hydrolysing tallow with potassium hydroxide, decomposing the solution of the resultant soap with a dilute acid, and purifying the liberated fatty acids from oleic acid by crystallisation from hot alcohol.   The pressed crystals consist essentially of a mixture of stearic and palmitic acids.   It should be purified by recrystallisation, and 4 parts dissolved in such a proportion of hot alcohol that nothing will separate out on cooling to 0°.   A solution of 1 part magnesium acetate in boiling alcohol is added and the liquid allowed to cool, when magnesium stearate will separate (page 522).   The precipitate is filtered off, washed with cold alcohol, boiled with water and hydrochloric acid, and the purity of the resultant stearic acid proved by a careful determination of the m. p. which should be 69.32° (de Visser).

The commercial product commonly termed "stearine" really consists of a mixture of free stearic and palmitic acids, and may be conveniently employed for the preparation of pure stearic acid, instead of tallow or other fat.   The "stearine" may be at once dissolved in hot alcohol and the solution precipitated with magnesium acetate as above described.   Commercial stearine often contains a considerable admixture of paraffin wax or other hydrocarbons, the absence of which should be proved before employing the substance for the preparation of stearic acid.

Stearic acid is less soluble in alcohol than is palmitic acid: 100 grm. of absolute alcohol dissolve 0.37 grm. of the acid at 0° and 2.5 grm. at 20°.   Methylated alcohol 95% dissolves 0.125 grm. at 0°, but larger quantities have been found owing to supersaturation (*Vide Supra*).   It dissolves readily in ether, benzene, or carbon disulphide.

Shea-butter, when obtainable, may be conveniently employed as a source of stearic acid, as the fatty acid produced by its hydrolysis consists solely of stearic and oleic acids, which can be separated perfectly by repeated crystallisation from hot alcohol.

Stearic acid presents the closest resemblance to palmitic acid, the following being the most tangible distinctions:

	Palmitic acid	Stearic acid
M. p.	62.62°	69.32°
B. p./100 mm.	271.5°	287°
Solubility in cold absolute alcohol.	9.3%	2.5%
Manner of crystallisation from alcohol.	Tufts of small white needles.	Nacreous laminæ, or needles.
Behaviour with magnesium acetate.	See page 522.	See page 522.
M. p. of lead soap.	108°–112°	125°
Refractive Index N_D^{80}	1.4324	1.4322
Sp. gr. at 80°	0.8412	0.8386

In the analysis of natural oils and fats the palmitic and stearic acids are usually obtained together, the oleic acid being separated by treating the lead soaps with ether, as described on page 530. In the mixture of palmitic and stearic acids thus obtained, the proportions of the two constituents can be approximately ascertained by one of the methods described on page 524 et seq., but the rigidly accurate analysis of such mixtures is not at present possible.

Commercial stearic acid differs much in quality and appearance according to it source, but usually consists of a mixture of stearic acid with more or less palmitic and, sometimes, oleic acid. Hydrocarbons and unsaponified fat may also be present, but the proportion of these impurities is seldom large. The method of analysis is similar to that employed for oleic acid, with the addition of ascertaining the solidifying point by the "titer test," from which the relative proportions of stearic and palmitic acids in the sample can be deduced; or, in the absence of hydrocarbons and unsaponified oil, the proportions of stearic and palmitic acids can be deduced from the results of the titration with standard alkali (page 521). The proportion of oleic acid may be ascertained by multiplying the iodine value by 1.11 (page 514).

Metallic Stearates.—Stearic acid forms a well-defined class of salts, all of which, with the exception of those of the alkali-metals, are insoluble in water, and mostly so in alcohol and ether.

The stearates present very close resemblances to the palmitates, the chief tangible points of distinction being the more ready solubility of magnesium palmitate in alcohol and the different m. p. of the lead salts. Lead palmitate melts at 108°, according to Maskelyne, and between 110° and 112°, according to Heintz, whilst lead stearate melts at 125°. Palmitates and stearates may also be distinguished by the m. p. and combining weights of the liberated fatty acids.

Potassium stearate may be prepared by saturating a hot alcoholic solution of stearic acid with alcoholic potassium hydroxide, phenolphthalein being used as indicator. On concentrating the solution and allowing it to cool, the potassium stearate crystallises in shining needles or laminæ. It also separates on cooling a solution of 1 part of stearic acid and 1 of potassium hydroxide in 10 parts of water. The opaque granules formed may be purified by crystallisation from alcohol. Or a boiling alcoholic solution of stearic acid may be mixed with an excess of a boiling aqueous solution of potassium carbonate, the liquid evaporated to dryness, the residue extracted with boiling alcohol, and the filtered solution allowed to cool, when crystals of potassium stearate will be deposited.

Potassium stearate dissolves in about 10 times its weight of water at the ordinary temperature, forming a mucilaginous mass. On heating the solution it becomes clear, and if diluted with a large proportion of cold water *potassium hydrogen stearate* of the composition $KH(C_{18}H_{35}O_2)_2$ separates in delicate, white, pearly laminæ, whilst a basic stearate remains in solution. An analogous decomposition by excess of water is suffered by other alkali-metal salts of the higher fatty acids, and is a leading cause of their application as soaps.

Ammonium stearate is obtained as a crystalline mass by incorporating strong ammonia with melted stearic acid, and keeping the product over sulphuric acid till the excess of ammonia has evaporated. On further keeping in this manner, it gradually loses ammonia (Wright and Thompson).

Sodium stearate resembles the potassium salt, but is harder. It is decomposed in a similar manner, but with greater facility, by excess of water, and is less soluble in alcohol than potassium stearate. Sodium stearate may be separated from sodium palmitate by fractional crystallisation from hot alcohol.

Barium amd calcium stearates are crystalline precipitates insoluble in water. The *magnesium* salt is similar, but is soluble in boiling alcohol.

Lead stearate, as prepared by double decomposition, forms a white amorphous powder, melting at 125° to a colourless liquid, which solidifies on cooling to an opaque amorphous mass. It is insoluble in water, alcohol, ether, or petroleum spirit. In these characters it resembles lead palmitate, myristate, arachidate, etc., but the lead salts of oleic acid and its homologues, as also of linolic and ricinoleic acids, are soluble in ether and petroleum spirit.

Stearic Esters.—*Ethyl stearate* is prepared by passing hydrogen chloride into a solution of stearic acid, in absolute alcohol. It is also formed by boiling tristearin with sodium oxide, or with a quantity of alcoholic potassium hydroxide insufficient for its complete saponification. Ethyl stearate is a crystalline, easily fusible, wax-like solid, m. p. 33.7°, readily soluble in alcohol and ether, and b. p. 224° with partial decomposition, b. p. in a vacuum 139° or 154° (Krafft, *loc. cit.*, p. 537).

Glyceryl stearates are obtainable synthetically by heating together, under pressure, suitable proportions of stearic acid and glycerol. Products containing either 1, 2, or 3 molecules of the stearic radicle are thus obtainable. Another method of obtaining stearin consists in heating α, β, γ-tribromopropane and sodium stearate at 170°–180° for 10 hours.

Monostearin and distearin do not appear to occur naturally, but *glyceryl stearate* is identical with the stearin which, in admixture with palmitin, constitutes the less fusible portion of solid fats. For brevity, this stearate is frequently called "stearin." It is not identical with commercial "stearine," which is a mixture of free stearic and palmitic acids obtained by the saponification of the neutral fats.

Stearin forms white, shining nodules, fine needles, or pearly laminæ resembling spermaceti. It is tasteless, neutral, and volatile almost without decomposition in a vacuum. Heated to a high temperature, it decomposes and gives off acrolein. It appears to exist in two isomeric modifications. As crystallised from ether, it has a m. p. of 71.6°, sp. gr. 0.8848/60° (Scheij, *loc. cit.*, p. 537). If the crystals so obtained be heated 4° or more above the m. p., they are converted into an unstable modification which solidifies to a waxy mass at 52°, and melts at 55°. If the latter be reheated a few degrees

above the m. p., the original substance, melting at 71.6°–72.2°, is obtained (see Nicolet, *J. Ind. Eng. Chem.*, 1920, **12**, 741).

Stearin is insoluble in water and nearly insoluble in rectified spirit. In boiling absolute alcohol it dissolves freely, and is deposited in flocks on cooling. Stearin also dissolves readily in boiling ether, but the liquid retains less than 0.5% on cooling. It is readily soluble in fixed and volatile oils, and in carbon disulphide. When heated in a vacuum it distils almost unchanged, but under the ordinary pressure it is decomposed with formation of carbon dioxide, acetic acid, water, free carbon, and olefines of b. p. ranging from 190° to 245°. A study of the melting points and refractive indexes of stearic acid, stearins, and palmitic acid and oleic acid and mixtures is given by Kremann and Klein (*Monats. Chem.*, 1913, **34**, 1291; 1914, **35**, 561) and Kremann and Pascal (*Bull. Soc. Chem.*, 1914, **15**, 360, 397).

Pure stearin does not change on exposure to air at the ordinary temperature. When impure, it is liable to become rancid, apparently owing to the presence of olein. Stearin readily undergoes saponification when heated with alkalis or other strong bases, with formation of a metallic stearate and glycerol.

OLEIC ACID

$$C_{18}H_{34}O_2 = C_{17}H_{33}COOH$$

Oleic acid is one of the most widely distributed fatty acids, occurring as an ester in most non-drying fixed oils, especially almond and olive oils, and in smaller proportion also in solid fats, such as lard, palm oil, butter, and goose fat. It occurs in several isomeric forms— the ordinary acid is stereo-isomeric with elaidic acid, the two being represented by the formulæ:

$$CH_3(CH_2)_7\ CH$$
$$\|$$
$$HC.(CH_2)_2CO_2H$$
Oleic acid

$$CH_3(CH_2)_7CH$$
$$\|$$
$$CO_2H(CH_2)_7CH$$
Elaidic acid
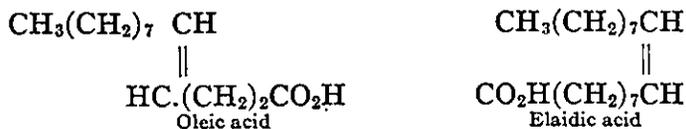
For the preparation of pure oleic acid an oil rich in olein, such as almond or olive oil, is saponified by alkali, the soap dissolved in water and decomposed by excess of dilute hydrochloric or sulphuric acid. White Castile soap may be employed as the starting-point, thus saving the trouble of saponifying. The use of commercial oleic acid is not to be recommended, owing to the frequent presence of

hydrocarbons. The liberated fatty acids are separated from the aqueous liquid, and heated for some time on the water-bath with about 1 part of finely ground lead monoxide for every 20 parts of oil taken for the operation. Excess of lead oxide should be avoided, as it occasions the formation of a basic oleate, which is subsequently treated with difficulty. The proportion of lead oxide prescribed is insufficient to combine with all the fatty acid, but the result is merely that a portion of the oleic acid remains in the free state, whilst palmitic and stearic acids form lead salts.

The product is next treated with about twice its volume of ether, which dissolves the lead oleate and free oleic acid, and leaves the lead palmitate and stearate unchanged. The solution is separated from the insoluble salts, and hydrochloric acid added until the aqueous liquid has a strongly acid reaction even after shaking. The lower layer now contains lead chloride, while the ether retains the oleic acid. It is separated from the acid liquid, washed by agitation with water, the ethereal layer removed and the ether evaporated off as rapidly and at as low a temperature as possible.

According to E. C. Saunders, rectified spirit (sp. gr. 0.82) may be advantageously substituted for the ether prescribed in the above process.

The oleic acid obtained by the foregoing process is apt to retain a little colouring matter and products of oxidation. To remove these, Bromeis recommends that it should be cooled below its solidifying-point, and subjected to strong pressure between folds of filter-paper. The residual oleic acid is melted, again cooled, and the purification by pressure repeated. Another method of purification consists in dissolving the oleic acid in twice its weight of alcohol and adding an equal volume of aqueous solution of lithium hydroxide sufficient just to neutralise the acid. On standing, a crystalline precipitate of lithium oleate separates which is collected on a filter, washed with dilute alcohol and the oleic acid liberated by dilute hydrochloric acid. The acid so obtained is distilled under reduced pressure and should be a colourless liquid, odourless, and having iodine value 90 and saponification value 284:

Pure oleic acid[1] is a colourless, odourless, tasteless oily liquid, having sp. gr. 0.900 at 11.8°, 0.897 at 19°, and 0.876 at 100°. When

[1] NOTE.—Lapworth and Pearson point out that the properties of the pure acid have not yet been ascertained with certainty, as the existing methods of isolation are unsatisfactory. The data given here refer to commercially pure oleic acid. (See Food Invest. Bd. *Rept*, 1921, H. M. Stationery Office, London, 1922.)

cooled to about 4°, it solidifies to a white crystalline mass, and on cooling its hot alcoholic solution is deposited in white needles, m. p. 14°. Its purity should be tested by means of the iodine value—the pure acid has an iodine value 90.

Pure oleic acid is not altered by exposure and is neutral, but the impure substance gradually absorbs oxygen, becomes yellow, and acquires an acid reaction and a rancid taste and smell. The altered product has a lower m. p. than the pure acid. Oleic acid is much thinner than the neutral fixed oils, and is less liable to leave a greasy stain. When applied to the skin it wets it almost like water, and is very rapidly absorbed.

Oleic acid is insoluble in water, but dissolves with facility in alcohol, ether, carbon disulphide, chloroform, and hydrocarbons, and is also miscible with neutral fats and essential oils. The solution of oleic acid in alcohol usually has an acid reaction to litmus, a fact said to be due to the presence of impurities. It turns milky when largely diluted with spirit, but the turbidity disappears on adding a few drops of hydrochloric acid. Oleic acid dissolves in ammonia and solutions of alkalis to form oleates, from which other salts may be obtained by double decomposition.

Oleic acid may be distilled in a vacuum or in a current of super-heated steam at 250° without material alteration; but if distilled in contact with air it is partially decomposed, with formation of carbon dioxide, hydrocarbons, acetic, caproic, caprylic, capric, sebacic, and other acids. It has b. p. 153°/0 mm., 264°/50 mm., 285.5°/100 mm.

Sebacic acid, $C_8H_{16}(COOH)_2$, is also produced when oleic acid is *rapidly* heated with excess of alkali. Its formation is a characteristic test for oleic acid and its immediate homologues. To detect it the alkaline residue should be treated with boiling water, and the liquid acidified with acetic acid, again boiled, and filtered hot. The filtered liquid will, on cooling, deposit brilliant needles of sebacic acid, m. p. 127°, and soluble in 1000 parts of cold or 50 of boiling water.

When more strongly heated with potassium hydroxide, oleic acid yields potassium palmitate, oxalate and acetate, and free hydrogen, secondary products being also formed. The temperature necessary for this change is 300° to 320°. The process is commercially employed for the production of palmitic acid. The following formula expresses the main change which occurs:

$$C_{18}H_{34}O_2 + 2KOH = KC_{16}H_{31}O_2 + KC_2H_3O_2 + H_2$$

Small quantities of sebacic acid, caproic acid, caprylic alcohol and other compounds are also produced. The details of this process of manufacturing palmitic acid, for which nearly all fatty substances, except mare's grease and suint fat, are available, have been described by W. Lant Carpenter (*J. Soc. Chem. Ind.*, 1883, **2**, 98. Compare also Lewkowitsch, *J. Soc. Chem. Ind.*, 1879, **16**, 390).

Oleic acid combines with a molecule of bromine to form dibromo-stearic acid, $C_{18}H_{34}O_2Br_2$ as a yellow viscous oil having a distinctive odour. Oleic acid also combines in a perfectly definite manner with Hübl's reagent, and may be estimated by that means.

Oleic acid is dissolved by concentrated sulphuric acid, a conjugate acid being formed which has been used in Turkey-red dyeing and calico-printing.

Strong nitric acid oxidises oleic acid, acids of the acetic and oxalic series (including succinic acid) being formed.

By oxidation with potassium permanganate in presence of an excess of potassium hydroxide, oleic acid yields dihydroxystearic acid, a crystalline compound, m. p. 131.5 to 132°, and solidifying at 119° to 122°. For details of preparation consult Le Sueur (*Trans. Chem. Soc.*, 1901, **79**, 1315).

When oleic acid is heated to 200° or 210° in a sealed tube with amorphous phosphorus and fuming hydriodic acid, it absorbs hydrogen, and is converted into stearic acid.

Iso-oleic Acid (Para-oleic, or Solid Oleic Acid).—Oleic acid, being unsaturated, may be hydrogenated catalytically, and is completely transformed into stearic acid; but during the hydrogenation an intermediate solid acid, "iso-oleic acid." is produced, the amount being dependent on the catalyst employed and on the temperature. In the case of partly hydrogenated oleic acid or its esters it may be nesessary to estimate the iso-oleic acid, liquid oleic acid and stearic acid in the mixture. For this purpose Moore's method may be employed (*J. Soc. Chem. Ind.*, 1919, **38**, 320T). The lead salts are prepared in the usual way (see p. 528) and the solid acids separated by ether, which may with advantage be anhydrous, then the ethereal solution of the lead salts of the liquid acids is cooled overnight at 0° to −5°. The further quantity of solid acid salts so obtained is added to the original solid acids, decomposed by hydrochloric acid, and the solid and liquid acids isolated. The liquid acid so obtained is practically pure oleic acid.

The solid acids still contain some oleic acid and are dissolved in 70% alcohol, cooled to 0° and allowed to stand for 12 hours, the precipitate of stearic and iso-oleic acid is separated, the alcohol is evaporated and the acids so obtained are once more treated by the lead salt and ether process. The iodine value of the solid acids is estimated, and from this the percentage of iso-oleic acid, which has iodine value of 90, is calculated, since stearic acid has iodine value *nil*.

When the red fumes generated by acting on nitric acid by starch or arsenious oxide, or by a mixture of sulphuric acid and sodium nitrite, are passed for a short time into oleic acid, carefully kept cold, the liquid gradually thickens, and in the course of an hour or so solidifies to a crystalline mass of an isomer of oleic acid, elaidic acid. If may be purified by agitation with boiling water, followed by crystallisation from alcohol.

Elaidic acid, $C_{18}H_{34}O_2$, forms large pearly plates, resembling benzoic acid, m. p. 51–52°, and distilling almost unchanged. B. p. 154°/0 mm., 266°/50 mm., 287.8°/100 mm. In the solid condition it is unchanged in the air, but in the melted state it readily absorbs oxygen, becoming yellow and pasty, and acquiring an odour like that of poppy oil. With bromine, fused potassium hydroxide, and phosphorus and hydriodic acid, elaidic acid behaves like oleic acid. Elaidic acid has a strong acid reaction, and forms a series of well-defined salts, all of which, if neutral, are said to be insoluble in water. *Sodium elaidate* crystallises from alcohol in silvery laminæ, and the *potassium* salt in glistening needles. The *barium* and *lead* salts are white precipitates.

The property of forming an isomer of higher m. p. under the influence of nitrous acid is not peculiar to oleic acid. It is exhibited also by olein, by its homologues hypogæic and erucic acids, and by ricinoleic acid, but not by the fatty acids characteristic of the drying oils.

Estimation of Oleic Acid.—When occurring in the free state and unmixed with other acids, oleic acid may be conveniently and accurately estimated by titration with standard alkali (page 10). In presence of acids of the stearic series it may be estimated from its iodine value, each c.c. of N/10 iodine aborbed corresponding to .00141 grm. of oleic acid. The estimation of oleic in presence of linolic acid is described on page 519.

Oleic acid may be estimated gravimetrically when in admixture with acids of the stearic series by utilising the solubility of its lead salt in alcohol, ether, or petroleum spirit, in the manner described for its preparation (page 543). The best method of applying the principle for analytical purposes is described on page 530.

According to F. Sear, palmitic and oleic acids can be separated by heating the mixture with excess of zinc oxide and digesting the product in the cold with carbon disulphide.

David's method for estimating oleic acid in the presence of stearic acid, based on the solubility of oleic acid in a liquid containing definite proportions of alcohol, acetic acid and water, is inaccurate.

A method for the approximate estimation of oleic and solid fatty acids in tallow is described on page 288.

Commercial Oleic Acid.—Commercial oleic acid is obtained by subjecting to hydraulic pressure the mixture of fatty acids produced by the hydrolysis of tallow, palm oil, and similar fats. The expressed liquid, technically known as "red oil," contains a considerable quantity of palmitic and stearic acids, which separate out on keeping the red oil for some time at a low temperature.

When fats are hydrolysed by the autoclave process, the products often contain a considerable proportion of unchanged fats. In consequence of the comparative facility with which palmitin and stearin are hydrolysed, the unaltered fat consists chiefly or wholly of olein, which, owing to its low m. p., becomes concentrated in the oleic acid expressed from the crude product. Hydrolysis under high pressure always tends to cause more or less decomposition of the higher fatty acids, and, when actual distillation has been resorted to, notable quantities of acetic, suberic, and sebacic acids are formed, and the two latter will remain with the oleic acid, together with certain hydrocarbons, apparently belonging to the paraffin series, which are always simultaneously produced.

Commercial oleic acid, which is frequently called "oleine," varies considerably in properties and composition. It is sometimes a clear liquid, ranging in colour from dark brown to pale sherry, "(saponification oleine)" whilst other specimens are quite pasty from separated solid fatty acids. By distillation in a current of steam, oleic acid may be obtained wholly free from colour, "(distillation oleine)" but possessing an acrid odour from the presence of decomposition products. Undistilled oleic acid usually

retains an odour suggestive of its origin.   The sp. gr. is also variable, ranging from about 0.887 to 0.908, or even more, according to the proportions of hydrocarbons, neutral oils, and solid fatty acids which happen to be present.   The iodine value of distilled acid varies between 80 and 85, whilst that of the saponification oleine may be much lower owing to presence of solid acids.

Mineral acids are sometimes present in sensible quantity in commercial oleic acid.   They rarely interfere with its applications; but, if necessary, may be detected and estimated as on page 92, or by titrating the alcoholic solution with alkali and methyl-orange.

The presence of an abnormal proportion of *oxidation* and *secondary products* of an acid character is indicated by agitating 50 c.c. of the oleic acid with 1 c.c. of a 10% solution of ammonia and 50 c.c. of water.   Both the oleic acid and the aqueous liquid should by this means be deprived of any acid reaction to litmus.

The presence of *palmitic* or *stearic acid* in commercial oleic acid may be detected by saponifying the sample with alcoholic potassium hydroxide, adding a drop of phenolphthalein solution, and then acetic acid, drop by drop, until the pink colour is just destroyed.   The liquid is then filtered, mixed with twice its weight of ether, and an alcoholic solution of lead acetate added.   Any white precipitate may consist of stearate or palmitate of lead, and may be filtered off, washed with ether, decomposed with dilute hydrochloric acid, and the liberated fatty acids weighed.   All ordinary commercial oleic acid will indicate the presence of foreign fatty acids when examined in this manner.

Neutral fats will be indicated by the gradual separation of oily drops when equal volumes of the sample and of alcohol are heated at 25° for some time, whilst a pure acid will give a clear solution when thus treated.   A very delicate test for neutral fats in oleic acid is described on page 535.

The presence of neutral fixed oils or hydrocarbon oils can also be inferred from the diminished proportion of alkali required when the sample is titrated as on page 10.   5 grm. of pure oleic acid will require 35.47 c.c. of $N/2$ potassium hydroxide, corresponding to 19.9% of KOH, and a combining weight of 282.   Hence the percentage of *oleic acid* in the sample may be found by dividing the percentage of KOH required by 0.199.   Any admixture of palmitic acid will *increase* the amount of alkali required.

The neutralised liquid resulting from the last process may be treated with a known amount of standard alcoholic potassium hydroxide, and examined by Köttstorfer's process, when each 1 c.c. of additional N/2 alkali neutralised will indicate the presence of 0.145 grm. of *neutral fixed oil* in the sample.

The liquid left after the second titration may be evaporated with a further quantity of alcoholic potassium hydroxide, the residual soap dissolved in water, and the solution agitated with ether, as described on page 90. The ethereal solution is then separated and evaporated, and the *unsaponifiable matter* weighed.

In the case of an oleic acid obtained by distillation of an ordinary fat with superheated steam, the unsaponifiable matter or ether-residue obtained in the last process consists of *hydrocarbons* presenting the closest resemblance to those contained in the lubricating oils manufactured from petroleum and bituminous shale. Hence no means exist at present by which an intentional addition of a moderate proportion of hydrocarbon oil to oleic acid can be positively detected. According to Allen, the hydrocarbons normally present in distilled oleic acid range from 3 to 7%; and therefore any proportion notably in excess of the latter figure may be attributed to an intentional adulteration of the product with mineral or shale oil. The addition of these adulterants to oleic acid is extensively practised, although their presence greatly reduces the suitability of the oleic acid for one of its most important applications, which is that of greasing wool during the process of spinning. Any admixture of hydrocarbons reduces the property of ready saponifiability for which oleic acid is chiefly valued.

The foregoing statement respecting the proportion of unsaponifiable matter present in distilled oleic acid applies to a product obtained by saponifying pure substances. Wool grease and the grease obtained by treating with acid the soapy liquors in which wool has been washed are much more impure articles. Besides the *hydrocarbons* formed on distilling such greases, the distilled product is liable to contain *actual* petroleum or shale products used in the wool-spinning, either intentionally or as adulterants of other oils, *petroleum* employed for antiseptic purposes on the living sheep, and *cholesterol* and other unsaponifiable matters contained in the "suint" or wool fat. Hence, an estimation of the "unsaponifiable matter" in such low-class oleic acids cannot be regarded as a reliable indi-

cation of the extent to which they have been adulterated by an actual addition of hydrocarbon oil. Some indication of the origin of the unsaponifiable matter may be obtained by treating the ether-residue with thrice its volume of rectified spirit, when the volume left undissolved may be regarded as indicating roughly the hydrocarbons present, whilst the cholesterol and solid alcohols from sperm or bottlenose oil pass into solution. (See "Wool Fat.")

The following table gives results obtained by Allen from an examination of specimens of commercial oleic acid of very different qualities. The "free fatty acids" were estimated by titration with standard alkali, and calculated to their equivalent of oleic acid; but in the case of the semi-solid samples containing much palmitic acid the result thus obtained is necessarily in excess of the truth. The percentage of ether-residue shows the "hydrocarbons, etc.," in the samples, while the esters were in some cases determined indirectly, in other cases calculated from the result of Köttstorfer's saponification process, and in others deduced from the difference between the free fatty acids of the original sample and the total fatty acids resulting from its saponification. The samples and ether-residues to which an *f* is affixed were noted as being distinctly fluorescent:

	A	B	C	D	E	F	G	H	I
Condition.......	Clear	Clear	Fluid, with slight deposit	Semi-solid	Semi-solid	Contained much solid	....	Fluid	Clear
Colour..........	Pale brown	Pale brown *f.*	Brown	Brown	Pale brown	Pale brown *f.*	....	......	Sherry brown *f.*
Sp. gr..........	0.8996	....	0.9055	0.9085	0.9014	0.8987	....	0.8894	0.9083
Free fatty acids..	96.3	93.8*f.*	80.3	83.7	96.2	84.5	89.4	77.2	55.3
Hydrocarbons, etc.............	1.3	3.9*f.*	2.2	2.9	4.8*f.*	10.3	2.0	26.8	35.9*f.*
Esters, direct....	....	....	....	13.4	....	3.3	....	......	11.6
Esters, by difference.........	2.5	2.3	17.5	17.0	....	2.0	8.6	4.0	8.8

The first 4 samples were manufactured by the autoclave process, A and C being derived from tallow. E and F were probably autoclave products, the latter being of French manufacture. G was obtained from tallow by lime-saponification, and H and I were probably distilled oleines from recovered grease.

Granval and Valser (*J. Pharm. Chim.*, [5], 1889, **19**, 232) have drawn attention to the fact that commercial oleic acid is sometimes

adulterated with the acids from linseed oil. Such samples have a sp. gr. of from 0.912 to 0.919 and do not dissolve completely in 9 volumes of rectified spirit. Shaken with an equal volume of sodium hydroxide solution, the mixture turns intensely yellow; pure oleic acid becomes grey. If the linseed oil acids be present in considerable proportion, they may be detected by the high iodine value. Hazura (*J. Soc. Chem. Ind.*, 1889, 8, 641) adopts the following method: 50 grm. of the sample are saponified on the water-bath with dilute alcoholic potassium hydroxide. The potash soap is freed from alcohol and dissolved in 1000 c.c. of water. This strong alkaline solution is gradually mixed with 1000 c.c. of a 5% solution of potassium permanganate. After $\frac{1}{2}$ to 1 hour, the manganese oxide is filtered off, the filtrate acidified with sulphuric acid, and again filtered. The filtrate thus obtained is neutralised with potassium hydroxide, concentrated to about 300 c.c., and again acidified with sulphuric acid, which produces a precipitate. The acid liquid, without removing the precipitate, is shaken with ether. If the precipitate dissolves in ether, it consists of azelaic acid ($C_7H_{14}(COOH)_2$), and the original oleic acid is free from linseed-oil acid. If it does not dissolve, it is filtered off, recrystallised several times from water or alcohol, with the addition of animal charcoal, and, after air-drying, its m. p. determined. *If this be above 160°, linseed oil acids are* undoubtedly present.

Sulpholeic Acid.—When a non-drying fixed oil is cautiously treated with strong sulphuric acid, complex changes occur, the precise nature of which depends on the conditions of the experiment. Olein treated in the cold with sulphuric acid yields two acids—one monobasic, the other dibasic—which appear to be addition products of sulphuric acid and olein. They are soluble in water. Oleic acid treated with sulphuric acid produces at first hydroxystearo-sulphuric acid, $C_{17}H_{34}(OSO_2H)CO_2H$, from which is formed hydroxystearic acid, $C_{17}H_{34}(OH)CO_2H$.

Metallic Oleates.—These form a well-defined series of salts, many of which have received practical applications. They may be obtained by dissolving the metallic oxide of which the oleate is required in warm oleic acid; but such a method does not give compounds of very definite composition. A preferable plan is to precipitate an aqueous solution of sodium oleate with a neutral solution of the salt of the metal of which the oleate is required. Zinc, alumi-

nium, iron, lead, copper, bismuth, and other oleates are readily obtained in this way.

These oleates are analysed by agitating them with ether and a dilute mineral acid, which should be sulphuric, hydrochloric, or nitric, according to the metal present. The metals pass into the dilute acid liquid, and may be estimated by the ordinary methods of mineral analysis. The oleic acid formed from the oleate is dissolved by the ether, and may be weighed after evaporating off the solvent. Any free oleic acid, neutral fat, or hydrocarbon (*e. g.*, vaseline) which may have been present in the original substance will also be found in the ether-residue, and may be ascertained by the methods indicated on page 528 *et seq.*

With the exception of the salts of the alkali metals, all the metallic oleates are insoluble in water, though they dissolve in many instances in alcohol, ether, carbon disulphide, and petroleum spirit. The calcium, magnesium, and iron oleates also dissolve in glycerol.

Potassium oleate is the principal constituent of soft soap. It is a white, friable, deliquescent substance, which with a small quantity of water forms a transparent jelly, soluble in 2 parts of alcohol or 4 parts of water; but decomposed on copious dilution into free alkali and a gelatinous hydrogen oleate, insoluble in water but readily soluble in alcohol.

Sodium oleate, m. p. 232–235°, is a constituent of hard soap. It may be prepared pure by neutralising an alcoholic solution of oleic acid with sodium hydroxide and evaporating off the alcohol. It may also be obtained by the addition of sodium carbonate to hot oleic acid. It is not deliquescent, but by contact with air becomes gelatinous. Pure sodium oleate may be obtained in crystals from its solution in absolute alcohol, but not from aqueous alcohol or from the syrupy solution in water.

Ammonium oleate is obtained in solution by treating oleic acid with cold aqueous ammonia. It is a gelatinous substance, soluble in water, and readily decomposing into ammonia and oleic acid.

Barium oleate, $Ba(C_{18}H_{33}O_2)_2$, is a light crystalline powder, insoluble in water, and difficultly soluble in boiling alcohol.

Magnesium oleate, $Mg(C_{18}H_{33}O_2)_2$, is insoluble in water, but soluble in alcohol and petroleum spirit.

Aluminium oleate is a soft, white, putty-like substance, insoluble in water, but soluble in ether and petroleum spirit. It has received a

curious application, owing to its great tenacity and peculiar property of stretching into a thin string without breaking. It is made by saponifying whale, cottonseed, or lard oil with sodium hydroxide, and adding the aqueous solution of the resulting soap gradually to a solution of alum. A tough, gummy precipitate of aluminium oleate, palmitate, etc., is formed, which constitutes the product known as "oil-pulp." This may be dissolved in 4 or 5 times its weight of mineral lubricating oil to form "thickener," which is employed to impart a factitious viscosity to oil.[1] Such oil will readily form threads in dropping, and has a thick, glairy character. The false viscosity thus produced cannot be regarded as really increasing the lubricating value of the oil, and the use of aluminium soap for the purpose can only be regarded as an adulteration.

Ferric oleate is dark red, but otherwise resembles the aluminium soap.

Cupric oleate is a dark green, wax-like substance, readily obtained by double decomposition. It becomes quite fluid at 100°, and dissolves with green colour in all proportions of alcohol, ether, and fixed oils.

Lead oleate $Pb(C_{18}H_{33}O_2)_2$, is the principal constituent of the "lead plaster" of pharmacy. As obtained by double decomposition it is a light white powder, melting at 80° to a yellow oil, and solidifying, on cooling, to a brittle translucent mass. Lead oleate is quite insoluble in water, but soluble in alcohol and in ether, especially when hot. It is also dissolved by oil of turpentine and by petroleum spirit, the hot saturated solution in the last solvent solidifying to a gelatinous mass on cooling. The solubility of lead oleate in ether is utilised in analysis for the separation of oleic from palmitic and stearic acids.

By boiling oleic acid with water and excess of lead oxide or basic lead acetate, a basic oleate is obtained which is nearly insoluble in ether.

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[1] A sample of "oil-pulp." the analysis of which is given in the *Oil and Colourman's Journal*, 4, 403. had the appearance of thick gelatin or soaked glue. It had a sp. gr. of 0.921. and is said to have contained:

	%
Paraffin oil of 0.906 sp. gr.	48
Lard oil (uncombined)	15
Fatty acids, 30 ⎱	36
Alumina, 6 ⎰	
Water, soda, and loss	1
	100

Zinc oleate is a white unctuous powder, soluble in carbon disulphide and petroleum spirit.

Many of the so-called commercial "oleates" are prepared by the use of Castile soap instead of pure sodium oleate. They are better described as "oleo-palmitates," and for pharmaceutical purposes are probably equally suitable.

Oleic Esters.

Ethyl oleate is prepared by passing dry hydrogen chloride into a solution of oleic acid in three times its volume of absolute alcohol. Esterification takes place very rapidly, and the ester separates from the liquid as an oily layer. It has a sp. gr. of 0.870 at 18°, is soluble in alcohol, and is decomposed by distillation. Nitrous acid and its equivalents slowly convert it into the isomeric ethyl elaidate.

The methyl, ethyl, propyl, isobutyl, amyl, benzyl, and glyceryl esters of oleic acid have been prepared and examined by Ellis and Rabinovitz (*J. Ind. Eng. Chem.*, 1916, 8, 1105); all are liquid at ordinary temperatures. Their characteristics before and after hydrogenation are as follows:

Ester	Acid value	Iodine value	Hydrogenated product	
			M. p.	Iodine value
Methyl oleate.................	1.3	87.0	37°	0.4
Ethyl oleate...................	0.6	83.3	31°	5.3
Propyl oleate.................	0.5	77.9	27°	1.3
Isobutyl oleate..	0.4	75.7	25°	0.2
Amyl oleate..................	0.7	71.3	22°	1.7
Benzyl oleate.................	0.7	62.3	28°	6.3
Glyceryl-mono-oleate..........	0.6	69.4	59°	6.5

Dodecatyl oleate and its *homologues* are said to constitute the greater part of sperm and bottlenose oils.

Glyceryl oleates are obtainable synthetically by heating oleic acid and glycerol together in sealed tubes at 200° for 24 hours. With excess of glycerol, the monolein is produced. With excess of oleic acid, *olein* is formed, and under special conditions the dioleate is said to be obtainable. Monolein and diolein are not known to occur naturally, but olein occurs in many fixed oils, and may be obtained approximately pure by agitating olive or almond oil with a

cold concentrated aqueous solution of sodium hydroxide, which, it is said, saponifies the palmitin and leaves the olein mostly unchanged. After 24 hours, water is added and the soap solution separated from the oily layer, which should be washed with dilute alcohol and filtered through animal charcoal. As thus prepared, olein is a colourless, tasteless oil, readily soluble in ether or in absolute alcohol, sp. gr. 0.900 to 0.920. Pure olein is obtained when $\alpha\beta\gamma$-tribromopropane is heated with sodium oleate, it has m. p. $-5°$ to $-4°$, b. p. $235°$ to $240°/18$ mm. (Guth, *loc. cit.*,). By treatment with nitrous acid it is converted into solid elaidin. It solidifies below $0°$, can be distilled in a vacuum, and on exposure to air oxidises and becomes acid.

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See bibliography under Fixed Oils and Fats. References to important papers are given in the text.

SOAPS

By ELBERT C. LATHROP, A.B, Ph.D.

Soap is the term ordinarily used to designate the alkaline salts, sodium, potassium and ammonium, of the non-volatile fatty acids beginning with those containing 8-carbon atoms. Strictly speaking, all metallic salts of fatty acids are soaps, but the salts of the alkaline metals and ammonium are the only ones which are appreciably soluble in water, and consequently the only ones commonly used as cleansers. The alkali salts of the resin acids are also used in soaps to a certain extent and have limited cleansing properties. A discussion of the fatty acid salts of the alkaline earth and heavy metals is outside the scope of this article although certain of these are of great technical importance. The importance of defining soap was demonstrated during the World War when, particularly in Germany and Austria, all manner of things were sold as soaps (Löffl, *Kunstoffe*, 1916, 6, 237). Conditions became such that these Governments passed laws defining what could be sold as soaps and as soap powders.

Soaps may be formed by direct union of fatty acids with sodium or potassium hydroxide or by heating the aqueous solutions of potassium or sodium carbonate with fatty acids. In the first case, water is eliminated, and in the second, carbon dioxide; both reactions are of technical importance. Lewkowitsch (Vol. 1, page 213, 1913, 5th ed.) remarks that from a physiological point of view it is interesting to note that whilst palmitic, stearic and oleic acids at a temperature of 37° (blood temperature) act but very slowly on a dilute solution of sodium carbonate, they form the respective sodium salts much more readily in the presence of bile secretions. Soaps may be obtained by adding boiling solutions of the carbonate to alcoholic solutions of the fatty acids, evaporating to dryness and extracting the residue with alcohol. If pure materials are used pure soaps

are obtained. These salts are neutral to phenolphthalein. The normal salts of the saturated acids have the general formula:

$$C_nH_{2n+1}CO.OM$$

where M, stands for Na, K or NH_4. Acid salts also exist having the formula $C_nH_{2n+1}CO.OM. C_nH_{2n}O_2$, which show in hot alcoholic solution an acid reaction to phenolphthalein.

The older method of preparing soaps and the one still used to a large extent is the treatment of the animal and vegetable fats and oils with sodium or potassium hydroxide. These oils and fats are mixed esters, and on such treatment yield glycerol and the sodium or potassium salts of the fatty acids, the reaction being represented by the equation:

$$C_3H_5(O.C_{18}H_{35}O)_3 + 3NaOH = C_3H_5(OH)_3 + 3C_{18}H_{35}O_2Na.$$
$$\text{stearin} \qquad\qquad \text{sodium hydroxide} \qquad\qquad \text{sodium stearate}$$
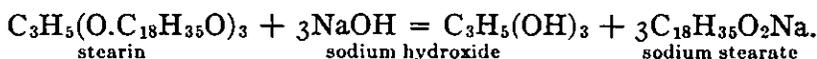
The breaking down a fat or oil into two separate portions, viz., (1) a mixture of fatty acids and (2) glycerol, may be brought about by the aid of superheated steam, acids, such as sulphonic acids (Twitchell reagent), enzymes, and by alkaline hydroxides. Saponification is the term applied to the splitting of an ester by water, forming an alcohol and a fatty acid. The term "hydrolysis" is perhaps better suited to this class of reactions in general, whilst the term "saponification" is more often applied to the splitting of fats and oils. For the general principles of these reactions and the laboratory methods see the section on "Esters" in Vol. 1.

Each fat and oil contains the glycerides of several fatty acids, the principal ones being stearic, palmitic and oleic acids. These different glycerides occur in varying quantities in the various fats and oils, the solid fats containing a larger proportion of stearin whilst the liquid fats or oils contain a larger proportion of olein. There are a large number of these glycerides and reference is made to the section of this volume on "Fixed Oils and Fats" for fuller information. Because of the complex character of these starting materials, soaps are themselves complex mixtures of salts of fatty acids, but are influenced in their general characteristics by the fatty acid predominating. The waxes can also be saponified, the process being generally strictly analogous to that with fats and oils, but appreciable amounts of glycerol are not obtained and such soaps are not in common use except for shoe polishes, etc.

In addition to the alkali salts of fatty acids, all soaps contain water and small amounts of impurities introduced by the raw materials and the process of manufacture. Certain other substances frequently enter into the composition of commercial soaps. These are added for legitimate or other purposes and many exaggerated claims have been made as to their detergent and cleansing power. It must be borne in mind by the reader that soaps are used for many purposes and that a soap which may be highly useful for a certain purpose may be of much less value elsewhere. Further, in evaluating a soap a number of factors, apart from its chemical composition, must be taken into consideration.

GENERAL PROPERTIES OF SOAPS AND SOAP SOLUTIONS

Broadly speaking, soaps are of technical importance because of their cleansing and detergent properties. Much attention has been devoted to this phase of the subject during the past decade, as well as to the physical chemistry of soaps and soap solutions. The economic situation brought on by the World War resulted in the diverting of much of the fat to nutritional uses, causing a scarcity of soap-making materials. Attention was, therefore, directed to the finding of substitutes having a high cleansing and detergent action. The researches of J. W. McBain and his co-workers (*Ber.*, 1910, 43, 321; *Z. physik. Chem.*, 1911; 76, 179; *J. Chem. Soc.*, 1911, 99, 91; 1912, 101, 2043; 1914, 105, 417; 1914, 105, 957; 1918, 113, 825; 1919, 115, 1279; 1920, 117, 532; 1920, 117, 1506; *J. Amer. Chem. Soc.*, 1920; 42, 426; *Proc. Roy. Soc. A.*, 1920, 97, 44) have been of the greatest importance in extending our knowledge of the properties of soap and soap solutions. See also, H. Pick, *Seifenfab.*, 1915, 35, 225, 279, 301, 323, and F. Auerbach, *Z. Deutsch. Öl-und Fettindustr.*, 1921, 41, 165.

As a general rule, potassium soaps are soft and deliquescent, whilst the sodium soaps are hard and in the absence of much free alkali are not deliquescent. The soaps of the saturated fatty acids are crystalline in structure, whilst those of the unsaturated fatty acids are only partially crystalline. Potassium and ammonium salts of oleic acid are plastic, and are said to form liquid crystals. McBain (*J. Soc. Chem. Ind.*, 1918, 37, 249) states that except in all but extremely dilute solutions all of the sodium soaps above the caprylate (C_8) are solid.

This solidification withdraws the soap from solution and is essentially crystallisation, the mother liquor being mechanically enclosed. The potassium soaps solidify at a much lower temperature and they possess a much greater tendency to exist as transparent liquids, which are often so viscous as to be almost, or quite, gelatinous. To obtain the same crystallisation phenomena it is necessary to use higher concentrations of potassium soaps of greater carbon content, and to have a much lower temperature than is the case with the sodium soaps.

With regard to the influence of position in the homologous series McBain (*loc. cit.*) states that the appearance, washing power, and conductivity of the caproates (C_6) distinctly marks the beginning of that deviation from the behaviour of the acetate, which rapidly and regularly increases throughout the other members of the homologous series until the typical character of the higher soaps is obtained. At the top of the scale is the *behenic acid* (C_{22}) often met with in the modern soaps. These soap solutions solidify at a high temperature. They tend to form mainly undissociated colloid, and the solutions have a distinct structure like that of starch. The laurates (C_{12}) are perhaps the most interesting, as they are in the middle of the series, the lowest really good soaps in whose solutions by suitable adjustment of concentration most of the typical phenomena of the soaps are produced. This is perhaps the most important constituent of industrial soft soaps.

The behaviour of the alkaline salts of the fatty acids to solutions in water is characteristic and demonstrates that the higher fatty acids are very weak acids. When a hot clear solution of a neutral soap is diluted with water and cooled it becomes turbid and, on shaking, a lather, which persists for some time, is formed. This turbidity is due to the hydrolysis of the soap into alkali hydroxide and an acid soap. The alkaline salts of the solid fatty acids do not dissolve in water, undecomposed, but undergo hydrolysis. Chevreul first studied this and found that by dissolving sodium stearate in 20 parts of boiling water and adding an additional 1000 parts of boiling water, on cooling, soap was precipitated, whilst free alkali and a very minute amount of stearic acid remained in the solution.

The technical importance of this is shown in the fact that soaps formed from the solid fatty acids of high molecular weight have little or no washing power in cold water, whilst those prepared from liquid

fatty acids, as well as from those of lower molecular weight, have high lathering and cleansing properties in cold water.

Aqueous soap solutions are representative of a type of solution of great theoretical interest, *viz.*, colloidal elcctrolytes. Indeed, owing chiefly to McBain, who chose soap as a most convenient type of colloid with which to work, our present knowledge of the physical chemistry of soap solutions has been obtained. In studying the nature of such solutions none but the most rigorous methods have been employed by him and his colleagues. In an article (*J. Soc. Chem. Ind.*, 1918, 37, 2497) he summarises his conclusions as follows: Commencing with the case of very dilute solutions the soaps are partially hydrolysed according to the following equation:

$$\text{Soap} + \text{water} \rightleftharpoons \text{acid soap} + \text{free alkali.}$$
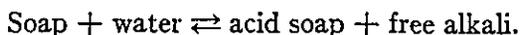
The acid soap is in suspension, either coarse or colloidal, as the case may be, and it consists of something between the neutral salt, NaR, and the acid soap, $NaHR_2$, where R is the radical of the fatty acid. Only excessively minute traces of free fatty acid can exist as such in soap solution even when a whole equivalent of excess fatty acid has been added, so that the equation just given must supersede the ordinary statement of the textbooks and publications. The data which established this are based upon analysis, conductivity measurements and measurement of the rate of hydrolysis of nitroso-triacetone-amine (the velocity of decomposition of which is directly proportional to the concentration of hydroxyl-ions). Later (1920) measurements of osmotic pressure and vapour pressure have confirmed these results. In $N/10$ solution, or somewhat less, soaps are chiefly composed of simple electrolytes in true solution with simple ions. Hydrolysis is still present but only in very minor degree, since the hydroxyl-ion concentration is shown by the two methods just cited to be only about $N/1000$ (sodium palmitate). As the concentration increases the fatty ions rapidly coalesce to form the ionic *miscelles* until in $N/2$ or $N/1$ solutions the colloidal electrolyte comprises all the soap, hydrolysis being still more insignificant. As the concentration increases the ionic *miscelles* becomes less solvated. Alcoholic solutions differ entirely in their behaviour, as the soap is a simple unhydrolysed electrolyte throughout.

In colloidal electrolytes such as soap solutions, the cation is the alkali metal, whilst the anion is not the fatty acid ion but a complex called by McBain "ionic miscelle" which carries a great number of

electric charges and consists of a large number of fatty acid ions associated with a considerable number of molecules of neutral soap. The *miscelle* is strongly solvated, although the solvation decreases with increasing concentration, whilst the conductivity increases within certain limits. This clears up the abnormal form of the curve for the molar conductivity of soaps which does not, as do normal salts, decrease regularly with increasing concentrations, but which instead passes through a maximum.

Soap solutions constitute perfectly reversible equilibria in which colloid, miscelle and crystalloid alike participate.

The following tables (McBain, *J. Soc. Chem. Ind.*, 1918, **37,** 250) show the equivalent conductivities of the sodium and potassium salts of certain fatty acids at 90° and 18°, respectively. The concentrations are expressed in grm. equivalents of soap per 100 grm. of water.

EQUIVALENT CONDUCTIVITIES OF SOAPS AT 90°

Concentration	1.0	0.5	0.1	0.01
Potassium stearate C_{18}	113.4	113.9	96.0	147.7
Sodium stearate	88.3	76.1	76.0	125.9
Potassium palmitate C_{16}	124.2	127.0	167.0	171.6
Sodium palmitate	84.66	89.48	82.51	137.7
Potassium myristate C_{14}	136.2	135.4	121.8	224.3
Sodium myristate	94.9	99.2	96.5	191.7
Potassium laurate C_{12}	143.2	146.0	159.7	233.0
Sodium laurate	104.2	109.5	125.5	193.9
Potassium acetate C_2	176.9	196.6	236.5	270.4
Sodium acetate	129.7	......	195.0	228.2

EQUIVALENT CONDUCTIVITIES OF SOAP AT 18°

Concentration	1.0	0.6	0.1	0.01
Potassium laurate C_{12}	47.1	46.2	44.0	75.4
Potassium caprylate C_8	48.6	51.9	69.5	....
Potassium oleate (unsaturated) C_{18}	....	37.3	29.7	51.9
Sodium oleate (unsaturated) C_{18}	....	20.8	20.5	30.1

The question of the hydrolysis of soaps has been under investigation since the time of Chevreul, and the great diversity of opinion

previously expressed as to whether soaps were only slightly or almost entirely hydrolysed was due to the use of such inadequate methods as direct titration in the study of this equilibrium, a procedure which could only lead to arbitrary and erroneous results. A discussion of this earlier work will be found in Lewkowitsch, Vol. i, pp. 127–131, 1921, 6th ed. The quantitative data obtained during the past decade shows that all soap solutions are alkaline, varying from N/3000 to N/300 for pure soap solutions down to N/30,000 for acid sodium palmitate. Several per cent of alkali are required to drive back this slight hydrolysis completely, but even in the presence of a large excess of alkali, not more than a small per cent. of the alkali can be sorbed by the soap. This means that the hydrolysis must be approximately equal to the alkalinity. The soaps of highest molecular weight are the most alkaline and the alkalinity is less at lower temperatures until the solution becomes heterogeneous, whereupon the alkalinity increases several fold. The alkalinity is less in the presence of moderate amounts of salt and McBain suggests that for this reason commercial soaps are all less alkaline than sodium palmitate.

Peck (*loc. cit.*) states than an N/2 solution of potassium palmitate at 90° is clear, a N/1 solution coagulates between 60° and 70°, whilst N/100 and N/50 solutions are weakly opalescent and give a small precipitate. A N/1 potassium stearate solution at 90° is clear and colourless but a N/20 solution is turbid and gives a precipitate equal to one-half the total volume.

F. C. Beedle and T. R. Bolam (*J. Soc. Chem. Ind.*, 1921 40, 27) studied the hydrolysis of pure and commercial soap, and report the alkali from hydrolysis of sodium oleate to pass through a maximum at N/20 concentration and that, whilst negligible at high concentrations, the hydrolysis increases rapidly in dilute solution. Sodium palmitate shows about the same hydrolysis alkalinity as sodium oleate and sodium resinate, but in more concentrated solutions, the oleate is less and the resinate is more hydrolysed. The hydrolysis alkalinity of soap solutions is essentially that produced by the most hydrolysable constituent. Free alkali accounts for only a fraction of the alkalinity in well made soaps. Cold process and toilet soaps made from the same material do not differ appreciably in this respect, the alkalinity being too small to have an effect on the most sensitive skin. Since coconut oil soap exhibits a very low degree of hydrolysis it cannot produce a skin irritation due to

alkali. The authors suggest that perhaps the laurate may be irritating.

The salting out of soaps and the methods of forming soap curd is of great technical importance and, further, this process has a bearing on the ultimate composition of the soap. When a clear soap solution is cooled, a transparent gel is formed, which is identical with the solution in all except mechanical properties. Out of the gel there separates a microcrystalline phase having a fibre structure and being of definite solubility. The gel becomes opaque and there is a drop in the conductivity and osmotic pressure. Zsigmondy and Bachman (*Z. Chem. Ind. Koll.*, 1912, 11, 156) report studies on the ultramicroscopic structure of soap and, later, W. F. Drake, J. W. McBain and C. S. Salmon (*Proc. Roy. Soc.* (London), 1921, 98A, 395) used the moving picture as a means of closely following this transition from solution through gel to curd. When a dilute soap solution is treated with an electrolyte there is reached a certain concentration of electrolyte which causes the separation of the mass into two phases—a soap free layer and above it a soap solution which is much poorer in electrolyte than the lower layer and corresponds to a soap gel. If more electrolye is now added the lower layer increases in volume whilst the soap layer decreases in volume. There is reached a concentration of electrolyte when flocculent masses begin to separate from the gel; this third or flocculent phase is called the curd in the soap industry. Generally, such concentrated solutions are used that the middle phase of this salting out, *viz.*, the gel, is not observable.

Our exact knowledge of the mechanism of this transition and the composition of the phases is due chiefly to the work of McBain and colleagues and to Martin H. Fischer. McBain states that with increasing concentration of the soap solution, the dissociation of the colloidal electrolyte decreases and the constitution of the miscelle (which, being colloidal, absorbs and adsorbs most of the available material, including probably the neutral colloid) approaches that of a neutral soap. Mere increase in concentration probably never makes this process complete, but it is rapidly and quantitatively effected by the addition of salts of any sort in sufficient concentration, resulting in the formation of a curd containing some combined water and other sorbed material. An ordinary analysis of such a curd gives but little clue to the solid part of it, since it is a heterogeneous

sponge or felt full of mechanically enclosed mother liquor. McBain and Taylor (*J. Chem. Soc.*, 1919, **115,** 1300) found that when salting out sodium palmitate with sodium hydroxide a marked negative sorption of the sodium hydroxide occurs. Soap curd is shown to be a mechanical mixture of hydrate (or sorption compound) and enmeshed lye. The degree of hydration was found to vary with the concentration of the lye as follows:

Lye	Sorption compound	% Fatty acids
3.0 N	NaP, 3.2 H$_2$O	76.28
2.5 N	NaP, 4.4 H$_2$O	71.67
1.9 N	NaP, 5.2 H$_2$O	68.89
1.5 N	NaP, 6.5 H$_2$O	64.81

It was found that by placing the curds under high pressure the degree of hydration could be considerably lowered. The same authors (*J. Chem. Soc.*, 1921, **119,** 1369) showed that when a N/1 solution of sodium palmitate is salted out with sodium chloride ranging from one-third to complete saturation, the mother liquor is alkaline only to the extent of N/500 to N/250 sodium hydroxide. Or, in other words, soap salted out with neutral sodium chloride contains an amount of sodium which is within 99.6% to 99.8% of that required to neutralise exactly the free fatty acids present. They remark that practical soap boilers frequently assert that it is necessary to salt out soaps in the presence of an excess of alkali if appreciable hydrolysis is to be avoided. It now appears that acid soaps, which are undoubtedly observed very often on a large scale, are due to incomplete saponification. The final stages of saponification are surprisingly slow. Sodium sulphate, sodium chloride and, to a slight extent, sodium hydroxide are all sorbed by the curd fibres, except in the presence of a large excess of a second salt. The empirical composition of curd fibres salted out with a saturated solution of sodium chloride was found by these authors to correspond with the proportions NaP : 2.1 H$_2$O : 0.16 NaCl; that is, the fibres themselves contain about 78.7% of anhydrous fatty acid and about 3% sodium chloride by weight. From more dilute lyes much more water and less salt is sorbed. McBain and

Salmon (*J. Chem. Soc.*, 1921, **119**, 1374) state that the composition of the solid portion of the curd is independent of the way in which it is prepared, *i. e.*, it responds to true chemical equilibria. The so-called "melting point" of aqueous soap curds is the temperature at which the whole of the fibres have just passed into solution and the hard opaque curd has finally turned to a transparent liquid or gel. They suggest that it should ultimately be possible to determine the real hydration of a commercial soap simply from a knowledge of its vapour pressure at room temperature, or from an analysis of the drops of "sweat" exuding from it. The degree of hydration of fibres of soap depends almost entirely upon the vapour pressure of the solution with which it has been in contact, being least for the most concentrated brines. There is a small but real increase in hydration with lowering of temperature. The hydration of sodium palmitate is distinctly greater than that of either the laurate or stearate.

Martin H. Fischer and M. O. Hooker (*Chem. Eng.*, 1919, **27**, 223) report studies on the salting out of potassium oleate with various salts and conclude that the potassium salts produce in general increase in viscosity, settling of gel and final dehydration.

Goldschmidt (*Ullmann*, 1922, **10**, 351) gives the following concentration of sodium hydroxide and sodium chloride required at boiling temperature to salt out the soaps of the more important fats and oils in technical practice.

Kind of fat or oil	Sodium hydroxide, ° Bé.	Sodium chloride solution, ° Bé.	Kind of fat or oil	Sodium hydroxide, ° Bé.	Sodium chloride solution, ° Bé.
Linseed oil	9.0	6.0	Sulphonated olive oil	11.0	6.0
Soya bean oil	8.5	6.0	Castor oil		Saturated
Corn oil	7.0	5.0	Palm oil	7.5	5.0
Cotton seed oil	8.0	5.5	Palm kernel oil	19.0	16.5
Rape oil	5.5	3.5	Coconut oil	23.0	19.0
Peanut oil	7.5	5.5	Lard	8.0	6.0
Olive oil, fresh	7.0	5.5	Tallow	7.0	5.0

The viscosity of soap solutions varies enormously, from about that of water to a value many thousand times greater, giving a perfectly continuous transition from very thin fluid through viscous liquids to a stiff clear jelly. McBain states that this change is not accompanied by a very great change in the electrical conductivity.

The increase in viscosity is directly proportional to increase in concentration, lowering of temperature, or rise within the homologous series of fatty acids. The addition of any electrolyte in small quantities reduces the viscosity slightly through a minimum and then increases it enormously. The reader is referred to Farrow (*J. Chem. Soc.*, 1912, 101–102, 374), Goldschmidt and Weismann (*Electrochem.*, 1912, 18, 380; *Kolloid-Zeit.*, 1913, 12, 18), Kurtzmann (*Kolloid Beih.*, 5, Heft 11/12 (1914), and E. Rothlin (*Biochem. Z.*, 1919, 98, 34) for a fuller discussion of the viscosity of soap solutions.

Soaps dissolve in alcohol to form real solutions, and the salts of the single fatty acids have definite solubilities. In general, the potassium soaps are more soluble in alcohol than the respective sodium soaps, and the salts of the saturated fatty acids are less soluble than those of the unsaturated fatty acids. Increase in molecular weight causes a decrease in solubility in alcohol; for example, the potassium soaps from castor oil, coconut oil, palm oil, cotton oil and olive oil, etc., are easily soluble in alcohol, whilst those from tallow are less so and those from commercial stearin but little soluble. Concentrated alcoholic solutions of soaps set to a jelly which has been used as a basis for the technical manufacture of the so-called "solid alcohols." Martin H. Fischer (*Science*, 1919, 49, 615; *Chem. Eng.*, 1919, 27, 155) has made an extensive study of the solution of soaps in various solvents. For example, solid gels were obtained in the case of 1 mol. of sodium stearate in 21 litres of alcohol, the actual soap content being 1.41%, whilst sodium arachidate formed a gel of 1 mol. of the salt to 27.5 litres of alcohol, the soap content being 1.21%.

The alkali soaps are but little soluble in dry ether, petroleum spirit, benzene, carbon tetrachloride, etc., a property utilised in the separation of unsaponified oils, fatty acids, hydrocarbons, etc., from soaps or soap solutions. However, the potassium soap from linseed oil dissolves to a clear solution in ordinary ether to which a few drops of absolute alcohol have been added. The corresponding sodium soap is less soluble. The acid soaps are more soluble than the neutral soaps and the preparation of the naphtha, benzene, etc., soaps is based on this fact. In preparing such soaps, acid soaps or free fatty acids are used in connection with the neutral soap to assist in retaining these solvents. In this connection it is claimed by

Schrauth (*Z. Deut. Öl.-Fett. Ind.*, 1921, **41**, 192) that the new technical hydrogenation products of phenols and naphthalene, *viz.*, cyclohexanol, tetralin, and decalin, dissolve to clear solutions like amyl alcohol in soap solutions, and may then serve as substitutes for sulphonated castor oil and also for benzene soaps which require the presence of free fatty acids. For example, settled soaps take up 10 to 20% of hexalin without much loss in hardness when made into cakes.

THE DETERGENT ACTION OF SOAP

Much interest is attached to the cleansing and detergent action of soap solutions, both from the practical and the theoretical side, and it is not unlikely that the solution of this problem may, to a certain extent, result in changes in soap technology. The older idea that the cleansing action of soaps is to be largely attributed to the alkalinity resulting from soap hydrolysis has been found untenable. The exact measurements of McBain and others have shown that the amount of alkali so resulting is so small that it cannot play an important part. Furthermore, as Goldschmidt (*Ullmann*, 1922, **10**, 349) states, the idea is shown to be untenable also from the practical standpoint, since it is generally agreed that the so-called fat-dissolving soap substitutes used during the war in no way replaced real soap.

The problem is being studied from the physico-chemical rather than the purely chemical point of view, and although the final solution of the problem must probably await a more thorough understanding of colloids in general, still much progress has been made. As is the case with colloids in general, soap markedly lowers the surface tension of water, making it possible to wet more easily the subtratum of grease and dirt and thus emulsify it. For the older work in this connection, see Botlazzi and Victorow (*Atti d. Reale Accad. dei Lincei (Rendiconti)*, 1910, **19**, 659), Mayer, Schaeffer and Terroine (*Compt. rend.*, 1908, **146**, 484), Hillyer (*J. Amer. Chem. Soc.*, 1903, **25**), Donnan (*Zeit. Phys. Chem.*, 1899, **31**, 42), Donnan and Potts (*Kolloid Zeitschr.*, 1910, **7**, 208). Hillyer studied the effect of surface tension of soap solutions on oils and attempted to base a quantitative method for determining the washing power of soaps. He used the stalagmometer of Traube and determined the change in drop number under different conditions.

THE DROP NUMBERS AND EFFICIENCIES OF CERTAIN COM-
MERCIAL SOAPS (Hillyer, *J. Amer. Chem. Soc.*, 1903, 25, 1262)

Soaps	Cold		Hot	
	Drops	Efficiency	Drops	Efficiency
Cold made, coconut oil...............	121	37	90	31
Hygienic coconut oil.................	56	13	67	21
Toilet.........................	114	34	221	77
Shaving............................	119	36	202	60
Tar, toilet.........................	84	22	80	28
Yellow laundry, rosin.................	75	19	103	35
Yellow laundry, rosin.................	100	28	135	45
Household for cold use...............	107	31	173	58
Household for cold use...............	98	27	150	50
Household for cold use...............	139	49	170	57
White laundry and toilet.............	97	27	206	71
White laundry and toilet.............	...	..	226	79
Prime yellow laundry.................	...	..	216	75
Prime yellow laundry.................	120	37	218	76
Steam laundry, tallow................	104	30	277	106
Castile, old and dry.................	142	54	...	..

Lehner and Buell (*J. Ind. Eng. Chem.*, 1916, 8, 701) and Lehner
and Bishop (*J. Phys. Chem.*, 1918, 22, 68) extended this work. They
studied the amounts of sodium oleate necessary to emulsify certain
oils, noting also effect of concentration and temperature. Emulsi-
fication was found to proceed better at a high temperature (100°)
than at a low temperature (20°) and the volume of water in which a
given soap is dissolved is an imporant factor in the detergent action.
These investigators found that when working in hot solution sodium
palmitate is more effective than sodium oleate or stearate. With
regard to the action of soap solutions on suspended matter, they
noted that the maximum suspension invariably occurred with about
N/320 solutions. A study of the amount of soap solutions required
to emulsify the following oils at 100°, cottonseed oil, corn oil, linseed
oil, olive oil, rapeseed oil, peanut oil, sesame oil, castor oil and sperm
oil, showed that all results were closely parallel. When small quan-
tities of oils are present a given additional quantity of oil requires
only a small quantity of soap for emulsification, whereas with large
quantities of oils a considerable quantity of soap is necessary to
secure any additional emulsification.

Shorter (*J. Soc. Dyers and Colorists*, 1915, **31**, 64; 1916, **32**, 99; 1919, **35**, 55; Shorter and Ellingsworth, *Proc. Roy. Soc.*, London, 1916, 92A, 231) has studied the detergent action of soap and the following are some of his conclusions from his experimental work: A detergent has three functions: (1) the wetting of a greasy surface, (2) the emulsification of grease, and (3) the stabilising of a very fine suspension of dirt and emulsion of grease which results from this emulsification.   The first and second of these functions depend upon the production of a low-tension layer at the surface between the solution and the grease, whilst the third depends on the colloidal nature of the detergent solution.   This layer may be formed (*a*) by the adsorption of the undecomposed soap, (*b*) by the interaction of the free fatty acids in the oil or grease, and the alkali set free in the solution by hydrolysis of the soap.   From his data it is shown that in solutions of neutral soap the surface activity of the hydrolysis alkali is only about 20% to 25% that of the undecomposed soap.   The hydrolysis alkali is capable of acting on fatty acid in an oil, though the effect of this action in producing a surface soap layer is small compared with that due to the adsorption of the undecomposed soap.   The view that the detergent action of soap is due to its colloidal nature suggests the idea that other colloids may possess detergent power.   The addition of alkali to a solution of neutral soap greatly increases the detergent power of the solution; the most obvious function of the alkali is, of itself, to influence the surface activity by acting on the greasy material which contains fatty acids.   The addition of alkali to a soap solution increases its detergent action on materials stained with mineral oil and charcoal.   With regard to the amount of soap to use it is shown that it is a waste to use soap in a much stronger solution than 0.4%.   Experiments on the effects of the amount of soap on the stability of fine suspensions shows that there is a maximum effect at 0.2% to 0.3%.   It is concluded that a maximum of 0.46% solution of soap is best for scouring purposes.   If the alkali in soap exceeds a small amount it tends to diminish the stabilising effect whilst it increases the emulsifying power.   This tends to result in a compromise in sacrificing stability for the sake of effecting rapid emulsification.   It is best to avoid using more than 1% alkali in the early stages of scouring in order to produce necessary, stabilising effect.

S. W. Pickering (*J. Chem. Soc.*, 1917, 111, 86) states that the detergent action of soap is due in part to (1) its power of emulsifying oil, the globules of which become enclosed in a pellicle which prevents them from rendering other substances oily, (2) the low surface tension between the oil and soap solution, and (3) to the union of the dirt with the acid soap formed by hydrolysis. A more important factor is that oils dissolve in soaps to form soluble compounds, which in some cases contain nearly equal amounts of oil and soap. When the oil is added in small amounts a certain proportion of it becomes emulsified and incapable of combining with the soap owing to the protective pellicle, and therefore considerable excess of oil must be taken for the soap to combine with the maximum amount of oil. The compound of soap and oil is not decomposed by an excess of water, but by diluting soap previous to its treatment with oil, less oil combines, since more of it is emulsified. The combining of oil and soap is accompanied by physical changes, a soluble limpid compound and an almost solid emulsion being formed. The proportions of oil and soap which will unite depend on the specific substances used.

White and Marden (*J. Phys. Chem.*, 1920, 24, 617) report that glycerol does not affect the surface tension between soap solutions and oil to any extent. A large amount of sodium carbonate raises the surface tension and is, therefore, not desirable in cleansing soaps.

Spring (*Kolloid Zeitschr.*, 1904, 4, 161; 1910, 6, 11, 109, 164) in a series of papers presents a mass of experimental data and discusses the washing power of soaps. His experiments are devoted more particularly to the action of soaps on non-fatty matter, such as lamp black, iron oxide, hydrated iron hydroxide, clay, silicic acid, cellulose, etc. He concludes that the washing power of soap solutions is due to the formation of adsorption complexes with material to be removed. In the formation of these compounds electrostatic forces play a rôle. Lehner and Bishop (*loc. cit.*) also studied the surface condensation of soaps in charcoal and found that the activity of the substances, tested in terms of the quantity of soap adsorbed, increased in the order:—graphite, willow charcoal, animal charcoal.

Neuberg (*Biochem. Zeitschr.*, 1916, 76, 108) describes a solution phenomenon, called by him hydrotropic action, which he observed

many substances to possess. Soap is one of the substances which causes the solution of ordinarily insoluble substances, and this phenomenon may play a part in the cleansing properties of soaps.

The sorptive power of the colloidal *miscelles*, the theory developed by McBain, undoubtedly is a most important factor in the detergent action.

According to J. Geppert (*D. mediz. Wochenschr.*, 1918, **44,** 51), the substratum is more easily wetted by the soap solution than the impure oil or fat which is thus lifted from the substratum and removed. The soap is thus more strongly adsorbed by the pure material than by the dirt, the surface of the purer material becoming saturated with adsorbed soap and the dirt drawn away.

S. S. Bhatnagar (*J. Chem. Soc.*, 1921, **119,** 61, 1760 and *Kolloid Zeitschr.*, 1921, **28,** 206) studied the effect of electrolytes on emulsion equilibria between neutral oils and soap solutions. His results show that the tervalent electrolytes have a greater effect on the inversion of these emulsions than the bivalent. The effect of dilution and of increasing the distance between the oil particles in an emulsion is essentially similar in nature to the effect of dilution in colloidal solutions. The difference in the amount of electrolyte required to bring about the reversal of phases with different soaps points to a probable difference in their protective action. Results indicate that soaps can be arranged in the order of their protective action as follows: Potassium stearate, sodium stearate, sodium and potassium palmitate, potassium oleate, sodium oleate for B. P. paraffin oil. Practically, the protective action of soaps will be considerably affected by the electrolytes in the wash water. Sodium linoleate and soaps with little free alkali should be good for cleansing purposes, as they give more finely grained emulsions than sodium oleate when pure water is used. Barium, calcium and magnesium salts in the water will be injurious to this action, as well as when neutral or acid soaps are employed, for the lathers are also easily transformed into water-in-oil emulsions which are very sticky and difficult to remove with water.

The Laundryowners' National Association (U. S.), through the agency of the Mellon Institute, is applying some of these principles in a practical way in the solutions of their problems. The following is some of the information developed in their studies. (Private communication.)

A solution of sodium oleate of the concentration used in the laundry is at its minimum surface tension at about 70° F., whereas a tallow soap of the same concentration reaches its minimum surface tension at about 140° F. Sodium oleate is at its maximum emulsifying power at 70° F., whereas the tallow soaps obtain their maximum emulsifying power around 140° F. Sodium oleate is completely soluble in water at 70° F., whilst tallow soap does not form a clear solution at so low a temperature. A 5% solution of sodium oleate at 70° F. is perfectly clear, and a 5% solution of a tallow soap at the same temperature is a thick jelly.

The following information with regard to surface tension is used in their work:

Substance	Surface tension in dynes per cm.	Temperature, ° C.
Water..................................	77	25
Sodium oleate 0.05%...........	30	25
Sodium oleate 0.05%.................	30	60
Swift's laundry soap 0.05%.............	35	25
Swift's laundry soap 0.05%........... .	29	60

They recommend that a tallow soap be used at a temperature of above 140° F., whilst a red oil or oleic acid soap be used at a temperature as low as 50° F. In general, the low titer soaps lend themselves to good washing and rinsing at a temperature well under 120° F. In case a fabric should be soiled with some such material as paraffin wax the washing temperature must of course be high enough to melt the paraffin.

For a more complete review of the theories concerning the washing power of soap see Margoches (*Seifenfab.*, 1918, **38**, 1) and Rasser (*Seifensieder Ztg.*, 1921, **48**, 268, 290, 309, 355).

RAW MATERIALS USED IN THE MANUFACTURE OF SOAPS

Fats and Oils.—A great variety of natural vegetable and animal fats and oils is used in the manufacture of soaps, depending on the nature of the soap required and the price and availability of the product. . Fatty acids have come into increased use, as methods of producing them in purer condition have been perfected. Large amounts of hydrogenated fats and oils are now used. As a result of

the growth of the hardened oil and fat industry for the production of edible and other fats, soap-stock, a by-product consisting of fatty acids and unsaponified oil, is a largely used raw material for making soaps. Soap-stock contains more or less oxidised fatty acids which tend to give a dark colour to soap and lead to a loss of soap-making materials. Blown oils, because they contain large amounts of such oxidation products, are unsuited, in general, for soap manufacture. Colophony, or rosin, is used to a considerable extent, especially in laundry or other cheaper soaps. The salts of the resin acids have detergent power, but are always used in conjunction with fats which yield hard soaps. In Germany and Austria, during the war, owing to the shortage of soap-making materials numerous attempts were made to synthesise fatty acids by the oxidation of various petroleum oils. Napthenic acid, a by-product of petroleum, particularly Baku, has been used for the preparation of soaps, but its strong odour is a serious objection. The soaps of this acid are extremely difficult to salt out and are said to have excellent detergent properties.

For the preparation of hard soaps, oils and fats especially are used which have a high content of saturated fatty acids, and although some oleic acid and to a smaller extent oils containing linolic acid are used in hard soaps, those containing much unsaturated acids and particularly those containing linolenic acid and clupandonic acid are entirely unsuited for the manufacture of hard soaps. This is due to the influence of the salts of such acids on the consistence of the soap. Further, the sodium salts of these acids are less stable than the respective potassium salts. On standing and exposure to the air hard soaps made from these acids darken and become ill-smelling due to the formation of oxy-fatty acids. Goldschmidt says that, in general, an oil should not be used for the production of a hard soap when its iodine number exceeds 110.

Some of the largely used fats and oils for the preparation of hard soap are as follows: beef tallow, mutton tallow, lard, bone fat, horse fat, olein (red oil) from stearin manufacture, palm oil, peanut oil, olive oil, especially the lower qualities, hardened (hydrogenated) fish oils, hardened linseed oil, hardened cotton oil, hardened corn (maize) oil, etc., as well as soap-stock containing the proper sort of acids from these oils. Cottonseed oil, soya bean oil, corn oil, sesame oil, and other semi-drying oils are used in conjunction with the

above fats for the manufacture of hard soaps. For preparing gelatinous hard soaps palm-kernel and coconut oils are used in the curd soap industry.

In the manufacture of hard soap the non-drying and semi-drying oils are mostly used, but in the soft soap industry the drying oils are best suited to the preparation of high quality products. Linseed oil is the classic example of an oil used for soft soap, others are soya bean oil, poppyseed oil, cottonseed oil, corn or maize oil, sunflower oil, various fish oils, etc., and the soap-stock prepared from these.

Because of their peculiar behaviour castor oil and rape oil form a special class. Ricinoleic acid forms a soap that is salted out with difficulty and the erucic acid from rape oil is extremely sensitive to electrolytes. These oils are never used alone ordinarily, but are used in mixtures with other oils. Castor oil plays an important part in the manufacture of transparent toilet soap.

In the manufacture of toilet soap pure fats or oils with as little odour or colour as possible are used. The hard fats are largely used, with the exception of mutton tallow, which unless very carefully prepared will impart an undesirable odour to the soap. Hardened fats and oils have come more and more into use for the preparation of high grade toilet soaps.

In the examination of a soap, where it is desired to determine the nature of the oils or fats used in the manufacture, it is well to bear in mind the wide range of materials from which a soap may be made, as well as to recognise that in some cases preparations such as hardened or treated oils have been used, concerning which there is no published record of analytical constants. The costs of the soap in many cases will be helpful in leading to a recognition of the unknown.

Alkalies and Fillers.—For the saponification of fats or oils either sodium hydroxide or potassium hydroxide are used, depending on the nature of the soap to be made. For certain types of soaps, mixtures of these two alkali hydroxides are used. For making soap by the double decomposition method, milk of lime is used to saponify the fat or oil. The calcium soap resulting is extracted with water to remove the glycerin completely and the sodium or potassium soap is made by heating the calcium soap with either sodium or potassium carbonate. For the manufacture of soaps from free fatty acids or soap-stock, sodium or potassium carbonates are used,

or if necessary some alkali hydroxide may be used in addition, or the alkali hydroxides may be used without any carbonate.

Soaps are liable to contain unsaponified oil or fatty acids on the one hand, and excess of alkali on the other. C. R. Alder Wright proposed the addition of ammonium salts, such as the sulphate or chloride, in quantity sufficient to react with the free alkali which is so objectionable an ingredient of toilet soaps. The latter may exist either as alkali or carbonate, in addition to which there may be sulphates, chlorides, silicates, traces of calcium, magnesium, aluminium, and iron compounds existing as impurities in the alkali used, common salt as a result of the precipitation of the soap with brine, and, in transparent toilet soaps, alcohol. The use of alcohol for purifying toilet soaps has the advantage of separating carbonates and neutral salts, but alkali dissolves with the soap. On subsequently evaporating the alcohol, the soap remains as a more or less translucent mass, the transparency of which can be further increased by an addition of glycerin or cane-sugar, the latter substance sometimes being present in large proportion in so-called "glycerin soaps," from most of which glycerol is absent.

Besides the foregoing accidental impurities, legitimate additions are frequently made to soap. Thus, potassium and sodium carbonates are added to "cold-water soap" to communicate the power of lathering readily with hard water and to increase the detergent properties generally; sodium silicate is often added to soap intended for manufacturing uses and, though objectionable in some cases, may be legitimate in others. Sodium aluminate is sometimes employed; and borax, which possesses some detergent properties, is used. Petroleum naphtha to the extent of 10% is sometimes incorporated with soap. It is said to increase the detergent action. Many processes have been patented for the addition of various other solvents, such as benzene, carbon tetrachloride, etc., the latest being concerned with the use of tetralin and decalin, the hydrogenation products of naphthylene. These latter solvents are claimed to greatly improve soaps for laundry and textile scouring purposes. A soap of this kind, now largely sold, is prepared by mixing the petroleum product with a rosin soap-mass and adding this to a common soap.

Small proportions of various substances are also added to soap as colouring and perfuming agents. Mottling is produced by iron salts, ochre, ultramarine, or even more objectionable matters, such

as vermilion and copper arsenite. Such additions remain as a residue on dissolving the soap in water or alcohol, and should never exceed 1%, even in mottled soap, and should be less in other varieties. The perfuming agents are mostly used in very small quantities and are ineffective, and in some of the medicated soaps the substances to which therapeutic properties of the soap are attributed are present in such small proportion that the same remark is applicable.

Many forms of medicated soaps are now sold. Among the substances added are carbolic and cresylic acids, thymol, naphthalene and creosote oils, petroleum, vaselin, camphor, formaldehyde, salicylic acid, iodine, chlorine, sodium perborate, flowers of sulphur, polymerised products of coal tar naphtha, mercuric acetate, chlorocresols, zinc stearate, zinc oxide, gelatin, etc., etc.

There are now on the market a number of varieties of soap which contain dyes, generally aniline dyes, and a description of these is to be sought in the patent literature. These soaps are used for the domestic washing of coloured fabrics either to retain the original colour or to dye the fabric some suitable tint. The colours so obtained are attractive, but fugitive in most cases.

Insoluble and inert organic and inorganic substances are added to soaps, either with the alleged object of imparting special characteristics or manifestly to act the part of "fillers" or adulterants. The following is a partial list of such substances found on analysis or taken from various formulas in books on the subject or from the patent literature: colloidal clay, china clay, magnesium silicate, talc, soluble fluorides, silicon fluorides, kaolin, kieselguhr, fuller's earth, potato flour, oatmeal, bran, sawdust, blood albumin, gliadin, glutenin, moss, glue, gelatin, barytes, whiting, pumice-stone, silex, cheese whey, skim milk, buttermilk, cotton fibres, ground corn, sulphite cellulose, burgundy pitch, sugar, sodium sucrate, potassium chlorate, hydrosulphite of soda, sodium sulphite, potassium chloride, beta-naphthalene sulphonic acids, sodium acetate, sodium peroxide, sodium perphosphate, ammonium chloride, ethyl acetate, ox gall carbon disulphide, ammonium acetate, pine oil, turpentine, citric acid, tannic acid, etc., etc. Leffman found 33% of mineral matter in a red Castile soap. The so-called "sand soaps" are largely used for scouring purposes and are usually mixtures of common soap, containing much rosin with some free alkali and a large proportion of more or less finely divided quartz. The proportion of quartz

is often over 80%. In a sample of much advertised soap said to contain milk and sulphur, neither of these substances was found, but there was much china clay and a notable amount of free alkali.

COMMERCIAL VARIETIES OF SOAP AND THEIR MANUFACTURE

Whilst it is not within the scope of this article to discuss in any detail the manufacturing operations used in the preparation of soap, still a general understanding of these is necessary in any analysis. For the interpretation of the more complete analyses and for other purposes of judging the quality of a soap, particularly for purposes of duplication, the knowledge of methods of manufacture must be fairly complete.

The "cold process" of making hard soda soaps is the simplest both in operation and in plant equipment. The plant consists of a tank into which the fat, most suitably of the coconut oil group, after being brought to a temperature of about 35°, is poured. Into it is stirred a concentrated sodium hydroxide solution. The tank is then covered and allowed to stand. During the standing the reaction of the fat and the soda develops heat which completes the saponification within about 24 hours. It is clear that such soaps contain all of the impurities which are contained in the raw materials and that there is no separation of glycerin. It is possible by a careful adjustment of conditions to prepare a neutral soap by this process, but the tendency is to prepare a soap which contains more or less free alkali and also possibly at the same time considerable unsaponified oil. These soaps are not easily "salted out" and are hence used for "marine soaps." Cold soap cannot be conveniently made from soap-stock, because the free fatty acids react so quickly with the strong alkali that lumps are formed occluding uncombined materials. Cold soaps can be made from castor oil, the soaps being transparent. In some cases only small amounts of castor oil are added to the other oils and the complete transparency is brought about by the addition of sugar.

Most **hard soaps** are made by boiling the glycerides of fatty acids with sodium hydroxide soda solution. This is practically the only process which yields soaps of high uniform quality, purity, colour and hardness, and at the same time makes it possible to recover the glycerine in a simple manner. The same type of soap may also be

prepared from free fatty acids, or soap-stock and either alkali hydroxide or soda ash. Generally the soap is boiled in open kettles, but the process may also be run under pressure or vacuum.

The oils or fats are agitated by steam whilst there is gradually added a dilute solution of the alkali lye. Emulsification of the oils first results, followed by hydrolysis. Strong lye cannot be used except with castor oil and oils of the coconut group. It requires some time to complete the hydrolysis, since its reaction velocity is much reduced towards the end of the boiling. McBain (*loc. cit.*) has made experiments on this phase of the reaction. This lessening of the speed of hydrolysis explains the presence of unsaponified fats in poorly made soaps. In order to separate the excess of alkali, which is always used in practice, and also to separate the glycerin, salt is added to the mass and, on standing, two layers separate: (1) an upper layer consisting of soap granules called "*curd*" which retains about 30 to 35% of water, and (2) a lower layer consisting of an aqueous solution of glycerin, excess lye, salt and other impurities. This lower layer is drawn off and used for glycerin recovery, whilst the upper soap curd layer is boiled up with water until a homogeneous mass is formed. This process is called "*closing*" the soap, and generally more lye is added during this boiling so as to insure complete saponification. The soap solution is again salted out and the curd is brought into the condition of a finished soap by a process called "*fitting.*" This consists in bringing the soap to a state so that it will contain just the proper amount of water so that the finished soap will be sufficiently dry and hard and yet permit the enmeshed heavier aqueous solution containing the metallic soaps and other impurities to settle out. The upper layer of soap called "*neat*" is then removed from the lower layer called "*niger*" and is allowed to cool and set in frames. It is cut into bars and is then worked mechanically to incorporate fillers, colouring matters, perfumes, medicaments, etc. Soaps of this class, when freshly made, contain about 63 to 64% of combined fatty acid and about 30% water.

Mottled soaps result when soaps made by boiling low grade greases are finished with strong lye. The impurities in such a case do not settle readily and tend to segregate, on cooling, causing a "mottled" appearance. Such soaps are likely to be more or less strongly alkaline. The proportion of fatty acids is somewhat lower

than in well fitted soaps, being about 61%. Such soaps find their greatest use in laundry and industrial processes.

Marseilles soap is a somewhat lower grade of mottled soap made originally from low grade olive oil. This is now made in many cases from olive oil foots, and because of the low quality of the foots many makers use, in addition, some tallow or sesame oil, although such a soap is not a Marseilles soap. At times the marbling is accentuated by the addition of iron sulphate or copper sulphate. This mottling used to be considered a sign of purity, but is no longer considered so. These soaps contain from 57 to 60% fatty acids and, in order that the soaps may be suitable for handling and shipping, they must be pickled in strong brine.

Eschweg soap, or blue mottled soap, is a cheap imitation of Marseilles soap, and is made by filling a genuine soap with such salts as sodium carbonate, sodium silicate, salt, etc. This soap contains about 47% fatty acids.

Filled soaps are made by working into neat soap the desired filler by a process known as *crutching*.

Milled soaps, to which type most of the toilet and medicated soaps belong, are made by grinding the soap bars into fine shavings and drying these in thin layers by steam. To the dried shavings perfumes, colouring matters, medicaments, etc., are added and the mass is then worked between rollers until these are thoroughly incorporated. The mass is then passed through dies and heated chambers under pressure, coming out in the form of a continuous bar, which is cut into suitable lengths and stamped into final shape.

Transparent soaps are made by dissolving the milled soap shavings in alcohol, or they may also be prepared by saponifying the oil with alcoholic alkali hydroxide. In this case the sodium carbonate and other salts separate out and the glycerin stays in solution. The alcoholic solution is decanted, most of the alcohol distilled off until a gelatinous mass is formed which is made into suitable bars. On standing in storage the cakes become transparent. Such soaps are of high purity and are largely made from tallow, coconut oil or castor oil. Transparent soaps are also made by filling with sugar, but these as well as those made by the cold process should be considered as an adulterated article. Transparent soaps are sometimes made from stock containing high proportions of rosin.

Shaving soaps are a type of milled soap made with a mixture of caustic soda and caustic potash to give the right hardness and lathering properties.

Floating soaps are made by blowing air or other gases into the soap whilst it is still in the crutchers in the paste form, or by incorporating substances which will produce gases in the soap before it is marketed.

Liquid soaps are made in various ways. Some are much diluted soaps, often potash soaps to which glycerin is added to prevent evaporation, or they may be alcoholic solutions of potash soaps to which glycerin is added. Other soaps, used in the textile industry, are partially or completely neutralised Turkey red oil. Solutions of soap in carbon tetrachloride or other solvents belong to this group.

Dry cleaning or benzene soaps are generally made from potash soaps, or from soda soaps containing goodly proportions of rosin. Into these soaps are incorporated solvents such as petroleum naphtha, benzene, etc. Oleic acid ammonium soaps with solvents are also made for this purpose. Soft gelatinised soaps and softeners are made for the textile trade. These are sometimes made from soda and sometimes from potash soaps and more frequently from a mixture of both. They are made from a variety of fats and contain in some cases free alkali.

Soft soaps are made largely from potash, although sometimes some sodium hydroxide is used in addition. Potassium soap cannot be separated in a way similar to the salting out of sodium soaps by the addition of potassium chloride. The hardness of the soap will depend on the fat saponified, it being possible to make a hard potash soap. The soft soap manufacture consists of but one operation, that of boiling the proper oil, chiefly linseed or like drying oils, with the alkali. The gelatinous mass after proper fitting is run directly into containers for marketing. The soft soap contains all of the glycerin and all of the impurities in the raw materials. It should be transparent, and a certain excess of caustic potash, or more often potassium carbonate, is nearly always present, excepting in certain textile soaps where appearance is not important. In cold weather, and in certain soft soaps, depending on the fats used, the harder potassium stearate crystallises out forming star-like clusters, known as "*figging*." This same effect may be produced by replacing a portion of the potash by soda.

ANALYSIS OF SOAPS

From the foregoing discussion it is evident that soaps may contain as frequent or occasional ingredients numerous substances and that the complete analysis of soap may be a tedious and very difficult matter. In the great majority of cases, however, the examination of soaps is restricted to a relatively small number of determinations, and of these some have a greater or lesser importance according to the purpose for which the soap is designed to be used.

The soap manufacturer, knowing the character of the raw materials used in making the soap, will be guided in the tests to be made on the finished soap by the specifications which it must meet. In general, the amount of unsaponified fat, the total alkali, the free caustic and carbonate, silicate or borate alkali, the unsaponifiable matter, the total fatty acids, the matter volatile at 105° and the insoluble matter will be of interest.

Textile soaps are usually examined for water, total alkali, combined alkali, free alkali, alkali hydroxide, fillers, rosin and fatty acids. Matthews ("Bleaching and Related Processes," 1921) states that the consensus of opinion from the best authorities on the subject is that a good scouring soap should be neutral; carbonated alkali is cheap as compared with soap, and, if its addition is desired by the scourer, it can be added to the scouring bath in proper amount when needed. The soap should be especially free from alkali hydroxide. It should not contain any unsaponified fat or free fatty acid, as just so much more of the soap is needed to emulsify this, and hence it will be less efficient in scouring. It should be free from rosin, mineral oil, and all other unsaponifiable matter, and finally it should be free from sodium silicate and any other filling matter.

Household and laundry soaps should, in general, be tested for the proportion of water, alkali as soap, alkali in other forms, total fatty acids and in addition frequently for the percentage of rosin and fillers as well as petroleum solvents and the like, and other unsaponifiable matter.

Toilet and fancy soaps should be tested for odour and appearance, water, alkali as soap, free alkali, alkali in other forms, fatty and resin acids, glycerol, sugar, insoluble matter and, in the case of shaving soaps and similar soaps, for lathering properties, presence of potash, and the general nature of the fatty acids.

Medicated soaps should be especially examined for the proportion of active or *quasi*-active constituent said to be present in addition to the other determination required under toilet soaps.

Liquid soaps should be examined for the proportion of total soap, free alkali, total alkali and in special cases glycerol, etc.

Automobile and similar soaps should be examined for water, free alkali, free acid, insoluble, rosin, and unsaponifiable matter.

Miscellaneous Soaps.—These should be tested to see if they are suitable for the particular purpose for which they are designed and to see if specifications have been met.

The above is merely suggestive and gives the tests which in general should be made. Frequently only a few tests need be made, and the number and kinds of tests must depend on specific cases. In cases where information is required as to the fats or oils from which the soap is made, or other information with regard to the manufacture of the soap is required, a more detailed examination will be required than those outlined above.

A comparative analysis of the soap content of different soaps can be effected in a useful and simple manner by ascertaining what volume of a standard solution of the sample must be added to 50 c.c. of a very dilute solution of calcium chloride or sulphate solution in order to obtain a persistent lather on shaking. The soap solution is made by dissolving 10 grm. of the sample in alcohol (sp. gr. 0.920), filtering, and diluting the filtrate with the same solvent to 1000 c.c. The test is made exactly as in estimating the hardness of waters, the soap solution being added to the standard hard water in small quantities at a time until a lather is obtained on shaking, which remains for at least 5 minutes when the bottle used for the operation is placed on its side. The standard hard water may conveniently be prepared by exactly neutralising 40 c.c. of N/10 sulphuric or hydrochloric acid by cautious addition of lime-water, and diluting the solution to 1000 c.c., when it will have a hardness of 14 degrees of Clark's scale.

A preliminary test for free alkali may be made by dropping an alcoholic solution of phenolphthalein on to a freshly cut surface of the soap. A pink coloration indicates the presence of free alkali hydroxide if the soap be dried out, but also of free alkalinity as carbonate, borate, trisodium phosphate, or silicate, if the soap be moist. If the soap be dried out the presence of these salts does not

affect the phenolphthalein. Legrandi (*Z. deut. Oel-Fett Ind.*, 1922, 42, 314) states that a hot alcoholic solution of a potash soap gives a red colour with phenolphthalein, disappearing on cooling, but reappearing on second heating. On excluding atmospheric carbon dioxide on cooling the solution retains its red colour. An alcoholic solution of potassium carbonate behaves in the same way, but parallel tests with sodium carbonate showed absence of colour in all cases. He concludes that the test is due to the hydrolysis of hot alcoholic solutions of potassium carbonate and potash soaps, but does not occur in the corresponding sodium compounds. Hydroxides or the alkaline salts will also be indicated by the black or grey coloration produced by dropping mercurous nitrate solution on the freshly cut surface.

A qualitative test for fillers may be made by dissolving the soap in hot alcohol and noting the insoluble matter.

Leitch (*J. Ind. Eng. Chem.*, 1914, 6, 811) gives the following qualitative test for the presence of silicates. To 1 grm. of the soap in 25 c.c. of water add 5 c.c. excess N/1 hydrochloric acid, with the use of Methyl Orange as indicator. Heat on the water bath until the fatty acids are clear, then filter and bring the filtrate to neutrality with N/1 sodium hydroxide solution. Add 10 c.c. of this solution to 5 c.c. of N/1 alcoholic potassium hydroxide solution, boil down to 10 c.c. on a water bath and pour this clear or filtered solution into a test tube containing 10 c.c. acetone and 1 c.c. of a solution made by dissolving 10 grm. of sodium aluminate and 2 grm. of salt in 1000 c.c. of water. If sodium silicate be present a gelatinous precipitate results. Dextrin and starch interfere and must be removed if present.

Two qualitative tests are used for the presence of rosin. The Halphen test is made by dissolving 2–3 grm. of the sample in hot water and adding a saturated solution of magnesium sulphate until no more precipitate is formed, and filtering hot. The resinate of magnesium remains in solution. To the hot filtrate sulphuric acid is added and, if a cloudiness be produced, rosin is indicated. Some fats (coconut oil) contain soluble volatile acids which produce a cloudiness under these conditions, but these may be driven off by boiling the solution for half an hour.

The Liebermann-Storch reaction is largely used for the qualitative test for rosin, although it is also given by cholesterol, certain

sulphurised oils, and other compounds. The test may be made by dissolving 1–2 grm. of the separated fatty acids (from the "titer") in warm acetic anhydride. Cool, pour sulphuric acid (sp. gr. 1.53) carefully down the side of the test tube containing the fatty acid solution. A reddish violet coloration which quickly fades to brown indicates rosin. The amount of cholesterol ordinarily present should give no more than a very faint trace of colour.

Cottonseed oil fatty acids may be tested for by the Halphen test. To 5 c.c. of the fatty acids in a 12 × 1 inch test tube add 10 c.c. of Halphen's reagent (4.5 grm. of sulphur dissolved in 150 c.c. of carbon bisulphide and 120 c.c. of amyl alcohol) and place the tube in saturated brine solution. Heat slowly until carbon disulphide is driven off and then boil for 45 minutes. Compare colour with original fatty acids. A red colour indicates cottonseed oil. Cottonseed oil is not always shown by this test.

The table on page 587 exhibits a systematic scheme for the complete analysis of even a complex soap. This table appeared in the last edition of this work and is mainly based on the scheme drawn up by C. R. Alder Wright and C. Thompson, which is a modification of that of A. R. Leeds, who appears in great measure to have derived his method from the first edition of this work. The plan of procedure is so arranged as to permit of the examination of ordinary soaps being very simply conducted, whilst allowing any special ingredient to be sought for and determined. This scheme will not be rigidly adhered to in the discussion which follows, but it will aid the analyst who has to make a complete examination of a soap, to coördinate the various procedures which may be followed. On the other hand, it must be understood that the complete examination of some soaps may prove to be a very difficult matter, and that to determine what each and every ingredient is, or was, when put into the soap, may require recourse to a wide variety of methods of isolation, identification and estimation.

Before discussing the various methods for determining constituents of soap the Standard Methods for the Sampling and Analysis of Commercial Soap and Soap Products of the American Chemical Society are given. These methods are the result of a study of several years on the part of leading producers and consumers of soaps in the United States, and represent the best commercial practice at this time for the determinations involved.

A.—Dry 10 grm. of the soap as described on page 603. The loss is _water_, with possible traces of alcohol and essential oils. Place the dried soap in a plaited filter, and exhaust it with redistilled petroleum spirit, in a Soxhlet tube.				**I.**—Exhaust 10 grm. of the sample with 200 c.c. of alcohol (96 %), or, preferably, absolute alcohol, avoiding exposure to air.	

B.—Solution will contain any _unsaponified_ and _unsaponifiable_ matters, the nature of which can be ascertained, as described on page 613. Their total amount may be found by distilling the whole or an aliquot part of the solvent solution, drying the residue at 100°, and weighing.	**C.**—Residue. Allow the adhering petroleum spirit to evaporate, and exhaust the residue thoroughly with boiling water. In some cases the previous drying and treatment with petroleum spirit may be omitted, in which case 10 grm. of the original soap are at once dissolved in water, and the solution shaken with petroleum spirit, if thought desirable, the solution being treated as at B. **D.**—The aqueous solution is filtered, decanted, or strained from any insoluble matter.		**K.**—Solution. Add a few drops of a neutral alcoholic solution of phenolphthalein. If a pink colour is produced, titrate cautiously with decinormal or seminormal acid, the volume of which responds to the _free caustic alkali_ of the soap. If no pink coloration be produced on adding phenolphthalein, titrate the liquid with decinormal caustic alkali, the volume required corresponding to _free fatty acids_ (see page 605).	**L.**—Residue. Dry at 100° and weigh (see page 603). Exhaust thoroughly with water at 60° or with boiling water, and filter, decant, or strain.	
	E.—Solution. Treat the hot liquid with a known volume of standard sulphuric acid, using a moderate excess. Agitate thoroughly, and pass the separated aqueous liquid through a filter (see page 621).	**H.**—Residue. Consists of _insoluble matters_, mineral and organic. It may be examined instead of, and in a manner similar to, Residue N.		**M.**—Solution. Divide into two equal parts (see page 609).	**N.**—Residue consists of _insoluble matter_. If considerable, dry at 100°, weigh, and examine as described on page 612.
	F.—Solution. Add Methyl Orange or Methyl Red and titrate with standard alkali or sodium carbonate free from chlorides. The difference between the free acid thus found and that previously added gives the equivalent of acid required to neutralise the _total alkali_ of the sample. Examine the neutralised liquid as on page 624.	**G.**—Oily Layer consists of _fatty_ and _resin acids_, and may be treated as described on page 628.		**1.**—Add Methyl Orange or Methyl Red and titrate with decinormal hydrochloric acid. Volume required corresponds to _alkali_ of _carbonate, silicate_, and _borate_ present. Employ neutralised liquid for determining _sulphates_, or to test for _starch_ and _gelatin_.	**2.**—Examine for _borate, silicate, aluminate_, and _sulphate_ as described on page 611.

STANDARD METHODS FOR THE SAMPLING AND ANALYSIS OF COMMERCIAL SOAPS AND SOAP PRODUCTS[1]

The *Committee on Methods of Analysis and Specifications of Commercial Soaps and Soap Products* of the *Division of Industrial Chemists and Chemical Engineers* of the AMERICAN CHEMICAL SOCIETY has given careful consideration to criticisms of its previous report (*J. Ind. Eng. Chem.*, 1919, 11, 785) and has also coöperated with the Soap Committee of the American Specialty Manufacturers' Association and with the Technical Committee on Soaps of the U. S. Government, with the result that the following report was unanimously adopted April 3, 1922.

ARCHIBALD CAMPBELL, *Chairman*, The Globe Soap Co., Cincinnati, Ohio.
C. P. LONG, The Globe Soap Co., Cincinnati, Ohio.
PERCY H. WALKER, Bureau of Standards, Washington, D. C.
J. R. POWELL, Armour Soap Wks,. Chicago, Ill.
R. E. DIVINE, Armour Soap Wks., Chicago, Ill.

Applicability of the Methods.—It is admitted that the methods of sampling may not in all cases yield samples that are truly representative of the whole lot, but any method that would do so would be so cumbersome and expensive as to defeat its own purpose.[2] The methods given do not favour either buyer or seller, and are believed to be as accurate as the economic considerations warrant and if mutually agreed upon should be satisfactory to all interested parties.

The methods of test differ somewhat in form and in some cases in substance from those given in the previous report, because the committee has attempted to cover methods that would be of importance in commercial transactions rather than methods that would be mainly of theoretical interest and only applicable in special cases. As presented, the methods of sampling and testing can be directly applied to commercial transactions, and it may be of interest to state that the methods prescribed in the specifications for various soap products recommended as U. S. Government Standards by the Federal Specifications Board are essentially the same as these.

1. **Sampling.**—The seller shall have the option of being represented at the time of sampling, and when he so requests shall be furnished with a duplicate sample.

I. Cake Soaps, Flake and Powdered Soap Products, when Packed in Cans or Cartons.—One cake (can or carton) shall be taken at random from not less than 1% of the vendors' shipping containers, provided such containers contain not less than 50 lb. In the case of smaller containers, a cake (can or carton) shall be taken at random from each lot of containers totaling not more than 5000 lb. The total sample shall in all cases consist of not less than three cakes (cans or cartons) taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 lb., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lb.

Wrap the individual cakes (cans or cartons) tightly in paraffined paper at once and seal by rubbing the edges with a heated iron. The inspector shall accurately weigh each wrapped cake (can or carton), record its weight and the date of weighing on the wrapper, place the wrapped cakes (cans or cartons) in an air-tight container which should be nearly filled, and seal, mark, and send to the laboratory for test. Samples should be kept cool until tested.

II. Flake and Powdered Soap Products When in Bulk.— A grab sample of not less than ½ lb. shall be taken at random from not less than 1% of the vendors' shipping containers, provided such containers contain not less than 100 lb. In case of smaller containers, a grab sample of not less than ½ lb. shall be taken at random from each lot of containers totaling not more than 10,000 lb. The total samples shall in all cases consist of not less than three grab portions taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 lb., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lb. The inspector shall rapidly mix the sample, place in an air-tight container, which shall be filled, and seal, mark, accurately weigh, record its weight and date of weighing on the package, and send to the laboratory for test. Samples should be kept cool until tested.

III. Liquid Soap.—A sample of not less than ½ pt. shall be taken at random from not less than 1% of the vendors' shipping containers, provided such containers contain not less than 10 gal. each. In case of smaller containers, a sample of not less than ½ pt. shall be taken at random from each lot of containers totaling not more than 1000 gal. The total sample shall

in all cases consist of not less than three portions of ½ pt. each taken at random from separate containers. Before drawing the sample from the container selected, the contents of the container shall be thoroughly agitated. The inspector shall thoroughly mix the samples drawn, place in clean, dry cans or bottles, which shall be completely filled and securely stoppered with clean corks or caps; seal, mark, and send to the laboratory for test.

IV. PASTE SOAP PRODUCTS.—(1) *When Packed in Cans or Cartons of 5 lb. or Less.*—One can or carton shall be taken at random from not less than 1% of the vendors' shipping containers, provided such containers contain not less than 50 lb. In case of smaller containers, a can or carton shall be taken at random from each lot of containers totaling not more than 5000 lb. The total sample shall in all cases consist of not less than 3 cans or cartons taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 lb., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lbs. Wrap, seal, mark, and send to laboratory for test.

(2) *When Packed in Bulk.*—Take a trial sample at random of not less than ½ lb. from not less than 1% of the vendors' shipping containers, provided such containers contain not less than 50 lb. In case of smaller containers a trial sample shall be taken at random from each lot of containers totaling not more than 5000 lb. The total sample shall in all cases consist of not less than 3 half-pound portions taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 10 lb., the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 10 lb. The inspector shall promptly place the combined sample in a clean, dry, air and water-tight container which shall be filled, and seal, mark and send to the laboratory for test.

2. **Preparation of Samples.**—I. CAKE SOAP.—In case of samples that can be easily disintegrated and mixed, run the entire sample through a suitable chopper. When the sample is large, each cake may be quartered and one-quarter of each cake run through the chopper. With samples that cannot be handled as above, select a cake of average weight, quarter it by cutting at right angles in the center and shave equally from all freshly cut surfaces sufficient

soap for analysis. Mix and weigh out all portions for analysis promptly. Preserve the remainder in an air-tight container in a cool place.

II. Powdered and Chip Soaps.—Rapidly disintegrate and mix the sample; if desired, quarter down to about 1 lb. and weigh out all portions for analysis at once. Unused portions of the sample for analysis shall be preserved in an air-tight container in a cool place.

III. Liquid Soap.—No preparation of the sample, other than thorough mixing, is necessary unless it is received during very cold weather, when it should be allowed to stand at least 1 hour after it has warmed up to room temperature (20° to 30°) before it is noted whether it forms a satisfactory lather.

IV. Paste Soap Products.—Mix thoroughly by kneading and quarter down to about 1 lb. Weigh out all portions for analysis promptly and preserve remainder in an air-tight container in a cool place.

3. **Methods of Analysis.**—When a determination shows nonconformity with the specifications a duplicate shall be run.

I. Matter Volatile at 105°.—Weigh 5 grm. of the sample in a porcelain or glass dish about 6 to 7 cm. in diameter and 4 cm. deep, dry to constant weight in an inert atmosphere at a temperature not exceeding 105°.

II. Total Matter Insoluble in—Alcohol. Free Alkali or Free Acid.—(1) *Matter Insoluble in Alcohol.* Digest hot a 10-grm. sample with 200 c.c. of freshly boiled ethyl alcohol neutral to phenolphthalein (94% or higher). Filter through a counterpoised filter paper neutral to phenolphthalein, or a weighed Gooch crucible with suction, protecting the solution during the operation from carbon dioxide and other acid fumes. Wash the residue on the paper, or in the crucible, with hot neutral alcohol until free from soap. Dry the filter paper, or crucible, and residue at 100° to 105° for 3 hours., cool, and weigh the total matters insoluble in alcohol.[1]

(2) *Free Alkali or Free Acid.*—Titrate the filtrate from the above, using phenolphthalein as indicator, with standard acid or alkali solution, and calculate the alkalinity to sodium hydroxide (or potassium hydroxide), or acidity to oleic acid.

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[1] The matter insoluble in alcohol will contain most of the alkaline salts such as carbonates, borates, silicates, phosphates and sulphates, as well as starch, and may be used for the approximate estimation of these constituents. These salts are not entirely insoluble in alcohol, so for accurate determinations separate portions of the soap should be used.
For estimation of carbonates see 3 X; for phosphates, 3 XI; for sulphates, 3 XII; for silicates, 3 IX; for borax, 3 VIII; for starch, 3 XIII(4).

(3) *Matter Insoluble in Water.*—Proceed as in the determination of matter insoluble in alcohol. After filtering and thoroughly washing the residue, extract it with water at 60° and wash the filter thoroughly. (When the matter insolube in water is all inorganic, boiling water may be used for the extraction and washing.) Dry the filter and residue at 100° to 105° for 3 hours, cool, and weigh matter insoluble in water. The nature of this matter may be determined by further examination.

(4) *Total Alkalinity of Matter Insoluble in Alcohol.*—(Alkaline salts.) Titrate the filtrate from the determination of matter insoluble in water with standard acid, using Methyl Orange as indicator. Calculate the alkalinity to sodium oxide (Na_2O), and, if desired, to any other basis agreed upon by the parties interested.

(5) *Combined Alkali. Total Anhydrous Soap.*—Dissolve 5 to 10 grm. of the sample, depending upon the anhydrous soap content, in 100 c.c. of water in a 250 c.c. Erlenmeyer flask. When solution is complete, add dilute sulphuric acid in slight excess, insert a small funnel in the neck of the flask, and heat the flask at a temperature not exceeding 60° until the fatty acids separate as a clear layer. Transfer to a separatory funnel, draw off the acid layer into a second separatory funnel and shake the acid aqueous liquid with two 20 c.c. portions of ethyl ether. Dissolve the fatty acids in the ether used for washing the aqueous liquid and shake with 10 c.c. portions of water until they are no longer acid to Methyl Orange. Unite the water portions used for washing and shake with 20 c.c. of ether. Wash this ether until the wash water is neutral to Methyl Orange. Save the acid water for chloride determination. Unite the ether solutions (if necessary, filter, washing the paper with ether) in a suitable weighed vessel, add 100 c.c. of neutral alcohol free from carbon dioxide, add phenolphthalein and titrate to exact neutrality with standard sodium hydroxide solution. Evaporate off the alcohol, dry to constant weight as in the determination of matter volatile at 105° and calculate the percentage of soda soap. This soap naturally includes any mineral oil and neutral fat, which, if determined separately, must be deducted from the result to obtain the true soap. Calculate the combined sodium oxide (Na_2O) and deduct from the weight of soda soap to give the anhydrides. If the original soap was potash soap, proper calculation must be made to reduce to potassium oxide (K_2O), or the titration made directly with stand-

ard potassium hydroxide solution. In case the soap shows an excess of free acid, proper corrections must be made in calculating the combined alkali in the original soap.[1] (See determination of rosin.) With soaps containing a large amount of soluble silicates and soap products containing a high percentage of finely divided material insoluble in water, the foregoing procedure cannot be applied as given. In such cases the filtrate obtained in the determination of total matter insoluble in alcohol can be used after neutralising any free acid or alkali. Evaporate off the alcohol on a steam-bath, take up in water and proceed as above.

With soap products containing a high percentage of matter insoluble in alcohol where approximate results will suffice, such as may be the case with cleansers, soap powders, scouring compounds, pastes, etc., and where agreed upon by the parties interested, the alcoholic solution, obtained after filtering off and washing the matter insoluble in alcohol, may be evaporated directly in a weighed vessel, dried at 105° to constant weight, and the result reported as soap.

III. CHLORIDE.—Neutralise with chlorine-free alkali the acid water obtained in paragraph 3 II(5). Titrate with standard silver nitrate solution, using potassium chromate as indicator, and calculate the result to sodium chloride or potassium chloride as the character of the soap indicates.

In case the total anhydrous soap is not to be determined it will be more convenient to use the following method (H. C. Bennet, *J. Ind. Eng. Chem.*, 1921 13, 813): Dissolve 5 grm. of the sample in 300 c.c. of water, boiling if necessary to effect solution. Add an excess of neutral, chlorine-free magnesium nitrate solution (about 25 c.c. of a 20% $Mg(NO_3)_2.6H_2O$ solution). *Without cooling or filtering*, titrate with standard silver nitrate solution, using potassium chromate as indicator.

IV. UNSAPONIFIED AND UNSAPONIFIABLE MATTER.—Weigh 5 grm. of the soap into a beaker and dissolve in about 100 c.c. of 50% alcohol on the steam-bath. If the sample has been found to contain free fatty acid, add just enough aqueous alkali to neutralise this. Evaporate off the bulk of the alcohol, take up with about 200 c.c. of hot water and transfer to a separatory funnel of about 500 c.c. capacity, designated as No. 1. When cool, rinse out the beaker with about 50 c.c. of ether and add it to the soap solution. Shake

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[1] A blank test should be made on the sodium or potassium hydroxide solution for neutral salts and the proper corrections made if necessary.

thoroughly for 1 minute. By the addition of small amounts of alcohol (5 c.c. portions and the total not to exceed 25 c.c.), a clear and rapid separation of the aqueous and ether layers is effected. After adding each alcohol portion, the separating funnel is not shaken but merely given a whirling movement. Draw off the aqueous portion into another separating funnel, designated as No. 2. Wash the ether solution with 10 c.c. portions of water until this water is no longer alkaline to phenolphthalein. Add all these washings to funnel No. 2, and extract this solution with 20 c.c. portions of ether until the ether is absolutely colourless (3 or 4 extractions should be sufficient). Combine these ether extracts in a third separating funnel (No. 3) and wash with 10 c.c. portions of water until the water is no longer alkaline to phenolphthalein. Now add the ether in Funnel 3 to that in Funnel 1, a small amount of ether being used to rinse out Funnel 3. Wash the ether solution with 20 c.c. of 10% hydrochloric acid solution and then successively with 20 c c. portions of water until the water is no longer acid to Methyl Orange. Filter the ether solution through a dry filter paper into a weighed beaker or flask. Evaporate or distil off the ether on the steam-bath, dry as under the determination of matter volatile at 105° and weigh the residue, then heat with alcohol and, when cool, neutralise with standard alkali, using phenolphthalein. Deduct any appreciable amount of fatty acid found by this titration from the weight of the residue. This residue consists of the unsaponifiable matter and any neutral fat that may have been present in the soap. In case it is desired to separate these, thoroughly saponify the residue with alcoholic alkali and repeat the foregoing procedure. The residue obtained is unsaponifiable matter only.

V. Rosin. *Wolff's Method (Chem. Z.,* 1917, **38,** 369, 382, 430; *C. A.,* 1914, **8,** 2495).—Dissolve 5 grm. of the sample in 100 to 200 c.c. of hot water, add a slight excess of dilute sulphuric acid, heat until the fatty acids collect in a clear layer, cool to room temperature, extract with a small portion of ether, draw off the aqueous layer and wash the ether solution with water until free from mineral acid. Transfer to a 200 c.c. Erlenmeyer flask, evaporate off the ether and dry 1 hour at 105°, cool and dissolve in 20 c.c. of absolute alcohol. Then add 10 c.c. of a solution of 1 volume of concentrated sulphuric acid (sp. gr. 1.84) and 4 volumes of absolute alcohol, and boil on the steam-bath for 4 minutes under a reflux condenser. Remove from steam-

bath, add to the liquid about 5 times its volume of 7 to 10% sodium chloride solution, and extract with ether. Shake out the aqueous portion 2 or 3 times with ether. Unite the ether solutions and wash with sodium chloride solution until the washings are neutral to Methyl Orange. Add 30 c.c. neutral alcohol, and titrate the rosin acids with standard sodium hydroxide solution, using phenolphthalein as indicator. Calculate to rosin or rosin soap, as desired (1 c.c. normal alkali = 0.346 grm. rosin or 0.377 grm. rosin soda soap). If the true fatty acid soap is desired, subtract the rosin soap from the total anhydrous soap obtained under 3 II(5).

VI. TITER TEST—(1) *Preparation of total fatty matter (fatty and rosin acids and unsaponified matter).*—Dissolve about 50 grm. of soap in 500 c.c. of hot water, add 100 c.c. of 30% sulphuric acid, heat until the fatty matter collects in a clear layer, siphon off the acid layer and wash the fatty matter free from sulphuric acid with hot water. Decant the fatty matter into a dry beaker, filter, using a hot-water funnel, or placing both funnel and receiving beaker in a water-jacketed oven, and dry for 20 minutes at the temperature of boiling water.

When other determinations are to made on the total fatty matter, and volatile and readily oxidisable fatty acids are present, the following method should be used: Dissolve about 50 grm. of the soap in 300 c.c. of hot water, transfer to a separating funnel, add 150 c.c. of approximately $N/2$ sulphuric acid, cool somewhat, add 120 c.c. of ether, shake, draw off the acid layer, and wash the ether layer free from acid with a strong salt (NaCl) solution. Then draw off the aqueous layer as completely as possible, transfer the ether layer to a flask (it is not necessary to transfer quantitatively), add 20 to 30 grm. of anhydrous sodium sulphate, stopper the flask, shake, and let stand at a temperature below 25° until the ethereal liquid becomes perfectly clear, showing that all water has been taken up by the sodium sulphate. Filter through a dry paper into another Erlenmeyer flask, and completely evaporate off the ether by passing through the flask a current of dry air and heating the flask to a temperature not above 50°.

(2) *Estimation.*[1] (a) *Thermometer.*—The thermometer shall be a standard "titer" thermometer graduated at zero and in tenth degrees from 10° C. to 65,° and certified by the U. S. Bureau of Standards.

[1] *Methods of Analysis of Assoc. Official Agri. Chem.*, 1920, 242. F. A. C. Methods, *J. Ind. Eng. Chem.*, 1919, 11, 1163.

(b) *Procedure.*—Transfer the fatty acids prepared as under VI(1), when cooled somewhat, to a titer tube 25 mm. by 100 mm. placed in a 16-oz. salt-mouth bottle of clear glass 70 mm. by 150 mm., fitted with a cork that is perforated so as to hold the tube rigidly when in position. Suspend the titer thermometer so that it can be used as a stirrer and stir the fatty acids slowly (about 100 r. p. m.) until the mercury remains stationary for 30 seconds. Allow the thermometer to stand quietly with the bulb in the centre of the tube and report the highest point to which the mercury rises as the "titer" of the fatty acids. The titer should be made in a room at about 20° for all fats having a titer above 30° and at 10° below the titer for all other fats.

VII. ACID NUMBER OF FATTY ACIDS—(1) *Preparation of fatty acids.* Follow procedure given under 3 VI.

(2) *Estimation.*—In a 250 c.c. Erlenmeyer flask dissolve 2 grm. of the fatty acids, accurately weighed, in 20 to 30 c.c. of neutral 95% ethyl alcohol. Titrate with standard alkali, using phenolphthalein as indicator. Calculate the acid number (mgs. of KOH per grm. of fatty acids).

VIII. BORAX ESTIMATION.[1]—Weigh 10 grm. of the soap (or 5 grm. if more than 5% of borax is present) into a platinum dish and add 2.15 grm. of fusion mixture (consisting of 200 grm. sodium carbonate, 15 grm. silica in fine powder). To this mixture add 15 c.c. of alcohol, mix with the aid of a glass rod and, after washing the rod with a little alcohol, evaporate the mass to dryness on the waterbath. Ignite until the combustible material is destroyed, cover the dish with a piece of platinum foil and fuse. Completely disintegrate the fused mass by boiling with water and transfer the solution to a 250 c.c. round-bottom flask. Acidify with 20 c.c. of dilute hydrochloric acid (1 : 1), heat nearly to boiling, and add a moderate excess of dry precipitated calcium carbonate. Connect with a reflux condenser and boil vigorously for 10 minutes. Filter out the precipitate through a folded filter, washing several times with hot water, but keeping the total volume of liquid below 100 c.c.

Return the filtrate to the flask, add a pinch of calcium carbonate and again boil under a reflux condenser. Remove the flame and connect the top of the condenser with a water pump. Apply the suction until the boiling has nearly ceased. Cool to ordinary

[1] Poetschke, *J. Ind. Eng. Chem.*, 1913, 5, 645.

temperature, add 50 c.c. of neutral glycerol and titrate the solution with N/10 sodium hydroxide, free from carbonate, using phenol-phthalein as indicator. After the end-point is reached add 10 c.c. more of glycerol and again titrate. Repeat this process until the addition of glycerol causes no further action on the end-point. The number of c.c. required multiplied by 0.00955 will give the equivalent of borax ($Na_2B_4O_7.10H_2O$) present in the solution.

IX. Estimation of Silica Present as Alkaline Silicates.—When the material contains no mineral matter that is insoluble in water, ignite a sample of the soap containing not to exceed 0.2 grm. of silica in a platinum dish at a low temperature. When charred, extract the soluble salts with water, return the paper and charred residue to the dish and complete the ignition. Unite the residue in the dish and the water extract, carefully acidify with hydrochloric acid, finally adding the equivalent of from 5 to 10 c.c. strong hydrochloric acid in excess. The dish or casserole containing the solution should be covered with a watch glass whilst adding acid so as to avoid loss by spray.

When the material contains mineral matter insoluble in water, or a determination of highest accuracy is not necessary, take a portion of the solution after titrating the matter insoluble in alcohol 3 II(4) containing not more than 0.2 grm. silica, and add 5 to 10 c.c. strong hydrochloric acid.

Evaporate the acidified solution (washing off and removing the cover glass if used) to dryness on steam bath or hot plate at a temperature not exceeding 200°. Cool, moisten with concentrated hydrochloric acid, leave for 5 to 10 minutes, breaking up all lumps with a stirring rod. Add about 25 c.c. of hot water. Heat a few minutes and filter through a small ashless paper. Wash thoroughly with hot water.

Evaporate the filtrate to dryness and repeat the above treatment, filtering on a second paper. Carefully ignite the two papers and contents in a weighed platinum crucible, first at a low temperature until the paper is consumed, but finally heating to constant weight over the blast lamp; cool in a desiccator before weighing. If extreme accuracy is desired, moisten the contents of the crucible with water, add 10 c.c. hydrofluoric acid and 4 drops of strong sulphuric acid, evaporate to dryness over a low flame, ignite at the temperature of the blast lamp for about 2 minutes, cool in a desiccator and weigh.

The difference between this weight and the previous weight is the weight of the silica (SiO_2).[1]

To calculate sodium silicate ($Na_2Si_4O_9$) multiply weight of SiO_2 by 1.26.

X. ESTIMATION OF CARBON DIOXIDE (CARBONATES).—For most determinations the dry matter insoluble in alcohol, as obtained in 3 II(1), will be suitable for this determination. In some cases it might be desired to run the test directly on an original sample of the soap. This should always be done when the highest accuracy is required. Any reliable absorption method for determining carbon dioxide may be used.[2]

The following is a method which has proved satisfactory:

A 250 c.c. Erlenmeyer flask is placed on a gauze over a burner. The flask is equipped with a 2-hole rubber stopper, through one opening of which is a 10 in. reflux condenser and through the other a thistle tube equipped at the outer end with a 3-way stopcock. The lower end of the thistle tube is drawn to a small point, which is placed very close to the bottom of the flask. To the straight-away end of the stopcock is attached a small funnel for the introduction of acid to the flask. The other opening of the stopcock is attached to receive air from a purifying train consisting of a wash bottle containing concentrated sulphuric acid and a second at the outer end of the train containing a 50% solution of potassium hydroxide. The top of the reflux condenser is attached first to a drying wash bottle containing concentrated sulphuric acid and then to a weighed absorbing train consisting of a Bender & Hobein or other suitable potash bulb charged with 50% potassium hydroxide, and a second containing concentrated sulphuric acid. This train is attached to a protective U-tube containing calcium chloride   The U-tube is attached to an aspirator.

Procedure.—Set up the apparatus, leaving out the weighed train, and aspirate with a slow stream of the dry carbon-dioxide-free air until the apparatus is freed from carbon dioxide. Insert the train and continue the aspiration for $\frac{1}{2}$ hour. Check the weight of the train to determine if the air is passing through too fast, or if the system is free from carbon dioxide. The system must be free from leaks. Weigh out 1 or 2 grm. of the sample into the Erlenmeyer

[1] See "The Analysis of Silicate and Carbonate Rocks," by W. F. Hillebrand, U. S. Geological Survey, *Bull.* 700, p. 102.
[2] "*Methods of Analysis,*" *Assoc. Official Agr. Chem.*, 1919, 277, 278.   *Bur. Chem., Bull.* 107, 169.

flask, cover with 20 c.c. freshly boiled distilled water, close the apparatus with the train in place. Add 20 c.c. dilute hydrochloric acid (1 : 1) through the funnel very slowly, with no heat being applied to the flask. The rate of adding acid should be carefully controlled so that the gas does not pass through the train too rapidly. As soon as the acid is added, start aspiration gently. When the absorption begins to stop the gas flow, start heating gently and continue until the contents of the flask have boiled 15 to 20 minutes. Stop heating and continue aspirating until the flask has cooled down. Remove the train and weigh. Calculate increase of weight as carbon dioxide. Carbon dioxide multiplied by 2.41 equals sodium carbonate.

XI. ESTIMATION OF PHOSPHATES.[1]—If a qualitative test has shown the presence of phosphates and their determination is desired, the matter insoluble in alcohol 3 III or the ash from the incineration of an original sample can be used. An original sample should always be used when the highest accuracy is desired.

(1) *Reagents.* (a) *Molybdate solution.*—Dissolve 100 grm. of molybdic acid in dilute ammonium hydroxide (144 c.c. of ammonium hydroxide (sp. gr. 0.90) and 271 c.c. of water); pour this solution slowly and w th constant stirring into dilute nitric acid (489 c.c. of nitric acid (sp. gr. 1.42) and 1148 c.c. of water). Keep the mixture in a warm place for several days or until a portion heated to 40° deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment and preserve in glass-stoppered vessels.

(b) *Ammonium nitrate solution.*—Dissolve 200 grm. of commercial ammonium nitrate, phosphate-free, in water and dilute to 2 litres.

(c) *Magnesia mixture.*—Dissolve 110 grm. of crystallised magnesium chloride ($MgCl_2.6H_2O$) in water, add 280 grm. of ammonium chloride, 261 c.c. of ammonium hydroxide (sp. gr. 0.090) and dilute to 2 litres.

(d) *Dilute ammonium hydroxide for washing.*—Dilute 100 c.c. of ammonium hydroxide (sp. gr. 0.90) to 1 litre.

(2) *Estimation.*—Weigh out a 2 grm. sample of the alcohol-insoluble or ash, and proceed as in 3 IX for removal of silica, saving the filtrate. Make up to 250 c.c., concentrating if necessary. Take an aliquot part corresponding to 0.50 grm. or 1 grm., neutralise with ammonium hydroxide, and clear with a few drops of nitric

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[1] *Methods of Analysis of Assoc. Official Agri. Chem.*, 1919, 1.

acid. Add about 15 grm. of dry ammonium nitrate or a solution containing that amount. To the hot solution add 70 c.c. of the molybdate solution for every decigram of phosphoric acid (P_2O_5) present. Digest at about 65° for an hour, and determine if the phosphoric acid has been completely precipitated by the addition of more molybdate solution to the clear supernatant liquid. Filter and wash with cold water or, preferably, ammonium nitrate solution. Dissolve the precipitate on the filter with ammonium hydroxide and hot water, and wash into a beaker to a bulk of not more than 100 c.c. Nearly neutralise with hydrochloric acid, cool, and from a burette add slowly (about a drop per second), stirring vigorously, 15 c.c. of magnesia mixture for each decigram of phosphoric acid (P_2O_5) present. After 15 minutes add 12 c.c. of ammonium hydroxide (sp. gr. 0.90). Let stand till the supernatant liquid is clear (2 hours is usually enough), filter, wash with the dilute ammonium hydroxide until the washings are nearly free from chlorides, ignite to whiteness or to a greyish white, weigh, and calculate to phosphoric acid (P_2O_5) or alkaline phosphate known to be present.

XII. ESTIMATION OF SULPHATES.—For most determinations the matter insoluble in alcohol obtained under 3 II may suffice. If a determination of the highest accuracy is desired, ignite a 10 grm. sample of the soap and use the ash from the ignition. Digest with 100 c.c. of water, cover with a watch glass, and neutralise carefully with hydrochloric acid. When neutralised, add 5 c.c. excess of hydrochloric acid, filter, and wash the residue thoroughly.[1] Make up the filtrate to 250 c.c. in a beaker and boil. To the boiling solution add 15 to 20 c.c. 10% barium chloride solution slowly drop by drop from a pipet. Continue boiling until the precipitate is well formed, or digest on a steam-bath over night. Set aside over night or for a few hours, filter through a prepared Gooch crucible, ignite gently, and weigh as barium sulphate. Calculate to sodium sulphate, or the alkaline sulphate known to be present.

XIII. ESTIMATION OF GLYCEROL, SUGAR, AND STARCH.— (1) *Estimation of glycerol in the absence of sugar.*

<div align="center">SOLUTIONS REQUIRED</div>

<div align="center">
Potassium dichromate 74.552 grm. per litre
Sodium thiosulphate N/10
Potassium iodide 10%
</div>

[1] Evaporation to dryness is unnecessary unless gelatinous silica should have separated and should never be performed on a bath heated by gas. See Hillebrand, *U. S. Geol. Survey, Bull.* **700,** 232.

Dissolve an accurately weighed sample of the soap[1] equivalent to not more than 3.0 grm. of glycerol in 200 c.c. of hot water in a 600 c.c. beaker. Decompose with 25 c.c. sulphuric acid (1 : 4). If alcohol be present, volatilise it by boiling for 20 to 30 minutes. Cool, remove, and rinse the cake of fatty acids, transfer the acid water and rinsings to a 500 c.c. graduated flask, add about 0.25 grm. silver sulphate to precipitate traces of chlorides and soluble fatty acids. Make up to volume and mix contents thoroughly.

Transfer a filtered, accurately measured 50 c.c. aliquot of the above to a 400 c.c. beaker, to this add 75 c.c. accurately measured potassium dichromate solution, followed by 25 c.c. of sulphuric acid (sp. gr. 1.84). Cover with a watch glass, and oxidise by heating in a steam-bath for 3 hours. Conduct a blank in like manner, but using 100 c.c. of water, 25 c.c. of sulphuric acid (sp. gr. 1.84) and 25 c.c. accurately measured potassium dichromate.

Cool and make up the solution to 1000 c.c. in graduated flasks. The excess of potassium dichromate is determined by taking 50 c.c. aliquot of the above, adding 50 c.c. of water, 20 c.c. of 10% potassium iodide solution, and titrating the liberated iodine with N/10 thiosulphate, with the use of starch solution as indicator.

Calculate the percentage of glycerol (1 c.c. of the potassium dichromate solution equals 0.0100 grm. of glycerol).

(2) *Estimation of sugar.*[2]—Dissolve 10 grm. of the soap in 200 c.c. of hot water in a 600 c.c. beaker. . Decompose with 25 c.c. of sulphuric acid (1 : 4), boil gently for 20 minutes to invert the cane sugar completely. Cool, remove, and rinse the cake of fatty acids. Extract the acid liquid with 25 c.c. of ether. Transfer the acid liquid to a 500 c.c. graduated flask, make up to volume and mix thoroughly. Estimate invert sugar in 50 c.c. of this solution by the Munson-Walker Method (*J. Am. Chem. Soc.*, 1906, 28, 663–86; *Bur. Chem., Bull.* 107; *Methods of Analysis of Assoc. Official Agri. Chem.*, 1920, p. 76, see Vol. I p. 401). To calculate sugar (sucrose) multiply the amount of invert sugar found by 0.95.

(3) *Estimation of glycerol in the presence of sugars* (Hoyt and Pemberton, *J. Ind. Eng. Chem.*, 1922, 14, 54; see also *Ibid.*, 1922, 14, 340).—Proceed as above under (1) taking a sample so that

[1] If starch be present, it will be necessary to remove the matter insoluble in water as described under this determination [3II (1) and (3)]. Combine the alcohol and water solutions, evaporate off the alcohol, and proceed.
[2] If starch is present, see note under glycerol estimation XII(1) and estimation of starch XII(4)

the sum of the glycerol and sugar is not more than 3.0 grm.[1] The solution must be boiled in all cases at least 20 minutes to insure complete inversion of cane sugar. Determine the amount of potassium dichromate solution required to oxidise both the sugar and glycerol. Determine also the sugar by the method given in (2).

Calculate the percentage of glycerol after deducting the amount of potassium dichromate required by the sugar.

> 1 c.c. potassium dichromate equals 0.0100 grm. glycerol.
> 1 c.c. potassium dichromate equals 0.01142 grm. invert sugar.

(4) *Estimation of starch* (*Methods of Analysis Assoc. Official Agri. Chem.*, 1920, 95; *Bur. Chem., Bull.* 107, 53).—Separate the matter insoluble in water as under 3 II(3), using a sample of soap that will give not more than 3 grm. of starch. Transfer the insoluble matter without drying to a beaker and heat for 2½ hours with 200 c.c. of water and 20 c.c. of hydrochloric acid (sp. gr. 1.125) in a flask provided with a reflux condenser. Cool, and nearly neutralise with sodium hydroxide. Complete the volume to 250 c.c., filter, and estimate the reducing sugars by the gravimetric method as given under method for the estimation of sugar.

Calculate the amount of dextrose (*d*-glucose) equivalent to the cuprous oxide obtained. ·This multiplied by 0.90 equals the amount of starch.

XIV. VOLATILE HYDROCARBONS.—Weigh not less than 250 grm. of the sample into a flask of about 5-litre capacity, which is so placed on a gauze that it can be heated. Add 2 to 3 litres of distilled water. Place a 2-holed rubber stopper in the flask, through one hole of which is inserted a copper or brass tube extending into the flask and terminating in a small circular ring of the tubing, bent so that the ring is in a horizontal position. Numerous small holes are drilled in the upper side of this ring and the end of the tube is sealed. This ring should be near the bottom of the flask.

Through the other hole of the stopper is inserted a glass tube provided with a trap of suitable form, the upper end of which is bent so as to be connected with a plain Liebig condenser. The end of the condenser tube is bent so as to extend into a burette graduated to 0.1 c.c.

Introduce steam (free from oil) into the flask through the brass tube and collect the distillate in the burette. When the

[1] See note if starch be present (XIII-1).

burette becomes full, draw off the water by opening the stopcock. The foam which forms in the flask may be controlled by momentarily shutting off the steam and by regulating heat applied to the flask.[1]

Read from time to time the amount of hydrocarbon distillate which collects on the top of the water in the burette, and when there is no further increase in this distillate the operation is finished. Allow the burette to stand over night, tightly stoppered, and then, after reading the amount of distillate, draw off the water as carefully as possible. Determine the sp. gr. of the distillate, and calculate the weight and percentage in the original sample.

Methods for sampling have been described under the A. C. S. method.

In weighing the soap, particularly a moist sample, all the precautions for preventing the loss of moisture during weighing must be resorted to. Lewkowitsch, in discussing the sampling of soap, calls attention to errors resulting in taking an average sample by means of a cork borer. In the cases where the loss of moisture between the time the soap has left the factory and is analysed is not known, as is provided for in the above methods, he advises cutting away the dried outer portion and taking a sample from the uniformly moist inner portion, this portion being located by inspection. With freshly made soaps (containing about 30% water) a fairly large portion should be weighed out rapidly. Soft soaps, according to this authority, should be sampled from the center of the keg.

In the case of isolated samples brought to the analytical chemist for examination he should be most careful to learn for what purpose the analysis is required and, if he has not sampled the soap, to learn what he can of the manner in which it was sampled or its previous history. There is no more potent source of error than that of sampling.

Estimation of Volatile Matter and Water.—In dealing with a substance like soap a clear distinction must always be made between loss on heating above 100° and the estimation of the actual water present. The reason for this is of course obvious. Lewkowitsch (*loc. cit.*) states that the direct determination of water in soaps is,

[1] Some find it an advantage to add 200 to 300 grm. calcium chloride to the flask containing the soap solution, to prevent foaming.

as a rule, an unnecessary operation. In the cases of genuine soaps it suffices for all practical purposes to calculate the fatty acids to anhydrides, to add their weight to the amounts of alkali in various forms and calculate the water by difference. Soaps reaching the laboratory have, as a rule, lost more or less water by drying; hence the determination of water does not afford a reliable means of evaluation. In the determination of water by loss on heating, the volatile ethereal oils, alcohol, glycerol, and solvents such as naphtha, etc., will also partly volatilise. Moreover, if a soap contains considerable portions of free sodium hydroxide, part of the loss in water will be compensated by the absorption of carbon dioxide from the atmosphere.

The American Chemical Society standard method has been given. Swift and Co. (private communication from W. D. Richardson) shave about 5 grm. of sample into a weighed 3 inch porcelain dish and dry to constant weight in a vacuum oven at 20–25° above the boiling point of water at the pressure used. The vacuum used should be at least 20 inches (240 mm.). An air-bath may be used, in which case the sample should be heated at 125–130° to constant weight (about 5 hours). When alcohol, light petroleum or coal tar distillates are present they must be estimated, and the moisture in the soap found by difference.

Another method for estimating the loss on heating is to dissolve 20 grm. of the soap in about 150 c.c. of hot water, transfer the solution whilst still hot to a 250 c.c. volumetric flask and dilute it to the mark. Mix thoroughly, transfer an aliquot part of 25 c.c. into a weighed platinum dish, evaporate to dryness on the steam-bath, and then dry to constant weight at 110°. The percentage of solid matter subtracted from 100 gives the per cent. moisture and other volatile matter (Griffin, "Technical Methods of Analysis," 1921).

The amount of volatile matter in a soap may also be estimated rapidly and with ample accuracy for most purposes by a method recommended by Watson Smith. From 5 to 10 grm. of the finely divided sample are placed in a large porcelain crucible or dish, set in a sand bath which is heated by a small bunsen flame. The soap is continually stirred with a glass rod (weighed with the crucible) having a roughed and jagged end, a peculiarity which greatly facilitates the stirring and breaking up of the lumps of soap formed

toward the end of the operation. The operation is usually complete in 20 to 30 minutes, and is known to be at an end when a piece of plate-glass placed over the crucible (the flame being removed) no longer collects moisture. Care is required to prevent burning of the soap, but the odour thus developed is so characteristic that the manipulation is easily controlled. Smith finds the results trust-worthy to 0.25%.

Direct Estimation of Water.—For the direct estimation of water in organic substances such as soap, the only reliable method is the so-called "xylene or solvent naphtha distillation." This pro-cedure is recommended by R. Hart (*J. Ind. Eng. Chem.*, 1918, **10**, 598), by Utz (*Seifenfarb.*, 1919, **39**, 225), and by Griffin (*loc. cit.*). Utz uses kerosene, whilst Hart and Griffin both use xylene. This type of estimation has been recommended by the American Society for Testing Materials (E. W. Dean and D. D. Stark, *J. Ind. Eng. Chem.*, 1920, **12**, 486) for the estimation of water in petroleum, and the apparatus devised by them is probably the most convenient for the use with soap.

It should be noted that, whilst the use of a high boiling solvent naphtha having a range from about 150 to 170° will give the quick-est and possibly most accurate determinations in general, that if more time is taken for the determination solvents such as toluene may be used satisfactorily. Utz notes that when soaps containing sugars are encountered the kerosene distillation method cannot be applied, since the sugars would be decomposed at the temperature of 150°. The use of toluene as a solvent would not be open to this and similar objections.

Griffin recommends using about 20 grm. of soap and acidifying with anhydrous $KHSO_4$ before distilling. His procedure is as follows, although for the details of his apparatus the ASTM. apparatus may be substituted, with the use of using toluene if it is felt that the xylene has too high a boiling point.

Weigh out 20 grm. of the soap on a balanced filter paper and place the soap and paper in a 300 c.c. Erlenmeyer flask. Add to this sufficient anhydrous $KHSO_4$ to completely decompose the soap, and 75 c.c. of xylene which has previously been saturated with water, as follows:

A convenient quantity of commercial xylene, say 500 c.c., is shaken up in a separatory funnel with water, and the xylene drawn off and

distilled slowly from a distilling flask. From this distillate a small amount of water will separate. The xylene standing above the water is poured off into a glass-stoppered bottle, with a tightly fitting stopper, and preserved for use.

Connect the flask containing the soap and xylene with a condenser, which must be perfectly dry. Heat the flask gradually in a bath of cylinder oil and distil the water and xylene slowly until the xylene comes over clear, collecting the distillate in a funnel tube with a stem graduated to 0.1 c.c. The bulk of the water comes over with the first 10 c.c. distillate. After the distillation is completed, wash down the condenser with water-saturated xylene and tap the funnel gently until any small drops of water clinging to the sides are brought down to the bottom. Read the volume of the water. Each 0.2 c.c. is equivalent to 1% of water in the soap, if a 20 grm. sample was used.

The proportion of water in soap differs greatly. In the so-called "dry soaps," and in some of the best kinds of curd soap, it does not exceed 16 to 20%, whilst in inferior soaps made from coconut oil it sometimes reaches 70 to 80%.

I. Exhaustion of the Soap with Alcohol.—If the original soap is tolerably dry, ordinary rectified spirit is usually sufficiently strong for the treatment at this stage; but if the sample contain much water, absolute or nearly absolute alcohol should be used, or the solution will have an objectionable tendency to gelatinise during filtration and other inconveniences will arise. In order to overcome this difficulty, if the soap contains over 40% moisture, Swift Co. dries the sample first in a vacuum oven so that the absorption of CO_2 and SO_2 is prevented. It is recommended by both Leeds and Wright that the portion of the soap to be treated with alcohol should be a part of that previously exhausted with petroleum spirit, but, as pointed out by C. Hope, it is difficult to dry soap effectually without a notable conversion of alkali into carbonate. The treatment with alcohol can be effected either in the Szombathy-tube, or by boiling the soap with the solvent, and filtering and washing in the usual way.

K. Examination of the Alcoholic Solution.—*Free alkali or free acid.* The estimation of the *free alkali* existing in soap can be effected very simply and accurately by the method of C. Hope (*Chem. News,* 1881, 219), described in the Amer. Chem. Soc. methods, the error rarely exceeding 0.25% of the total free alkali present. The test may be applied qualitatively by dropping an alcoholic solution of

phenolphthalein on to a freshly cut surface of the soap, when a red coloration will be produced, the intensity of which increases with the proportion of the alkali present. Hydroxide or carbonated alkali will also be indicated by the black or grey coloration produced by dropping mercurous nitrate on the freshly cut surface. Each 1 c.c. of N/1 acid neutralised represents 0.0471 grm. of potassium oxide, 0.0561 of potassium hydroxide, 0.031 of sodium oxide, or 0.040 of sodium hydroxide. Should it be desired to ascertain which is present, the method described on page 608 must be employed.

It is possible to have a *negative* alkalinity shown at this stage. This result is due to the presence of fatty acid or a diacid salt, but acidity of the alcohol may produce the same effect. The volume of standard alkali required to be added before a pink colour appears should be calculated to its equivalent of *oleic acid*, which is stated in the analysis as existing in the free state. Any difference between this amount and that found in the petroleum spirit solution is due to a partial neutralisation of the free acid coexisting in the imperfectly mixed soap.

The following method of treating the alcoholic solution of a soap in such a manner as to allow of the estimation of the leading constituents in a very rapid manner has been communicated by C. Hope: 2 grm. of the soap are dissolved in hot absolute alcohol, a drop of phenolphthalein solution added, and carbon dioxide passed till any pink coloration is destroyed. The liquid is then filtered, the residue, consisting of *total impurities*, washed with hot alcohol, weighed, and then titrated with N/10 acid and Methyl Orange to find the *alkali not existing as soap*. The alcoholic solution is evaporated to dryness at 100°, and the residue of *dry soap* weighed when constant. It is then ignited gently, treated with water, and the solution titrated with decinormal acid and Methyl Orange to find the *alkali existing as soap*. The difference between this and the total residue before ignition gives the *fatty* anhydrides, which, multiplied by 1.03, gives the *fatty acids*. The *water* is found with sufficient accuracy by subtracting the sum of the weights of the impurities and dry soap from 100.

If the soap contains both free alkali and free fat, the above methods are open to the objection that during the heating of the soap with alcohol the free alkali hydroxide will saponify some of the fat. Another objection to the alcohol method is that the alka-

line salts are not wholly insoluble in alcohol. Also, the solution must be filtered hot causing carbonisation of some of the alkali hydroxide.

Herrman (*Chem. Ztg.*, 1904, 53) and others have suggested the addition of $BaCl_2$ solution to an aqueous solution of the soap and a titration of the alkali with acid in the usual way. A modification of this method is the use of a 50% alcoholic solution to repress the hydrolysis of the barium soaps. Izmail'ski (*J. Russ. Phys. Chem.*, 1916, 8, 411) and Bosshard and Huggenberg (*Z. angew. Chem.*, 1914, 27, 11) have discussed the errors in this method and in the method of salting out with Na_2SO_4 recommended by Dietrich and Helfen (*Ann.*, 1886, 1887, 1889). (See also F. H. Newington, *J. Soc. Chem. Ind.*, 1916, 35, 95.) Bosshardt makes the estimation as follows: 5 grm. of soap are dissolved in 100 c.c. of 50% alcohol in a flask supplied with reflux condenser by heating on a water-bath. The solution is rapidly cooled and 15–20 c.c. of 10% $BaCl_2$ solution are added together with 2–5 c.c. of α-naphtholphthalein indicator solution (prepared by dissolving 0.1 grm. in 150 c.c. alcohol and 100 c.c. of water). The solution is now titrated with N/40 stearic acid (prepared by dissolving 7.1 grm. stearic acid in 1000 c.c. of alcohol and used a similarly prepared barium soap solution with known excess of stearic acid until one is familiar with the end-point). It is said that the end-point of this titration cannot be seen in rosin soaps or other dark coloured soaps. Izmail'ski proceeds as follows: 10 grm. of soap, freshly cut from the middle of the cake, are dissolved in 200 c.c. of freshly boiled hot water, and to the hot solution, constantly rotated, 20 c.c. of a perfectly neutral 30% $BaCl_2$ solution are slowly added. The mixture is boiled for a short time, is then cooled under the tap and filtered, and the filter is washed with 100 c.c. of water, in three portions. The free alkali is titrated with N/10 acid with the use of phenolphthalein as indicator. The author claims that the alkali found does not actually represent that existing in the free condition in the soap, but that part of it results from hydrolysis, and that the figure should be called the "alkali number."

It is necessary to avoid confusion between the real alkali, *i. e.*, existing in a soap in the form of potassium or sodium hydroxide, the apparent alkali, which corresponds to the soap, and that corresponding to carbonate, silicate, or borate. If the estimation is made

in the alcoholic solution, as recommended, the actual hydroxide, for practical purposes, will alone be present, the other compounds capable of neutralising acid being almost entirely insoluble in spirit. On the other hand, the standard acid required to neutralise the aqueous solution of the soap (page 607) includes that corresponding to any soluble *carbonate, silicate, borate, aluminate* or *tri-basic phosphate* in the sample.

The alcoholic solution of the soap rendered neutral to phenolphthalein may be conveniently employed to estimate the *alkali existing in combination with the fatty and resin acids* of the sample. To effect this, it is merely necessary to add a few drops of Methyl Orange solution to the neutralised liquid, and then at once titrate with standard sulphuric or hydrochloric acid. The point of neutrality is sharply marked by the production of a pink colour, and the accuracy of the results is all that could be desired.

In order to prevent misunderstanding, the volumetric method of ascertaining the proportions of alkali existing in soap in various conditions may be recapitulated as follows:

In alcoholic solution of soap.—1. Acid required to establish neutrality to phenolphthalein corresponds to *free alkali*, and is calculated to oxide or hydroxide, according to circumstances. 2. Acid subsequently required by same solution to produce neutrality to Methyl Orange represents the *alkali converted into soaps* of fatty and resin acids.

In residue insoluble in alcohol.—3. Acid required to produce neutrality to Methyl Orange corresponds to *alkali corresponding to carbonate, silicate, borate,* and *tribasic phosphate.*

In aqueous solution of soap.—4. Acid required to produce neutrality to Methyl Orange corresponds to *total alkali*, whether existing as such or converted into true soap, resin soap, carbonate, silicate, borate, aluminate, tribasic phosphate and soluble lime. This estimation should therefore agree with the sum of 1, 2, and 3, or if any 2 of these have been determined the third will be the difference between their sum and the total alkali (4).

The volumetric estimation of the alkali in soap gives no information as to its nature. To ascertain this it is necessary to separate them as sulphates or chlorides. This is best effected by treating the alcoholic solution of the soap which has been used for the estimation of alkali, and is neutral to Methyl Orange, with strong solution

of barium hydroxide, until the formation of a permanent pink tint shows that the liquid is distinctly alkaline to phenolphthalein. A saturated solution of barium chloride is then added, as long as further precipitation occurs, when the liquid is filtered from the barium sulphate and barium soap. The filtrate is evaporated to dryness, and the residue cautiously ignited at the lowest possible temperature. The residue is dissolved in water, the solution filtered and treated with ammonia and ammonium carbonate, the precipitate filtered off, the filtrate again evaporated to dryness, and the residue gently ignited and weighed. In the mixed *chlorides* thus obtained, the potassium and sodium may be indirectly deduced from the percentage of chlorine present, obtained by dissolving the residue in water, and carefully titrating ½ of the solution with N/10 silver nitrate, using neutral potassium chromate as an indicator.

From this datum approximate calculation may be made by the following formula:

$$\text{Per cent. of sodium chloride} = \frac{\text{Per cent. of total chlorine} - 47.53}{0.1310}.$$

If greater accuracy is desired, the potassium may be estimated with platinum chloride in the usual way.

L. **Residue Insoluble in Alcohol.**—After the residue obtained at this stage has been dried and weighed, a minute quantity of it may be advantageously examined under the microscope, by which many substances will be revealed by their characteristic structure. Iodine solution will colour starch granules blue and render them more distinct.

If starch is found by the microscope, it is sometimes desirable to treat the residue with cold water, and examine the solution thus obtained separately from that subsequently obtained by the use of boiling water. Starch and gelatin will be contained in the latter only, but sodium silicate may be present in both solutions—a serious complication.

Frequently the only data required will be the weight of the insoluble portion in alcohol together with its total alkalinity.

M. **Examination of the Aqueous Solution of the Residue.**— Before dividing the aqueous solution and titrating with standard acid in the manner described in the Amer. Chem. Soc. methods, it is sometimes desirable to make a direct estimation of the carbon

dioxide evolved on treatment with acid, so as to obtain a means of calculating the amount of *soluble carbonate* present. This is necessary when the soap contains borate or silicate in addition, but otherwise the carbonate can be deduced with accuracy from the titration of the solution with standard acid. To ascertain the carbonate directly, proceed as directed under the Amer. Chem. Soc. methods X, page 597.

1. After the last of the carbon dioxide has been expelled by warming the acidified liquid, the solution should be divided into two or more equal parts, in 1 of which the excess of acid is estimated by titrating back with standard sodium carbonate and Methyl Orange, and hence the sum of the alkali existing in the forms of *carbonate, silicate, borate, aluminate*, and tribasic phosphate ascertained, whilst the other portion is examined for borate, silicate, and aluminate as in 2.

The solution which has been employed for the estimation of the total alkali of the residue may then be divided into 2 or more equal parts, which may be employed for estimating *sulphates* by precipitation with barium chloride. This residue may be further examined for certain organic constituents by a procedure recommended by Marcusson (*Kgl. Materialprüfungsamt; Chem. Rev. Fett-Harz Ind.*, 21, 1-3) for rosin soaps. The residue is tested for the presence of nitrogen; if none is present, gluten, albumin, casein, gelatin, etc., are excluded. Several grm. of the residue should be extracted with 300 c.c. cold water, which will dissolve gum arabic, dextrin, vegetable slimes (linseed, salep, gum tragasol), soluble starch, leaving behind starch and viscose. Starch is identified by means of the microscope and by the iodine reaction and other methods described in Vol. I. Viscose (alkali cellulose xanthate) is recognised by treatment with dilute mineral acid which decomposes it into hydrogen sulphide and cellulose hydrate. Gum arabic is precipitated from its solution by lead acetate, dextrin remaining in solution. These constituents are further identified by the tests given under the analyses of these compounds. Vegetable slimes are precipitated by lead acetate as a glutinous mass (gum arabic as dense lumps) and are separated from the gum arabic by precipitating the former with a ·5% tannin solution, gum arabic remaining in the solution. If nitrogen is found to be present, the residue is treated with cold water, which dissolves glue egg albumin, and if

combined with alkali also gluten and casein; if uncombined, gluten and casein remain undissolved. The aqueous solution is acidified with acetic acid and heated, precipitating egg albumin; the glue is precipitated by tannin solution. Soluble gluten and soluble casein are precipitated by alcohol. Casein is identified by means of rennet. Gluten (like albumin and casein) forms lead sulphide when treated with a solution of alkaline lead oxide. To test for gum arabic and dextrin in the aqueous extract, remove the nitrogen compounds with excess tannin solution, evaporate the filtrate to dryness, redissolve in water and filter off any further tannin precipitate. Treat the aqueous solution with excess of alcohol, which dissolves the excess tannin and precipitates dextrin and gum arabic, which are identified as above. It is understood that this scheme is only suggestive, and that other compounds than the above may be present. For the complete examination of this material recourse to many methods of identification must be had. A single test such as mentioned for the various compounds cannot be interpreted as more than an indication of the presence of the material in question. To identify the compound completely as many confirmatory tests as conclusively define the substance must be made.

2. The other half of the aqueous solution of the residue insoluble in alcohol should be rendered distinctly acid with hydrochloric acid, and evaporated at 100° in porcelain. A slip of turmeric paper should be immersed in the liquid toward the end of the operation, and allowed to remain until the evaporation is complete. If a *borate* is present, the paper will become brownish-red in colour, and will be changed to green, blue, violet, or black on addition of sodium hydroxide solution. (See Amer. Chem. Soc. methods, VIII, p. 595.) The residue is treated with hydrochloric acid, water added, and the solution filtered. The residue of *silica* is washed, dried, ignited, and weighed. As the *sodium silicate* (see also Amer. Chem. Soc. method for determining silicate, IX) present in soap is not of constant composition, though usually approximately corresponding to the formula $Na_2Si_4O_9$, it is not possible to deduce the amount of alkali existing as silicate from the weight of the silica found; but, in the absence of borates, it may be ascertained by estimating the carbon dioxide evolved on treating the aqueous solution of the residue insoluble in alcohol with dilute acid. This estimation will give the means of calculating the alkali existing as *carbonate*, and the

remainder of the alkali of the residue must exist as *silicate* (or aluminate or phosphate).

The variable composition of sodium silicate must be taken into consideration. This variation depends upon the composition of the original silicate and the amount of alkali used in the manufacture of the soap, as any excess of free alkali hydroxide used will tend to be absorbed by the silicate filler, causing the disappearance of free alkali hydroxide and the formation of a more alkaline silicate. On this account, soaps containing an appreciable quantity of silicate filler usually show little or no free hydroxide alkalinity. Likewise, since silicate of soda can be decomposed by carbon dioxide, soaps, especially in the chip form, that have contained large quantities of silicate of soda may have absorbed sufficient carbon dioxide during long exposure to the air to decompose the silicate more or less completely. In such cases, the quantity of carbonate will be increased and a corresponding quantity of free silicic acid found in the water insoluble portion. Since the combination of soda and silicic acid is so variable, it is preferable to determine the total alkalinity by titration, using Methyl Orange, and to determine the carbon dioxide, silicic acid and boric anhydride, if present, separately. After the proper quantity of soda to combine with the carbon dioxide and boric acid found has been calculated, the remaining sodium oxide and the silicon dioxide are reported as soda and silica combined as silicate, without attempting to use a definite formula for the silicate.

The filtrate from the silica may be conveniently employed for estimating *sulphates* by precipitation with barium chloride (see Amer. Chem. Soc. methods, XII, p. 599), or of *aluminium* by precipitation with ammonium hydroxide or phosphate by Amer. Chem. Soc. Method XI, page 598, and of *calcium* in the filtrate by precipitation with ammonium oxalate. C. Hope states that free lime is not unfrequently present in soap, and may be detected and estimated at this stage. Its presence would tend to increase the "alkali" of the residue insoluble in alcohol.

N. **Residue Insoluble in Petroleum Spirit, Alcohol, and Water.—** After drying the residue at 100° and noting its weight it is desirable to examine it under a low microscopic power, with a view of recognising characteristic organic structures, which can be seen much more distinctly after the removal of the soluble matters.

Whether any further examination of the residue is requisite neces-
sarily depends on its amount and nature and the object of the
analysis. Among the various constituents of such a residue the
following list comprises those most likely to be present:

1. *Insoluble Organic Matters*, such as sawdust, bran, woody fibre
from oatmeal, etc., etc.

2. *Mineral Pigments and Colouring Matters*, as red ochre, burnt
umber, various other ferruginous materials, red lead, vermilion,
Scheele's green, chrome green, ultramarine.

3. *Mineral Matters used as Scourers*, such as sand, powdered
quartz, pumice, and infusorial earth.

4. *Mineral Matters used as Adulterants or "Fillings,"* such as
china clay, steatite, barium sulphate, chalk, and whiting.

The systematic recognition and estimation of these and other
possible additions belong to inorganic analysis. It is sufficient
here to indicate the following simple method of classification with a
view to facilitate further examination.

Organic matters may be approximately estimated by igniting an
aliquot portion of the residue. The loss will include the volatile con-
stituents of china clay, whiting, red ochre, etc., as well as any ver-
milion which may be present. Lantos (*Chem. Ztg.*, 1920, 44, 35)
calls attention to the fact that when organic substances containing
calcium are ashed in the usual way the calcium is left in the form of
$CaCO_3$. He recommends adding a small amount of $NH_4 NO_3$,
when the calcium will appear in the ash as CaO.

By treatment with dilute hydrochloric acid, the original or ignited
residue may be divided into *soluble* and *insoluble constituents*. The
former include whiting, chalk, ultramarine, Scheele's green, oxide of
iron, and the greater part of the ferruginous pigments; whilst barium
sulphate, steatite, sand, quartz, pumice, kieselguhr, china clay,
chrome green and vermilion are but little acted on.

Unsaponified and Unsaponifiable Matter.—Under ordinary cir-
cumstances the Amer. Chem. Soc. method IV, p. 592, may be followed
for these estimations. If a more complete examination is desired the
petroleum spirit (ether) extraction outlined in the table on page 586
may be followed, but since this extraction requires considerable
time and care to insure its being complete, it is frequently more
satisfactory to extract a solution of the soap (p. 592). However, as
soap is very readily hydrolysed in water it is not permissible to use

this solvent alone, as considerable quantities of fatty acids would be extracted besides the ether-soluble compounds existing free in the soap. It will be found that if a solvent consisting of about equal parts of water and alcohol be used, the hydrolysis of the soap will be so slight that no serious error will be introduced (D. Holde, *Zeit. Electrochem.*, 1910, 16, 436). The solution obtained should be extracted by shaking out with several portions of petroleum spirit. If troublesome emulsions are formed, they can usually be broken by the addition of a little more alcohol. Naturally this extraction gives both the unsaponified and unsaponifiable matter present. These may be separated by making an alcoholic potash or soda saponification of the residue obtained on the evaporation of petroleum spirit, then extracting a second time, using the same precautions as above. This will give the unsaponifiable matter only (p. 592).

Petroleum Spirit Solution.—Ordinarily, the material dissolved from dry soap on treatment with petroleum spirit consists merely of *unsaponified fats* or of *free fatty acids*. Insignificant proportions of unsaponifiable matter natural to fixed oils may also be present, and nitrobenzene and essential oils used for scenting the soap will also be dissolved. If Yorkshire grease has been used in manufacturing the soap, the residue may contain *cholesterol*. *Cetyl alcohol* from spermaceti and *myricyl alcohol* from beeswax and carnaüba wax will also be present ·if these waxes have been employed. If added to the made soap, of course the unsaponified *waxes* will be dissolved out, instead of simply the solid alcohols resulting from their saponification. If the presence of waxes is suspected beforehand, or from the amount or appearance of the residue obtained on evaporating a portion of the solution, the residual soap should be further exhausted with boiling toluene, which dissolves the wax-alcohols better than petroleum spirit.

The residue from medicated soaps may also contain metallic *oleates* and free *carbolic* and *cresylic acids*, *thymol*, and *hydrocarbons*, such as vaseline and other neutral petroleum and tar products.

When the nature or amount of the residue obtained on evaporating a small aliquot part of the petroleum spirit solution indicates the desirability of further examining it, the unevaporated portion should be treated in the manner directed in the following table:

SYSTEMATIC SEPARATION OF UNSAPONIFIED MATTERS FROM SOAP

Agitate the solution in petroleum spirit with dilute hydrochloric acid, and separate.

a. Acid Solution. Examine for *h e a v y metals* (*e. g.*, Pb, Hg, Cu, Zn) and *aluminum*, which, if found, must have existed in the soap as *oleates*. Potassium and sodium oleates may also have been dissolved if the soap contained much hydrocarbon. If metals are found at this stage, the amount of fatty acids dissolved by petroleum spirit must be corrected to ascertain the fatty acids existing in the soap in a free state.

b. Petroleum Solution. Wash free from mineral acid by repeatedly agitating with small quantities of water. Add some alcohol and titrate liquid with standard alkali and phenolphthalein for estimation of *fatty acids* (page 10). Separate and agitate petroleum spirit several times with small quantities of sodium hydroxide solution, separating as before.

c. Petroleum Solution. Evaporate at a low temperature and observe odour, especially toward the end. Weigh residue and then estimate *unsaponified fat* by Köttstorfer's process (page 16). In absence of waxes, the potassium hydroxide required divided by 0.19 gives the weight of true fats, which deducted from whole residue gives that of the *hydrocarbons, wax-alcohols*. If desired, these may be isolated and further examined.

d. Alkaline Solution. Evaporate to small bulk, dilute with three volumes of strong brine, and filter.

e. P r e c i p i t a t e c o n s i s t s o f sodium salts of *fatty acids* existing in the soap either in the free state or as aluminium or other metallic oleates.

f. Solution. Acidulate with dilute sulphuric a c i d, and s e p a r a t e layer of *phenols*, or titrate portion of diluted s o lution with bromine, etc. (See p a g e 617 and "Creosote Oils," Vol. III.)

Hydrocarbons, such as petroleum, vaseline, and coal-tar oils, are sometimes, to a considerable extent, introduced into soap. Though incapable of saponification, they may exist in notable proportion without being suspected; for if not used in excessive amount, and especially if certain combinations be added, they remain in apparent solution when the soap is dissolved in water or alcohol, and, on decomposing the solution with an acid, they pass wholly into the oily layer of fatty and resin acids.

Hydrocarbons may sometimes be detected by the fluorescence exhibited by the ethereal solution of the fatty acids. If in considerable quantity, they may be partially separated by subjecting the dry soap to a gradually increasing heat, when the hydrocarbons will distil, together with any other volatile matter which may be present.

A satisfactory means of detecting and estimating hydrocarbons in soap is to extract them by agitating the aqueous solution of the sample with ether and alkali as described below. Any *unsaponified fat* will, however, be simultaneously dissolved by the ether, and must be separated by saponifying the ether-residue with alcoholic potash, and again agitating the solution of the resultant soap with ether, or the original soap may be evaporated with alcoholic potassium hydroxide, and the residue dissolved in water and treated

with ether. This method is particularly valuable when heavy petroleum or hydrocarbons non-volatile with steam are present.

Somewhat similar to the Amer. Chem. Soc. method XIV, p. 601, for determining volatile hydrocarbons is a method developed by the Larkin Co. (private communication), for the estimation of naphtha in naphtha soap. 50 grm. of soap are dissolved in 500–600 c.c. of water in a 1000 c.c. distillation flask. The soap is cracked with sulphuric acid and the sample is then distilled with superheated steam, the distillate being received in a flask provided with a narrow graduated neck. After recording the volume of the naphtha its sp. gr. is taken, the simplest method being to place a drop of naphtha in alcohol and dilute with water until the naphtha barely sinks, and then determining the sp. gr. of the mixture with a Westphal balance. From this the per cent. of naphtha by weight is calculated. In the case of soaps containing much coconut or palm-kernel oils some water-insoluble volatile fatty acids will distil with the naphtha and will tend to give high results, but in most soaps the error from this source is very small.

In connection with the separation of hydrocarbons two qualitative methods which are said to separate fatty oil and fatty acids from hydrocarbons are of interest. Holde (*Seifenfabr.*, 1920, **40**, 113) states that aniline is a solvent in which mineral oils are insoluble, whilst fatty oils, fatty acids, rosin oils, and naphthenic acids are soluble. The method is only designed to be qualitative. Verona-Rinati (*Ann. Chim. applicata*, 1914, **2**, 201) gives a method depending on the fact that fatty acids and their glycerides are soluble in dichlorohydrin, whilst the hydrocarbons are insoluble, especially if the reagent is saturated with water. Into a small test tube about 1 cm. in diameter, graduated in 0.1 c.c. run 7 c.c. of, dichlorohydrin (water free), then 1–2 c.c. water, and then 1.43 grm., carefully weighed, of the substance to be tested. The well-closed tube is kept at 65° in a beaker. From time to time the tube is removed and well shaken. It is allowed to stand 10 minutes and the upper volume of undissolved liquid read, allowed to stand for 10 minutes after shaking, and the volume again read. Each 0.1 c.c. corresponds to 5 hydrocarbons of mineral origin.

For purposes of identifying the fats and oils from which the soap was manufactured the determination of cholesterol and phytosterol is important. For the details of these methods see page 763. In

this connection Marcusson and Meyerheim (*Z. angew. Chem.*, 27, 201) state that during the hydrogenation of oils or fats cholesterol becomes resinified to the extent of 75% at a temperature of hydrogenation of 200°, whilst phytosterol is hardly attacked at this temperature. After hydrogenation at 250° cholesterol no longer. gives any crystalline substance whilst, phytosterol yields some.

The directions given in the foregoing table do not require further comment, except in the case of the method indicated for the estimation of *phenols*. Phenol and cresylic acid, and some other substances, are dissolved on treating the soap with petroleum spirit, and can be separated from the admixed fatty acids by treating the alkaline solution with brine, but the method is faulty for the following reason: soaps, and especially common household and soft soaps, are liable to contain free alkali which will react with the coal-tar acids added, to form substances not dissolved by petroleum spirit, and hence the phenols obtained are only that portion not taken up by the alkali present in the soap.

The analysis of soap for the percentage of *phenols* and other *coal-tar products* is most conveniently and accurately effected by the following process, which was extensively used by Allen: 5 grm. weight of the sample is dissolved in warm water with addition of from 20 to 30 c.c. of a 10% solution of sodium hydroxide, according to the proportion of phenols believed to be present. The cooled solution is then agitated with ether, and the ethereal layer separated and evaporated at a low temperature and weighed. The odour toward the end of the evaporation and that observed on heating the residue will give considerable information as to the nature of the admixture. Odours suggestive of gas-tar and burning gutta-percha are very common. The alkaline liquid separated from the ether is then treated in a capacious separator with excess of strong brine, which completely removes the fatty acids as sodium salts, whilst the phenols remain in solution. The liquid is well agitated to cause the soap to filter and is then passed through a filter. If the soap does not coagulate, an addition of a small quantity of tallow or palm-oil soap, previously dissolved in water, will usually determine separation. The precipitated soap is washed twice by agitating it with strong brine, the washings being filtered and added to the main solution, which is then diluted to 1 litre. 100 c.c. of this solution (= 0.5 grm. of the sample of soap) is then placed in a globular separator, and acidified with dilute sulphuric

acid, when it should remain perfectly clear. A precipitation at this stage indicates the incomplete removal of the fatty acids. In such case, 200 c.c. of the alkaline solution should be treated with common salt in powder, the solution filtered through a dry filter, and 100 c.c of the filtrate acidified as before. Standard bromine-water is then added from a burette, the stopper of the separator inserted, and the contents shaken vigorously. (A standard KBr.KBrO$_3$ solution is somewhat easier to work with than the bromine-water.) More bromine-water is then added, and the agitation and addition repeated alternately until the liquid acquires a faint but permanent yellow tint, showing that a slight excess of bromine has been used. If crystallised phenol had been employed for making the soap, the addition of the bromine-water causes the precipitation of tribromophenol, C$_6$H$_3$Br$_3$O, in snow-white crystalline flocks, which allow the faintest yellow tint due to excess of bromine to be observed with great facility. If cresylic acid is the chief phenol present, the precipitate is milky and does not separate well from the liquid, but the end of the reaction can still be observed. The addition of a solution containing a known amount of crystallised phenol is a useful device in many cases, as the precipitate then curdles readily, and the yellow coloration can be easily seen.

The bromine solution is made by mixing in a separator one volume of saturated bromine-water with two volumes of water. This solution is approximately 1%, and should be run out from the tap of the separator into the Mohr's burette used for the titration. The burette should be closely covered, and the last few c.c. of the solution contained in it should never be employed for the titration, as it is apt to have become weak. The bromine-water must be standardised immediately before or after use, upon a solution of phenol of the quality that is indicated in the sample acid, according to the kind of acid the titration has indicated to have been present in the soap. This solution is made by dissolving 0.5 grm. of the phenol in 20 c.c. of a 10% solution of sodium hydroxide, together with 5 grm. of a non-phenolic soap. The solution is then treated with brine in the same manner as the sample, the filtrate diluted to 1000 c.c., and 100 c.c. acidified and titrated with the bromine used for the sample. The volume of bromine solution used is that required by 0.050 grm. of phenol of approximately the same quality as that contained in the soap.

The remaining portion of the liquid filtered from the precipitate of soap may be evaporated to a small bulk, acidified with dilute sulphuric acid, and the separated phenols measured, but the quantity is not sufficient to make the method satisfactory. It is generally better to employ the solution for the isolation of the bromo-derivatives. For this purpose it is acidified with dilute sulphuric acid (without previous concentration), and bromine-water added in slight excess. From 5 to 10 c.c. of carbon disulphide are then added, the liquid well agitated, and the carbon disulphide drawn off into a small beaker. The aqueous liquid is agitated with fresh quantities of carbon disulphide (5 of 5 c.c. each) till it no longer acquires a red or yellow colour. The carbon disulphide is then allowed to evaporate spontaneously, when a residue is obtained consisting of the brominated derivatives of the phenols present in the soap. If *crystallised* phenol of fairly good quality had been introduced into the soap, the bromo-derivative is obtained in fine long needles having very little colour, and, if all heating was avoided during the evaporation of the carbon disulphide, the weight of the residue multiplied by 0.281 gives a fair aproximation to the amount of phenol; but if a crude liquid article has been employed, consisting mainly of *cresylic acid*, the bromo-derivative will be deep yellow, orange, or red, with little or no tendency to crystallise, and the weight will not afford even a rough indication of the amount of coal-tar product present.

Lewkowitsch considers the following rapid process sufficiently accurate for practical purposes: A somewhat large amount of the sample, say 100 grm., is weighed off, dissolved in hot water, the solution rendered strongly alkaline with sodium hydroxide, the soap precipitated with sodium chloride, the curd separated and washed with strong sodium chloride solution, the solution of the phenolate boiled down to a small bulk, transferred to a stoppered measuring cylinder of 50 or 100 c.c. capacity, sufficient salt added so that some remains undissolved, and the liquid acidified with sulphuric acid. The volume of the separated phenols is then read off, and the number of c.c. taken as so many grm.

The following table shows some of the results obtained in Allen's laboratory in the analysis of representative samples of commercial carbolic soap. The descriptions given by the manufacturers are

strictly adhered to. Two samples described in the same words were manufactured by different firms:

Description of soap	Phenols		Ether-residue	
	Per-centage	Nature	Per-centage	Odour on heating
1. Medical carbolic soap; 20% pure	30.5	Pure phenol	....	....
2. Medical carbolic soap; 20% pure....................	17.0	Pure phenol	4.2	Gutta-percha.
3. Carbolic toilet soap; 10%... .	3.6	Pure phenol	2 0	Cayenne.
4. Carbolic toilet soap; 10%.... .	3 4	Pure phenol	1.0	Gutta-percha.
5. Transparent carbolic soap .. .	3.2	Pure phenol	....	....
6. Transparent coal-tar soap ...	1.5	Pure phenol	....	....
7. Domestic carbolic soap.... .	4.8	Pure phenol	.. .	....
8. Domestic carbolic soap.... .	6.4	Common carbolic	.... .	....
9. No. 1 carbolic soap........ .	5.4	Common carbolic	....	....
10. No. 2 carbolic soap..........	3.5	Common carbolic	.... ..	....
11. Carbolic soap..............	1.1	Common carbolic	1 0	....
12. Carbolic soap............. .	0.5	Impure carbolic	... .	....
13. Carbolic soft soap; 10%... ..	9.9	Common carbolic	... ...	....
14. Carbolic soft soap; 10%.... .	8.2	Common carbolic	.. .	....
15. Carbolic soft soap....... ...	0.16	Common carbolic	... .	....
16. Disinfectant soap...........	none	....	4.6	Coal-tar oils.
17. Sanitary soap.......... . .	0.75	Impure carbolic	4.6	Coal-tar oils.

It will be observed that in No. 1 sample, described as containing 20% of crystallised carbolic acid, 30.5% was actually found, which result was confirmed by weighing the tribromophenol, which crystallised in well-formed colourless needles. In some cases the proportion of phenols found was notably less than the amount stated to be present, and this was especially the case with Nos. 3 and 4, though these were made by different firms. It must, however, be borne in mind that a loss of 2 or even 3% of phenol is liable to occur through evaporation.

Cresols.—For a rapid analysis of cresol soap preparations similar to the official disinfecting compounds, M. Seiger (*Seifenseider Ztg.*, 1911, **38**, 986) proceeds as follows: 20 grm. of solution with the addition of 500 c.c. of water are twice evaporated to dryness to drive off the cresol. The residue is dissolved in 40 c.c. of water, transferred to a 160 c.c. graduated cylinder and decomposed by adding 5 grm. of sodium chloride and 10 c.c. of strong hydrochloric acid. 20 grm. of petroleum spirit are added and the whole is shaken up and allowed to separate. 20 c.c. subtracted from the volume of the petroleum spirit solution gives the volume of the fatty acid, which multiplied by 0.92 is considered the weight. Another 20 grm. of the original compound are diluted with 20 c.c. of water and treated

exactly as above without evaporating. In this case, the upper layer consists of the cresols and fatty acid. The factor 1.04 is used to convert the volume of the cresols to the weight.

C. Residue Insoluble in Petroleum Spirit.—The portion of the sample not volatile at 100° and insoluble in petroleum spirit constitutes the *soap proper*.

In analysing soap of known origin and general composition it is often wholly unnecessary to go through the previous operations of drying and exhaustion with petroleum spirit. In such cases it is evidently preferable to weigh out 10 grm. of the original soap and treat it at once with hot water as described in the *Amer. Chem. Soc.* method 3 II(5).

D. Aqueous Solution of the Purified Soap.—In most cases soap will dissolve almost completely in boiling water, but if a large quantity of the solvent is employed, hydrolysis occurs to a serious extent, and if such a liquid be filtered, a notable quantity of acid soap may be removed. Hence it is better, when possible, to separate any insoluble matter by decantation. When the proportion of insoluble matter is inconsiderable, there is no occasion to separate it, as with proper management it will not interfere with the subsequent operations. An exception occurs in the case of calcium carbonate, which, if not removed, will neutralise acid and render the figure for the total alkali too high.

In many cases the aqueous solution of the soap may be advantageously agitated with ether at this stage. Such treatment obviates the necessity of previously extracting the dried soap with petroleum spirit, while it removes *hydrocarbons, unsaponified oil*, and *free fatty acids* in a very satisfactory manner. (See Amer. Chem. Soc. method IV.) The ethereal solution may then be treated in exactly the same manner as is directed for the petroleum spirit solution on page 616, whilst the aqueous liquid can be at once titrated with standard acid, though for convenience of subsequent manipulation of the fatty acids it is desirable first to remove the dissolved ether by boiling the solution in a capacious flask.

E. Separation of Fatty Acids.—For decomposing the aqueous solution of the soap, N/1 sulphuric acid possesses some advantages, and should be used in moderation, an excess of 5 c.c. beyond that necessary to combine with alkali present being sufficient. Wright and Thompson prefer to substitute standard nitric acid, as it enables

the sulphates to be estimated by barium chloride in one portion of the filtrate, and the chlorides by silver nitrate in another.

The method of manipulation for the separation of the oily layer of fatty acids from the aqueous liquid depends on what tests are to be made upon them, and upon their nature.

When the soap is chiefly a stearate or palmitate, as that made from tallow or palm oil, the liberated fatty acids are solid when cold, and in such cases there is no better plan than to effect their precipitation in a beaker or vessel of such shape that the cake can be directly removed, wiped with blotting-paper, and weighed. Precipitation in a conical flask is advantageous in some cases.

If the fatty acids are liquid at the ordinary temperature or form a cake deficient in consistence, a known weight of dry, bleached beeswax, stearic acid or paraffin wax (which does not give off volatile matter at 100°) may be added to the hot liquid. The fatty acids become amalgamated with the melted wax, and, on cooling, a firm coherent cake is formed, which may be at once wiped and weighed. Should the cake show any cavities (which occurs only when the fatty matter has not been properly heated) enclosing water and perhaps mineral acid, the cake should be remelted over water as described above. The weight of wax added (which should be about the same as that of the soap employed) being deducted from that of the cake, the weight of the crude fatty acids is at once found.

As a rule, it is preferable to effect the decomposition of the soap solution in a stoppered separator, running off the aqueous liquid through a wet filter, and subsequently allowing the fatty acids also to run on to the filter, where they are washed with boiling water, and subsequently treated as described on page 22. This method of treatment is the best when it is desired to make a further examination of the separated fatty acids. (See Amer. Chem. Soc. method VI, p. 594.)

Coconut and palm-nut oil soaps yield acids not wholly insoluble in hot water. In such cases the precipitation of the acids should be conducted in a tolerably concentrated liquid, which may be advantageoulsy saturated with common salt. The washing of the separated acids should be restricted, and brine may be advantageously used, whilst the drying should be effected with as little exposure to heat as possible.

Instead of estimating the fatty acids by the cake method some analysts, after having decomposed the soap, prefer to dissolve the layer of acids in petroleum spirit, drawing off the acid water by means of a separating funnel and filtering the spirit solution into a tared flask or beaker. If the filter has previously been saturated with the petroleum spirit and is kept saturated during the operation, any small quantities of the aqueous solution that may be accidentally transferred to the filter will be held back. After the solution has been extracted with several small portions of the petroleum spirit and the funnel and filter carefully washed with the same, the solvent is evaporated and the acids weighed directly. A convenient method of driving off the last traces of petroleum spirit is to heat the acids on a steam-bath under a moderate current of air directed into the flask or beaker from a suitable nozzle. It will be found that the acids may be brought to a more nearly constant weight by this method than by heating in an air-bath. The danger of oxidation of acids from the drying oils by this method should be noted and the use of a vacuum oven is recommended in such cases.

Whatever method is used in estimating the fatty acids, the danger of volatilisation must be considered. In fats having a saponification value of about 200, this danger is comparatively slight when reasonable care is used, but with fats containing acids of low molecular weight the loss may be very appreciable. Moreover, in soaps that have become rancid with the development of a high free acidity, probably due to the decomposition of fat, volatile acids are present to a very considerable extent. Such a loss, if occurring, may be estimated by taking the fatty acids after weighing, dissolving them in neutral alcohol and titrating, then calculating the combined alkali from this titration. If the results so obtained are less than the combined alkali as estimated by other methods, the indication is that acids have been volatilised. This loss may also be checked by making two extractions, in one of which the acids are weighed and then titrated, whilst in the other the titration is done directly and a correction made in the weight for any loss indicated by a difference of titrations (A. Besson, *Chem. Zeit.*, 1914, **38**, 645, 686).

It is almost impossible to separate, or even extract, the fatty acid from the decomposed mass obtained from soaps that contain large quantities of fillers insoluble in water or sodium silicate, which gives

a gelatinous precipitate of silicic acid when decomposed with acid. When such difficulties arise, the best procedure is to separate the soap from such material by dissolving it in alcohol, filtering, and washing the matter insoluble in alcohol carefully so as to insure the removal of all soap. The alcohol is then evaporated and the fatty acids estimated in the purified soap obtained. Several methods have been proposed in which the soap is decomposed and the fatty acids collected in a narrow graduated tube, the volume read off and the weight calculated from the gravity. The method is rapid and with suitable apparatus quite accurate (O. Schutte, *Seifensieder Ztg.*, 1913, 40, 551). For a more detailed comparison and discussion of various methods of fatty acid estimation, see G. Fendler and L. Frank (*Zeit. angew. Chem.*, 1909, 22, 252, 541).

F. **Solution Separated from the Fatty Acids.**—The method described in the table for determining the *total alkali* of soap is, in most cases, highly satisfactory. The result is not affected by the omission to treat the soap with petroleum spirit before dissolving it in water, and ordinary insoluble matters do not interfere. If, however, an insoluble carbonate be present, it will neutralise acid, and must be separated, or the figure for alkali will be too high.

It will be noted that the Amer. Chem. Soc. method 3 II(5), p. 591, determines the *combined alkali* by separating the fatty acids, exactly neutralising these with standard sodium hydroxide solution, drying and weighing the soap so formed.

Instead of at once adding an excess of standard acid, then titrating back, and thus ascertaining the volume required to neutralise the alkali of the soap, the standard sulphuric acid may be added gradually to the soap solution, until the neutral point, as indicated by methyl-orange, is reached. An excess of acid is then added and the fatty acids separated as before.

The volumetric method of estimating alkali does not distinguish between potassium hydroxide and sodium hydroxide, and hence, if the nature of the alkali present be unknown, the estimation is simply an expression of the alkali in terms of one or the other.

The solution separated from the fatty acids and neutralised with standard alkali will, of course, contain *alkali sulphates.* In addition, it may contain many other substances, among which are, *sodium chloride, soluble fatty acids, glycerol, sugar, dextrin, starch, gelatin.*

For the detection and estimation of these it is necessary to operate on separate aliquot portions of the solution.

If nitric acid has been used instead of sulphuric acid at the previous stage of the process, the sulphates may be estimated by treating an aliquot part of the solution with barium chloride.

a. Sodium chloride may be estimated by titration with decinormal silver nitrate (see Amer. Chem. Soc. method III, p. 592) or deduced from the weight of the silver chloride precipitate.

b. Soluble fatty acids rarely require estimation in soap. Swift & Co. continue the titration with N/2 alkali phenolphthalein being used as indicator. 1 c.c. N/2 NaOH = 0.0750 grm. water-soluble fatty acids in foots soap = 0.0875 grm. water-soluble fatty acids in laundry soap. If the precautions on page 622 are adopted in separating the fatty acids from coconut and palm-nut oil soaps, only insignificant quantities of soluble fatty acids will remain in the aqueous liquid. If desired, these may be estimated by distilling the acidified solution, as described on page 21, but their amount may also be ascertained in the following simple manner: Titrate a certain volume of the solution with standard alkali, using phenolphthalein as an indicator. Titrate another portion of equal measure with the same alkali, using Methyl Orange to indicate the point of neutrality. The alkali consumed in the second case corresponds to the free mineral acid only, whilst the difference between this and the first estimation gives the volume of alkali required to neutralise the soluble acids present. 1 c.c. of N/1 alkali corresponds to 0.144 grm. of *caprylic acid*.

Allen suggested the following as a method for estimating the total fatty acids in coconut and palm-nut oil soaps: Separate the fatty acids in the ordinary manner, but in as concentrated a solution as possible. Agitate the aqueous liquid with a little ether, separate, and extract any dissolved fatty acids from the ether by agitating with dilute sodium hydroxide solution. Employ the alkaline solution obtained to neutralise the main quantity of fatty acids, and add a few drops of phenolphthalein, and then more alkali, drop by drop, until the pink colour just remains permanent. Then treat the hot liquid with a slight excess of magnesium sulphate, filter, wash with hot water, dry the precipitate at 100° and weigh. Ignite the precipitate and weigh the residual oxide. The difference is the weight of fatty anhydrides forming insoluble salts with magnesium. Evaporate the filtrate, dry the residue at 100°, and weigh. Ignite and

weigh again. The difference is the weight of fatty anhydrides forming soluble salts with magnesium.

J. A. Wilson employs the following process in the presence of soluble fatty acids:

1. The alkali in all forms is estimated by titration with standard acid in the usual manner.

2. Another weighed quantity of the soap is decomposed in an Erlenmeyer flask with a slight excess of dilute sulphuric acid, and the flask kept on the water-bath until the fatty acids separate quite clear. The flask is placed in ice-water to cool and then filtered. The fatty acids are washed 3 times successively with 250 c.c. of boiling water, allowed to cool each time, and filtered. The united filtrates are diluted to 1000 c.c., and 500 c.c. placed in a beaker and tinted with Methyl Orange; N/10 alkali is then run in until the liquid acquires the usual colour, after which a little phenolphthalein is added and the addition of standard alkali continued until a permanent pink is established. The amount used in the latter titration is due to soluble acids and is calculated to caprylic acid. The fatty acids in the flask and that on the filter are dried and weighed, and then dissolved in alcohol and titrated with N/2 alkali. The amount so used, together with that required for neutralisation of the soluble acids, deducted from the total alkali, gives the alkali existing in forms other than as soap.

If desired, the soap may be decomposed with standard sulphuric acid, Methyl Orange added, and the alkali required for neutralisation noted; this, deducted from the total acid used, would give the acid equivalent to the alkali existing in all forms. In this manner are ascertained: Total alkali; combined alkali; insoluble fatty acids; and soluble fatty acids.

c. *Glycerol* may exist in soap. The Amer. Chem. Soc. method XIII, p. 599, is recommended for the determination of glycerol, sugar and starch. In the absence of sugar, it may be estimated with considerable accuracy by the permanganate process. When glycerol is present in considerable amount in soap, Lewkowitsch makes the estimation by dissolving it in water, separating the fatty matter with acid, and filtering off. The filtrate is then neutralised with barium carbonate and boiled down to the consistency of syrup. The residue is next extracted with a mixture of 3 parts of 95% alcohol and 1 part ether, and the alcoholic solution filtered and evaporated on the water-

bath to small bulk, and finally dried under a desiccator. The glycerol in the residue may be estimated by the acetin method. A more convenient method is that of Hehner with potassium dichromate (see under "Glycerol"). The presence of sugar renders the above methods (with the exception of the Amer. Chem. Soc. method) wholly useless.

d. Sugar is rarely present except in transparent toilet soaps, but in these it sometimes exists to the extent of 20 to 30% of the entire weight, or in a proportion approaching that of the anhydrous soap present. Such soap is sometimes sold as "glycerin soap," though wholly destitute of glyercol.

According to Donath and Mayrhofer (*Zeit. anal. Chem.*, 1881, 383), the estimation of sugar and glycerol may be made by adding to the solution slaked lime sufficient to combine with the sugar and an equal quantity of washed and ignited sand, boiling down to the consistency of syrup, pulversing the cooled residue and exhausting it in a closed vessel with 80 to 100 c.c. of a mixture of equal parts of ether and alcohol. The glycerol will pass into solution, and, after cautious evaporation of the solvent, may be estimated by methods given under "Glycerol."

Sugar may be estimated by Fehling's solution, after inversion, without previous separation of the glycerol, but the solution should be dilute and the boiling very limited in duracion, or the glycerol may cause some reduction.

In an aqueous liquid containing no other substances than sugar and glycerol, the amount of glycerol may be deduced from the sp. gr. of the liquid. The sugar having been previously estimated by Fehling's solution or other means, its effect on the sp. gr. can be readily calculated; and, this being deducted from the observed sp. gr., gives that due to the glycerol present in the liquid. See section on "Glycerol."

Organic matters, such as starch, dextrin, gelatin, may be detected by special tests; but their recognition is more easy and certain in residue L, left on treating the purified soap with alcohol.

G. **Examination of the Oily Layer of Fatty Acids.**—The separation of the liberated fatty acids from the acidified aqueous solution has already been described. If wax or stearic acid has been employed for the purpose of obtaining a solid cake, the further treatment of the fatty acids is practically limited to drying them and determining

their weight. In many cases, however, it is of interest or importance to make a further examination of the oily layer, which in that case should be treated as described on page 23.

The oily layer may contain *fatty acids*, the acids of *resin* or *colophony*, *coal-tar products* which existed as salts in the original soap, and other substances of acid character and limited solubility in water. If the treatment with petroleum spirit has been omitted, the oily layer may contain various *hydrocarbons*, *waxes* and *wax alcohols*, *unsaponified fat*, etc. In such a case the proximate analysis is best made as indicated in the table on page 615. When only fatty and resin acids are to be estimated, they may be estimated by the method of Wolff (see Amer. Chem. Soc. method V). They may also be estimated by Twitchell's method, but it must be remembered that any unsaponified oil may contaminate the resin acid and be estimated as such. Resin acids may be detected by the Liebermann-Storch test.

It is often important to ascertain the origin of the fatty acids from soap. Rosin is very frequently present, and it is best to remove it altogether from the fatty acids before proceeding with the other tests. This is accomplished by using a large quantity of the mixed fatty acids + rosin and proceeding as in the Twitchell method. After neutralising the rosin acids, the esters of the fatty acids are shaken out of the aqueous soap solution with ether, the ether evaporated, and the esters hydrolysed by boiling with alcoholic potash, evaporating off alcohol, dissolving the soap paste in water and acidifying with mineral acid. The fatty acids thus obtained are free from rosin acids, but contain any unsaponifiable matter occurring originally in the rosin.

In some cases their origin may be satisfactorily solved by a study of their physical and chemical properties. Thus, the melting and solidifying points of the fatty acids from various sources are given on pages 594 to 595 (see Amer. Chem. Soc. method VI). Archbutt has communicated the following observations of the sp. gr. of the acids from several oils. The observations were made at the b. p. of water by means of a Sprengel tube, and the figures express the sp. gr. of the fatty acids at the b. p. of water, compared with water at 15.5°.

Fatty acids from	Sp. gr.	Fatty acids from	Sp. gr.
Olive oil, genuine...........	0.8422	Nigerseed oil...............	0.8546
Olive oil, genuine...........	0.8404	Linseed oil.................	0.8583
Olive oil, Gallipoli average...	0.8423	Train oil...................	0.8580
Colza oil....................	0.8448	Lard oil....................	0.8438
Rape oil.....................	0.8423	Tallow......................	0.8364
Cottonseed oil...............	0.8478	Palm oil....................	0.8367

In the examination of fatty acids separated from a soap with the object of obtaining some idea as to their source, it is to be remembered that in the last few years fats from various sources hardened by hydrogenation have appeared on the market and are extensively used in the manufacture of soap. Since the hardening of various oils converts the oleins and other unsaturated acids or their esters more or less completely into the corresponding saturated compounds, the characteristics of the fat are entirely changed. This is probably most noticeable in the reduction in the iodine value and the rise in melting point or "titer." Valuable information may, however, be obtained by the examination of the acids as to the probable action of the soap in use and, possibly, as to the nature of fats required to make a similar product, but it would be very difficult to form even an approximate idea of the source of fats that have been used if they have been hydrogenated.

Much information can be gained by ascertaining the combining weight as described in Amer. Chem. Soc. method VII, p. 595. The figures yielded by the acids from various oils are given on page 513, and in other cases they may be calculated from the saponification equivalents recorded on page 19. The combining weight of the insoluble acids is usually less than the saponification equivalent of the oil by about 13 to 14. This statement only applies to those oils yielding about 95 to 96% of insoluble fatty acids on saponification.

Similarly, the iodine values of the insoluble fatty acids (p. 513) are more or less characteristic of their origin, but are subject to the same limitations as are stated above to apply to the saponification equivalents.

In cases in which the acids are practically insoluble in water, a titration in alcoholic solution with standard alkali and phenolphthalein affords a simple and accurate means of ascertaining the

proportion of *alkali existing in combination with the fatty and resin acids*, as it is evident that the amount of alkali required for neutralisation of the separated acids must be the same as that with which they had been previously in combination. (See Amer. Chem. Soc. method 3 II (5), p. 591.)

The fact that the soaps produced by the saponification of *coconut* and *palm-nut oils* are not readily precipitated by solution of common salt may, according to W. Lant Carpenter, be employed for detecting the presence of these oils in soap. A sufficient quantity of the soap should be dissolved in hot water, and the fatty acids liberated by acidifying the solution, and separated without special washing or use of ether. 10 grm. of the fatty acids are treated with 39 to 40 c.c. of N/1 sodium hydroxide or a volume just sufficient to dissolve them completely. The whole is then boiled, and the weight of the liquid brought to 50 grm. by evaporation or cautious addition of water. A saturated solution of common salt (previously boiled with a few drops of sodium carbonate and filtered from any precipitate) is then run in gradually from a burette, the liquid being constantly stirred and kept gently boiling. The addition is continued until the soap suddenly precipitates—a point which is usually sharply marked. The soap from ordinary oils is precipitated when from 8 to 10 c.c. of the salt solution have been added, but that from coconut oil requires an addition of more than 50 c.c. Mixtures of the fatty acids from coconut or palm-nut oil with those from other oils will of course require a volume of brine intermediate between these two limits.

The Polenske Value (see page 417) and the Reichert-Meissl Value (see page 25) are recommended by a number of authorities to assist in the identification of coconut and palm-kernel oils. Estimation of the octabromide value, and acetylation value and determination of the refractive index of the fatty acids will be found to be of value in certain cases.

The American editors in their laboratory have found the estimation of the oxidised fatty acids to be of value in seeking the cause of poorly made soaps, particularly those made from foots and soap-stock, where the colour was very bad. These oxidised acids comprise a class occurring in oils and fats which have undergone a natural process of oxidation by exposure to the atmosphere, such as highly rancid oils, or by blowing of oils or fats with air or oxygen (*cf.*

Lewkowitsch, Vol. 11, 592, 6th Ed.). The method of Fahrion (*Z. angew. Chem.*, 1898, 782; 1903, 79; 1904, 1199, see also Kassner, *Z. angew. Chem.*, 1904, 1853; Hodes, *Chem. Ztg.*, 1912, 41, 492; Davidsohn, *Seifensieder Ztg.*, 1921, 48, 926) is as follows: 3–4 grm. of the fatty acids are shaken in a separatory funnel with equal volumes of water and petroleum spirit, boiling below 80°, and allowed to stand until the mixture has separated completely into two layers. The insoluble oxidised fatty acids will be found to adhere to the sides of the funnel, or to form a sediment in the petroleum spirit layer. The aqueous layer is drawn off, the petroleum spirit layer is poured off, if necessary through a filter, and the oxidised fatty acids are washed with petroleum spirit to remove adhering soluble fatty acids. In case the amount of oxidised fatty acids is large, it is advisable to dissolve them in alkali, decompose the soap with hydrochloric acid, and shake out again with petroleum spirit in order to remove completely any occluded soluble fatty acids. The oxidised fatty acids are then dissolved in warm alcohol, or ether, and the solution is transferred to a tared dish or flask, the solvent evaporated off, and the residue dried to constant weight and weighed. H. Stadlinger (*Z. Oel-Fett-Ind.*, 1920, 40, 437) gives the following directions for estimation by the German Soap Syndicate Goldschmidt-Weiss Method (*Seifenfab.*, 1919, 39, 49; *Z. angew. Chem.*, 1919, 32, 33, 96): Warm the total fatty acids to melt any solid acids, and then dissolve them by adding 50 c.c. petroleum spirit in a fine stream from a wash bottle. If allowed to stand for several hours the oxidised fatty acids usually cling to the sides of the flask. Filter, wash, dissolve the oxidised fatty acids in warm alcohol, or in a 1:1 alcohol-chloroform mixture, filter, evaporate off the solvent, dry and weigh. Stadlinger states that the quality of the petroleum spirit influences the final results. Commercial gasoline, redistilled at 70°, showed in 7 samples 1.3 to 6.5% oxidised acids, whilst Kahlbaum's "normal" benzine (sp. gr. at 15° of 0.695–0.705, boiling 65–95°) showed 7.1 to 14.0% oxidised acids. Not only the b. p., but also the presence of cyclic compounds in the gasoline influences the results.

Estimation of Special Constituents.—Formaldehyde is present in a number of medicinal soap preparations and may be estimated as follows: The soap is dissolved in 4 or 5 times its weight of water and the soap precipitated either with barium chloride or sulphuric

acid, filtered and made up to some definite volume. The formalde-
hyde is estimated in an aliquot of the filtrate by titrating by the
iodometric method (Vol. I, p. 328) (O. Alleman, *Zeit. Anal. Chem.*,
1910, **49**, 265, *Seifensieder Ztg.*, 1913, **40**, 49).

Peroxide soaps or powders are frequently met with in which the
peroxygen component may be sodium perborate, percarbonate or the
peroxide of some heavy metal, the nature of which will have been
determined in the course of analysis. The available oxygen of such
a soap may be estimated by dissolving the soap in water and decom-
posing with acid, care being taken that the solution is kept cool and
sufficiently dilute to prevent the peroxide liberated from being
decomposed. The acids are filtered off, with the use of kieselguhr,
if necessary, to obtain a clear filtrate, the residue wasted and
the filtrate and washings made up to definite volume. To an
aliquot of the filtrate, potassium iodide is added and the liberated
iodine titrated with standard sodium thiosulphate solution, or if
preferred, the peroxide in the filtrate may be estinated by
acidifying with sulphuric acid and titrating with potassium perman-
ganate (F. M. Litterschied and P. B. Guggari, *Chem. Zeit.*, 1910,
37, 677 and 690), 1 c.c. of an $N/10$ solution in either case being
equivalent to 0.0008 grm. oxygen.

Grün and Jungmann (*Seifenfab.*, 1916, **36**, 753) have studied the
effects of saponins on this determination and find that it is un-
necessary to remove them before making the estimation.

H. Trickett (*Analyst*, 1920, **45**, 88) gives a method for the estima-
tion of perborates which may be applied to soap powders without
the previous separation of soap or fatty acids, or the decomposition
of the sodium carbonate present: Mix the material, containing about
0.2 grm. $Na_2B_4O_7$, with about 20 c.c. of water in a beaker, transfer
the mixture to the outer vessel of a nitrometer decomposing bottle,
fill the inner vessel with a clear saturated solution of bleaching
powder (about 15 c.c.), and carry out the estimation with the usual
precautions. Note the volume of oxygen after 5 minutes inter-
mittent shaking of the reaction mixture. In the case of a $Na_2B_4O_7$
mixture giving 8.45% by the potassium iodide method 8.32 and 8.54%
were found.

Nitrobenzene in soap may be estimated by the method of G.
Armani and L. Barboni (*Ind. Saponiara Giorn. farm. Chim.*, 1913, **62**,
126). The aqueous solution of the soap, previously acidified with

dilute sulphuric acid, is steam distilled. The first 10–15 c.c. of the distillate are shaken out with ether, the ethereal solution evaporated, and the residue is dissolved in alcohol, and treated with zinc and dilute sulphuric acid. The aniline formed may be estimated by the usual methods.

Occasionally it is necessary to estimate the amount of alcohol left in transparent soaps. Lewkowitsch gives the following method: The alcohol is estimated by distilling a weighed amount of the soap with steam. If frothing cannot be prevented in this distillation, a weighed quantity of the soap is decomposed with sulphuric acid, the fatty acids are separated by filtration, and the filtrate is distilled. From the sp. gr. of the first 50 c.c. of the distillate and, if need be, from the second fraction, the amount of alcohol is found.

Colouring matters are demanded in certain classes of soaps, and are extensively used in some of the tinting soaps now on the market. The identification of the aniline or vegetable dyes or mineral pigments requires recourse to the special methods outlined in other volumes.

Essential oils have become a necessary ingredient in most classes of toilet soaps, etc., and, if identification of these is required, special methods will have to be devised to suit the case in hand.

Soap Powders, Scouring Powders and Scouring Soaps.—The general methods of soap analysis will usually apply to products of the above class, but since the proportions of the various constituents are entirely different, precautions must sometimes be taken. In soap powders the percentage of soap is frequently quite low, the bulk of the powder being composed of sodium carbonate with water of crystallisation. In such cases, estimation of moisture, the weight of the alcohol extract, considered as true soap, and the alkalinity of the alcohol insoluble portion, calculated as sodium carbonate, may give all the data required. A qualitative examination of the matter insoluble in alcohol should be made, as various other alkalies may have been used, including sodium hydrogen carbonate, silicate, aluminate, triphosphate and borate. Potassium salts are seldom found, except in soft soaps, both on account of their greater cost to the manufacturer and their hygroscopic nature.

Scouring powders usually consist of a large percentage of abrasive material with a comparatively small quantity of soap, moisture and

alkali. Frequently a short method of analysis, similar to that suggested above, but including an estimation of water-insoluble matter, would answer all requirements. A microscopic and more or less practical examination of the abrasive material might give valuable information. The abrasive material should be sharp and have decided mechanical cleansing value, but should not be too hard, or it may be destructive to the surfaces on which it is used. Likewise, it should be practically free from extremely fine or clay-like impurities.

Scouring soaps are similar in their general composition to the powders described above, except that they are in bar form. The quantity of abrasive material in such soap varies from that in an ordinary household bar soap containing a few per cent., to that in a scouring brick which contains only enough soap or other agent to act as a binding material.

Interpretation of the Results of Analysis of Soaps.—Calculating from the equation of the reaction between sodium stearate, and any strong acid, it is found sodium stearate yields 92.8% of stearic acid. Similarly, the alkali used in forming the soap would be 10.13%, so that the analysis would be—

Stearic acid..........................	92.81%
Sodium hydroxide...................................	10.13%
	102.94%

This statement shows an excess of nearly 3%, owing to the hydrolysis which takes place. It is evident that if the basic constituent of a soap be stated as anhydrous alkali, a correction must be made in the actual weight of fatty acid found, to bring it to the corresponding quantity of anhydride. 568 parts of stearic acid correspond to 550 of stearic anhydride, and the proportions of the respective anhydrides corresponding to palmitic and oleic acids are not very different from the above. Hence, in soaps made from palm oil, olive oil, and tallow the necessary correction of the observed weight of fatty acids to the corresponding quantity of fatty anhydrides may be made by multiplying by the factor 0.97, 100 parts of stearic acid representing approximately 97 of stearic anhydride. In the case of coconut and castor-oil soaps, and many others made with mixed oils, this factor is far from accurate, and hence it is in all cases decidedly preferable to determine the mean combining weight

Description of soap	Origin	Fatty and resin anhydrides	Sodium oxide existing as soap	Silica	Sodium oxide existing as silicate	Sodium carbonate and hydroxide	Sodium chloride	Sodium sulphate	Lime, iron oxide	Water	Total	Fatty and resin acids
1. "White," No. 1	Tallow	69.06	8.98	0.01	None.	.27	.49	.16	.07	21.14	100.18	71.20
2. "White," No. 2	Tallow and coconut oil.	60.50	6.82	0.06	None.	.06	.11	.12	.16	32.20	100.03	62.36
3 "White," No. 3	Tallow and coconut oil.	55.71	6.90	0.03	None.	.92	.18	Trace.	.08	36.54	100.36	57.44
4. "White," No. 4	Tallow and coconut oil.	44.27	6.23	7.02	2 36	.75	.32	.34	.34	38.14	99.77	45.64
5. "Cold water," No. 1	Tallow, rosin, and cottonseed oil.	71.30	7.98	1.07	0.48	.75	.36	.30	.16	17.44	99.84	73.50
6. "Cold water," No. 2	Tallow, rosin, and cottonseed oil.	49.95	7.00	2.34	1.01	.33	.51	.00	.50	38.18	99.82	51.50
7. "Olive oil," No. 1	Olive oil	71.20	7.58	0.06	0.03	.22	.66	.17	.20	19.70	99.82	73 40
8. "Marseilles," No. 1	Chiefly olive oil	62 66	7.27	0.06	0 03	.77	.76	.30	.16	28.20	100.21	64 60
9. "Palm oil," No. 1	Palm oil	59.28	6.65	0.42	0.01	.39	.47	.13	.16	32.35	99.86	61.08
10. "Mottled"	Palm-nut oil	38.89	5 76	6.40	1.29	1.62	1.78	.72	.03	38.70	95.19	40.10
11 "Satinet"	Tallow and rosin.	59.92	6.76	0 02	None.	.92	.41	.37	.05	31.30	99.75	61.77
12. "Glasgow Almond"	Tallow and rosin.	42.41	4.14	5.64	1.59	2.76	.37	Trace.	.14	42.88	99.93	43.72
13. "Pale rosin," No. 1	Tallow and rosin.	60 90	7.22	0.04	None.	.10	.46	.12	02	31.22	100.08	62.78
14. "Pale rosin," No. 2	Tallow and rosin.	48.20	5.00	0 42	1.18	.15	.65	.10	.10	45.00	99.80	49.65
15. "Pale rosin," No. 3	Tallow and rosin.	39.92	4 70	0.62	0.25	.20	1.48	.18	.15	52.40	99.90	41.15
16. "Milling"	....	63.06	7.25	0.02	None.	.10	1.65	.15	.30	27.47	100.00	64.95
17. "Yellow" (for foreign markets)	....	10.90	1.36	0.03	None.	Trace.	2.57	.56	.14	84.00	99.56	11.26
18. "Marine" for emigrants	Palm-nut oil	19.42	3.11	9.00	3.98	3.00	5.13	.35	.16	53.32	97.47	20.02

of the isolated fatty and resin acids, as described on page 512, and calculate the corresponding weight of fatty anhydride therefrom. The mean combining weight of the anhydride is always 9 less than that of the corresponding acid. The usual figures for the fatty acids isolated from various fatty oils are given on page 513.

Numerous analyses of soaps have been published, but many are not trustworthy. In many cases the observers appear to have stated the amount of fatty acids and alkali as deduced from the ash, the remainder being entered as "water, etc." C. Hope furnished the valuable analytical data contained in the table on page 635. Samples 10 and 18 were prepared by the "cold process," and hence contained the glycerol produced by the saponification. This accounts for the sum of the estimated constituents being sensibly below 100. Samples 3, 4, and 12 were the only three which contained free alkali, and in these it only reached the proportions of 0.16, 0.26, and 0.15% of sodium hydroxide, respectively. Hope points out that a striking feature of the analyses is the variable composition of the silicate existing in the soap, although, as added, it is tolerably constant in composition. This is attributed by Hope to the property possessed both by rosin and fats of taking alkali from sodium silicate, in which case the change will occur only in those soaps to which the silicate was added before saponification was complete.

W. Lant Carpenter gives the following analyses in his treatise on *Soaps and Candles:*

Description of soap	Fatty acids	Soda as soap	Soda in other forms	Silica	Neutral salts	Water	Total
Primrose soap as in south and west of England	62.3	6.7	......	......	0.2	32.8	102.0
Primrose soap as in north of England	42.66	5.41	1.21	0.94	0.55	50.40	101.17
Genuine "cold-water" soap	70.2	7.3	1.8	1.6	0.4	22.0	103.3
Manufacturers' neutral curd soap	67.9	7.0	0.0	......	0.2	28.0	103.1
Manufacturers' brown oil soap, from oleic acid	68.60	7.88	1.00	......	1.00	21.00	99.48

The following table gives a list of typical analyses of various classes of soaps commonly found on the American market.

Kind of soap	Fatty anhydride	Rosin acids	Combined alkali	Free caustic	Free carbonate	Silicate[1] of soda	Salt	Water insoluble	Glycerin and undetermined	Volatile matter
Milled toilet....	79.39	.....	9.24	0.08	0.37	.....	0.12	......	0.38	10.42
Milled toilet...............	68.51	.....	7.98	0.12	0.55	.....	0.18	11.21[4]	0.43	11.02
Floating....................	53.24	.....	8.23	0.02	0.33	.....	0.35	......	0.52	27.31
Coconut....................	57.95	.....	8.58	0.01	0.17	.....	0.21	....→	6.12	26.96
Transparent[2]................	43.33	.....	5.50	0.12	0.73	.....	0.60	......	10.51	24.58
Household bar, yellow........	41.56	18.83	6.30	0.04	1.87	2.38	0.28	trace	0.45	28.29
Household bar, yellow.......	28.28	20.45	5.10	0.02	2.34	3.18	0.40	11.28[5]	0.38	28.57
Household bar, white.........	43.48	.....	5.64	0.02	2.05	11.11	0.23	......	0.98	36.49
Laundry chip................	78.99	.....	9.20	0.22	0.64	.....	0.10	......	0.44	10.41
Laundry chip...............	57.54	.....	6.82	0.03	3.95	7.91	0.18	......	0.70	22.87
Soft potash[3]................	40.52	.....	6.92	0.06	1.19	.....	0.45	......	5.92	45.21

[1] Silicate of soda calculated on the basis of 1 part of Na_2O combining with 3.14 parts of SiO_2.
[2] Contained 14.63 % sugar.
[3] All alkalies calculated as potassium compounds.
[4] Water insoluble material was starch.
[5] Water insoluble material was silica.

Partial analyses of various representative samples of carbolic soap are given on page 620.

Analyses of soft soap published show the proportion of water in samples of good quality is usually between 35 and 45%. The potassium oxide ranges from 8.8 to 11.2%.

In forming an opinion as to the quality of a soap, the application to be made of it is a primary consideration. In practice, water in moderate proportion must be regarded as a useless but unavoidable constituent; but, if present in the enormous proportion sometimes observed, it can only be regarded as an adulterant.

In some of the best brands of opaque toilet soap, made by special methods, the proportion of water does not exceed 10 or 12%, but the majority of the best qualities of soap, known as Marseilles, curd, brown Windsor, honey, and primrose, contain from 17 to 24% of water. In some of the transparent toilet soaps, made by solution in alcohol, the proportion of water is very small (9 to 10%), but this advantage is more than counterbalanced by the presence of 20 to 30% of sugar. Transparent soaps made in other ways, as by the "cold process," rarely contain half their weight of actual soap, the remainder consisting of water and sugar.

Practically, the proportion of *alkali* in a soap is the best single test of its quality, but here again a distinction must be drawn between alkali existing in combination with fatty and resin acids, or, in other words, as true soap, and that existing in other conditions, particularly

the caustic state.   Wright arranges toilet soaps in three classes,
according to the proportion the "free" or *inorganic alkali* bears to
the *alkali existing as soap*.   Thus, soaps containing less than 2.5 parts
of free alkali for 100 of alkali as soap are arranged in the first class;
those containing between 2.5 and 7.5 in the second, and those contain-
ing more than 7.5 in the third class.   In judging of the quality of
toilet soap, Wright also takes into account the freedom of the soap
from adulterants, "filling," water, and "closing up" agents, and
from poisonous colouring matters; as also the nature and quality of
the fatty matters used as basis and their freedom from rancidity.

Although the absence of a notable proportion of "free" alkali is
important in the case of toilet soaps, owing to its powerful action on
the skin, it does not follow that a similar absence is advantageous
under other conditions.   On the contrary, for scouring and household
purposes, a limited proportion of alkali is advantageous, and in the
case of some soaps used by manufacturers the presence of   con-
siderable proportion of alkali is essential to success, a solution of
alkali with sufficient soap in it to cause lathering being preferred.   A
neutral soap, however pure, will for such uses be regarded as deficient
in "strength," and will often cause trouble through the precipitation
of free fatty acid or acid soap in the fabric with which the soap is
used.

The nature and origin of the acids are sometimes of interest in
judging of the suitability of a soap for certain purposes.   The pres-
ence of rosin acids and of the acids from coconut or palm-nut oil can
be ascertained as noted under G (p. 627), and it is rarely of interest to
inquire further, unless the question of duplication is in mind.

The examination of the oils used in the composition of soap differs
from most other cases in the fact that only the mixed fatty acids are
available, the oils or fats having been split by saponification.   Fryer
and Weston in their book, Oils, Fats and Waxes, Vol. II, 252, give
examples of the interpretation of the examination of the fatty acids
as follows:

Example 1.—A sample of household soap (in bars).

Appearance of soap—fairly firm, light yellow colour, pleasant
odour.[1]

Percentage of fatty acids 57.5%.

Tested for rosin by Liebermann-Storch.   Rosin present.

[1] Most household soaps are scented with low grade perfumes (citronella, etc.).

Took large quantity (30 grm.) of mixed fatty acids and proceeded as above, removing the rosin acids.

Proportion of rosin by Twitchell's methods = 22%.

The fatty acids free from rosin acids gave the following figures:

Iodine value.. 38.5
Mean molecular weight................................. 252.5
"Titer" test.. 33°
Cotton oil was present by the Halphen reaction.

The mean molecular weight shows coconut oil present to the extent of about 30% of the *fatty* acids.

A Polenske estimation of the mixed fatty acids (Fryer, *J. Soc. Chem. Ind.*, 1918, **37**, 262) confirmed this figure.

The presence of tallow or a hardened fat was indicated by the iodine value. The "titer" test was lower than would have been expected with hardened fat, considering the amount of cottonseed oil which is indicated. Assuming tallow present, the iodine value gives about 15% of cottonseed oil.

$$\text{(Coconut } \quad \frac{9.7 \times 30}{100} = 2.9; \ 38.5 - 2.9 = 35.6 : 35.6 \times \frac{100}{70} = 50.$$

Tallow at iodine value = 42; cotton at iodine value = 100.

By inspection this indicates about 15% cottonseed oil.)

It was therefore inferred that the *composition of the fatty acids was:*

Tallow... 55
Cottonseed oil....................................... 15
Coconut oil.. 30

Adding rosin found, we obtain:

Rosin.. 20
Tallow... 44
Coconut oil.. 24
Cottonseed oil....................................... 12
                                                    ———
                                                    100

The above analytical data would not, taken alone, fully justify the conclusions arrived at. These were also based upon a wide knowledge and experience of the materials likely to be employed, together with their relative value at the time of manufacture. Additional help was also given by the general appearance of the soap and the odour of the fatty acids. In case of doubt "the insoluble bromide" value would have excluded drying oils, whilst the examination of the liquid fatty acids (lead salts soluble in ether) would have given additional information as to the amount of cottonseed oil present.

This is a good instance of the value of practical experience in commercial analyses, referred to above.

Example 2.—A sample of potash soft soap.

The soap was transparent, light yellow and of medium consistence. The odour was suggestive of linseed oil.

Fatty acids = 39.5%.

The mixed fatty acids (pronounced odour of linseed) gave figures as follows:

Iodine value... 153.0
"Titer" test... 21.0°
Mean molecular equivalent of fatty acids........ 283
No rosin by Leibermann-Storch test.

These figures pointed to linseed oil and another oil as present. The insoluble bromide value was 20.2.

The proportion of linseed was thus about 50–60%.

Cotton seed oil was not detected by Halphen's test.

Current prices of oils made it probable that only *soya bean oil* would be employed, besides linseed oil, in a soft soap. This supposition agreed with the observed lack of distinctive odour and the general appearance of the soap.

About equal quantities of linseed and soya bean oil was indicated by all the tests.

The composition was therefore taken as:

Linseed oil... 50
Soya oil.. 50
                                                       ———
                                                       100

Example 3.—Sample of "soda soft" soap.

This was transparent at 20°, slightly cloudy under 15° and firm in consistence. Odour of linseed oil and rosin.

The fatty acids (+ rosin) were 50.5%.

Rosin was present by the Liebermann-Storch test.

The Twitchell estimation gave *rosin* 15%.

The rosin acids were not separated, and the following figures apply to (rosin + mixed fatty acids):

Iodine value... 145.5
"Titer" test indefinite (on account of rosin present)....... 25°
Insoluble bromide value.............................. 22.2

The last figure gave linseed about 60% present, and this raised a presumtion of the presence of some other oil, with iodine values

about 80–100. Castor oil was suspected for other reasons. The acetyl value of the fatty acids was then estimated. This gave 35.5, corresponding to 25% of castor oil in the fatty acids.

The iodine value obtained corresponded with this mixture of oils and rosin, and as no other oil would be likely to be employed under the existing market conditions, the *composition was taken to be:*

Linseed oil...	60
Castor oil..	25
Rosin...	15
	100

The permissibility of additions to soap must be judged on the merits of each case, but, as a general rule, the less extraneous matters present the better. It is said that, for some purposes, as in the treatment of wool and silk, a small proportion of starch is an advantage. In contracting to supply manufacturers of textile fabrics, the soap-maker is frequently obliged to settle definitely the proportions of fatty acids, resin, alkali, and potato-starch which shall be present in the soap. A soap suitable for fulling cloth and for other purposes should not contain less than 40% of fatty acids nor more than 5% of rosin and 6 of potato-starch.

A continued effort has bee made to develop a method of estimating the working or cleansing value of soap. McBain, Harborne and King (*J. Soc. Chem. Ind.*, 1923, 42, 3735) have standardized a method using carbon black, which gives concordant results. The "carbon number" which is obtained may be taken as a measure of the detergent action of the material. McBain believes that the action of soaps on carbon black may be specific and in so far be not quite parallel to the effect on oily matter, which would limit, but not destroy, the value of the data from such a procedure.

Holde gives in the table on page 642 the specifications for soap used on continental European railways, in 1913.

The table on page 644 gives the specifications for various grades of soap adopted by the Federal Specification Board of the United States Government in 1922. These specifications were arrived at by consultation with many producers, and may be said to be representative of American practice. For more complete specifications for special soaps, such as those used for textile scouring, etc., reference should be made to text books dealing with the technology of the special industry.

RAILWAY SPECIFICATIONS FOR SOAPS IN FORCE 1913

Material	State	External appearance	% of fatty acids	Other properties
Soft soap	Prussia, 1903	Clear and translucent, odourless.	At least 40	(Brown or green soap) should be free from silica, silicates, aluminium compounds, starch and other filling material and foreign substances; should be solid at 25°. Fish oils and bad smelling oils should not be used in the manufacture of the soap. Rosin may be added but, not more than 5 % of the weight of fat used.
Soft soap	Bavaria, 1900	Light brown, translucent on the edges, of thick salve-like consistence even in summer.	At least 35	Must be purest soap free from rosin, should contain no foreign caustic or weighting materials and should have the power of cleaning and lubrication. Not more than 45 % water, 10 % ash (K_2CO_3), 3.85 % impurities should be present. Unsaponified fat or free alkali should not be present. On storage, no liquid particles should separate.
Soft soap	Saxony, 1902	Thick and viscous.	. . . . . .	Must be prepared from linseed oil, must be free from injurious substances and contain at least 45 % fat.
Soft soap	Württemberg, 1904	Thick salve-like, viscous, light brown, translucent on the edges.	At least 35	Must be the purest soap free from rosin, should contain no foreign caustic or filling materials (starch or oxides of earth metals). Must cleanse and lubricate when mixed with water and mix uniformly with luke warm water. Mineral oil and unsaponifiable fat are not allowed. Ash (aside from combined alkali) less than 5 %. Traces of free alkali.
Soft soap	Baden, 1910	Thick salve-like, viscous, light brown, translucent at the edges.	At least 35	Must be purest soap free from admixture or filling material, free from mineral oil and unsaponifiable fat, with only a trace of free alkali. On storage, no liquid particles should separate. Ash content not over 5 %.
Soft soap	Imperial Territory, 1912	Clear and translucent, should not have a bad odour.	At least 40	(Green soaps) from linseed oil without admixture of fish oils, rosin, etc. Free from impurities, additions, colouring matter. Should not crumble on storage nor separate water, nor liquify. Should not be prepared from old rancid oil.
White soap (curd soap)	Prussia, 1903	Should not have a noticeable odour; neither a bad odour nor artificially perfumed.	At least 60	Should be a neutral curd soap, free from rosin, silica, silicates, aluminum compounds, starch and foreign materials. Lathering when used for washing. Must be dry, and should lose not more than 5 % of the original weight when left 5 days in the air at 20°.
White soap (curd soap)	Württemberg, 1904	. . . .	60	(Curd soap) should be free from rosin silica, and impurities. Should be dry, water not over 25 %.
White soap (curd soap)	Baden, 1910	Should be solid, not greasy, and should not be too dark coloured.	At least 60	Must be unfilled, free from foreign admixture and unsaponified fat, with traces of free alkali. Not more than 30 % moisture. Olein and rosin soaps not allowed.
White soap (curd soap)	Imperial Territory, 1912	Not greasy, white, hard.	At least 60	Must be a neutral curd soap, free from impurity, salted out, 7.5 % soda, not more than 30 %, no free alkali or free fatty acid.

Holde-Mueller, "Examination of Hydrocarbon, Oils and Saponifiable Fats," pages

SPECIFICATIONS FOR SOAP
Federal Specification Board, U. S. Government 1922

	Specification 123, white floating soap	Specification 126, salt water soap	Specification 128, white chip soap	Specification 132, hand grit soap	Specification 124, liquid soap	Specification 129, laundry soap (ordinary)
General description.............	From soda, high grade tallow and 25 to 30 % coco-nut oil	From pure coco-nut oil and necessary alkali	From soda and fats	High grade cake soap, firm, smooth cakes	From pure vege-table oil, potash or potash and soda, with, or *without alcohol and glycerol*	From soda and fats, no excessive proportion o f rosin
Volatile matter at 105°	Shall not exceed 34 %	Shall not exceed 55 %	Shall not exceed 15 %	Shall not exceed 25 %		Shall not exceed 36 %
Sum of free alkali, total matter insoluble in alcohol and NaCl.	Shall not exceed 2.0 %		Shall not exceed 3.0 %			Not less than 2.0 % Not more than 10.0 %
Sum of free alkali and total matter insoluble in alcohol.						
Combined alkali...............						
Alkali as alkaline salts calc. as Na_2CO_2.				Shall not exceed 1.0 %		
Free alkali as NaOH...........	Shall not exceed 0.15 %	Shall not exceed 0.5 %	Shall not exceed 0 5 %	Shall not exceed 0.1 %		Shall not exceed 0.5 %
Free alkali as KOH.............					Shall not exceed 0.05 %	
Free acid calc. as oleic acid......						
Anhydrous soap...............					Not less than the equivalent o f 15 % potash soap	
Sum of Na_2CO_3 and anhydrous soap.						

Sodium carbonate...					
Chlorides as NaCl..............	Shall not exceed 1.0%	Not less than 2.5% Not more than 3.5%			
Chlorides as KCl..............					Shall not exceed 0.3%	
Total matter insoluble in alcohol		Not less than 2.0% Not more than 3.0%			Shall not exceed 0.5%	
Total matter insoluble in water...	Shall not exceed 0.2%	Shall not exceed 0.5%	Shall not exceed 0.2%			Shall not exceed 1.0%
Acid number of separated fatty acids.	Not less than 212	Not less than 250				
Titer test of separated fatty acids.			Not less than 39° C.			
Rosin........................						Shall not exceed 25%
Unsaponified matter............						
Rosin, sugar and foreign matter.	Shall not be present	Shall not be present		Shall not be present		
Insoluble siliceous matter........				Not less than 25% Not more than 40%		
Specifications of insoluble siliceous matter.				Not less than 98% through No. 100 screen Not less than 90% through No. 200 screen		
					Clear solution and must quickly form satisfactory lather	
					More than traces of sulphates and sugar shall not be present	

SPECIFICATIONS FOR SOAP.—(*Continued*)

	Specification 127, automobile soap	Specification 130(a), grit cake soap for fine work	Specification 130(b), grit cake soap for scouring and scrubbing	Specification 125, soap powder	Specification 131(a), scouring compound for fine marble floors	Specification 131(b), scouring compound for tile and ceramic floors	Specification 131(c), soap scouring compound
General description	Pure vegetable oil, paste soap	Compact cake soap, light grey or white colour	Compact cake soap, light grey or white colour	Uniform mixture of soap and sodium carbonate in powdered form	Finely divided siliceous material and soap or sodium carbonate	Finely divided siliceous material, soap, sodium carbonate, or both	Light coloured siliceous material, sodium carbonate and powdered soap
Volatile matter at 105°	Shall not exceed 55%	Shall not exceed 4.0%	Shall not exceed 5.0%		Shall not exceed 10.0%	Shall not exceed 10%	Shall not exceed 10%
Sum of free alkali, total matter insoluble in alcohol and NaCl.							
Sum of free alkali and total matter insoluble in alcohol.	Shall not exceed 1.0%						
Combined alkali							
Alkali as alkaline salts calc. as Na2CO3.		Shall not exceed 1.0%	Shall not exceed 3.0%				
Free alkali as NaOH	None	Shall not exceed 0.1%	Shall not exceed 0.1 %		Shall not exceed 0.1%	Shall not exceed 0.1%	Shall not exceed 0.1%
Free alkali KOH							
Free acid calc. as oleic acid	Shall not exceed 0.2%						
Anhydrous soap				Not less than 15.0%			Not less than 5.0% Not more than 10.0%
Sum of Na2CO3 and anhydrous soap.				Not less than 55%	Not less than 2.0% Not more than 7.0%	Not less than 2.0% Not more than 10.0%	

Sodium carbonate............				Not less than 30.0%			Not less than 15% Not more than 20%
Chlorides as NaCl..........							
Chlorides as KCl............							
Total matter insoluble in alcohol.							
Total matter insoluble in water.	Shall not exceed 0.2%						
Acid number of separated fatty acids.							
Titer test of separated fatty acids.							
Rosin.....................	Shall not be present						
Unsaponified matter..........	Shall not exceed 4.0%						
Rosin, sugar and foreign matter	.	Shall not be present	Shall not be present				
Insoluble siliceous matter......		Not less than 88% Not more than 93%	Not less than 75% Not more than 85%		Not less than 85% Not more than 95%	Not less than 85% Not more than 95%	Not less than 60% Not more than 80%
Specifications of insoluble siliceous matter.		All pass No. 100 screen; 95% through No. 200 screen. Mainly ground feldspar	All pass No. 100 screen, must be mainly quartz		All pass No. 100 screen; 95% through No. 200 screen	90% through No. 80 screen; 99% through No. 60 screen	90% through No. 80 screen; 99% through No. 60 screen
					Must not scratch marble		

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GLYCERIN

By J. W. LAWRIE, Ph.D.

Glycerol was discovered in 1779 by K. W. Scheele (Crell's Chem. Annal., 1783–99) and was called by him Ölsüss (principe doux des huiles—sweet principle of oils). It was more fully investigated by M. E. Chevreul, who named this sweet principle *glycerin*. Berthelot and several other chemists established the fact that glycerol is a trihydric alcohol, indicated by the formula $C_3H_5(OH)_3$. It occurs in a free state in palm oil and possibly in some other oils. It was not made use of extensively until the discovery and development of trinitroglycerin. This was first obtained in 1846 by Sobrero (Mem. Acad. Torino, 1847) but its large use was made possible through the work of Nobel in 1868, who discovered that nitroglycerin could be rendered comparatively safe by absorbing it in kieselguhr. The importance of glycerin became greater from this time on, but the only source of supply for a long time was from the saponification of fats and oils. During the World War, the demands for glycerin were much greater than the supply and it was necessary to look for other sources. In 1873 Pasteur found in the ordinary yeast-fermentation of sugars, etc., for the production of ethyl alcohol, that about 3.3% of the fermentable sugars were converted into glycerin. This fact, discovered by Pasteur, was made use of by Connstein and Lüdecke in Germany and as much as 2000 tons of glycerin was produced per month from some 61 factories by the use of a process in which sugar was fermented by large quantities of yeast in the presence of sodium sulphite. Fermentation glycerin will be discussed in more detail under its own heading. It will be seen, however, that a new source of producing glycerin has been developed which is of extreme importance and that it is no longer necessary to rely on fats and their saponification for our glycerin supplies. Glycerol can also be produced synthetically in several ways. Berthelot produced it from acetylene by conversion into acetaldehyde, oxidised this to acetic acid, from which he prepared acetone, which in turn was con-

verted into isopropyl alcohol, and then into propylene. Propylene was converted to the dibromide and then to the tribromide, and the three bromine atoms were next displaced by acetyl groups, which in turn were hydrolysed to produce glycerol. There are, however, several new methods for the synthesis of glycerol from propylene, which is produced as a by-product in the Burton still process in the production of gasoline. The name glycerol has been given to the pure chemical $C_3H_6O_3$ trihydoxypropane. The term glycerin is used to represent the commercial varieties of impure glycerol, such as crude, dynamite and C. P. glycerin.

Pure glycerol, according to the determinations of G. E. Jacobson and W. F. Giaque (*J. Amer. Chem. Soc.*, **45**, 93), has a m. p. of 291.00° K. This corresponds to 17.9°. This determination is correct within ±0.001° and the purity of the glycerol used is given as 99.94%, with 0.06% moisture present. Other determinations show m. p. 17.0° (Henninger, *Ber.*, 1875, **8**, 643); 20.0° (Nitsche, *Jahres. Ber.*, 1873, 323). The b. p. of glycerol has been determined as 290.0° at 760 mm., by Mendelejeff (*Annal.*, 1860, **16**, 114–117); 210° at 50 mm. (Bolas, *Trans.*, 1871, **9**, 84) 162° to 163° at 10 mm. (Richardson, *Trans.*, 1886, **49**, 764); 143° at 0.2 mm. (Fischer and Harries, *Ber.*, 1902, **35**, 2158).

Manufacture of Glycerin.—The ordinary method of preparing glycerin on a commercial scale at present is by the saponification of fats for the production of soaps. The spent lyes from the saponification are concentrated and separated from precipitated salts, etc., and are distilled under high vacuum and with a current of superheated steam. There are several well-known methods for this procedure such as the Jobbins and van Ruymbeke, the Garrigues, and the Wood systems, which are largely used in the United States. The glycerin from the distillation of the concentrated soap lyes, etc., is usually of sufficient purity for use in making dynamite. It, however, is nearly always yellow in colour and, "for the so-called C. P. grades," it is usually redistilled and decolourized with chars to obtain a water-white glycerin.

Uses for Glycerin.—The greatest consumption of glycerin is in the production of explosives, which use trinitroglycerin as a base. The second largest use is in the manufacture of tobacco for smoking and chewing. The glycerin keeps the tobacco moist, is sweet to taste and is a partial antiseptic. It is used to a considerable extent

in toilet preparations, such as skin lotions, creams, soaps, etc. Recently it has found a use in the preparation of flavouring extracts, especially in the United States, where the prohibition laws have restricted the use of ethyl alcohol. A recent patent held by the Standard Oil Co. (1) of New York describes a stable foam containing a large portion of glycerin that is employed to prevent evaporation of gasoline, etc., from large oil storage tanks. It is also used in the tanning and leather industries, in foods, in the production of many pharmaceutical preparations such as glycero-phosphates, glyceryl borates, phenolates, tannates, etc. The so-called "Glycerylphosphoric acid" (glycero-phosphoric acid), obtained by heating glycerol with phosphoric acid (compare Power and Tutin, *Trans.*, 1905, **87**, 249), appears to be a mixture of α-glycerylphosphoric acid, $OH.CH_2.CH(OH).CH_2.O.PO_2.H_2$, and β-glycerylphosphoric acid, $(OH.CH_2)_2.CH.O.PO_3H_2$ (Tutin and Hann, *Trans.*, 1906, **89**, 1749). A somewhat differently constituted mixture of the same acids is obtained by the hydrolysis of lecithin, a complex compound of these acids with choline and the fatty acids, stearic acid and palmitic acid, occurring in the yolk of egg and in brain tissue. (For the estimation of glycerophosphates, see A. Astruc, *J. Pharm.*, 1898, (6), **7**, 5; A. Trillat, *ibid.*, 163; Imbert and Pages, *ibid.*, 378.)

Glycerol dissolves large quantities of arsenious oxide to form a compound of the formula $C_3H_5AsO_3$, glyceryl arsenite, which has been employed by calico-printers for fixing aniline colours. It is an amber-yellow, fatty substance, melting at 50° to a thick liquid, soluble in glycerol and in water, but decomposed by excess of the latter liquid.

When 3 parts of glycerol are heated to about 160° with 2 of boric acid, glyceryl borate, $C_3H_5BO_3$, is formed, which has been patented as a preservative agent under the name of "boroglyceride." Glycerin is used extensively as an ingredient in the namufacture of printer's rolls, printer's inks, etc.

Another interesting and promising field for the use of considerable quantities of glycerin is in the production of artificial resins. Several patents have been taken out. One of these, by Downs and Weisberg, Br. Pat. 173225, 1920, describes the method for the production of a resin by heating a polyhydric alcohol (such as glycerol) with a polybasic aliphatic acid or anhydride, such as fumaric, maleic, etc., to form first a sticky mass that solidifies on cooling to a fusible

solid, on further heating gives an infusible mass insoluble in acetone, and on still further heating results in the formation of a resin insoluble in acetone and other organic solvents, resistant to cold and boiling water and acids at ordinary temperature, but decomposed by caustic soda (hot).   The General Electric Co. (U. S.) have also a series of patents for making condensation products from glycerol and succinic and phthalic acids and anhydrides.

U. S. Pharmacopœia, 1915.—The specifications and tests for glycerin as given in the Pharm. of the U. S. (1915) are as follows:

A liquid obtained by the hydrolysis of vegetable or animal fats, or fixed oils, purified by distillation and containing not less than 95% of the trihydric alcohol $C_3H_5(OH)_3$ or $CH_2OH . CHOH-CH_2OH$ (92.06).

Glycerin is a clear, colourless liquid, of a thick syrupy consistence, having not more than a slight characteristic odour which is neither harsh nor disagreeable, sweet to the taste and producing a sensation of warmth in the mouth; when exposed to the air, it absorbs moisture.·

Glycerin is miscible with water or alcohol; insoluble in chloroform, ether, benzene, petroleum spirit, carbon disulphide or fixed or volatile oils

An aqueous solution of glycerin (1 in 20) is neutral to litmus.

Sp. gr. not below 1.249 at 25°.

Glycerin does not appreciably volatilise from weak aqueous solutions.   When of a strength of between 70 and 100%, it volatilises at boiling temperatures.

When a few drops of glycerin are heated with about 0.5 grm. of potassium hydrogen sulphate; pungent vapours of acrolein are evolved.

Glycerin is colourless when viewed transversely in a tube of colourless glass about 30 mm. in diameter, held in a vertical position.

Heat 50 grm. of glycerin in an open shallow, 100 c.c. porcelain or platinum dish until it ignites, then allow it to burn without further application of heat in a place free from draught; not more than 0.15% of carbonaceous and mineral residue remains.   Subject this residue to a low red heat until combustion is complete; not more than 0.007% of mineral ash remains.   This ash when dissolved in 10 c.c. of distilled water and titrated with N/100 silver nitrate, using potassium chromate T. S. as indicator, shows, in the original 50 grm. of glycerin,

not more than 0.001% of chlorides calculated as sodium chloride. Each c.c. of N/100 silver nitrate consumed corresponds to 0.0005846 grm. of NaCl.

Mix 5 c.c. of glycerin by vigorous shaking with an equal volume of sulphuric acid in a glass stoppered cylinder; the liquid does not become darker than yellow on standing 1 hour (*readily carbonisable impurities.*)

Mix 50 grm. of glycerin with 50 c.c. of freshly boiled distilled water and 5 c.c. of N/2 potassium hydroxide and boil the mixture for 5 minutes. When cold, it requires not less than 4 c.c. of N/2 hydrochloric acid for neutralisation, using phenolphthalein T. S. as indicator (*fatty acids* and *esters*).

An aqueous solution of glycerin (1 in 10) remains clear on the addition of calcium chloride T. S. (oxalic acid); another portion of the solution is not affected by barium chloride T. S. after acidification with a few drops of diluted hydrochloric acid (*sulphate*).

An aqueous solution of glycerin does not respond to the test for heavy metals.

An aqueous solution of glycerin meets the requirements of the test for arsenic.

A mixture of 5 c.c. of glycerin and 5 c.c. of an aqueous solution of potassium hydroxide (1 in 10) does not become yellow when kept for 5 minutes at 60° (*acrolein, glucose*), nor emit an odour of ammonia (*ammonium* compounds).

British Pharmacopœia, 1914.—The following are the requirements.

Glycerinum.—Sp. gr. 1.260. Neutral to litmus. An aqueous solution (1 in 10) yields no characteristic reaction for ammonium compounds, chlorides, or sulphates. Assumes when heated not more than a faint yellow but no pink coloration, and yields not more than a very slight charred residue and no odour of burnt sugar (absence of sugar), undergoes no darkening in colour when mixed with an equal volume of solution of ammonia and a few drops of solution of silver nitrate, the mixture being kept protected from light and the observations made after the lapse of 5 minutes (absence of *formic acid* and *acrolein*). Gently warmed with an equal volume of diluted sulphuric acid, the mixture being vigorously shaken, not more than a faint odour is noticeable (absence of *fatty acids*). Shaken with an equal volume of sulphuric acid, the mixture being kept cool, not more than a very slight straw coloration is produced (absence of *extraneous*

organic matter). A mixture of 10 c.c. of glycerin with 40 c.c. of water, 1 drop of solution of ammonia and 1 drop of solution of tannic acid assumes not more than a faint and transient pink or purple coloration (limit of *iron*). When tested for lead according to the quantitative test described in the B. P., Appendix V, but using 10 grm. in each Nessler glass, no difference is observed upon the addition of the solution of sodium sulphide to one of the solutions (absence of *lead*); when the foregoing test is repeated, but omitting the addition of solution of ammonia and of solution of potassium cyanide and adding to each solution 1 c.c. of diluted hydrochloric acid, no difference in colour is observed upon the addition of solution of hydrogen sulphide to one of the solutions (absence of *copper*). Arsenic limit 2 parts per million. No appreciable ash.

QUALITATIVE TESTS FOR GLYCERIN

If glycerol or solutions containing it are heated rapidly in an open vessel and especially in the presence of any salts, it burns with formation of acrolein. The penetrating odour of acrolein is very distinct and serves as the most characteristic test for the detection of small quantities of glycerol. For this test, it is best to mix the substance under examination with some dehydrating material such as potassium hydrogen sulphate, and on heating, acrolein is readily formed. The acrolein can be detected either by its odour or by leading the products of distillation into an ammoniacal solution of silver nitrate, producing a silver mirror. A solution of rosanilin that has been decolorised by sulphur dioxide (Schiff's reagent) is restored to its pink colour by acrolein. Grünhut (*weit. anal. Chem.*, 1899, 41) mixes the substance under examination with twice its weight of finely powdered potassium hydrogen sulphate in a test-tube or flask fitted with a stopper and bent glass tube. The mixture is heated on a sand bath and the gases are condensed in a test-tube kept in a freezing mixture. The condensate, if glycerol is present in the unknown liquid, will smell distinctly of acrolein. If to the condensate are added a few drops of alkaline ammoniacal silver nitrate solution, a silver mirror will be produced.

The following tests are less characteristic but may be used as qualifying the acrolein test. If 2 drops of concentrated glycerol are treated in a dry test-tube with 2 drops of melted phenol and 2

drops of strong sulphuric acid, and the mixture heated very carefully over a flame or bath to about 120°, a brownish-yellow mass will be produced which, after cooling, is soluble in water; on adding a few drops of ammonia to this aqueous solution, a carmine-red colour appears.

Reichl's test for minute quantities of glycerol is to boil the solution with the addition of a minute quantity of pyrogallol and a few drops of sulphuric acid, when a red colour will appear, which changes to violet red on addition of stannic chloride. None of these colour tests, however, are distinctive of glycerol. An excellent method of determining the presence of glycerol, even in a rather complex mass, is to distil a sample large enough so that a weighable amount of glycerol can be obtained. The method of distillation and a description of the equipment will be given under "Fermentation Glycerin."

Glycerol itself and in solution in water has high solvent properties. It dissolves many substances more easily than either water or ethyl alcohol. The following table contains a partial list of the solubilities of many substances in glycerol at 15°:[1]

100 parts of glycerol dissolve at 15°; 98 parts crystal sodium carbonate; 60 parts sodium borate; 50.5 parts potassium arsenate; 50.0 parts sodium arsenate; 50.0 parts zinc chloride; 48.8 parts tannic acid; 40.0 parts alum; 40.0 parts zinc iodide; 40.0 parts potassium iodide; 35.2 parts zinc sulphate; 32.0 parts potassium cyanide; 30.0 parts copper sulphate; 25.0 parts ferrous sulphate, 25.9 parts potassium bromide; 20.0 parts lead acetate; 20.0 parts ammonium carbonate; 20.0 parts arsenious acid; 20.0 parts arsenic acid; 20.0 parts ammonium chloride; 15.0 parts oxalic acid; 11.0 parts boric acid; 10.0 parts barium chloride; 10.0 parts copper acetate; 10.0 parts benzoic acid; 8.0 parts sodium bicarbonate; 7.5 parts mercuric chloride; 5.0 parts calcium sulphide; 3.7 parts potassium chloride; 3.5 parts potassium chlorate; 1.9 parts potassium iodate; 1.0 parts calcium sulphate; 0.1 parts sulphur; 0.25 parts phosphorus.

Crystals of glycerol are quite difficult to obtain, but are often found in shipments of glycerol that have been exposed for a long period of time to low temperatures. If a drum of glycerol is cooled below 17.0° and is seeded with a crystal of glycerol, it immediately starts to crystallise, but at a very slow rate, so that it is sometimes months before all the glycerol in the drum is in crystalline form. (The crystals are hard, gritty and deliquescent.) It is then exceedingly difficult to melt the glycerol on account of its poor heat conductivity. When cooled to −40°, glycerol forms a gum-like mass.

Glycerol is highly hygroscopic, absorbing as much as 20% of its weight of water when exposed to moist air. It is miscible with

[1] Merton, Industrial Organic Chemistry, p. 130.

water, alcohol and aniline in all proportions but is insoluble in chloro-
form, benzene, petroleum spirit, carbon disulphide. It is nearly
insoluble in ether, from which it separates alcohol and water. It is
soluble in a mixture of 2 volumes of absolute alcohol and 1 volume
of ether, a fact which may be employed to separate it from sugars,
gums, gelatin and certain salts. It is soluble in a mixture of equal
weights of chloroform and alcohol, and can be thus separated from
sugars, dextrin and gums, as these products are insoluble in this
mixture.

On mixing water with glycerol, a contraction of volume and an
increase in temperature takes place. The greatest increase in
temperature, 5°, is produced when 50 parts of glycerol by weight
are mixed with 42 parts of water. The greatest contraction in
volume equals 1.1% (Gerlach).

Glycerol, in certain cases, acts as an antiseptic, but it has recently
been shown that glycerol, in solutions containing as high as 50%
glycerol by weight, has, by the action of certain bacteria, been con-
verted to trimethylene glycol and other products. It acts as an
antiseptic, however, to most yeasts in dilutions as low as 12%. It
is said to yield normal butyl alcohol and 1.3 propanediol by schizo-
mycetic fermentation. On fermenting glycerol with different
organisms, butyric, lactic, and succinic acids, glycerose and dioxy-
acetone, and trimethyleneglycol are produced.

Glycerol removes ferric chloride, ferric thiocyanate, gold chloride
and some other salts from ether solutions on agitation with them. It
also prevents the precipitation from solution of many substances.
The precipitation of mercuric and chromic salts by ammonia and of
copper salts by alkalies is wholly or partially prevented by the presence
of glycerol. With alkaline earths and lead oxide, glycerol forms
compounds that are soluble in water and gives solutions that are not
decomposed by carbonic acid.

Glycerol reacts readily with the alkali, alkaline earth hydroxides
and lead oxide to form chemical compounds. Calcium, strontium
and barium hydrates are precipitated from such solutions by carbon
dioxide, but not quantitatively. In the presence of alkali hydrox-
ides, glycerol dissolves ferric oxide, cupric oxide and bismuth oxide,
attributed to the formation of soluble metallic glyceroxides. Many
glyceroxides have been prepared in the pure state such as the mono-,
di-, and tri-sodium; calcium, barium and mono-lead, and mixed

metallic glyceroxides, such as di-sodium manganese and mono-sodium copper oxide. Glycerol also forms complex compounds with many metallic salts, such as zinc sulphate, nickel sulphate, cobalt sulphate and copper sulphate. These compounds have been called glycerinates by Grün and Bockisch (*Ber.*, 1908, 3465).

On distillation, pure glycerol undergoes very slight decomposition under atmospheric pressures, but if it contains even traces of salts, it undergoes noticeable decomposition, giving rise to the production of acrolein, water and polyglycerides. Glycerol heated in the presence of potassium hydrogen sulphate or phosphorus pentoxide, is almost completely converted into acrolein and water. In the presence of small amounts of alkali, glycerol is readily polymerised at its b. p. to diglycerol and higher polymerisation products.

Glycerol yields a variety of oxidation products, according to the conditions under which it is treated. When carefully oxidised with dilute nitric acid, it is converted into glyceric acid: CH_2-$OHCHOHCH_2OH + O_2 = CH_2OHCHOHCOOH + H_2O$. With stronger nitric acid, it is converted into a mixture of glyceric, oxalic and carbonic acids. In the presence of ferrous sulphate, it is readily oxidised by an aqueous solution of hydrogen peroxide to glycerose. In the presence of sulphuric acid and potassium dichromate, it is oxidised completely to carbon dioxide and water. In the presence of alkaline permanganates, it is oxidised to oxalic acid and carbon dioxide. The last two reactions have been used extensively for the quantitative estimation of glycerol. Glycerin in the presence of mixtures of sulphuric and nitric acids is converted into trinitro-glycerin which is the main constituent entering into the production of dynamite, and many other explosives. Glycerin reacts readily with organic acids to produce esters. This fact is made use of in the quantitative estimation of glycerin in which triacetin is produced by treating the glycerin with anhydrous acetic acid under definite conditions. Mono- and di-acetins are also produced from glycerol by treatment with acetic acid. Concentrated hydrochloric acid reacts on glycerin in a manner similar to acetic acid and depending on the conditions, one or more atoms of chlorine are substituted for the hydroxyl groups yielding either mono-, di- or tri-glycerin chlorhydrins.

On heating glycerol with the theoretical amount of hydriodic acid, allyl iodide and propylene are formed. In the presence of

an excess of hydriodic acid, allyl iodide and propionic acid are formed with small quantities of propane. Zeisel and Fanto (*Zeit. Landw. Versusch. SW. in Österr.*, 1902, 1) have developed a method of estimating the amount of glycerol present by conversion into isopropyl iodide, using an excess of strong hydriodic acid. This method, however, has not found any great favour and is not in general use.

On electrolysing glycerol, using platinum anodes, McCay (*Amer. Chem. Jour.*, 1892, **15**, 656) found that glycerol is decomposed into carbon monoxide, carbon dioxide, acetic acid, glyceraldehyde and probably glyceric acid. Electrolysing in 5% sulphuric acid solutions, using lead anodes, formaldehyde is produced in considerable quantity.

Estimation of Glycerol.—A quantitative separation of glycerol from complex mixtures has not been worked out altogether satisfactorily. Solutions of glycerol cannot be concentrated at high temperatures without serious loss from volatilisation. The first step in the quantitative estimation of glycerol ordinarily consists in separating it from the other substances with which it is mixed or combined, so as to obtain it as pure as possible. This can be accomplished in most cases qualitatively in a satisfactory manner, but it often happens that evaporations are necessary steps in a quantitative estimation, and there is a loss of glycerol by volatilisation which renders results of little value for quantitative purposes. Proteins and some other foreign substances may be separated from a solution containing glycerol by adding a solution of basic lead acetate and removing the excess of lead from the filtered solution by hydrogen sulphide or other means. This method may be employed for the analysis of pharmaceutical preparations, such as "glycerol of tannic acid" and "glycerol of gallic acid," and is also used in the clarification of soap lyes for the estimation of their glycerol content.

Proteins and some other organic substances may be removed completely by treating the slightly alkaline solution with zinc chloride. The precipitate is filtered off and the filtrate rendered faintly acid, when a further precipitation will often occur. The last traces of zinc may be removed from the solution by potassium ferrocyanide, which is also a good precipitant of albumin.

Dilute glycerol may be further purified by evaporating the water at as low a temperature as possible, and treating the residue with absolute alcohol, a mixture of alcohol and ether or a mixture of

alcohol and chloroform, according to circumstances. Absolute alcohol readily dissolves glycerol, whilst many classes of salts (e. g., metallic sulphates, phosphates, tartrates, etc.) are insoluble. The alkali-metal chlorides are not completely separated by alcohol alone, but a mixture of equal volumes of absolute alcohol and dry ether leaves them undissolved. The same solvent serves to separate glycerol from sugar, but the use of a mixture of 2 volumes of absolute alcohol with one of chloroform is preferable. If the filtered solution be treated with about twice its volume of water, chloroform separates from the diluted alcohol, and often carries troublesome colouring matters with it.

Any process of estimating glycerol that involves the evaporation of an aqueous or alcoholic solution and isolation of the glycerol in substance is usually deficient in quantitative accuracy, as evaporation of glycerol towards the end of the concentration is difficult, and the loss from this cause is often considerable. Even absolute glycerol is sensibly volatile at 100°, the loss of weight varying with the mode of heating, the shape and material of the containing vessel, and the surface exposed.

The following figures, due to Nessler and Barth (*Zeit. anal. Chem.*, 1884, **23**, 323), show the rate of evaporation of glycerol under different conditions. The experiments were made with glycerol that had been heated for 6 hours over a water-bath at 100°, and then for 6 hours longer in an air-bath at 100°. In one series of experiments, the glycerol was exposed in a water-oven at 100° in a platinum dish 20 mm. high, 80 mm. diameter at the top and 60 mm. at the bottom; in the other, it was heated in a beaker of thin glass 40 mm. high and 48 mm. in diameter:

	PLATINUM DISH	GLASS BEAKER
1.0 grm. lost, in first 2 hours	46 mg.	36 mg.
1.0 grm. lost, in second 2 hours	29 mg.	14 mg.
1.0 grm. lost, in third 3 hours	21 mg.	5 mg.
Average for last 3 hours	7 mg.	1.7 mg.
0.5 grm. lost in first 2 hours	36 mg.	45 mg.
0.5 grm. lost in second 2 hours	28 mg.	11 mg.
0.5 grm. lost in third 3 hours	23 mg.	6 mg.
Average for last 3 hours	7.7 mg.	2 mg.

The following figures show the loss of weight when heated on an open water-bath kept briskly boiling:

	PLATINUM DISH	GLASS BEAKER
1.0 grm. lost, in 1 hour	37–39–29–30 mg.	30–18 mg.
0.5 grm. lost in 1 hour,	34–29–24–30 mg.	11– 2 mg.

Other experiments conducted in platinum and glass vessels of various diameters showed that the loss increased with the diameter of the vessel (*i. e.*, with the surface of glycerol exposed), and that the rate of evaporation was less in a vessel composed of a material of low heat conducting power.

The volatilisation of glycerol during the evaporation of an aqueous liquid may be prevented by adding an excess of lime, which forms a compound with it, but Clausnizer has shown (*Zeit. anal. Chem.*, 1881, **20**, 58) that from the product the glycerol cannot be dissolved by absolute alcohol. If hydrated alcohol is employed, alkalies resulting from the action of the lime on phosphates may pass into the alcoholic liquid, and carry with them substances not otherwise soluble. Even if excess of lime be avoided, the glycerol cannot be extracted completely from the residue by *cold* alcohol or ether-alcohol.

General Methods for the Estimation of Glycerol

It will be convenient first to consider the general methods used in estimating glycerol, and then to deal later with the application of these methods to special cases, as, for example, to soap lyes or commercial forms of glycerin.

Chemical Methods.   A. Volumetric

1. *Permanganate Oxidation Process.*—This is best carried out by Benedikt and Zsigmondy's modification (*Chem. Zeit.*, 1885, **9**, 975) of Wanklyn and Fox's method. 0.2 to 0.3 grm. of the concentrated glycerin (or a quantity of dilute glycerin corresponding to this amount and calculated approximately from the sp. gr. of the sample) is mixed with 250 c.c. of water in a large flask, 10 grm. of solid potassium hydroxide added, and a 5% solution of potassium permanganate run in at the ordinary temperature until the liquid ceases to be green and becomes blue or black in colour. Finely powdered potassium permanganate can be used in place of its solution. The mixture is then boiled, when hydrated manganese dioxide is precipitated and the solution becomes red. A solution of sulphurous acid or of sodium sulphite is then cautiously added, *drop by drop*, until the liquid just becomes colourless, and the solution is then

filtered through a filter sufficiently large to take at least half the liquid at one time. The precipitate is thoroughly washed with hot water. The last washings sometimes become turbid, owing to the formation of manganese hydroxide, but the turbidity disappears when acetic acid is added to render the solution acid before precipitating with calcium chloride. The precipitation is effected by adding 10 c.c. of a 10% solution of calcium chloride to the boiling liquid. The calcium oxalate is left for some time in order to complete the precipitation, collected on a filter, and, after washing thoroughly with hot water, is transferred to a flask and titrated with N/10 permanganate in the usual way.

1 c.c. N/10 permanganate (corresponding with 0.0045 grm. $H_2C_2O_4$) = 0.0046 grm. glycerol.

In the permanganate method, excess of sulphurous acid must be carefully avoided, as in presence of hydrated manganese dioxide it destroys oxalic acid. Allen suggested the use of sodium sulphite instead of sulphurous acid, but on adding acetic acid before precipitation, sulphurous acid is liberated, which may cause the loss of oxalic acid if any small quantity of manganese dioxide has passed through the filter. There is, moreover, the danger of calcium sulphite being precipitated with the calcium oxalate.

Herbig has, therefore, suggested the use of hydrogen peroxide in place of sulphite, and employs a smaller quantity of potassium permanganate. Mangold (*J. Soc. Chem. Ind.*, 1891, 10, 803) reports favourably on the method, and recommends the following procedure: To 0.2–0.4 grm. of glycerol, dissolved in 300 c.c. of water containing 10 grm. potassium hydroxide, as much of a solution containing 5% potassium permanganate is added as will correspond with 1.5 times the theoretical quantity of glycerol (for 1 part glycerol 6.87 parts of potassium permanganate). The operation is conducted in the cold and the solution must be agitated on adding the permanganate. After standing for about half an hour at ordinary temperature, sufficient hydrogen peroxide is added to completely decolourise the liquid. The whole is now made up to 1000 c.c., well shaken, and 500 c.c. filtered through a dry filter. After heating the filtrate for half an hour to destroy all hydrogen peroxide, and cooling to about 60°, sulphuric acid is added and the liquid titrated with permanganate. Heating after addition of the permanganate is superfluous. A number of results of analysis by the above method are given

which prove it to be accurate even in the presence of 90% of butyric acid.

2. *Oxidation with Potassium Dichromate (Hehner's Method).*—The solutions required are as follows:

1. Potassium dichromate solution containing in 1000 c.c. about 74.56 grm. of potassium dichromate and 150 c.c. of strong sulphuric acid. The exact oxidising value of the solution must be ascertained by titration with solutions of known ferrous iron content.

2. Ferrous ammonium sulphate solution containing about 240 grm. in 1000 c.c.

3. Potassium dichromate solution $\frac{1}{10}$ the strength of No. 1. The ferrous solution is exactly standardised against the stronger dichromate solution, 1 c.c. of which should correspond to 0.01 grm. glycerol.

With pure glycerol, the oxidation is quantitative. Crude glycerins must be treated as follows: For the removal of chlorine and of aldehydic compounds, some silver oxide is added to a weighed quantity of the sample (about 1.5 grm.), which is placed in a 100 c.c. flask. After slight dilution, the sample is allowed to stand with the silver oxide for about 10 minutes. Basic lead acetate is then added in slight excess, the bulk of the fluid made up to 100 c.c., and a portion filtered through a dry filter; 25 c.c. of the filtrate are placed in a beaker, previously well cleaned with sulphuric acid and potassium dichromate to remove all traces of fat, from 40 to 50 c.c. of the standard dichromate are added, accurately measured, and about 15 c.c. of strong sulphuric acid, and the beaker, covered with a watch-glass, is heated for 2 hours in boiling water. After that time, the excess of dichromate is titrated back with ferrous ammonium sulphate solution.

As the dichromate solution is necessarily a somewhat strong one, the measurements must be made with the greatest care, attention being paid to the temperature. Check results are easily obtained and the method is rapid. It is open to the objection that by the use of lead acetate the impurities may not be perfectly removed, any left being oxidised and counted as glycerol. However, all higher fatty acids and all resin acids, as well as albuminoids, sulphides, thiocyantes, and aldehydes, are completely removed, and the lower fatty acids, such as acetic and butyric acid, are not attacked by chromic acid. Hehner allows for variation of temperature by assum-

ing an expansion of the dichromate solution of 0.05% per 1°. This value he found for a dichromate solution, prepared as above. Lewkowitsch avoids a temperature correction by maintaining the solutions at the normal temperature during titration by surrounding them with a large water-jacket.

Several alterations in the procedure have been suggested by Richardson and Jaffé (*J. Soc. Chem. Ind.*, 1898, 17, 330), a stronger solution of dichromate being used and the time of boiling much reduced.

A modified dichromate method for the estimation of glycerol and trimethylene glycol in crude and dynamite grade glycerins as well as for glycerol C.P. has been developed by Fachini and Somazzi. (*Bolletino del Industria degli Olii e dei Grassi*, Oct., 1923; *Chem. Trade Jour.* and *Chem. Eng.*, 73, 127, 703.) Crude glycerin is purified by treatment with basic lead acetate prepared as follows:

A 10% solution of lead acetate is boiled with an excess of litharge for one hour. The hot solution is filtered under conditions whereby contamination with carbon dioxide is avoided. Even if the basic acetate solution deposits a precipitate after standing some time, its efficiency is not reduced. This solution precipitates the proteins and albuminoids by coagulation, the organic acids as insoluble salts and the alkaline carbonates as insoluble carbonates. By cooling the purified mixture for one hour to 0°, practically all of the chlorides are removed as lead chloride. The final traces of chlorides are removed by a slight excess of silver carbonate. The presence of a slight excess of basic lead acetate will not affect the accuracy of the resultas as lead cetate below 120° is not oxidized by chromic acid.

About 20 grm. of soap lye or 2 grm. of 80% crude gylcerin are weighed accurately into a 250 c.c. graduated flask. Water is added to bring the volume to about 50 c.c. and 5 c.c. of the basic lead acetate as prepared above is added. The flask is well shaken and the mixture left to settle for 30 minutes. A small additional quantity of basic lead acetate solution is added cautiously and if an additional precipitate is formed, the analysis is started over again using a smaller weight of sample. If no further precipitate is formed, the contents of the flask are made up to 250 c.c. at 15° and are then cooled to 0° for one hour. The liquid is then filtered through a dry cool filter and is then brought to a temperature of

15°; 25 c.c. are pipetted to an oxidation flask and the analysis is continued as for pure glycerin.

The oxidation flask is fitted with a rubber stopper with three holes, through one of which is inserted a small tap funnel; through another, a tube for the entrance of air, reaching to the bottom of the flask; and through the third an exit tube for the air and carbonic acid. This exit tube is connected to a small water jacketed condenser and this in turn to a U-tube containing small glass beads moistened with concentrated sulphuric acid and then to three other U-tubes filled with lime-free anhydrous calcium chloride.

The absorption bulb for the carbon dioxide (the ordinary potash absorption bulb used in combustion work) is weighed and is connected to the last of the three calcium chloride tubes above and to this absorption tube is connected another calcium tube which has been weighed and which is in turn protected by an additional calcium tube to take up any moisture from the atmosphere.

For each gram of glycerin present in the sample there is added 1.5 grm. approximately of pure potassium dichromate accurately weighed (1 grm. of glycerol equals 0.4564 grm. potassium dichromate). The flask is connected to the apparatus and about 12 c.c. of 66° Be. sulphuric acid is added slowly through the tap funnel in such a way as to eliminate any sudden formation of carbon dioxide. It is best to have a slight air pressure on the tap funnel and this can be done using a slight air pressure through a rubber tube which can be closed with a pinch cock. A small residue of acid should be left in the funnel. After the acid has entered the flask and the stream of carbon dioxide has almost ceased, the flask is heated slowly in a beaker of water and the water is kept boiling for two hours. Air is now admitted through the proper tube with the heat still on and the carbon dioxide is swept out of the flask. After 15 minutes the water bath is allowed to cool and for an additional 30 minutes the air flows through the equipment. The absorption tube is now disconnected and weighed with its single calcium chloride tube to determine the amount of carbon dioxide produced from the glycerol in the sample as well as any trimethylene glycol which may have been present.

The contents of the flask are transferred quantitatively into a graduated 500 c.c. flask and made up to the mark with distilled water at 15°. 50 c.c. are pipetted into a glass beaker and 2 grm.

of crystallized potassium iodide and 25 c.c. of 20% hydrochloric acid are added and sufficient water to bring the volume to about 500 c.c. The excess of dichromate is determined by titration with normal sodium thiosulphate solution, using starch as the indicator. This gives the actual amount of potassium dichromate used in producing the carbon dioxide weighed above. The reactions involved in the oxidation of glycerol and trimethylene glycol follow:

$$C_3H_5(OH)_3 + 7O = 3CO_2 + 4H_2O$$
$$C_3H_6(OH)_2 + 7O = 3CO_2 + 4H_2O$$
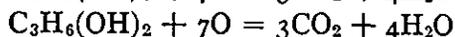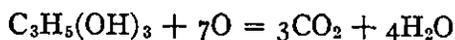
1 grm. CO_2 equals 0.57624 grm. trimethylene glycol.

1 grm. CO_2 equals 0.69745 grm. glycerol.

1 grm. glycerol equals 7.4564 grm. potassium dichromate.

1 grm. dichromate in excess equals 0.7748 grm. trimethylene glycol.

X is amount glycerol present in sample.

Y is amount of trimethylene glycol in sample.

B is weight of potassium dichromate reduced.

D is theoretical quantity of dichromate calculated from the amount of CO_2 produced.

C is the weight of CO_2 produced.

G is the weight of glycerol calculated from the CO_2 produced.

G equals $C \times 0.69745$.

B equals $G \times 7.4564$.

Y equals $(B - D) \times 0.7748$.

X equals $G - \dfrac{Y \times 92.064}{76.064}$

The authors claim that this method is more accurate that the regular dichromate method and that it gives more consistent results than the acetin method. It is too new to have the backing of a large number of tests by different analysts but it looks very promising.

3. *Acetin Method.*—The *acetin method* of Benedikt and Cantor (*J. Soc. Chem. Ind.*, 1888, **7**, 696) depends upon the formation of triacetin (glyceryl triacetate) when glycerol is heated with acetic anhydride. The triacetin is then saponified with sodium hydroxide solution, and the amount of the latter used gives a measure of the glycerol. Lewkowitsch has shown that the method gives closely concordant results in the case of moderately pure "crude glycerins," and recommends its adoption in all cases in which the glycerol is

first isolated in a fairly pure state, as in its estimation in fats and oils (*v. infra*) (Lewkowitsch, *Chem. Zeit.*, 1889, **13,** 93, 191, 559; Hehner, *J. Soc. Chem. Ind.*, 1889, **8,** 6).

Solutions required:

1. $N/2$ or $N/1$ hydrochloric acid (accurately standardised).

2. Sodium hydroxide solution, 20 grm. sodium hydroxide per 1000 c.c. Its strength need not be accurately known.

3. A 10% sodium hydroxide solution.

Solutions 2 and 3 must be kept free from the access of carbon dioxide.

Procedure.—1 to 1.5 grm. of the crude glycerol, 7 or 8 grm. of acetic anhydride, and about 3 grm. of anhydrous sodium acetate (previously dried in an oven) are heated from 1 to 1.5 hours in a reflux apparatus. The mixture is allowed to cool, 50 c.c. of water are added, and the heating is continued (still with the condenser, as triacetin is volatile in a current of steam) until it begins to boil. When the oily deposit at the bottom of the flask is dissolved, the liquid is filtered from a white flocculent precipitate, which contains most of the impurities of the crude glycerol, allowed to cool, phenolphthalein added, and dilute sodium hydroxide (No. 2 solution) run in until neutrality is obtained. Care must be taken not to pass the neutral point, as triacetin is easily saponified.

During the operation, the solution must be agitated continually, so that the acid may not be in excess locally any longer than is unavoidable. The point of neutrality is reached when the solution becomes reddish-yellow. It must not be allowed to become pink. The estimation is inaccurate if the solution is more than neutralised even for the shortest time. 25 c.c. of the strong sodium hydroxide are now added from a pipette. The mixture is then heated for 15 minutes and the excess of alkali titrated back with N or $N/2$ hydrochloric acid. The strength of the alkali used is ascertained at the same time by titrating another 25 c.c., measured with the same pipette. The difference between the titrations gives the amount of alkali consumed in saponifying the acetin, and from this, the quantity of glycerol is calculated.

B. Gravimetric Methods.—I. *Zeisel and Fanto's* method (*Zeit. landw. Versuchswesen Oest.*, 1902, **5,** 729). This method is based on the fact that when glycerol is boiled with an excess of hydriodic acid (sp. gr. 1.7, b. p. 127°) it is converted quantitatively into *iso*propyl

iodide, which can be estimated by passing it into a solution of silver nitrate in absolute alcohol, and weighing the silver iodide formed.

$$C_3H_5(OH)_3 + 5HI = C_3H_7I + 3H_2O + 2I_2$$
$$C_3H_7I + AgNO_3 = AgI + C_3H_7NO_3.$$
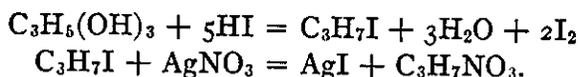
Materials Required.—1. It is advisable to keep a stock of hydriodic acid of sp. gr. 1.9, containing 68% by weight of HI; this acid can then be suitably diluted with water (3 vols. hydriodic acid to 1 vol. water), so that the acid acting on the glycerin is of sp. gr. 1.7. Is must be free from sulphur and, in a blank experiment carried out at described below, give no precipitate of silver iodide in the alcoholic silver nitrate solution.

2. 40 grm. of pure silver nitrate are dissolved in 100 c.c. of water and made up to 1 litre with commercial absolute alcohol; after 24 hours the solution is filtered. The solution must be kept in the dark.

3. Red phosphorus. This must be washed with carbon disulphide, ether, alcohol, and water, and dried in the air.

The apparatus used (see Fig. 16) is a modification of the well-known Zeisel apparatus for the estimation of methoxyl. The flask *a*, capacity 40 c.c., has a side tube attached as shown, which serves to pass carbon dioxide through the apparatus. Through the condenser, *b*, circulates water maintained at 60° ± 10° by means of an Ehmann's heating arrangement, *g*; the tube of the condenser is ground into the neck of flask, *a*, and the joint held in position by means of the small springs shown. The bulb, *c*, immersed in water at 60–70°, serves to count the bubbles of gas and is filled to about a third with a thin mixture of red phosphorus and water (a solution of potassium arsenite can be used in place of phosphorus, but the latter is preferable). The Erlenmeyer flasks, *e* and *f*, the larger with a mark showing 45 c.c., the smaller with a mark at 5 c.c., contain the clear alcoholic silver nitrate up to the marks aforesaid. The glycerin is weighed into *a*, the quantity taken being such as to give not more than 0.4 grm. of silver iodide. A fragment of pumice is introduced into *a*, 15 c.c. of the hydriodic acid (sp. gr. 1.7) added, and the flask immediately connected with the condenser and with a carbon dioxide apparatus supplying carbon dioxide, which must be washed by passing it through dilute sodium carbonate solution. The carbon dioxide is passed at the rate of about 3 bubbles per second. The boiling flask is immersed in a glycerin bath so that the levels

inside and outside of the flask are the same; the bath is heated by a small flame so as to keep the hydriodic acid boiling gently during the whole operation. When the liquid above the precipitated silver iodide becomes clear and the operation is complete, the contents of
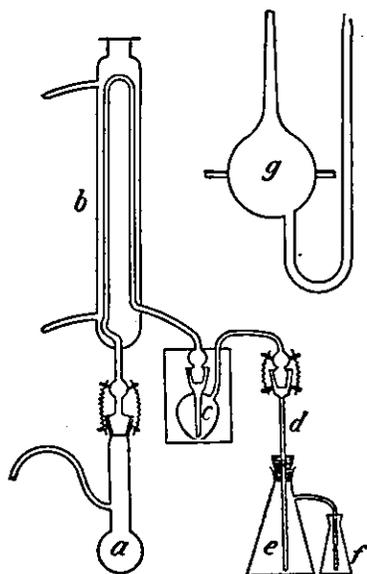
the Erlenmeyer flasks are transferred to a large beaker; water is added so as to make a volume of 450 c.c., and then 10 to 15 drops of dilute nitric acid; the liquid is then heated in a water-bath so as to make the silver iodide readily filterable, and, on cooling, the precipitate is collected and weighed. The weight of silver iodide $\times$ 0.3920 gives the weight of glycerol present. The time of distillation varies from 2 to 4 hours; the completion of the operation is controlled by substituting for flask e a flask containing fresh silver nitrate solution and again distilling.

Lewkowitsch (*Analyst*, 1903, 28, 108) states that the above method does not give accurate results for crude glycerin on account of the presence of impurities in the latter. Other workers, however, highly commend it (Schuch, *Ztsch. für landw. Versuchswesen Oest.*, 1904, 7, 111; Hertmann, *Beiträge z. chem. Physiologie u. Pathologie*, 5, 422). From a very detailed comparative study of the different methods of estimating glycerol, Schuch (*vide infra*) has concluded that the Zeisel-Fanto method is the most accurate under all conditions of all the methods yet devised for estimating glycerol.

Instead of the special apparatus described by Zeisel and Fanto, a modification of Perkin's form of the ordinary Zeisel apparatus would probably prove more simple in use.

II. *Shukoff and Schestakoff's Method* (*Zeit. angew. Chem.*, 1905, 18, 294).—This is a direct method based on the fact that on mixing a glycerol solution with sodium sulphate dehydrated by ignition and extracting the mass with acetone the whole of the glycerol passes into solution. The method is tedious, and in many cases gives values as much as 1% in error (compare Landsberger, *Chem. Rev.*

Fett Harz. Ind., 1905, **12**, 150; Dynamitfabrik Schlebusch, *Zeit. angew. Chem.*, 1905, **18**, 1656). It will be described in more detail under fermentation glycerin.

Specific Gravity.—The most widely used method of estimating the strength of glycerol solutions is by specific gravity determinations. Several investigators have made studies of this method. The most important tables developed are those by Gerlach[1], Nichol,[2] Lenz,[3] Strohmer,[4] Fabian, Metz, Schey[5] and Skalucit,[6] Mendelejeff.[7] The tables of Lenz, Strohmer, Gerlach and Nicol are given below:

SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS OF PURE GLYCEROL
(LEWKOWITSCH)

Glycerol %	Lenz Sp. gr. at 12–14°/12°	Strohmer Sp. gr. at 17.5°/17.5°	Gerlach Sp. gr. at 15°/15°	Gerlach Sp. gr. at 20°/20°	Nicol Sp. gr. at 20°/20°
100	1.2691	1.262	1.2653	1.2620	1.26348
99	1.2664	1.259	1.2628	1.2594	1.26091
98	1.2637	1.257	1.2602	1.2568	1.25832
97	1.2610	1.254	1.2577	1.2542	1.25572
96	1.2584	1.252	1.2552	1.2516	1.25312
95	1.2557	1.249	1.2526	1.2490	1.25052
94	1.2531	1.246	1.2501	1.2464	1.24790
93	1.2504	1.244	1.2476	1.2438	1.24526
92	1.2478	1.241	1.2451	1.2412	1.24259
91	1.2451	1.239	1.2425	1.2386	1.23900
90	1.2425	1.236	1.2400	1.2360	1.23720
89	1.2398	1.233	1.2373	1.2333	1.23449
88	1.2372	1.231	1.2346	1.2306	1.23178
87	1.2345	1.228	1.2319	1.2279	1.22907
86	1.2318	1.226	1.2292	1.2252	1.22636
85	1.2292	1.223	1.2265	1.2225	1.22365
84	1.2265	1.220	1.2238	1.2198	1.22094
83	1.2238	1.218	1.2211	1.2171	1.21823
82	1.2212	1.215	1.2184	1.2144	1.21552
81	1.2185	1.213	1.2157	1.2117	1.21281
80	1.2159	1.210	1.2130	1.2090	1.21010
79	1.2122	1.207	1.2102	1.2063	1.20739
78	1.2106	1.204	1.2074	1.2036	1.20468
77	1.2079	1.202	1.2046	1.2009	1.20197
76	1.2042	1.199	1.2018	1.1982	1.19925
75	1.2016	1.196	1.1990	1.1955	1.19653
74	1.1999	1.193	1.1962	1.1928	1.19381
73	1.1973	1.190	1.1934	1.1901	1.19109
72	1.1945	1.188	1.1906	1.1874	1.18837

[1] *Chem. Indus.*, 1884, **7**, 277. *Zeit. anal. Chem.*, **24**, 109.
[2] *Pharm. Jour. Trans.* (3), 1887, **18**, 302.
[3] *Zeit. anal. Chem.*, 1880, **19**, 302.
[4] *Monat. f. Chem.*, 5, 61. *Zeit. anal. Chem.*, **24**, 107.
[5] *Recueil des travaux chem. des Pays Bas*, 18, 181.
[6] *Pharm. Jour. Trans.*, 1887, **8**, 297.
[7] *Vergl. Benedikt-Ulzer, Analyse der Fette und Wachsarten*, Aufl. 1898, **5**, S-450.

SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS OF PURE GLYCEROL (LEWKOWITSCH).—(*Continued*)

Glycerol %	Lenz Sp. gr. at 12–14°/12°	Strohmer Sp. gr. at 17.5°/17.5°	Gerlach Sp. gr. at 15°/15°	Gerlach Sp. gr. at 20°/20°	Nicol Sp. gr. at 20°/20°
71	1.1918	1.185	1.1878	1.1847	1.18565
70	1.1889	1.182	1.1850	1.1820	1.18293
69	1.1858	1.179	......	......	1.18020
68	1.1826	1.176	......	......	1.17747
67	1.1795	1.173	......	......	1.17474
66	1.1764	1.170	......	......	1.17201
65	1.1733	1.167	1.1711	1.1685	1.16928
64	1.1702	1.163	......	......	1.16654
63	1.1671	1.160	......	......	1.16380
62	1.1640	1.157	......	......	1.16107
61	1.1610	1.154	......	......	1.15834
60	1.1582	1.151	1.1570	1.1550	1.15561
59	1.1556	1.149	......	......	1.15288
58	1.1530	1.146	......	......	1.15015
57	1.1505	1.144	......	......	1.14742
56	1.1480	1.142	......	......	1.14469
55	1.1455	1.140	1.1430	1.1415	1.14196
54	1.1430	1.137	......	......	1.13923
53	1.1403	1.135	......	......	1.13650
52	1.1375	1.133	......	......	1.13377
51	1.1348	1.130	......	......	1.13104
50	1.1320	1.128	1.1290	1.1280	1.12831
45	1.1183	.....	1.1155	1.1145	1.11469
40	1.1045	.....	1.1020	1.0110	1.10118
35	1.0907	.....	1.0885	1.0875	1.08786
30	1.0771	.....	1.0750	1.0740	1.07469
25	1.0635	.....	1.0620	1.0610	1.06166
20	1.0498	.....	1.0490	1.0480	1.04884
15	1.0374	.....	......	......	1.03622
10	1.0245	.....	1.0245	1.0235	1.02391
5	1.0123	.....	......	......	1.01184
0	1.0000	.....	1.0000	1.0000	1.00000

The purity of the glycerol used by Gerlach was established by the constant b. p. of 290° at 760 mm.; Lenz determined the purity by elementary analysis, Strohmer used crystals of glycerol from which adhering liquor had been removed by pressure, and Nicol used glycerol with a constant boiling temperature of 210° at 50 mm. pressure, which he also analysed for its elementary composition.

These values for the sp. gr. of pure glycerol at 15°/15° range from 1.262 (Strohmer) to 1.269 (Lenz). For the higher concentrations

the sp. gr. alters according to these determinations by 0.0025 to 0.0030 for each 1% of water. Grün and Wirth (*w. angew. Chem.*, 1919, 32, 59; *J. Sci. Chem. Ind.*, 1919, 38, 295-A) found by twice distilling glycerol in vacuum and then drying for 5 months over P_2O_5 in vacuum that the sp. gr. at $15°/15°$ was 1.2653 ± 0.0001. This value agrees with that given by Gerlach. Gerlach's determinations, on the other hand, were not carried out with the best type of equipment. He made use of the plummet or Westphal type of sp. gr. balance, a means that is impossible of the accuracy to be had using a proper type of pyknometer such as is used almost universally at present and with which accurate results to the fourth decimal place are possible. The type of pyknometer as shown on page 668, for use in the determination of the sp. gr. of dynamite glycerin, has been found to be very accurate. In making sp. gr. determinations by use of the pyknometer, the glycerin should be very carefully freed from all air bubbles, after having been thoroughly mixed, by allowing the sample to stand at room temperature until perfectly clear. · A pyknometer that has been carefully calibrated is then filled with the glycerin and a glass tube fitted with a rubber connection is fastened over the expansion outlet neck. The thermometer is inserted so as to avoid any air bubbles, and the excess glycerin rises in the tube, due to the space occupied by the thermometer. The pyknometer is now brought to constant temperature in the water-bath, and after the thermometer inside of the glycerin reads the same as that in the water-bath, it is held for some 10 minutes to insure the uniformity of temperature throughout all the glycerin. It is then taken out of the bath, the rubber tube is disconnected and the ground surface of the outlet neck is wiped clean with a dry finger. The glass cap is then put on and the outside of the pyknometer is wiped clean and dry. For experimentally accurate work, it is necessary to take into consideration the displacement of the air by the pyknometer and also by the brass weights used in the balance. This, however, is not necessary for routine work. The determination may be made exact to the fourth decimal if the weights are reduced to vacuum. Complicated calculation is avoided by ascertaining once for all the necessary corrections for the pyknometer when filled with water. Suppose the weight p has been found in air, then the corrected weight P will be:

$$P = p + pR$$

For brass weights, the correction R for the sp. gr. likely to occur is found from the following table:

Sp. gr.	Correction (R)	Sp. gr.	Correction (R)
1.00	0.00106	1.10	0.00095
1.02	0.00103	1.15	0.00090
1.04	0.00101	1.20	0.00086
1.06	0.00099	1.25	0.00082
1.08	0.00097	1.30	0.00078

Gerlach (*Chem. Ind.*, 1884, 277) made actual determinations on 100%, 90%, 80% glycerol, etc., every 10%, and interpolated the in-between figures. His figures are probably accurate to the third place. The fourth decimal figure for each 10% difference is o, excepting for 100% glycerol and 10% glycerol, where this figure is 5. For the percentages between 80 and 100, he interpolated the results to the fourth decimal place. This gives the table an apparent accuracy, which was not determined by actual experimental work. In spite of this, the table gives figures that are apparently close to the true ones. A. C. Langmuir, using a very carefully purified sample of glycerol and with thermometers and weights calibrated by the U. S. Bureau of Standards, found a sp. gr. for 100% glycerol at 60° F. of 1.2653 and for 95% glycerol at 60° F. 1.2524, which would correspond to 1.2655 and 1.2525 at 15° respectively. Gerlach's table at 20° is unquestionably wrong. His figures more nearly correspond with the true sp. gr. for glyercol solutions as determined at 25°.

Gerlach (*Zeit. anal. Chem.*, 24, 111) determined the coefficient of expansion of glycerol at various temperatures. Hehner (*J. S. C. I.* 1889, 8, 8) states that this amounts to 0.00058 for each degree centigrade in the neighborhood of 15.5°. It can be calculated from the results of Gerlach's observations that the value of this factor varies with the temperatures according to the following table:

TEMPERATURE, ° C.	COEFFICIENT OF EXPANSION
5.0	0.0057
12.5	0.000587
20.0	0.00060
30.0	0.000619

From these figures, it can be seen that it is necessary to use a factor corresponding closely to the temperature at which the specific

gravities are made. Comey and Backus (*J. Ind. Eng. Chem.*, 1910, **2**, 11) have made accurate determinations of this factor, and their figures have been accepted in general as being standard. The average coefficients of expansion from their tables are as follows:

TEMPERATURE, ° C.	COEFFICIENT OF EXPANSION
20°	0.000612
25°	0.000617
30°	0.000622

The formula deduced by them for calculating the sp. gr. at the higher concentrations at a given temperature to another temperature is:

$$\text{Sp. gr. } \frac{t}{t'} = \frac{w}{c} \cdot \frac{1}{1 + a(t' - t)} + B\,(t' - t)$$

in which t is the temperature at which the gravity is desired, say $\frac{15.5}{15.5}$, w is the weight of glycerin at t' temperature, c is capacity pyknometer in grams of water at t temperature, a is thermal coefficient of expansion of glass and was taken as 0.000025 per 1°, B = thermal coefficient of expansion of glycerol, t' is observed temperature. Gravity determinations were made on the same lot of glycerol at different temperatures with these corrections applied and, when calculated to the same temperature, the corrected gravities were alike. A table showing the influence of temperature on sp. gr. of glycerol solutions of strengths 5% to 50% is given below:

INFLUENCE OF TEMPERATURE ON SP. GR. FOR GLYCEROL

% Glycerol	Temperature, °							
	15/15	20/20	25/25	30/30	35/35	40/40	45/45	50/50
5	1.0122	1.0117	1.0113	1.0108	1.0103	1.0098	1.0092	1.0087
10	1.0245	1.0237	1.0233	1.0227	1.0221	1.0215	1.0209	1.0203
15	1.0370	1.0358	1.0354	1.0350	1.0346	1.0340	1.0334	1.0328
20	1.0495	1.0489	1.0481	1.0474	1.0467	1.0460	1.0453	1.0446
25	1.0631	1.0610	1.0605	1.0600	1.0593	1.0586	0.0579	1.0572
30	1.0753	1.0747	1.0737	1.0729	1.0721	1.0713	1.0705	1.0697
35	1.0885	1.0889	1.0860	1.0861	1.0853	1.0845	1.0837	1.0829
40	1.1023	1.1017	1.0905	1.0896	1.0887	1.0878	1.0869	1.0860
45	1.1156	1.1150	1.1142	1.1134	1.1125	1.1116	1.1106	1.1095
50	1.1290	1.1283	1.1274	1.1263	1.1253	1.1240	1.1229	1.1220

The percentages of glycerol in water solution, together with the gravities and the grams of glycerol per 100 c.c., and also c.c. of pure glycerol per 100 c.c. of the various strength solutions is given in the following table prepared by E. Lewis, *J. Soc. Chem. Ind.*, 1922, 97T:

Sp.gr. 20°/20°	Grm. glycerol in 100 grm.	C.c. glycerol in 100 grm.	Grm. glycerol in 100 c.c.	C.c. glycerol in 100 c.c.
1.0117	5.00	4.94	5.06	4.09
1.0237	10.00	9.76	10.24	8.10
1.0358	15.00	14.48	15.54	12.30
1.0489	20.00	19.06	20.98	16.60
1.0610	25.00	23.56	26.53	21.00
1.0747	30.00	27.91	32.24	25.42
1.0880	35.00	32.17	38.08	30.05
1.1017	40.00	36.31	44.07	34.89
1.1150	45.00	40.36	50.17	39.72
1.1283	50.00	44.31	56.41	44.56
1.1418	55.00	48.17	62.80	49.72
1.1550	60.00	51.95	69.30	54.86
1.1691	65.00	55.59	75.99	60.16
1.1827	70.00	59.18	82.79	65.54
1.1964	75.00	62.69	89.73	71.04
1.2091	80.00	66.16	96.73	78.58
1.2237	85.00	69.46	104.01	82.35
1.2368	90.00	72.77	111.31	88.13
1.2506	95.00	75.96	118.81	94.06
1.2631	100.00	79.17	126.31	100.00

Other determinations are given in Marie, Vols. I, and III.

Kailan (*Z. anal Chem.* 51, 83) has determined the vapour tension of pure glycerol at various temperatures:

TEMPERATURE, °	V. P. MM. HG
166–166.5	9
170.5–174.5	12
171	13
172.5	14
176–177	15
182	20
185	23
190	28
192	30
193	32

Kailan's determinations are in close agreement with Richardson's as given below:

TEMPERATURE, °	V. P. MM. HG
118.4	0.238
130.8	1.891
141.0	2.588
151.9	4.083
161.2	6.527
171.0	12.694
183.2	20.461
195.3	34.369
201.3	45.61
211.5	65.61
220.3	100.813
229.5	137.95
241.8	201.225
250.3	281.872
260.4	385.326

The refractive index of glycerol is an important check on its purity. It has been determined by Lenz to be 1.4758 at 12.5° to 12.8° for pure glycerol. He found the following indices of refraction at 12.5° to 12.8° for aqueous solutions of pure glycerol:

TABLES OF THE REFRACTIVE INDEX, N_D AT 12.5 TO 12.8°, OF AQUEOUS SOLUTIONS OF GLYCEROL (LENZ)

% anhydrous glycerol	N_D	% anhydrous glycerol	N_D	% anhydrous glycerol	N_D
100	1.4758	66	1.4249	32	1.3745
99	1.4744	65	1.4231	31	1.3732
98	1.4729	64	1.4213	30	1.3719
97	1.4715	63	1.4195	29	1.3706
96	1.4700	62	1.4176	28	1.3692
95	1.4686	61	1.4158	27	1.3679
94	1.4671	60	1.4140	26	1.3666
93	1.4657	59	1.4126	25	1.3652
92	1.4642	58	1.4114	24	1.3639
91	1.4628	57	1.4102	23	1.3626
90	1.4613	56	1.4091	22	1.3612
89	1.4598	55	1.4079	21	1.3599
88	1.4584	54	1.4065	20	1.3585
87	1.4569	53	1.4051	19	1.3572
86	1.4555	52	1.4036	18	1.3559
85	1.4540	51	1.4022	17	1.3546
84	1.4525	50	1.4007	16	1.3533
83	1.4511	49	1.3993	15	1.3520
82	1.4496	48	1.3979	14	1.3507
81	1.4482	47	1.3964	13	1.3494
80	1.4467	46	1.3950	12	1.3480
79	1.4453	45	1.3935	11	1.3467
78	1.4438	44	1.3921	10	1.3454
77	1.4424	43	1.3906	9	1.3442
76	1.4409	42	1.3890	8	1.3430
75	1.4395	41	1.3875	7	1.3417
74	1.4380	40	1.3860	6	1.3405
73	1.4366	39	1.3844	5	1.3392
72	1.4352	38	1.3829	4	1.3380
71	1.4337	37	1.3813	3	1.3367
70	1.4321	36	1.3798	2	1.3355
69	1.4304	35	1.3785	1	1.3348
68	1.4286	34	1.3772	0	1.3330
67	1.4267	33	1.3758		

In order to avoid the necessity of maintaining a known constant temperature and of accurately ascertaining the zero error of the instrument, Lenz recommends that the refractive index of the glycerol solution and of pure water be observed successively. The following table gives the differences between the refractive index of water and of aqueous solution of glycerol of different concentrations:

TABLE OF DIFFERENCES BETWEEN REFRACTIVE INDICES OF
AQUEOUS SOLUTIONS OF GLYCEROL AND OF PURE WATER.
(N_D SOLUTION—N_D WATER)(LENZ)

% glycerol	Difference	% glycerol	Difference	% glycerol	Difference	%‑glycerol	Difference	% glycerol	Difference
100	0.1424	80	0.1133	60	0.0806	40	0.0526	20	0.0261
99	0.1410	79	0.1119	59	0.0792	39	0.0510	19	0.0238
98	0.1395	78	0.1104	58	0.0780	38	0.0495	18	0.0225
97	0.1381	77	0.1090	57	0.0768	37	0.0479	17	0.0212
96	0.1366	76	0.1075	56	0.0757	36	0.0464	16	0.0199
95	0.1352	75	0.1061	55	0.0745	35	0.0451	15	0.0186
94	0.1337	74	0.1046	54	0.0731	34	0.0438	14	0.0173
93	0.1323	73	0.1032	53	0.0717	33	0.0424	13	0.0160
92	0.1308	72	0.1018	52	0.0702	32	0.0411	12	0.0146
91	0.1294	71	0.1003	51	0.0688	31	0.0398	11	0 0133
90	0.1279	70	0.0987	50	0.0663	30	0.0385	10	0.0120
89	0.1264	69	0.0970	49	0.0659	29	0.0372	9	0.0108
88	0.1250	68	0.0952	48	0.0645	28	0.0358	8	0.0096
87	0.1235	67	0.0933	47	0.0630	27	0.0345	7	0.0083
86	0.1221	66	0.0915	46	0.0616	26	0.0332	6	0.0071
85	0.1206	65	0.0897	45	0.0601	25	0.0318	5	0.0058
84	0.1191	64	0.0889	44	0.0587	24	0.0315	4	0.0046
83	0.1177	63	0.0861	43	0.0572	23	0.0302	3	0.0033
82	0.1162	62	0.0842	42	0.0556	22	0.0288	2	0.0021
81	0.1148	61	0.0824	41	0.0541	21	0.0275	1	0.0008

The viscosity of various solutions of glycerol at 20° has been
determined by Schöttner (*Seitzungsberichte der Kaiserlichen Aka-
demie der Wissenschaften Wien*, 1878, **77**, 682; 1879 **79**).
The viscosities in dynes per sq. cm. for glycerol solutions in steps
of 5% increase in concentrations has been developed from this
table by Archbutt (Lubrication and Lubricants, 1st Ed. p. 161)
and are given below:

% glycerol	Density grm. per c.c. of glycerol	Viscosity C. G. S. units	Viscosity kine‑mater C. G. S. units
5	1.0098	0.01181	0.01170
10	1.0217	0.01364	0.01335
15	1.0337	0.01580	0.01529
20	1.0461	0.01846	0.01765
25	1.0720	0.02585	0.02411
35	1.0855	0.03115	0.02780
40	1.0989	0.03791	0.03450
45	1.1124	0.04692	0.04218
50	1.1258	0.05908	0.05248
55	1.1393	0.07664	0.06727
60	1.1528	0.1031	0.08943
65	1.1797	0.2149	0.1822
75	1.1932	0.3371	0.2825
80	1.2066	0.5534	0.4586
85	1.2201	1.025	0.8401
90	1.2335	2.076	1.683
95	1.2465	4.801	3.852

The b. p. and vapour pressures of glycerol solutions from 0% to 100%, as given in Thorpe's Dictionary II, 768, and determined by Gerlach, are given below:

% glycerol	B. p. °	Vapour pressure at 100° mm, Hg.
100	290	64
99	239	87
98	208	107
97	188	126
96	175	144
95	164	162
94	156	180
93	150	198
92	145	215
91	141	231
90	138	247
85	127.5	326
80	121	396
75	116.7	450
70	113.6	496
65	111.3	553
60	109	565
55	107.5	593
50	106	618
45	105	639
40	104	657
35	103.4	675
30	102.8	690
25	102.5	704
20	101.8	717
10	100.9	740
5	100.5	...

Boiling Points of Pure Glycerol Solutions.—Grün and Wirth (*Zeit. angew. Chem.*, 1919, **32**, 59) recommend the b. p. method of determining the strength of glycerol solutions of high concentrations. The glycerol used in their experiments was distilled twice *in vacuo* and dried over P_2O_5 for 5 months and had a sp. gr. at 15°/15° of 1.2653 ± 0.0001. They found the b. p. of this glycerol and dilutions to be:

Glycerol % strength	Water %	Boiling point ° at 760 mm.
Unmixed	0.04	282
99	0.94	226
98	2.01	194
97	2.98	179
96	4.00	167
95	4.93	160

They determined the b. p. of solutions of glycerol at 760 mm. pressure as below for each $\frac{1}{2}\%$ difference:

GLYCEROL, %	B. P. IN ° AT 760 MM.
100	283-4
99.5	243-4
99.0	224-5
98.5	207-8
98.0	195-6
97.5	185-6
97.0	178-9
96.5	171-2
96.0	167-8
95.5	163.4
95.0	160.1

It will be noted that the undiluted sample had a b. p. of 283-4° but that it contained 0.04% moisture. Even this minute quantity of water gave a lowering of the b. p. They found on distilling a considerable quantity of this very pure glycerol (0.04 water) that the b. p. rose to 290° and remained constant. The presence of 1% of water lowers the b. p. from 290° to 224° at 760 mm. Schleiermacher's (*Ber.*, 24, 944, 2251) method, in which the glycerol is heated over mercury in a sealed capillary extension U-tube, may be used for this determination. Gerlach (*Chem. Ind.*, 7, 277) shows the b. p. of glycerol solutions at 760 mm. to be:

GLYCEROL, %	° C.
100	290
99	239
98	208
97	188
96	175
95	164

The b. p. of pure glycerol at low pressures has been determined and comparisons made with the calculated b. p.

Pressure in mm.	B. p. as found, °	B. p. as calculated, °
15	176	176
12	174.5	171.5
12	173.5	171.5
15	177	176
20	182	183
23	185	186.5
28	190	190.5
30	192	192
32	193	193.5
9	166	166
9	166.5	166
14	172.5	174.5
13	171.0	173.0
12.5	170.8	172.0
12.0	170.5	171.2

The results obtained by actual experimentation are very close to the calculated results.

Lewis (*J. Soc. Chem. Ind.*, 41, 99T) determined the boiling points of aqueous solutions of pure glycerol at 760 mm. pressure. He dried the pure glycerol in thin layers over phosphorus pentoxide under vacuum. He used the boiling point method as described by Schleiermacher (*Ber.*, 1891, 24, 944, 2251). His results are given in the table following:

% GLYCEROL	B. P., ° C.	% GLYCEROL	B. P., ° C.
100	290.0	70	113.5
99	225.5	65	111.0
98	196.0	60	108.8
97	179.5	55	107.2
96	168.0	50	106.0
95	160.0	45	105.5
94	156.0	40	104.2
93	149.5	35	103.5
92	145.5	30	103.0
91	141.0	25	102.4
90	137.5	20	102.0
85	126.8	15	101.5
80	121.5	10	101.0
75	116.5	5	100.5

These figures differ somewhat from those of Gerlach but are in close agreement with those of Grün and Wirth and are therefore probably nearer correct that Gerlach's.

In determining the strength of glycerol solutions by the sp. gr. method, the presence of more than very small amounts of trimethylene glycol will give incorrect results. A method has been developed by Cocks and Salway for the determination of this material in glycerol solutions (*J. Soc. Chem. Ind.*, 1922, 41, 17T). The work in preparing this method was undertaken, in connection with the proposal of the Committee for the revision of the International Standard Methods of Glycerin Analysis, to introduce a standard method of determining trimethylene glycol in crude glycerin. The sp. gr. of a series of mixtures containing known proportions of glycerol, trimethylene glycol and water were determined and from the figures so obtained, tables were constructed by which the T. M. G. content of any distilled glycerin of known sp. gr. and apparent glycerol content could be deduced. The glycerol used by them was a sample of purified and standardised glycerol (90% strength) furnished by the Expert Committee on Crude Glycerin Analysis. The trimethylene glycol was especially prepared from so-called "catch box" liquor, obtained in the commercial concentration of a distilled glycerin and which contained about 40% by weight of trimethylene glycol. This liquor was fractionated under reduced pressure and the trimethylene glycol fraction was further fractionated at ordinary pressure using a small fractionating column. A large portion boiling at 210–211° (uncorr.) was obtained and 500 c.c. of this fraction was redistilled under slightly reduced pressure. The first 100 c.c. were rejected and the next 150 c.c. were used. This boiled at 171° (174 mm.) and had a sp. gr. at 20°/20° of 1.0552. The acetyl value of this material showed it to be 99.5%, trimethylene glycol. By interpolation, the true sp. gr. of trimethylene glycol is given as 1.0554 at 20°/20°. The b. p. and sp. gr. of pure trimethylene glycol are given in the literature as follows: (sp.gr. having been calculated to 20°/20°):

Sp. gr.: Noyes and Watkins (*J. Am. Chem. Soc.*, 1895, 17, 890), 1.0550; Freund (*Monatsh.*, 1881, 2, 638), 1.0518; Rojahn (*Z. anal. Chem.*, 1920, 58, 433), 1.0553; Cocks and Salway (*J. Soc. Chem. Ind.*, 1918, 37, 123T, 158T), 1.0554.

B. p.: Noyes and Watkins, 214–217°; Henry (*Ann. Chim.*, 1878, (5), 14, 491), 210; Raboul, 216–17; Rojahn, 210; Cocks and Salway, 210–211°.

The general procedure recommended for the estimation of trimethylene glycol in crude glycerin follows:

A known weight (100 grm.) of the crude glycerin is introduced into a 600 c.c. distillation flask, which is fitted with a cork and capillary inlet tube. To the distilling flask is fitted an air condenser about 2 ft. 6 in. or 3 ft. long, and a receiver to collect the distillate. The apparatus is then evacuated (15–30 mm. pressure) and distillation is commenced. For heating the glycerin, an oil bath at 230–240° may be used, but occasionally trouble arises due to frothing. It has been found preferable to use a carefully manipulated smoky gas flame by which means the frothing can be kept under better control. The heating should be so regulated that the distillation proceeds at about one drop per second, and the distillation is continued until approximately 30% of the weight of the original crude glycerin has collected in the receiver. In the early stages of the distillation the material loses its water, some of which escapes condensation. This is an advantage, as it obviates the necessity for concentrating the distilled liquor.

If any foaming has occurred during distillation, the distillate must be redistilled. For analysis, the sp. gr. and acetin value of the distillates are determined and the amount of trimethylene glycol present may then be read off from curves, or may be calculated by taking the difference between the sp. gr. of the mixture under examination and the sp. gr. of glycerin at a dilution represented by the acetin figure of the mixture and then dividing by a given factor. This factor increases with the acetin figure as follows: 50% trimethylene glycol, factor is 0.00134 per 1% trimethylene glycol; 55%, 0.00138; 60%, 0.00143; 65%, 0.00148; 70%, 0.00152; 75%, 0.00157; 80%, 0.00162; 85%, 0.00168; 90%, 0.00174; 95%, 0.00179. For use of these factors, the sp. gr. of the glycerin mixture is taken at 20/20°. The method is said to be fairly accurate.

The carbon dioxide-bichromate method for the estimation of trimethylene glycol in the presence of a large quantity of glycerin devised by Fachini and Somazzi and described under the estimation of glycerol by the dichromate method (page 663) would seem to be a more accurate way of determining the amount of trimethylene glycol than the specific gravity-acetin method above.

GLYCERIN SPECIFICATIONS

Ordinary glycerin in commercial operations is divided into three grades: (1) crude glycerin; (2) distilled or dynamite glycerin; (3) chemically pure glycerin.

British Standard Specifications for Crude Glycerins.—The following standard specifications were drawn up by the British Executive Committee on crude glycerin analysis and approved at a general meeting of crude glycerin makers, buyers and brokers held in London, on Oct. 3, 1912.

Soap Lyes Crude Glycerin.—Analysis to be made in accordance with the International Standard Methods.

Glycerol.—The standard shall be 80% of glycerol. Any crude glycerin tendered which tests 81% of glycerol or over shall be paid for at a *pro rata* increase, calculated as from the standard of 80%. Any crude glycerin which tests under 80% of glycerol, but is 78% or over, shall be subject to a reduction of $1\frac{1}{2}$ times the shortage, calculated at a *pro rata* price as from 80%. If the test falls below 70% the buyer shall have the right of rejection.

Ash.—The standard shall be 10%. In the event of the per-centage of ash exceeding 10%, but not exceeding 10.5%, a percentage deduction shall be made for the excess calculated as from 10% at *pro rata* price, and if the percentage of ash exceeds 10.5% but does not exceed 11% an additional percentage deduction shall be made equal to double the amount in excess of 10.5%. If the amount of ash exceeds 11% the buyer shall have the right of rejection.

Organic Residue.—The standard shall be 3%. A percentage deduction shall be made of 3 times the amount in excess of the stand-ard of 3% calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 3.75%.

Saponification Crude Glycerin.—Analysis to be made in accord-ance with the International Standard Methods, 1911.

Glycerol.—The standard shall be 88%. Any crude glycerin tend-ered which tests 89% or over shall be paid for at a *pro rata* increase calculated as from the standard of 88%. Any crude glycerin which tests under 88%, but is 86% or over, shall be subject to a reduction of $1\frac{1}{2}$ times the shortage, calculated at *pro rata* price as from 88%. If the test falls below 86% the buyer shall have the right of rejection.

Ash.—The standard shall be 0.5%. In the event of the ash exceeding 0.5%, but not exceeding 2.0%, a percentage reduction shall be made equal to double the amount in excess of 0.5%. If the amount of ash exceeds 2.0% the buyer shall have the right to reject the parcel.

Organic Residue.—The standard shall be 1%. A percentage deduction shall be made of twice the amount in excess of the standard of 1%, calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 2%.

The lack of uniformity in the methods and processes of analysis, together with the irregularity of the results obtained, have made necessary the establishment and adoption of standard methods for the analysis of crude glycerols. With this object in view, committees were formed in the United States, France, Germany and Great Britain. The following methods have been approved by these committees and have been accepted in these countries as standard methods of analysis:

1. *Crude Glycerin.*

Three kinds of crude glycerin may be distinguished: saponification glycerin, distillation glycerin, soap lye glycerin or soap glycerin.

Saponification Glycerin.—This glycerin is obtained by the autoclave process of hydrolysing fats by heating with water under high pressure, either alone or in the presence of a small proportion of lime or magnesia. It is evaporated to a sp. gr. 1.240–1.242, and is then known as "28° B.," "raw glycerin," "saponification glycerin" or "candle glycerin." It has a sweet taste, and varies in colour from bright yellow to dark brown. It gives but a slight precipitate with basic lead acetate, and with hydrochloric acid should give no turbidity. The valuation of such glycerin includes the estimation of glycerol, ash (which should not exceed 0.3 to 0.5%), organic impurities and moisture.

The methods recommended by the International Committee for the analysis of crude glycerin follow. The actual quotations from the "recommended methods" are given in quotation marks. The other paragraphs are given in explanation of the methods and serve to make more clear the reasons for the methods and also the results obtained by using these methods.

CRUDE GLYCERIN

I. *References:*

    J. Ind. Eng. Chem., 1911, **3**, 682.

    Zeit. angew. Chem., 1911, **24**, 865.

    Examination of Hydrocarbon Oils and Saponifiable Fats,

        Holde (Mueller), First English Edition, 1915, p. 394.

II. *Principle.*—The estimations designated under "VI Procedure" as "(A) Estimation of Free Caustic Alkali;" "(B) Estimation of Ash and Total Alkalinity," and "(C) Estimation of Alkali Present as Carbonate," are all simple volumetric estimations of the specified alkaline constituents of the crude glycerin. The constituent designated as "(D) Alkali Combined with Organic Acids" is derived from these estimations by deducting from the per cent of Na_2O found under "C" the sum of the per cent of Na_2O found under "A" and "B."

In case the glycerin shows an acid reaction on diluting and adding phenolphthalein indicator, this acidity is probably due to the presence of lower fatty acids, especially butyric and formic acids. The acidity is titrated with standard NaOH solution and expressed in terms of grm. of Na_2O required to neutralise 100 grm. of th sample.

The total residue at 160° consists of the inorganic ash and the non-volatile organic constituents present in the crude glycerin. Since glycerol is completely volatilised by careful and long continued heating at 160° in the presence of water, the residue should contain no glycerol. However, if the directions are not accurately followed, there is danger of polymerising some of the glycerol and obtaining an abnormally high residue. In the subsequent acetin estimation, a correction is made for the acetin value of this non-volatile residue.

By subtracting the ash, as estimated under "(B) Estimation of Ash and Total Alkalinity," from the total residue at 160°, the organic residue at 160° is obtained.

The acetin method depends upon the formation of triacetin. (glyceryl triacetate) when glycerol is heated with acetic anhydride and sodium acetate. The triacetin is then saponified with sodium hydroxide solution and the amount of the latter used gives a measure of the glycerol.

The dichromate method is based on the fact that $K_2Cr_2O_7$ in the presence of H_2SO_4 completely oxidises glycerol to CO_2 and H_2O. With pure glycerol the oxidation is quantitative. Crude glycerins are treated for the removal of chlorine and aldehydic compounds with silver carbonate and basic lead acetate. The method is open to the objection that by precipitation by lead acetate the impurities may not be perfectly removed, anything left being oxidised and counted as glycerol. However, all higher fatty acids and all resin acids, as well as albuminoids, sulphides, thiocyanates and aldehydes, are completely removed, and the lower fatty acids, such as acetic and butyric, are not attacked by chromic acid.

III. *Status.* —The method of analysis of crude glycerin, as herein presented, is the official method agreed upon by the International Committee on Glycerin Analysis which met in London in October, 1910. The matter in quotation marks is taken directly from the report of the American Sub-committee.[1]

The report of the sub-committee contains no mention of a method for the estimation of water. However, the Eastern Laboratory (du Pont's) has made an exhaustive study of this estimation as applied to all types of glycerin, and the method referred to under "VI Procedure" is entirely applicable to crude glycerin.

"As a result of our researches, we [the committee] have unanimously decided that the acetin method is the basis on which glycerin should be bought and sold. The dichromate method is of value in factory control and for routine work in the analysis of crudes of known good character. For this reason we have felt it necessary to retain the dichromate in a properly standardised form, but we advise against its use in general analytical work."

[The acetin process] "is the process to be used (if applicable) whenever only one method is employed. On pure glycerins, the results are identical with those obtained by the dichromate process. For the application of this method, the crude glycerin should not contain over 60% water."

"Neither the acetin nor the dichromate method is correct in theory or practice on crudes containing trimethylene glycol or polyglycerols. We know that the acetin is less affected by these

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[1] *J. Ind. Eng. Chem.,* 1911, **3**, 682. "A sub-committee of the Committee on Fats, Soaps and Glycerin of the Division of Industrial Chemists and Chemical Engineers. The report has received the approval of the Supervisory Committee on Standard Methods of Analysis, American Chemical Society."

substances than the dichromate. They are not precipitated by basic lead acetate or silver salts, and are, therefore, left to exert the full reducing power of the molecule on the dichromate. With the acetin method, on the other hand, action is proportional to the number of OH groups directly attached to the chain. For example, a crude glycerin containing 80% glycerol and 1% trimethylene glycol would show by the dichromate 81.38% and by the acetin 80.81% glycerol. With triglycerol, a 1% addition would increase the dichromate test by 1.15% and the acetin by 0.64%. A comparison of the results obtained by the acetin and dichromate methods will, therefore, often throw light on the nature and quantity of the impurities present.'

"In the absence of a chemical method which will show glycerol only in such mixtures, we must, therefore, prefer the acetin, because it gives the same results as the dichromate on pure glycerin and high grade crudes and lower or much lower results on bad crudes. In the acetin method, the error caused by the presence of poly-glycerols is partially offset by the determination of the acetylisable matter in the non-volatile residue at 160° which will hold the higher polyglycerols. The lower polyglycerols and trimethylene glycol are volatile at 160°, and are, therefore, figured as glycerol. Trimethyl-ene glycol is more volatile than glycerol, and may be distilled off with the glycerin in the first portions of the distillate, where it may be determined by the spread between the acetin and dichromate tests."

"We have met with some bad crudes, which cannot with safety be analysed by any chemical method known to us. The only method which will give even approximate results on crudes high in glycol or crudes containing still residues is a distillation in a still adapted to quantitative work. A crude containing a large amount of glycol tested 81.8% dichromate, 76.2% acetin and 71.0% by distillation. A crude made from still residues showed 73% by the dichromate, 48% by the acetin and only 30% by distillation. These are extreme cases, but serve to show that a marked spread between the acetin and the dichromate tests is an indication that both are probably incorrect."

"The acetin test is not looked upon with favour by some chemists on the ground that results are unreliable unless precautions are taken out of the reach of the busy laboratory. This opinion is largely the

result of erroneous statements in the text books and literature. The danger of saponifying triacetin by standing in aqueous solution and during neutralisation of the acetic acid is greatly exaggerated. A point in favour of the acetin method is the avoidance of the purification required by the dichromate test. Two of the members of this committee have made the change from the dichromate to the acetin without any trouble, although they had but little experience with the acetin. In their hands the acetin has given results of greater uniformity and accuracy than the dichromate. Every member of our Committee has had by this time some experience with the acetin in comparison with the dichromate and a few of us have had a very extensive experience, covering several years. It is our opinion that with proper attention to details, which are not in the least onerous, chemists will be able to obtain results which are more concordant than those obtainable by the dichromate and at the same time nearer the actual glycerol present."

"It is not possible to carry through as many acetin tests per day as dichromate, but with many crudes the difference between results is so wide that it is not any longer a question as to which method is the quicker or more convenient."

It[1] has been shown by experience that in good crude glycerin the sum of the water, total residue at 160°, and corrected glycerin content will be equal to 100 ± 0.5%. Moreover, with such samples, the dichromate method will agree with the acetin result to within 1%.

If larger differences are found, then impurities, such as polyglycerins or trimethylene glycol, are present. An approximation to the quantity of trimethylene glycol present can be obtained by isolating some of the more volatile distillate and running acetin and dichromate determinations on this distillate. Trimethylene glycol shows by the first method 80.69% and by the second 138.3% glycerin. The spread[2] multiplied by 1.736 will give the trimethylene glycol. In valuing the crude glycerin for some purposes, the estimation of its approximate content of arsenic, sulphides, sulphites and thiosulphates is necessary. The methods for the estimation of these components were not included in the report of the committee.

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[1] Examination of Hydrocarbon Oils, etc., Holde (Müller). 1915, p. 402.
[2] "Spread" means the difference in % of glycerin as determined by the action and dichromate method.

IV. *Reagents and Apparatus:*

(A) *Reagents.*

1. *Miscellaneous Estimations:*

Standard hydrochloric acid solution (N/10).

Standard sodium hydroxide solution (N/10).

Phenolphthalein indicator.

Methyl Orange indicator.

2. *Acetin Method:*

"(a) *Best Acetic Anhydride.*—This should be carefully selected. A good sample must not require more than 0.1 c.c. normal NaOH for saponification of the impurities when a blank is run on 7.5 c.c. Only a slight colour should develop during digestion of the blank.

"The anhydride may be tested for strength by the following method: Into a weighed stoppered vessel, containing 10 to 20 c.c. of water, run about 2 c.c. of the anhydride, replace the stopper and weigh. Allow to stand with occasional shaking for several hours to permit the hydrolysis of all the anhydride; then dilute to about 200 c.c., add phenolphthalein and titrate with N/1 NaOH. This gives the total acidity due to free acetic acid and acid formed from the anhydride. It is worthy of note that in the presence of much free anhydride a compound is formed with phenolphthalein, soluble in alkali and acetic acid, but insoluble in neutral solutions. If a turbidity is noticed toward the end of the neutralisation it is an indication that the anhydride is incompletely hydrolysed and inasmuch as the indicator is withdrawn from the solution, results may be incorrect.

"Into a stoppered weighing bottle containing a known weight of recently distilled aniline (from 10 to 20 c.c.) measure about 2 c.c. of the sample, stopper, mix, cool and weigh. Wash the contents into about 200 c.c. of cold water, and titrate the acidity as before. This yields the acidity due to the original, preformed, acetic acid plus one-half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated to 100 grm.) and double the result, obtaining the c.c. N/1 NaOH per 100 grm. of the sample. 1 c.c. N/1 NaOH equals 0.0510 grm. anhydride."

(The above paragraph shows the method recommended by the glycerin committee. However, experience has shown that simple

neutralisation with alkali and titration of the excess of the latter is more reliable.)

"(b) *Pure Fused Sodium Acetate.*—The purchased salt is again completely fused in a platinum, silica or nickel dish, avoiding charring, powdered quickly and kept in a stoppered bottle or desiccator. It is most important that the sodium acetate be anhydrous."

"(c) *A Solution of Sodium Hydroxide for Neutralising, of About Normal Strength, Free from Carbonate.*—This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide) and allowing to settle until clear, or filtering through an asbestos or paper filter. The clear solution is diluted with water free from carbon dioxide to the strength required."

"(d) *N Sodium Hydroxide Free from Carbonate.*—Prepared as above and carefully standardised. Some sodium hydroxide solutions show a marked diminution in strength after being boiled; such solutions should be rejected."

"(e) *N Acid.*—Carefully standardised."

"(f) *Phenolphthalein Solution.*—0.5% phenolphthalein in alcohol and neutralise."

(3) *Dichromate Method:*

"(a) *Pure potassium dichromate* powdered and dried in air, free from dust or organic vapours, at 110° to 120°. This is taken as the standard."

"(b) *Dilute Dichromate Solution.*—7.4564 grm. of the above dichromate is dissolved in distilled water and the solution made up to 1000 c.c. at 15.5°."

"(c) *Ferrous Ammonium Sulphate.*—It is never safe to assume this salt to be constant in composition and it must be standardised against the dichromate as follows: Dissolve 3.7282 grm. of dichromate (a) in 50 c.c. of water. Add 50 c.c. of 50% sulphuric acid (by volume), and to the cold undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulphate, and titrate with the dilute dichromate (b). Calculate the value of the ferrous salt in terms of dichromate."

"(d) *Silver Carbonate.*—This is prepared as required for each test from 140 c.c. of 0.5% silver sulphate solution by precipitation with about 4.9 c.c. N. sodium carbonate solution (a little less than the calculated quantity of N. sodium carbonate should be used, as an

excess prevents rapid settling). Settle, decant and wash once by decantation."

"(e) *Sub-acetate of Lead.*—Boil a 10% solution of pure lead acetate with an excess of litharge for 1 hour, keeping the volume constant, and filter whilst hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide."

"(f) *Potassium Ferricyanide.*—A very dilute solution containing about 0.1%."

(B) *Apparatus.*

No apparatus other than that constituting regular laboratory equipment is required for any of the estimations.

The Freas type thermostatic electric oven, equipped with a simple fan to keep the air in agitation, is entirely satisfactory for the estimation of total residue at 160°. A convenient fan may be made by cutting two disks of light sheet metal so that five or six blades, resembling electric fan blades, may be fashioned out of each. Attach one propeller to each end of a glass rod by means of sections of rubber stoppers, first inserting the rod through a glass tube which acts as a journal for the glass-rod shaft. The tube is inserted through a rubber stopper which fits tightly through the central hole in the top of the oven. When assembled, one fan is inside of the oven in a position directly over the evaporating dishes, and the other fan is outside of the oven. By directing a jet of air from a constricted tube at the fan blades, sufficient motive power is furnished to keep the fan rapidly revolving.

V. *Preparation of the Sample:*

"The most satisfactory method available for sampling crude glycerin liable to contain suspended matter, or which is liable to deposit salt on settling, is to have the glycerin sampled by a mutually approved sampler as soon as possible after it is filled into drums, but in any case before any separation of salt has taken place. In such cases, he shall sample with a sectional sampler (see Fig. 693) then seal the drums, brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of the same made in his certificate, together with the temperature of the glycerin. Each drum must be sampled. Glycerin which has deposited salt or other solid matter cannot be accurately sampled from the drums, but an approximate sample can be obtained by means

of the sectional sampler which will allow a complete vertical section of the glycerin to be taken including any deposit.

"The usual method of sampling crude glycerin hitherto has been by means of a glass tube, which is slowly lowered into the drum with the object of taking as nearly as possible a vertical section of the glycerin contained in the drum. This method has been found unsatisfactory, owing to the fact that in cold climates glycerin runs into the tube very slowly so that owing to the time occupied, it is impossible to take a complete section of the crude. Another objection to the glass tube is that it fails to take anything approaching a correct proportion of any settled salt contained in the drum.

"The sampler which is described herein has been devised with the object of overcoming the objections to the glass tube as far as possible. It consists of two brass tubes, one fitting closely inside the other. A number of ports are cut out in each tube in such a way that when the ports are opened a continuous slot is formed which enables a complete section to be taken throughout the entire length of the drum. By this arrangement, the glycerin fills into the sampler almost instantaneously. There are a number of ports cut at the bottom of the sampler, which renders it possible to take a proportion of the salt at the bottom of the drum. The instrument is so constructed that all the ports, including the bottom ones, can be closed simultaneously by the simple action of turning the handle at the top; a pointer is arranged which indicates on a dial when the sampler is open or closed. In samplers of larger section (1 in.), it is possible to arrange a third motion whereby the bottom ports only are open for emptying, but in samplers of smaller dimensions (⅝ in.) this third motion must be dispensed with, otherwise the dimensions of the ports have to be so small that the sampler would not be efficient.

"In using the sampler, it is introduced into the drum with the ports closed, and when it has touched the bottom the ports are opened for a second or two, then closed and withdrawn, and the sample discharged into the receiving vessel by opening the ports. When the drum contains salt which has deposited, the ports must be opened before the sampler is pushed through the salt, thus enabling a portion to be included in the sample. It is, however, almost impossible to obtain a correct proportion of salt after it has settled in the drum, and it is, therefore, recommended that the drum be sampled before any salt has deposited. A sampler 1 in. in diameter withdraws
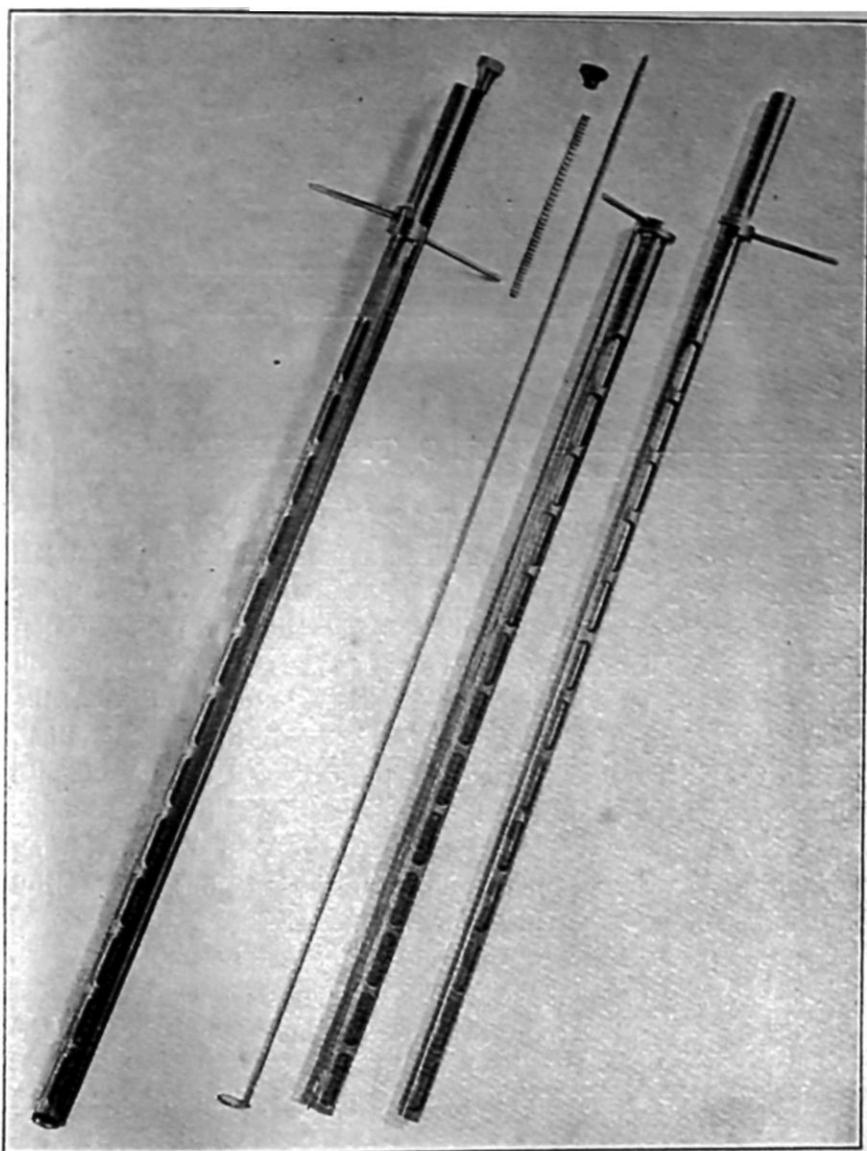
FIG. 17.—Sample thief for crude glycerin. Length overall 40 in. Length of immersible portion from tip to metal shoulder containing valve handle 33 in. 13 parts each 2 in. long and $\frac{1}{2}$ in. wide. First part $3\frac{1}{2}$ from shoulder. Diameter of main tube 1 in. Thickness of wall $\frac{1}{32}$ in. Diameter inside tube $1\frac{3}{16}$ in. Thickness of wall $\frac{1}{16}$ in.

approximately 10 oz. from a 110 gal. drum. A sampler ⅝ in. in diameter will withdraw about 5 oz."

VI. *Procedure:*

(*A*) "*Estimation of Free Alkali Hydroxide.*"

"Weigh 20 grm. of the sample into a 100 c.c. flask, dilute with approximately 50 c.c. of fresh boiled distilled water, add an excess of neutral barium chloride solution, 1 c.c. of phenolphthalein solution, *make up to the mark and mix. Allow the precipitate to settle, draw* off 50 c.c. of the clear liquid and titrate with N/1 acid. Calculate to % of Na_2O existing as hydroxide."

Calculation:

$$\frac{\text{c.c. acid} \times \text{N.} \times 3.1}{\text{wt. of sample in aliquot}} = \% \ Na_2O \ \text{(Free Alkali Hydroxide)} \ (A)$$

(*B*) "*Estimation of Ash and Total Alkalinity.*"

"Weigh 2 to 5 grm. of the sample in a platinum dish, burn off the glycerin over a luminous Argand burner or other source of heat giving a low temperature, to avoid volatilisation and the formation of sulphides. When the mass is charred to the point that water will not be coloured by soluble organic matter, lixiviate with hot distilled water, filter, wash and ignite the residue in the platinum dish. Return the filtrate and washings to the dish and carefully ignite without fusion. Weigh the ash.

Dissolve the ash in distilled water and titrate total alkalinity, using as indicator Methyl Orange, cold, or litmus, boiling." (Methyl Orange gives a better endpoint for this purpose.

Calculation:

$$\frac{\text{wt. of ash} \times 100}{\text{wt. of sample}} = \% \ \text{Ash} \qquad\qquad (B_1)$$

$$\frac{\text{c.c. acid} \times \text{N.} \times 3.1}{\text{wt. of sample}} = \% \ Na_2O \ \text{(Total Alkalinity)} \qquad (B_2)$$

(*C*) "*Estimation of Alkali Present as Carbonate.*"

"Take 10 grm. of the sample, dilute with 50 c.c. distilled water, add sufficient N/1 acid to neutralise the total alkali found at (*B*), boil under a reflux condenser for 15 to 20 minutes, wash down the condenser tube with distilled water, free from carbon dioxide, and then titrate back with N/1 NaOH, using phenolphthalein as indicator. Calculate the percentage of Na_2O. Deduct the Na_2O found in (*A*).

The difference is the percentage of Na_2O existing as carbonate."
  Calculation:

$$\frac{(\text{c.c. st'd acid} \times N - \text{c.c. st'd NaOH} \times N) \times 3.1}{\text{wt. of sample}} A = \% \ Na_2O$$

(Alkali present as Carbonate) (C)

  (D) "Alkali Combined with Organic Acids."
  "The sum of the percentages of Na_2O found at (A) and (C), deducted from the percentage found at (B) is a measure of the Na_2O or other alkalies combined with organic acids."
  Calculation:

$B_2 - (A + C) = \%$ Na_2O as Alkali combined with Organic
Acids (D)

  (E) "Estimation of Acidity."
  "Take 10 grm. of the sample, dilute with 50 c.c. distilled water free from carbon dioxide, and titrate with N/1 NaOH and phenolphthalein. Express in terms of Na_2O required to neutralise 100 grm."
  Calculation:

$$\frac{\text{c.c. st'd NaOH} \times N \times 3.1}{\text{wt. of sample}} = \text{grm. } Na_2O \text{ required to neutralise}$$

100 grm. of sample (E)

  (F) "Estimation of Total Residue at 160°."
  "For this estimation the crude glycerin should be slightly alkaline with Na_2CO_3, not exceeding 0.2% Na_2O, in order to prevent loss of organic acids. To avoid the formation of polyglycerols, this alkalinity must not be exceeded.
  "10 grm. of the sample are weighed into a 100 c.c. flask, diluted with water and the calculated quantity of N/1 HCl or Na_2CO_3 added to give the required degree of alkalinity. The flask is filled to 100 c.c., the contents mixed, and 10 c.c. measured into a weighed Petrie or similar dish 2.5 in. in diameter and 0.5 in. deep, which should have a flat bottom. In the case of crude glycerins abnormally high in organic residue, a smaller amount should be taken, so that the weight of the organic residue does not materially exceed 30 to 40 mg."
  "The dish is placed on a water bath (the top of the 160° oven acts equally well) until most of the water has evaporated. From

this point, the evaporation is effected in the oven. Satisfactory results are obtained in an oven measuring 12 in. cube, having an iron plate 0.75 in. thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf halfway up the oven. On these strips the dish containing the glycerin is placed.[1]

"If the temperature of the oven has been adjusted to 160° with the door closed, a temperature of 130° to 140° can be readily maintained with the door partially open, and the glycerin, or most of it, should be evaporated off at this temperature. When only a slight vapour is seen to come off, the dish is removed and allowed to cool.

"An addition of 0.5 to 1.0 c.c. of water is made, and by a rotary motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water bath or top of the oven until the excess water has evaporated and the residue is in such a condition that on returning to the oven at 160°, it will not spurt. The time taken up to this point cannot be given definitely, nor is it important. Usually 2 or 3 hours are required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained at 160°, for 1 hour, when it is removed, cooled, the residue treated with water, and the water evaporated as before. The residue is then subjected to a second baking of 1 hour, after which the dish is allowed to cool in a desiccator over sulphuric acid and weighed. The treatment with water, etc., is repeated until a constant loss of 1 to 1.5 mg. per hour is obtained.

"In the case of acid glycerin, a correction must be made for the alkali added. 1 c.c. N/1 alkali represents an addition of 0.03 grm. In the case of alkaline crudes, a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the NaOH and Na_2CO_3 to NaCl. The corrected weight multiplied by 100 gives the percentage of *total residue at* 160°.

"This residue is taken for the estimation of the non-volatile acetylisable impurities (see acetin method)."

Calculation:

$$\frac{(\text{wt. of residue} - \text{correction}) \times 100}{\text{wt. of sample in aliquot}} = \% \text{ Total Residue at } 160° \ (F)$$

[1] See description of oven under "IV. Reagents and Apparatus."

(G) *"Organic Residue."*

"Subtract the ash from the total residue at 160°. Report as organic residue at 160°. (It should be noted that alkaline salts of fatty acids are converted to carbonates on ignition and that the CO_2 thus derived is not included in the organic residue.)"

Calculation:

$$F - B_1 = \% \text{ Organic Residue at } 160° \qquad (G)$$

(H) *Moisture.*

Determine moisture by the procedure described on page 721.

Calculation:

$$\frac{\text{Loss in wt. of bottle} \times 100}{\text{wt. of sample}} = \% \, H_2O \qquad (H)$$

(I) *"Acetin Process for the Estimation of Glycerol."*

"Into a narrow mouthed flask (preferably round bottomed), capacity about 120 c.c., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1.25 to 1.5 grm. of the glycerin. A Grethan or Lunge pipette will be found convenient. Add about 3 grm. of the anhydrous sodium acetate, then 7.5 c.c. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside diameter. The flask is connected to the condenser by either a ground glass joint (preferably) or a rubber stopper. If a rubber stopper is used, it should have had a preliminary treatment with hot acetic anhydride vapour.

"Heat the contents and keep just boiling for 1 hour, taking precautions to prevent the salts drying on the sides of the flask.

"Allow the flask to cool somewhat and through the condenser tube add 50 c.c. of distilled water, free from carbon dioxide, at a temperature of about 80°, taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapours from the flask on adding water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment, bearing in mind that the anhydride in excess is much more effectively hydrolysed in hot than in cold water. The contents of the flask may be warmed to, but must not exceed, 80°, until the solution is complete

except a few dark flocks representing organic impurities in the crude. By giving the flask a rotary motion, solution is more quickly effected.

"Cool the flask and contents without loosening from the condenser. When quite cold, wash down the inside of the condenser tube, detach the flask, wash off the stopper or ground glass connection into the flask, and filter the contents through an acid washed filter into a Jena glass flask of about 1 litre capacity. Wash thoroughly with cold distilled water, free from carbon dioxide. Add 2 c.c. of phenolphthalein solution (f), then run in caustic soda solution (c), or (d), until a faint pinkish yellow colour appears throughout the solution. This neutralisation must be done most carefully; the alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralised, as indicated by the slower disappearance of the colour developed locally by the alkali running into the mixture. When this point is reached, the sides of the flask are washed down with carbon dioxide free water and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

"Now run in from a burette 50 c.c. or a calculated excess of N/1 NaOH (d), and note carefully the exact amount. Boil gently for 15 minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate the excess of NaOH with N/1 acid (e), until the pinkish yellow or chosen endpoint colour just remains. A further addition of the indicator at this point will cause an increase of the pink colour; this must be neglected, and the first end point taken.

"From the N/1 NaOH consumed, calculate the percentage of glycerol (including acetylisable impurities) after making the correction for the blank test described below."

"1 c.c. N/1 NaOH = 0.03069 grm. Glycerol."

"The coefficient of expansion for normal solutions is 0.00033 per c.c. for each degree rise in temperature. A correction should be made on this account, if necessary."

"*Blank Test.*"

"As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test using the same quantities of acetic anhydride and sodium acetate as in the

analysis. It is not necessary to filter the solution of the melt in this case, but sufficient time must be allowed for the hydrolysis of the anhydride before proceeding with the neutralisation. After neutralisation, it is not necessary to add more than 10 c.c. of the N/1 alkali (d) as this represents the excess usually present after the saponification of the average soap lye crude. In estimating the acid equivalent of the NaOH, however, the entire amount taken in the analysis, 50 c.c., should be titrated after dilution with water free from carbon dioxide and without boiling."

"*Estimation of the Glycerol Value of the Acetylisable Impurities.*"

"The total residue at 160° is dissolved in 1 or 2 c.c. of water, washed into the acetylising flask and evaporated to dryness. Then add anhydrous sodium acetate and acetic anhydride in the usual amounts and proceed as described in the regular analysis. After correcting for the blank, calculate the result to glycerol."

Calculations:

"*Instructions for Calculating the Actual Glycerol Content.*"

"1. Estimate the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylisable impurities if any are present.

"2. Estimate the total residue at 160°.

"3. Estimate the acetin value of the residue at (2) in terms of glycerol.

"4. Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol. If volatile acetylisable impurities are present, these are included in this figure."

$$\frac{\text{c.c. st'd NaOH required in (3) corrected for blank} \times N \times 3.069}{\text{wt. of sample}} = \% \text{ Glycerol.}$$

Uncorrected Acetin Value of Sample. (I_1)

$$\frac{\text{c.c. st'd NaOH required in (3) corrected for blank} \times N \times 3.069}{\text{wt. of sample}} = \% \text{ Glycerol.}$$

Acetin Value of 160° Residue. (I_2)

$I_1 - I_2 = \%$ Glycerol. Corrected Acetin Value of Sample. (I_3)

(J) "*Dichromate Process for Glycerol Estimation.*"[1]

[1] Notes on Dichromate Process.—"1. It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.
"2. Before the dichromate is added to the glycerin solution, it is essential that the slight excess of lead be precipitated with sulphuric acid as stipulated.
"3. For crudes practically free from chlorides the quantity of silver carbonate may be reduced ½ and the basic lead acetate to 0.5 c.c."
"4. It is sometimes advisable to add a little potassium sulphate to ensure a clear filtrate."

"Weigh 20 grm. of the glycerin, dilute to 250 c.c. and take 25 c.c. Add the silver carbonate, allow to stand, with occasional agitation, for about 10 minutes, and add a slight excess (about 5 c.c. in most cases) of the basic lead acetate (*e*), allow to stand a few minutes, dilute with distilled water to 100 c.c. and then add 0.15 c.c. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 c.c., and return the filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate. (In the great majority of cases, 5 c.c. is ample, but occasionally a crude will be found requiring more, and in this case another aliquot of 25 c.c. of the dilute glycerin should be taken and purified with 6 c.c. of the basic acetate.) Care must be taken to avoid a marked excess of basic acetate.

"Measure off 25 c.c. of the clear filtrate into a flask or beaker (previously cleaned with potassium dichromate and sulphuric acid). Add 12 drops of sulphuric acid (1 : 4) to precipitate the small excess of lead as sulphate. Add 3.7282 grm. of the powdered potassium dichromate (*a*). Rinse down the dichromate with 25 c.c. of water and leave with occasional shaking until all the dichromate is dissolved. (No reduction will take place in the cold.)

"Now add 50 c.c. of 50% sulphuric acid (by volume) and immerse the vessel in boiling water for 2 hours and keep protected from dust and organic vapours, such as alcohol, till the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulphate (*c*) making spot tests on a porcelain plate with the potassium ferricyanide (*f*). Titrate back with the dilute dichromate. From the amount of dichromate reduced, calculate the percentage of glycerol."

Calculations:

"1 grm. glycerol = 7.4564 grm. dichromate.
1 grm. dichromate = 0.13411 grm. glycerol."

The percentage of glycerol obtained above includes the oxidisable impurities present after the purification. A correction for the non-volatile impurities may be made by running a dichromate test on the residue at 160°."

$$\frac{\text{Total g. } K_2Cr_2O_7 \text{ added} - K_2Cr_2O_7 \text{ equiv. of } Fe(NH_4)_2(SO_4)_2.6H_2O \times 13.411}{\text{wt. of sample in aliquot}} =$$

% Glycerol in Sample — Dichromate Process (*J*)

VII. *Form of Report.   Results of Complete Analysis.*

A (*A*) If the original sample is alkaline to phenolphthalein.

A convenient form for reporting the analysis of crude glycerin is given below:

A. Free alkali hydroxide as Na_2O....................... %
B_2. Total alkalinity as Na_2O................................
C. Alkali present as carbonate as Na_2O.....................
D. Alkali combined with organic acids as Na_2O.............
B_1. Ash...
F. Total residue at 160° C ....
G. Organic residue.....................................
H. Moisture..
I_3. Glycerol by acetin (corrected acetin value)............
    I_1. Uncorrected acetin value of sample.................
    I_2. Acetin value of 160° residue.......................
J. Glycerol by dichromate process........................

....

100% Analysis
From Acetin Value

H. Moisture... %
I_3. Glycerol..   ....
F. Total residue at 160° C...............................
    Over or under 100%................................

                                                100%

(*B*) If the original sample is acid to phenolphthalein, the items designated "*A*," "B_2," "*C*," and "*D*" are omitted from the report and item "*E*" is substituted, as below:

E. Grm. Na_2O required to neutralise 100 grm. of sample........%

Methods for reporting the analysis of refined glycerin follow.

REFINED GLYCERIN

I. *References:*
   Ardeer Factory Analytical Method Book, Part II–A, Method No. 33.
   J. Ind. Eng. Chem., 1910, **2**, 11.

II. *Principle and Status.*—In addition to the estimations required for the regular specification analysis of refined glycerin, the detailed procedure includes directions for making the silver test, and reference is also made to the acetin method for the estimation of the glycerol content, and the method for the estimation of moisture.

The method for the estimation of sp. gr. has been standard for a number of years, and yields unquestionably accurate results.   Under "IV. Reagents and Apparatus," the method for standardising the

pyknometer is given with special reference to its use with glycerin. Duplicate capacity estimations should agree within 0.005%, a difference equivalent to approximately 0.00005 in subsequent sp. gr. estimations. The greatest allowable tolerance between the sp. gr. obtained by two laboratories working on the same sample of glycerin is + 0.00015. The estimation is made at the temperature which is most easily kept constant, provided it is between 15.6° and 30°. For instance, if the room temperature is 25°, the evaporation of the water in the bath will cause it to remain practically constant at 23°, at which temperature the estimation should be made. The advantage of making the sp. gr. estimation at $t°$ rather than at 15.6° is that the bath can be more easily kept at a constant temperature. Moreover, if the estimations were made at 15.6°, the average temperature of the air being considerably above this, a deposition of moisture would occur on the cool surface of the pyknometer, necessitating a delay in weighing until equilibrium with the atmosphere could be established. A laboratory regularly making sp. gr. estimations should be provided with at least six pyknometers, which will permit covering a carload lot of thirty drums, and thus by making the estimations simultaneously, save much time and labour.

The published tables on the relation between the purity and the sp. gr. of glycerin exhibit no agreement among themselves, sometimes differing by as much as 1.0% in the strength ascribed to a given sp. gr. For this reason, Table IV has been appended, though not concerned with the particular specifications forming the basis of this Specification Analysis. This table represents the opinion of the Glycerin Committee and therefore has official status.

Most samples of refined glycerin show an acid reaction with phenolphthalein. This acidity was formerly supposed to be due to the presence of fatty acids, but it has been found to be due in the majority of cases to resin acids. The distinction between the presence of vegetable or animal fats or fatty acids and mineral oils may be detected by the camphor test.[1]

[1] *Camphor Test for Fatty Acids.* —Place a minute fragment of camphor, about the size of a pin head, on the surface of about 200 c.c. of very pure distilled water contained in a beaker absolutely free from all traces of grease. The camphor will immediately acquire a rotary motion. Add a few c.c. of the diluted glycerin sample to the beaker; if either animal or vegetable fats or fatty acids are present, this rotary motion of the camphor fragment will be immediately arrested, and it will float quietly on the surface of the water. Mineral oils are without effect. The sensitiveness of the test is such that merely drawing the finger through the hair of the head and then immersing it in the water will immediately check the motion of the camphor. Under these circumstances, the most scrupulous cleanliness is required in the execution of this test.

Whilst the percentage of "char" is not reported separately in the specification analysis, the directions for making the routine test are given. By the term "char" is meant the carbonaceous residue left when glycerin, having been once heated to ignition, is allowed to burn without further application of external heat until all combustible matter is consumed. The residue consists chiefly of carbon, together with a small amount of incompletely carbonised organic matter, the proportion of the latter usually increasing with the total amount of residue.

In the estimation of ash, the complete combustion of the carbonaceous residue can seldom be effected without volatilising a portion of the NaCl, but if the amount of NaCl and other chlorides present does not exceed the specifications limit (0.01% chlorides calculated as Cl) the error from this source is insignificant. In case the glycerin has a high salt content, or when special accuracy is required, the soluble salts are extracted from a sample of the charred residue by lixiviating with boiling water and filtering, subsequently recovering them by evaporation. The insoluble residue is then ignited and the weight of the ash added to the weight of the residue from the evaporation gives the weight of the total ash.

A more accurate estimation of the chlorine present as chlorides may be made by running the chlorine estimation on the evaporated residue from the extracted char, to which has been added the soluble portion of the ignited char, though for ordinary purposes the estimation made on the ash is sufficiently accurate. A direct titration of the chlorides by merely diluting the glycerin invariably yields low results for, although the foreign organic matter increases the consumption of $AgNO_2$, its action imparts a brownish tinge which it is impossible to distinguish from the true end-point colour produced by Ag_2CrO_4.

The tests for odour and suspended matter are entirely arbitrary and so much depends on the personal element that these tests are of little value except in extreme cases.

The silver test was intended for the detection of acrolein, formic and butyric acids, and in general such organic substances as will reduce silver nitrate   The test is entirely empirical and is now held to be of little significance except in extreme cases.

The acetin method when applied to samples of refined glycerol yields quantitative results, and is useful where there is suspicion of

adulteration with impurities which would not affect the sp. gr. estimation.

Estimations *A* to *F* (incl.) are always required for the specification analysis of glycerin. The other tests are only made in special cases or on request.

III. *Reagents and Apparatus:*

(*A*) *Reagents.*

Standard NaOH and HCl solutions (approximately 0.3 N.).

Phenolphthalein indicator (5 grm. per litre of 50% alcohol).

Standard AgNO₃ solution (approximately 0.01 N.).

Silver nitrate solution (10%).

(*B*) *Apparatus.*

Pyknometer.—The pyknometer used in the sp. gr. estimation on glycerin should be of the standard 50 c.c. Geissler type (see Fig. 18), provided with a piece of glass tubing 6 cm. in length and attached to the side tube of the pyknometer by means of a piece of rubber tubing 2.5 mm. in diameter and 2 cm. in length. The thermometers should be calibrated at four points, namely, 15°, 20°, 25° and 30°, and each nstrument should be furnished with the thermometer corrections for these four temperatures. (See also description of pyknometer without thermometer, page 718.)

Prepare the pyknometer either for standardisation or for use by first cleaning the interior with chromate cleaning solution, thoroughly rinsing with water, alcohol and ether, and expelling the ether by a current of air, which has passed through a drying train, which will free it from dust, grease, moisture and acid. Under no circumstances subject the pyknometer to any considerable elevation of temperature. Wipe the pyknometer first with a damp cloth and then with a dry cloth or with filter paper. This standard method for preparing the pyknometer for accurate weighing insures uniformity with respect to the invisible film of moisture present on glass surfaces.

The method of standardising the pyknometer should parallel the procedure indicated under "VI" for the estimation of glycerin, except that freshly boiled distilled water, which has been cooled to about the temperature of the constant temperature bath, is substituted for the glycerin. The capacity in grm. of water at 15.6° is calculated from the weight of water obtained at $t°$, corrected by the following formula:

$$C = W \cdot \frac{D}{d} \cdot \frac{1}{1 + a\,(t - 15.6)}$$

in which t = Observed Temperature.

$\qquad W$ = Capacity in grm. at $t°$.

$\qquad C$ = Capacity in grm. at 15.6°.

$\qquad D$ = Density of water at 15.6°.

$\qquad d$ = Density of water at $t°$.

$\qquad a$ = Thermal coefficient of cubical expansion of glass = 0.000025 per 1°.

Table II gives the values for "D" and "d," the density of pure water free from air. Table III gives the logarithm for the values of the expression.

$$\frac{D}{d} \cdot \frac{1}{1 + a\,(t - 15.6)}$$

for every 0.1° from 15.6–30°. To use this table, add the logarithm opposite the observed temperature to the logarithm of the weight of water contained "W"; the sum represents the logartithm of the capacity.

IV. *Preparation of the Sample:*

Glycerin being very hygroscopic, the samples should be taken, if possible, in clear, dry weather, with a "thief" which will deliver a portion of each drum in the least possible time. A "thief" made of glass tubing 2 cm. inside diameter and 70 cm. in length, having one end fused so that the thumb will cover the air hole, will deliver from 125 to 150 c.c. of glycerin, depending upon the time allowed to drain and the viscosity of the glycerin. One thief full from each drum will suffice and will be delivered in less time than if a thief of smaller diameter be used, thereby lessening the time of exposure to the atmosphere with less chance of taking up moisture. The standard thief described on page 693 should be used if available.

Strip the "thief" as it is drawn from the drum, of the outer coating of glycerin by pulling it through the hand while tightly clasped around it, and allow the drippings to flow back into the drum. Rinse at least twice, in the same way as the sample is taken, in the glycerin of the new drum when changing from one drum to another before taking the sample. In filling the thief, lower into the glycerin

very gradually so that a thief full will represent every stratum in the drum. In this way, a column of glycerin can be taken out of the drum, whilst if it is lowered to any one point and allowed to fill a local sample is obtained. Make a composite sample for each 5 drums of a shipment unless a special sample is required. Provide special standard bottles to contain the sample as it is taken. These are glass stoppered, wide mouth bottles of at least 800 c.c. capacity. Mark the stoppers and bottles so that the stoppers will be returned to the proper bottles after being washed and dried, thus insuring perfectly fitting stoppers. Before using, they should be thoroughly dried either with alcohol and ether and blown dry with dry air or placed in a hot air oven for some time, being stoppered after drying.

After taking the sample, wipe any glycerin from the outside of the neck and stopper of the sample bottle with a dry cloth to prevent the glycerin between the stopper and neck from absorbing moisture upon allowing the sample to stand.

Shake the sample, which should represent 5 drums (unless otherwise specified), and set aside until all air bubbles disappear. Before transferring the glycerin from the original sample bottle to another bottle, take care to wipe the lip and inner neck of the bottle and the stopper with a dry cloth before and after pouring the glycerin, so that if any glycerin around the stopper has taken up moisture it will not get into the sample.

V. Procedure:

(A) Specific Gravity:

Place the tubing attachment firmly over the end of the pyknometer capillary, and transfer the glycerin to the pyknometer, avoiding air bubbles. Wipe the lip and inside of the neck of the sample bottle with a clean, dry cloth before and after pouring out the glycerin to prevent getting any diluted glycerin in the pyknometer. Also wipe the stopper of the sample bottle with a dry cloth before replacing it in the bottle. After filling the pyknometer, carefully draw up the glycerin in the tubing attachment until it appears well up in the capillary. Set the thermometer firmly in place, and wash the whole apparatus free of the surplus glycerin. Set the pyknometer in a constant temperature water bath and maintain the temperature of the bath constant until the thermometer in the pyknometer and the thermometer in the bath register the same temperature, and allow to remain for a period of 10 minutes

longer to make sure that the temperature of the glycerin is the same throughout the pyknometer. Carefully remove the tubing attachment, and wipe the excess glycerin from the top of the capillary with a dry finger before removing the pyknometer from the water. After removing the pyknometer from the water, wipe the ground portion of the capillary quickly with a piece of filter paper and replace the cap tightly. Wipe the whole pyknometer, first with a wet cloth and then with a dry cloth, and weigh rapidly.

Calculation:

$$\frac{G}{C} \cdot \frac{1}{1 + a\,(t - 15.6)} + B\,(t - 15.6) = \text{sp. gr. at } \frac{15.6°}{15.6°}$$

in which t = Observed temperature.

G = Grm. glycerin at $t°$.

C = Capacity of pyknometer in grams of water at 15.6°.

a = Coefficient of expansion of glass = 0.000025 per 1°.

B = Thermal Coefficient of Expansion of

Glycerin = 0.00061 between 15.6° and 20°.

0.000615 between 20° and 25°.

0.00062 between 25° and 30°.

Table I, p. 711, gives the logarithms of the values of the expression $1 + a(t - 15.6)$ and the values of the expression $B(t - 15.6)$ in the above formula for every 0.1° from 15.7–30°. Add the logarithm of the value $1 + a(t - 15.6)$ corresponding to the observed temperature of the glycerin to the logarithm of the capacity of the pyknometer used at 15.6°, "C," and subtract the sum from the logarithm of the weight of the glycerin "G." The number corresponding to the remaining logarithm plus the value of $B(t - 15.6)$ at the observed temperature gives the sp. gr. of the sample at $\frac{15.6°}{15.6°}$.

Table IV gives the best data available on the conversion of corrected sp. gr. readings to per cent. glycerol.

(B) *Acidity or Alkalinity.*

Measure 50 c.c. of glycerin in a 50 c.c. graduate, and pour into a beaker. Wash out the graduate with 100 c.c. of freshly boiled, distilled water to which 0.5 c.c. phenolphthalein indicator has been added, and sufficient acid or alkali to bring to exact neutrality. Titrate the glycerin solution to neutrality with 0.3 N HCl solution or 0.3 N. NaOH solution as required.
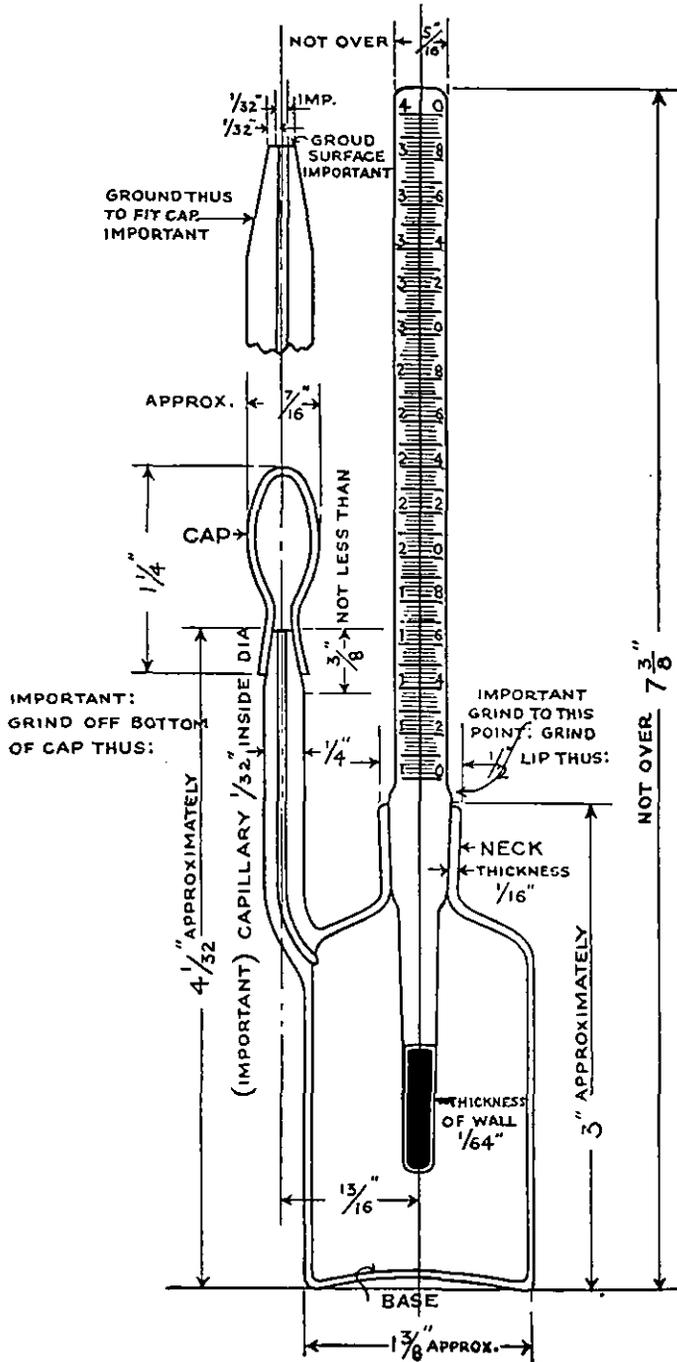
FIG. 18.

Calculation:

$$\text{c.c. NaOH} \times \text{N.} = \text{c.c. N. NaOH per 50 c.c.}$$

or

$$\text{c.c. HCl} \times \text{N.} = \text{c.c. N. HCl per 50 c.c.}$$

(C) Ash.

Weigh about 50 grm. of the glycerin in a tared platinum dish and heat until the vapour continues to burn after the withdrawal of the flame. Allow the combustion to proceed until it dies out. Carefully protect the operation from draughts, especially during the latter part of the combustion, as a premature extinguishing of the flame, even by but a few seconds, materially lessens the carbonisation of the residue. Cool in a desiccator and weigh if the char estimation (see below) is to be made.

Ignite the residue in the platinum dish avoiding a greater heat than necessary to secure complete combustion of the carbonaceous residue. Cool and weigh the ash.

Calculation:

$$\frac{\text{wt. of ash} \times 100}{\text{wt. of sample}} = \%\ \text{Ash.}$$

In case a separate report on the char is desired the char is the first residue (carbonaceous) minus the second residue (ash).

$$\frac{(\text{wt. of carbonaceous residue} - \text{wt. of ash residue}) \times 100}{\text{wt. of sample}} = \%\ \text{Char.}$$

(D) Chlorides.

Add about 10 c.c. of hot distilled water to the ash residue in the platinum dish and triturate with the end of a glass rod. Finally wash the contents of the dish onto a filter and wash thoroughly

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PYKNOMETER SPECIFICATIONS (see p. 708).

Base: Bottom slightly concave as shown, to stand on flat surface.

Neck: Should be thoroughly ground with tight joint. Thermometer rigid when in place with no indentation between tip of neck and thermometer.

Thermometer: Thickness of glass as near as possible to $\frac{1}{64}$ in. Extremities of bulk approximately equidistant from shoulder and base of body of pyknometer. The joint at the lower end of the thermometer should contain no unground portions and should project slightly above the top of the neck. Scale range from $10°$ to $40°$ graduated in $\frac{1}{5}°$. Accuracy to be guaranteed within $0.2°$ between $15°$ and $30°$. Scale of opalescent glass to be sealed rigidly in place.

Capillary: Ground portion fitting into cap to be ground true without shoulder below lower end of cap to prevent ridge forming or wearing.

Numbering: All instruments to be numbered serially, same number to be shown on bottle, cap and thermometer of each instrument and manufacturer's initials to be etched on bottle.

Capacity: Approximately 50 c.c.

Note: Each pyknometer to be packed in separate box.

with hot water, collecting the filtrate in a porcelain evaporating dish or casserole. Add 1 c.c. of potassium chromate indicator and 1 to 2 mg. of Na_2CO_3. Titrate to the first permanent reddish tint with 0.01 N. $AgNO_3$ solution.

Calculation:

$$\frac{\text{c.c. } AgNO_3 \times \text{N.} \times 3.546}{\text{wt. of sample}} = \% \text{ Chlorides as Cl.}$$

(*E*) *Odour.*

Observe the odour of the original sample.

(*F*) *Suspended Matter.*

Estimate by observation in an ordinary test-tube.

(*G*) *Silver Test.*

Place 10 c.c. of a 10% solution of $AgNO_3$ in a small glass stoppered cylinder, and add 10 c.c. of the glycerin sample. Mix thoroughly by repeated inversions of the cylinder, but avoid vigorous agitation. Conduct the operation in a subdued light as rapidly as possible, and, when completed, allow the cylinder to stand for 10 minutes in a perfectly dark place. At the expiration of this time, inspect the appearance of the mixture by transmitted light and report any change in colour or formation of a precipitate.

(*H*) *Glycerol Content by the Acetin Method.*

Estimate the glycerol content of the sample of refined glycerin in the same manner as described under Method 697 for crude glycerin.

(*I*) *Moisture.*

Estimate moisture by the procedure described on page 721.

It has been found almost impossible to purchase or have made pyknometers having thermometers which are sufficiently accurate for use in determining the specific gravity of refined glycerin. Usually only approximations of the true temperature of the glycerin inside the pyknometer are possible and the final temperature is best determined by means of an accurate thermometer in the constant temperature water bath, keeping the sample in the bath long enough for the glycerin to come to this same temperature throughout. The solt glass, ordinarily used in making pyknometers, chips easily on grinding and with usage. On account of the above difficulties, a better pyknometer was desirable and the Walker[1] type, made from

[1] Walker, *Bull.* 109, U. S. Bureau of Chemistry.

TABLE I

Logarithm of the value of the expression $1 + a(t - 15.6)$ and value of the expression $B(t - 15.6)$.

In the formula: $\dfrac{G}{C} \cdot \dfrac{1}{1 + a(t - 15.6)} + B(t - 15.6) = $ sp. gr. at $\dfrac{15.6°}{15.6°}$

Temp.	Log. values of $1 + a(t - 15.6)$	Values of $B(t - 15.6)$	Temp.	Log. values of $1 + a(t - 15.6)$	Values of $B(t - 15.6)$
15.6	.0000000	.00000	19.1	.0000380	.00213
15.7	.0000011	.00006	19.2	.0000391	.00220
15.8	.0000022	.00012	19.3	.0000402	.00226
15.9	.0000033	.00018	19.4	.0000412	.00232
16.0	.0000043	.00024	19.5	.0000423	.00238
16.1	.0000054	.00030	19.6	.0000434	.00244
16.2	.0000065	.00037	19.7	.0000445	.00250
16.3	.0000075	.00043	19.8	.0000456	.00256
16.4	.0000087	.00049	19.9	.0000467	.00262
16.5	.0000098	.00055	20.0	.0000478	.00268
16.6	.0000109	.00061	20.1	.0000489	.00274
16.7	.0000119	.00067	20.2	.0000500	.00280
16.8	.0000130	.00074	20.3	.0000510	.00286
16.9	.0000141	.00080	20.4	.0000521	.00293
17.0	.0000152	.00086	20.5	.0000532	.00299
17.1	.0000162	.00092	20.6	.0000543	.00306
17.2	.0000174	.00098	20.7	.0000554	.00312
17.3	.0000185	.00104	20.8	.0000565	.00319
17.4	.0000196	.00110	20.9	.0000575	.00325
17.5	.0000207	.00117	21.0	.0000586	.00331
17.6	.0000217	.00122	21.1	.0000597	.00337
17.7	.0000228	.00129	21.2	.0000608	.00343
17.8	.0000239	.00135	21.3	.0000619	.00350
17.9	.0000250	.00141	21.4	.0000629	.00356
18.0	.0000261	.00147	21.5	.0000640	.00362
18.1	.0000272	.00153	21.6	.0000651	.00368
18.2	.0000283	.00159	21.7	.0000662	.00374
18.3	.0000294	.00165	21.8	.0000673	.00380
18.4	.0000304	.00171	21.9	.0000684	.00386
18.5	.0000315	.00177	22.0	.0000695	.00393
18.6	.0000326	.00183	22.1	.0000705	.00399
18.7	.0000336	.00189	22.2	.0000716	.00405
18.8	.0000347	.00195	22.3	.0000727	.00411
18.9	.0000358	.00201	22.4	.0000738	.00418
19.0	.0000369	.00207	22.5	.0000749	.00424

TABLE. I.—(*Continued*)

Temp.	Log. values of $1 + a(t - 15.6)$	Values of $B(t - 15.6)$	Temp.	Log. values of $1 + a(t - 15.6)$	Values of $B(t - 15.6)$
22.6	.0000760	.00430	26.6	.0001194	.00681
22.7	.0000771	.00436	26.7	.0001205	.00687
22.8	.0000782	.00442	26.8	.0001216	.00693
22.9	.0000792	.00449	26.9	.0001226	.00700
23.0	.0000803	.00455	27.0	.0001237	.00706
23.1	.0000814	.00461	27.1	.0001248	.00712
23.2	.0000825	.00467	27.2	.0001259	.00719
23.3	.0000836	.00474	27.3	.0001270	.00725
23.4	.0000847	.00480	27.4	.0001281	.00731
23.5	.0000858	.00486	27.5	.0001292	.00737
23.6	.0000869	.00492	27.6	.0001303.	.00743
23.7	.0000879	.00499	27.7	.0001313	.00750
23.8	.0000890	.00505	27.8	.0001324	.00756
23.9	.0000901	.00511	27.9	.0001335	.00762
24.0	.0000912	.00517	28.0	.0001346	.00769
24.1	.0000922	.00524	28.1	.0001357	.00775
24.2	.0000933	.00530	28.2	.0001368	.00782
24.3	.0000944	.00536	28.3	.0001379	.00788
24.4	.0000955	.00543	28.4	.0001390	.00794
24.5	.0000966	.00549	28.5	.0001400	.00800
24.6	.0000977	.00555	28.6	.0001411	.00807
24.7.	.0000988	.00562	28.7	.0001422	.00813
24.8	.0000999	.00568	28.8	.0001433	.00819
24.9	.0001010	.00574	28.9	.0001443	.00826
25.0	.0001021	.00580	29.0	.0001454	.00832
25.1	.0001032	.00587	29.1	.0001465	.00838
25.2	.0001042	.00593	29.2	.0001476	.00844
25.3	.0001053	.00600	29.3	.0001487	.00851
25.4	.0001064	.00606	29.4	.0001498	.00857
25.5	.0001075	.00612	29.5	.0001509	.00864
25.6	.0001086	.00618	29.6	.0001520	.00870
25.7	.0001096	.00624	29.7	.0001530	.00876
25.8	.0001107	.00630	29.8	.0001541	.00882
25.9	.0001118	.00637	29.9	.0001552	.00889
26.0	.0001129	.00643	30.0	.0001563	.00895
26.1	.0001139	.00649	30.1	.0001574	.00901
26.2	.0001150	.00655	30.2	.0001585	.00908
26.3	.0001161	.00662	30.3	.0001596	.00914
26.4	.0001172	.00668	30.4	.0001607	.00920
26.5	.0001183	.00674	30.5	.0001618	.00927

TABLE IA

(For use with pyrex pyknometers)

Logarithm of the value of the expression $1 + a(t - 15.6)$ and value of the expression $B(t - 15.6)$

In the formula: $\dfrac{G}{C} \cdot \dfrac{1}{1 + a(t - 15.6)} + B(t - 15.6) =$ sp. gr. at $\dfrac{15.6°\text{ C.}}{15.6°\text{ C.}}$

Temp.	Log. values of $1 + a(t - 15.6)$	Values of $B(t - 15.6)$	Temp.	Log. values of $1 + a(t - 15.6)$	Values of $B(t - 15.6)$
15.6	.0000000	.00000	19.1	.0000121	.00213
15.7	.0000003	.00006	19.2	.0000125	.00220
15.8	.0000007	.00012	19.3	.0000128	.00226
15.9	.0000010	.00018	19.4	.0000132	.00232
16.0	.0000014	.00024	19.5	.0000135	.00238
16.1	.0000017	.00030	19.6	.0000139	.00244
16.2	.0000021	.00037	19.7	.0000142	.00250
16.3	.0000024	.00043	19.8	.0000145	.00256
16.4	.0000027	.00049	19.9	.0000149	.00262
16.5	.0000031	.00055	20.0	.0000152	.00268
16.6	.0000034	.00061	20.1	.0000156	.00274
16.7	.0000038	.00067	20.2	.0000160	.00280
16.8	.0000041	.00074	20.3	.0000163	.00286
16.9	.0000045	.00080	20.4	.0000167	.00293
17.0	.0000048	.00086	20.5	.0000170	.00299
17.1	.0000052	.00092	20.6	.0000174	.00306
17.2	.0000055	.00098	20.7	.0000177	.00312
17.3	.0000059	.00104	20.8	.0000181	.00319
17.4	.0000062	.00110	20.9	.0000184	.00325
17.5	.0000066	.00117	21.0	.0000187	.00331
17.6	.0000069	.00122	21.1	.0000191	.00337
17.7	.0000073	.00129	21.2	.0000195	.00343
17.8	.0000076	.00135	21.3	.0000198	.00350
17.9	.0000080	.00141	21.4	.0000202	.00356
18.0	.0000083	.00147	21.5	.0000205	.00362
18.1	.0000087	.00153	21.6	.0000208	.00368
18.2	.0000090	.00159	21.7	.0000211	.00374
18.3	.0000094	.00165	21.8	.0000215	.00380
18.4	.0000097	.00171	21.9	.0000219	.00386
18.5	.0000101	.00177	22.0	.0000222	.00393
18.6	.0000104	.00183	22.1	.0000226	.00399
18.7	.0000107	.00189	22.2	.0000229	.00405
18.8	.0000111	.00195	22.3	.0000233	.00411
18.9	.0000115	.00201	22.4	.0000236	.00418
19.0	.0000118	.00207	22.5	.0000240	.00424

TABLE LI.—(*Continued*)

Temp.	Log. values of $1 + a(t - 15.6)$	Values of $B(t - 15.6)$	Temp.	Log. values of $1 + a(t - 15.6)$	Values of $B(t - 15.6)$
22.6	.0000243	.00430	26.6	.0000382	.00681
22.7	.0000247	.00436	26.7	.0000386	.00687
22.8	.0000250	.00442	26.8	.0000389	.00693
22.9	.0000254	.00449	26.9	.0000393	.00700
23.0	.0000257	.00455	27.0	.0000396	.00706
23.1	.0000261	.00461	27.1	.0000400	.00712
23.2	.0000264	.00467	27.2	.0000403	.00719
23.3	.0000268	.00474	27.3	.0000406	.00725
23.4	.0000271	.00480	27.4	.0000410	.00731
23.5	.0000275	.00486	27.5	.0000413	.00737
23.6	.0000278	.00492	27.6	.0000417	.00743
23.7	.0000282	.00499	27.7	.0000420	.00750
23.8	.0000285	.00505	27.8	.0000424	.00756
23.9	.0000289	.00511	27.9	.0000427	.00762
24.0	.0000292	.00517	28.0	.0000431	.00769
24.1	.0000295	.00524	28.1	.0000434	.00775
24.2	.0000299	.00530	28.2	.0000437	.00782
24.3	.0000302	.00536	28.3	.0000441	.00788
24.4	.0000306	.00543	28.4	.0000444	.00794
24.5	.0000309	.00549	28.5	.0000448	.00800
24.6	.0000313	.00555	28.6	.0000451	.00807
24.7	.0000316	.00562	28.7	.0000455	.00813
24.8	.0000319	.00568	28.8	.0000458	.00819
24.9	.0000323	.00574	28.9	.0000462	.00826
25.0	.0000326	.00580	29.0	.0000465	.00832
25.1	.0000330	.00587	29.1	.0000469	.00838
25.2	.0000333	.00593	29.2	.0000472	.00844
25.3	.0000337	.00600	29.3	.0000476	.00851
25.4	.0000340	.00606	29.4	.0000479	.00857
25.5	.0000344	.00612	29.5	.0000483	.00864
25.6	.0000347	.00618	29.6	.0000486	.00870
25.7	.0000351	.00624	29 7	.0000490	.00876
25.8	.0000355	.00630	29.8	.0000493	.00882
25.9	.0000358	.00637	29.9	.0000497	.00889
26.0	.0000362	.00643	30.0	.0000500	.00895
26.1	.0000365	.00649	30.1	.0000503	.00901
26.2	.0000369	.00655	30.2	.0000507	.00908
26.3	.0000372	.00662	30.3	.0000510	.00914
26.4	.0000376	.00668	30.4	.0000514	.00920
26.5	.0000379	.00764	30.5	.0000517	.00927

TABLE II

Density of pure water free from air
Values of D and d

Deg. C.	0	1	2	3	4	5	6	7	8	9	Mean differences
0	0.9998681	8747	8812	8875	8936	8996	9053	9109	9163	9216	+ 59
1	9267	9315	9363	9408	9452	9494	9534	9573	9610	9645	+ 41
2	9679	9711	9741	9769	9796	9821	9844	9866	9887	9905	+ 24
3	9922	9937	9951	9962	9973	9981	9988	9994	9998	*0000	+ 8
4	1.0000000	*9999	*9996	*9992	*9986	*9979	*9970	*9960	*9947	*9934	− 8
5	0.9999919	9902	9884	9864	9842	9819	9795	*9769	9742	9713	− 24
6	9682	9650	9617	9582	9545	9507	9468	9427	9385	9341	− 39
7	9296	9249	9201	9151	9100	9048	8994	8938	8881	8823	− 53
8	8764	8703	8641	8577	8512	8445	8377	8308	8237	8165	− 67
9	8091	8017	7940	7863	7784	7704	7622	7539	7455	7369	− 81
10	7282	7194	7105	7014	6921	6826	6729	6632	6533	6432	− 95
11	6331	6228	6124	6020	5913	5805	5696	5586	5474	5362	−108
12	5248	5132	5016	4898	4780	4660	4538	4415	4291	4166	−121
13	4040	3912	3784	3654	3523	3391	3257	3122	2986	2859	−133
14	2712	2572	2431	2289	2147	2003	1858	1711	1564	1416	−145
15	1266	1114	0962	0809	0655	0499	0343	0185	0026	*9865	−156
16	0.9989705	9542	9378	9214	9048	8881	8713	8544	8373	8202	−168
17	8029	7856	7681	7505	7328	7150	6971	6791	6610	6427	−178
18	6244	6058	5873	5686	5498	5309	5119	4927	4735	4541	−190
19	4347	4152	3955	3757	3558	3358	3158	2955	2752	2549	−200
20	2343	2137	1930	1722	1511	1301	1090	0878	0663	0449	−211
21	0233	0016	*9799	*9580	*9359	*9139	*8917	*8694	*8470	*8245	−221
22	0.9978019	7792	7564	7335	7104	6873	6641	6408	6173	5938	−232
23	5702	5466	5227	4988	4747	4506	4264	4021	3777	3531	−242
24	3286	3039	2790	2541	2291	2040	1788	1535	1280	1026	−252
25	0770	0513	0255	*9997	*9736	*9476	*9214	*8951	*8688	*8423	−261
26	0.9968158	7892	7624	7356	7087	6817	6545	6273	6000	5726	−271
27	5451	5176	4898	4620	4342	4062	3782	3500	3218	2935	−280
28	2652	2366	2080	1793	1505	1217	0928	0637	0346	0053	−289
29	0.9959761	9466	9171	8876	8579	8282	7983	7684	7383	7083	−298
30	6780	6478	6174	5869	5564	5258	4950	4642	4334	4024	−307
31	3714	3401	3089	2776	2462	2147	1832	1515	1198	0880	−315
32	0561	0241	*9920	*9599	*9276	*8954	*8630	*8304	*7979	*7653	−324
33	0.9947325	6997	6668	6333	6007	5676	5345	5011	4678	*4343	−332
34	4007	3671	3335	2997	2659	2318	1978	1638	1296	0953	−340
35	0610	0267	*9922	*9576	*9230	*8883	*8534	*8186	*7837	*7486	−347
36	0.9937136	6784	6432	6078	5725	5369	5014	4658	4301	3943	−355
37	3585	3226	2866	2505	2144	1782	1419	1055	0691	0326	−362
38	0.9929960	9593	9227	8859	8490	8120	7751	7380	7008	6636	−370
39	6263	5890	*5516	5140	4765	4389	4011	*3634	3255	2876	−377
40	2497	2116	1734	1352	0971	0587	0203	*9818	*9433	*9047	−384
41	0.9918661										

TABLE III

Logarithm of the value of the expression $\dfrac{D}{d} \cdot \dfrac{1}{1 + a\,(t - 15.6)}$

In the formula: $C = W \cdot \dfrac{D}{d} \cdot \dfrac{1}{1 + a(t - 15.6)}$

Temp.	Logarithm	Temp.	Logarithm	Temp.	Logarithm	Temp.	Logarithm
15.6	0.0000000	19.2	0.0002389	23.0	0.0005567	26.8	0.0009380
.7	0.0000059	.3	0.0002464	.1	0.0005660	.9	0.0009487
.8	0.0000116	.4	0.0002540	.2	0.0005753		
.9	0.0000175	.5	0.0002616	.3	0.0005845	27.0	0.0009595
		.6	0.0002693	.4	0.0005939	.1	0.0009701
16.0	0.0000235	.7	0.0002769	.5	0.0006032	.2	0.0009813
.1	0.0000294	.8	0.0002850	.6	0.0006126	.3	0.0009927
.2	0.0000356	.9	0.0002924	.7	0.0006223	4	0.0010036
.3	0.0000411			.8	0.0006317	.5	0.0010147
.4	0.0000475	20.0	0.0003002	.9	0.0006415	.6	0.0010258
.5	0.0000538	.1	0.0003078			.7	0.0010369
.6	0.0000600	.2	0.0003158	24.0	0.0006510	.8	0.0010480
.7	0.0000663	.3	0.0003240	.1	0.0006607	.9	0.0010591
.8	0.0000727	.4	0.0003320	.2	0.0006704	28.0	0.0010708
.9	0.0000790	.5	0.0003401	.3	0.0006802	.1	0.0010821
		.6	0.0003481	.4	0.0006900	.2	0.0010936
17.0	0.0000855	.7	0.0003566	.5	0.0006997	.3	0.0011047
.1	0.0000917	.8	0.0003646	.6	0.0007095	.4	0.0011164
.2	0.0000985	.9	0.0003732	.7	0.0007197	.5	0.0011279
.3	0.0001047			.8	0.0007295	.6	0.0011396
.4	0.0001115	21.0	0.0003812	.9	0.0007398	.7	0.0011512
.5	0.0001182	.1	0.0003896			.8	0.0011628
.6	0.0001251	.2	0.0003980	25.0	0.0007496	.9	0.0011744
.7	0.0001317	.3	0.0004065	.1	0.0007596		
.8	0.0001383	.4	0.0004150	.2	0.0007699	29.0	0.0011869
.9	0.0001454	.5	0.0004233	.3	0.0007801	.1	0.0011978
		.6	0.0004319	.4	0.0007903	.2	0.0012096
18.0	0.0001521	.7	0.0004408	.5	0.0008004	.3	0.0012214
.1	0.0001592	.8	0.0004493	.6	0.0008109	.4	0.0012332
.2	0.0001659	.9	0.0004582	.7	0.0008212	.5	0.0012451
.3	0.0001730			.8	0.0008315	.6	0.0012569
.4	0.0001803	22.0	0.0004667	.9	0.0008420	.7	0.0012690
.5	0.0001875	.1	0.0004755			.8	0.0012810
.6	0.0001946	.2	0.0004845	26.0	0.0008525	.9	0.0012930
.7	0.0002017	.3	0.0004933	.1	0.0008632		
.8	0.0002091	.4	0.0005021	.2	0.0008739	30.0	0.0013052
.9	0.0002167	.5	0.0005110	.3	0.0008841	.1	0.0013171
		.6	0.0005200	.4	0.0008948	.2	0.0013290
19.0	0.0002238	.7	0.0005293	.5	0.0009056	.3	0.0013414
.1	0.0002313	.8	0.0005382	.6	0.0009167	.4	0.0013534
		.9	0.0005477	.7	0.0009274	.5	0.0013660

TABLE IV

Per cent. glycerol corresponding to sp. gr. at $\dfrac{15.6°}{15.6°}$

Sp. gr.	0	1	2	3	4	5	6	7	8	9
1.252	.....	.....	.....	......	95.00	95.03	95.07	95.11	95.15	95.19
1.253	95.23	95.27	95.31	95.35	95.39	95.43	95.46	95.50	95.54	95.58
1.254	95.62	95.65	95.69	95.73	95.77	95.80	95.84	95.88	95.92	95.96
1.255	96.00	96.03	96.07	96.11	96.15	96.19	96.23	96.26	96.30	96.34
1.256	96.38	96.42	96.46	96.50	96.54	96.58	96.62	96.66	96.70	96.74
1.257	96.78	96.82	96.86	96.90	96.94	96.98	97.02	97.05	97.09	97.13
1.258	97.17	97.21	97.24	97.28	97.32	97.36	97.40	97.44	97.48	97.52
1.259	97.56	97.60	97.64	97.68	97.72	97.76	97.80	97.84	97.88	97.92
1.260	97.96	98.00	98.03	98.07	98.11	98.15	98.19	98.23	98.26	98.30
1.261	98.34	98.38	98.41	98.45	98.49	98.53	98.57	98.60	98.64	98.68
1.262	98.72	98.76	98.80	98.84	98.88	98.92	98.96	99.00	99.03	99.07
1.263	99.11	99.15	99.19	99.22	99.26	99.30	99.34	99.37	99.41	99.45
1.264	99.49	99.53	99.56	99.60	99.64	99.68	99.72	99.76	99.80	99.84
1.265	99.88	99.92	99.96	100.0						

pyrex glass, with a soft glass capillary tube, was found to be much better than the thermometer type already described. The coefficient of expansion of pyrex glass is very low and extremely uniform. This coefficient for soft glass is 0.000025 and for pyrex glass it is 0.000008 per degree difference in temperature. This difference in expansion has made necessary the recalculation of Table I for the value of the expression $\dfrac{G}{C} \cdot \dfrac{1}{1 + a(t - 15.6°)} + B(t - 15.6°) =$ sp. gr. at $\dfrac{15.6°}{15.6°}$ and Table III for the expression $\dfrac{D}{d} \cdot \dfrac{1}{1 + a(t - 15.6°)}$. The new tables[1] are marked IA and IIIA—"For use with Pyrex Pyknometers."

[1] The tables were recalculated by Mr. George Lewis of the Eastern Laboratory, E. I. duPont deNemours & Co.

TABLE IIIA

(For use with pyrex pyknometers)

Logarithm of the value of the expression $\dfrac{D}{d} \cdot \dfrac{1}{1 + a(t - 15.6)}$

In the formula: $C = W \cdot \dfrac{D}{d} \cdot \dfrac{1}{1 + a(t - 15.6)}$

Temp.	Logarithm	Temp.	Logarithm	Temp.	Logarithm	Temp.	Logarithm
15.6	0.0000000	19.2	0.0002655	23.0	0.0006113	26.8	0.0010207
.7	0.0000067	.3	0.0002738	.1	0.0006213	.9	0.0010320
.8	0.0000131	.4	0.0002820	.2	0.0006314	27.0	0.0010436
.9	0.0000198	.5	0.0002904	.3	0.0006413	.1	0.0010549
16.0	0.0000264	.6	0.0002988	.4	0.0006515	.2	0.0010669
.1	0.0000331	.7	0.0003072	.5	0.0006615	.3	0.0010791
.2	0.0000400	.8	0.0003161	.6	0.0006717	.4	0.0010907
.3	0.0000462	.9	0.0003242	.7	0.0006820	.5	0.0011026
.4	0.0000535	20.0	0.0003328	.8	0.0006922	.6	0.0011144
.5	0.0000605	.1	0.0003411	.9	0.0007027	.7	0.0011262
.6	0.0000675	.2	0.0003498	24.0	0.0007130	.8	0.0011380
.7	0.0000744	.3	0.0003587	.1	0.0007234	.9	0.0011499
.8	0.0000816	.4	0.0003674	.2	0.0007338	28.0	0.0011623
.9	0.0000886	.5	0.0003763	.3	0.0007444	.1	0.0011744
17.0	0.0000959	.6	0.0003850	.4	0.0007549	.2	0.0011867
.1	0.0001027	.7	0.0003943	.5	0.0007654	.3	0.0011985
.2	0.0001104	.8	0.0004030	.6	0.0007759	.4	0.0012110
.3	0.0001173	.9	0.0004123	.7	0.0007869	.5	0.0012231
.4	0.0001249	21.0	0.0004211	.8	0.0007975	.6	0.0012356
.5	0.0001323	.1	0.0004302	.9	0.0008085	.7	0.0012479
.6	0.0001399	.2	0.0004393	25.0	0.0008191	.8	0.0012603
.7	0.0001472	.3	0.0004486	.1	0.0008298	.9	0.0012725
.8	0.0001546	.4	0.0004577	.2	0.0008408	29.0	0.0012848
.9	0.0001624	.5	0.0004668	.3	0.0008517	.1	0.0012974
18.0	0.0001699	.6	0.0004762	.4	0.0008627	.2	0.0013100
.1	0.0001777	.7	0.0004859	.5	0.0008735	.3	0.0013225
.2	0.0001852	.8	0.0004951	.6	0.0008848	.4	0.0013351
.3	0.0001930	.9	0.0005047	.7	0.0008957	.5	0.0013477
.4	0.0002010	22.0	0.0005140	.8	0.0009067	.6	0.0013603
.5	0.0002080	.1	0.0005234	.9	0.0009180	.7	0.0013730
.6	0.0002168	.2	0.0005332	26.0	0.0009192	.8	0.0013858
.7	0.0002246	.3	0.0005427	.1	0.0009406	.9	0.0013985
.8	0.0002327	.4	0.0005523	.2	0.0009520	30.0	0.0014115
.9	0.0002410	.5	0.0005619	.3	0.0009630	.1	0.0014242
19.0	0.0002489	.6	0.0005717	.4	0.0009744	.2	0.0014368
.1	0.0002572	.7	0.0005817	.5	0.0009860	.3	0.0014500
		.8	0.0005914	.6	0.0009979	.4	0.0014627
		.9	0.0006015	.7	0.0010093	.5	0.0014761

3. PURE GLYCERIN

Chemically pure glycerin comes on the market in three grades: sp. gr. 1.24, sp. gr. 1.25, sp. gr. 1.26, respectively. The "glycerinum" of the British Pharmacopœia has a sp. gr. 1.26; that of the United States Pharmacopœia of 1.25.

The percentage of glycerol in pure glycerin can be ascertained by taking the sp. gr. and observing the refractive index in the manner

SCALE: FULL SIZE
(DETAILS TWICE FULL SIZE)

11 mm
TOL.: 2 mm

1·5 mm DIA.
TOL.: 0·2 mm

32 mm
TOLERANCE: 3 mm

10 mm
TOL.: 2 mm

IMPORTANT:
GRIND SURFACE
FLAT AND SMOOTH

IMPORTANT:
GRIND BOTTOM OF CAP
FLAT AND SMOOTH

7·5 mm DIA.
TOL.: 0·5 mm

CAPILLARY:
1·0 mm DIA.
TOL.: 0·2 mm

15 mm DIA.
TOL.: 1·5 mm

10 mm
TOL.: 1·0 mm

145 mm
TOLERANCE: 8 mm

19 mm
TOL.: 2 mm

75 mm
TOLERANCE: 5 mm

36 mm
TOLERANCE: 3 mm

4 mm
TOL.: 0·5 mm

3·5 mm
TOL.: 0·2 mm
ON EACH

DETAIL OF TOP
OF STEM

2·5 mm
TOL.: 0·5 mm

IMPORTANT:
GROUND PORTIONS
MUST EXTEND BELOW
BOTTOM OF CAP
AND ABOVE NECK
AS SHOWN

IMPORTANT:
GRIND TOP OF NECK
THUS, AND POLISH.
AVOID INDENTATION
BETWEEN INNER
EDGE OF NECK
AND STEM.

2·5 mm
TOL.: 0·5 mm

THICKNESS OF
WALL OF NECK
2 mm. TOL.: 0·5 mm

10 mm
TOL.: 1 mm

DETAIL OF NECK

10 mm
TOL.: 0·5 mm

11 mm
TOL.: 0·5 mm
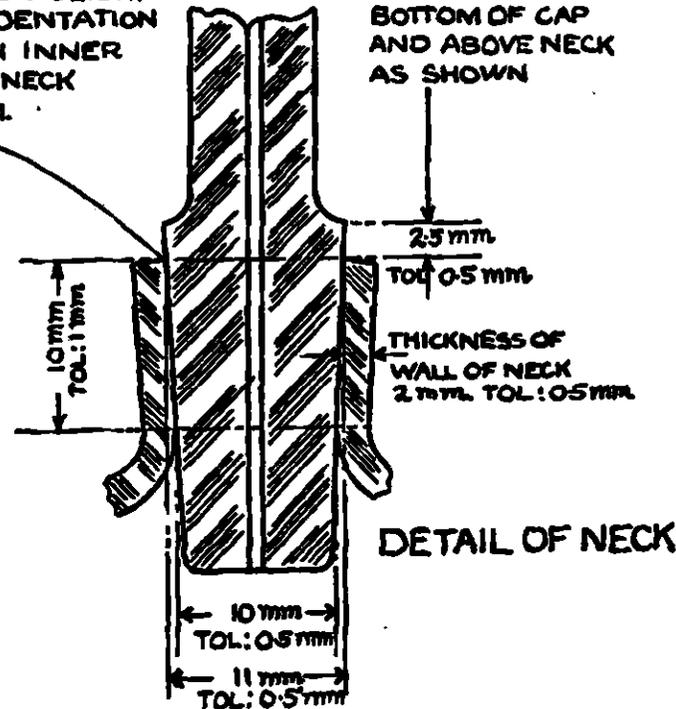
SLOPE OF STEM INDICATED BY
DIFFERENCE OF 1·0 mm DIA. IN
VERTICAL DISTANCE OF 10 mm
AS SHOWN

FIG. 19.

PYKNOMETER

GENERAL DESCRIPTION: Pyknometer or Specific
gravity bottle, consisting of three
parts, viz.: bottle, capillary stem
and cap.

CAPACITY: 50 ml., Tolerance 5 ml.

MATERIAL: Bottle and Cap to be made of Pyrex
glass, capillary stem to be made of
regular stock, all parts to be thorough-
ly annealed.

GRINDING: To be done with the utmost care,
insuring perfect fitting of stopper por-
tion of capillary stem into neck of
bottle, and of cap on upper end of
capillary stem.

BASE: Bottom slightly concave as shown, to
stand on flat surface.

SPECIAL MARKING: Manufacturer's serial
number, and name, initials or trade-
mark to be engraved on each instrument,
the same serial number to appear on
each of the three separate parts.

DIMENSIONS: To be as shown and within the
specified tolerances.

CASE: Each instrument to be packed in
separate box.

already described.(page 674). With dilute solutions the percentage of glycerol is best ascertained by means of the dichromate method; Lewkowitsch also recommends the permanganate method for this purpose (compare above).

Ash *plus* polyglycerins should not exceed 0.03%; *ash* alone should not exceed 0.01%.

Acrolein (and other reducing substances) are best detected by adding a few drops of silver nitrate solution to the diluted glycerin; after standing 24 hours there should be no visible blackening. The test is made more sensitive by using ammoniacal silver nitrate.

L. F. Kebler and H. C. Fuller have examined a number of samples of commercially pure glycerin in order to ascertain to what extent commercial glycerin complies with the requirements of the U. S. Pharmacopœia. Eleven samples were obtained from American manufacturers, whilst 2 were of foreign origin, purchased in the open market. The sp. gr. at 25° ranged from 1.248 to 1.258, all exceeding the Pharmacopœia standard of 1.246. In every case reduction occurred when the samples were submitted to the pharmacopœal test with ammoniacal silver nitrate. This test is therefore regarded as inconclusive and Hager's test is preferred; according to this, 5 c.c. of the glycerin are mixed with 5 c.c. of 26% ammonia and 5 drops of silver nitrate solution and the mixture left in the dark for 15 minutes at the ordinary temperature.

Two of the samples gave a pronounced reduction, 5 a slight coloration whilst with 6 there was no reduction. The quantity of arsenic ranged from *nil* to 0.75 parts per million with the exception of a foreign sample which contained 3.75 parts. On the basis of this examination the authors conclude that glycerin of the best quality should answer to the following requirements: It should be neutral to litmus, leave no ash on ignition and have a sp. gr. of about 1.25 at 25°. It should emit only a slight odour when heated on the water-bath and not give off an unpleasant ethereal or a fruity odour when warmed with alcohol and sulphuric acid. When mixed with an equal volume of sulphuric acid there should be no disagreeable odour nor any *coloration deeper than* yellow. In Hager's test no coloration, or at most a yellow coloration, should be developed. It should not contain sulphates, chlorides, oxalates, metals or sugars, and when mixed with an equal volume of water should not reduce Fehling's solution. Arsenic

in excess of the limit fixed by the U. S. Pharmacopœia should not be present.

Aldehydic Impurities in Glycerol.—The impurities to which the reducing properties of the majority of the better qualities of glycerol are due are derived from acrolein. According to Bergh (*Apoth. Zeit.*, 1908, 23, 689) glycerol and acrolein combine in equimolecular proportions forming *glycerol-acrylol*, which possesses the properties of an acetal. It does not reduce Fehling's solution and only slightly reduces ammoniacal silver nitrate. It is slowly dissociated by water, more rapidly on heating, and is decomposed by dilute acids. Its presence may be detected by means of *fuchsine* sulphite solution or by its reducing action on Fehling's solution, obtained after liberating the acrolein by carefully warming with dilute sulphuric acid.

Estimation of Glycerol in Fats.—Willstätter and Madinaveitia (*Ber.*, 1912, 45, 2825) state that the drawbacks (due to incomplete hydrolysis) of the method of Zeisel and Fanto, when applied to fats, are obviated by using hydriodic acid of sp. gr. 1.8, with small quantities of the fat (0.15 to 0.35 grm.). About 0.2 grm. of the glyceride is treated with 10 c.c. of the hydriodic acid (sp. gr. 1.8) in Zeisel and Fanto's apparatus, the mixture being heated at 110–115° until the action starts; the temperature is then kept constant for 20–40 minutes, until the silver solution in the absorption flask becomes clear again, after which the heating is continued for 1 hour at 130–140°. The glycerol is then calculated from the amount of isopropyl iodide as in the original method. Results are given by the authors which show that when the method is carried out in the manner described, it possesses a very considerable degree of accuracy.

Volatile fatty acids are detected as on page 653.

Arsenic must not exceed 1 part in 250,000. The best test for arsenic is the Gutzeit test, which is carried out as follows:

Place in a tall test-tube about 1 grm. of pure zinc, 5 c.c. of diluted sulphuric acid (6%), and 2 c.c. of the sample. The mouth of the test-tube is then covered with a tightly-fitting cap, made of 3 thicknesses of filter-paper. A drop of a 50% solution of silver nitrate is placed on the inner surface layer and the tube allowed to stand for 10 minutes in the dark. If arsenic is present, a bright yellow stain will appear on the filter-paper, which, on the addition of water, becomes black or brown. A blank test should always be made to establish

the absence of arsenic in the reagents. Sulphides (which may be detected by substituting lead acetate for the silver nitrate in the above test) must be oxidised to sulphates before applying the test.

The test is extremely sensitive. A less rigorous test may be made by substituting a drop of a saturated solution of mercuric chloride for the silver nitrate. If no yellow coloration appears after 10 minutes, the sample may be considered free from arsenic.

Pure glycerol does not acquire a yellow or brown colour when very gradually mixed with an equal volume of cold concentrated sulphuric acid. Sugar and certain other impurities cause a marked darkening, or even charring, and in presence of any considerable quantity of formic or oxalic acid the mixture effervesces when warmed. *Oxalic acid* may be recognised more certainly by the formation of a white turbidity on adding calcium acetate to the diluted sample. It is not infrequently present in raw, but never in distilled samples.

Pure dilute glycerol does not sensibly reduce Fehling's solution when heated with it to 100° for a few minutes, but prolonged boiling causes precipitation of cuprous oxide. Dextrose and arsenious acid will reduce the solution even before the b. p. is reached. Arsenic occurs in glycerin recovered from soap-lyes which have been neutralised by crude hydrochloric acid, owing to the fact that it volatilises (probably as a compound of glycerol) when the glycerol is distilled. *Cane-sugar* can be recognised by the same test, if the sample is previously heated to 70° or 80° for 10 minutes in 5 times its volume of water and half its volume of strong hydrochloric acid, and the inverted solution be neutralised and tested for reducing sugars dy the Fehling method.

ESTIMATION OF MOISTURE IN GLYCERIN

The estimation of moisture is of great importance, both for crude, dynamite and C.P. glycerins. A method was developed by C. A. Rojohn (*Zeit. anal. Chem.*, 1919, 58, 440–41) in which the moisture was removed from the glycerin by a distribution of the glycerin over a large area in a tared bottle held in a desiccator over phosphorus pentoxide under reduced pressure of 12 to 15 mm. This method has been thoroughly investigated and improved upon by the Eastern Laboratory (Lewis and Bond) of the duPont Company, and its details have been privately communicated for this article. The

Rojohn method has been changed in several details and much more efficient apparatus has been developed. On samples containing up to 5% of water results are accurate to within 0.05% absolute error. The apparatus used for this estimation consists of glass weighing bottles which are shown in the accompanying drawing (Fig. 723). The bottles are filled to a depth of 1 cm. with fine glass wool and the drying is conducted in a 6" vacuum desiccator, charged with phosphorus pentoxide. It is very necessary to use heavy, strong desiccators, as light desiccators are liable to collapse after being used for some period. For this reason, desiccators should be enclosed in a wooden or metal box provided with a small hole at the top through which the stop-cock projects. In case satisfactory desiccators are not available, the determinations may be conducted under a Bell jar placed on a greased ground glass plate, the vacuum tube going through an outlet placed in the top or side of the jar. In order to avoid the use of the usual cumbersome calibrated manometer to determine the degree of evacuation of the desiccator, with the accompanying necessity of reading the barometric figures, the following simple device may be utilised.

A piece of 5 mm. glass tubing from 2 in. to 3 in. long is sealed at one end and completely filled with clean mercury. By placing in a vacuum and tapping, any air bubbles adhering to the walls of the tube may be dislodged and removed. A small bottle or vial is filled to a depth of about 2 cm. with mercury and the tube is inverted into this bottle, being careful to avoid trapping any bubbles of air. At a distance of 12–15 mm. above the level of the mercury in the bottle, a mark is made on the tube to indicate the level at which the mercury in the tube should stand when the desiccator is evacuated to the proper degree. This apparatus is placed in the desiccator and remains there continually, thus indicating at all times whether or not the desiccator is properly exhausted.

Preparation of the Sample.—Due to the extremely hygroscopic nature of glycerin, great care should be exercised in securing a sample for analysis. If necessary, a piece of tubing may be slipped over the end of the auxiliary pipette, so that a sample may be drawn directly from the bottle of glycerin. This extra tube is then removed and the pipette is quickly introduced into the adapter opening, after removing the stopper. After distributing the required amount of sample over the glass wool, the pipette is removed, the stopper

replaced and the bottle quickly weighed. Thus all absorption of atmospheric moisture is avoided.

MOISTURE WEIGHING BOTTLE
FOR THE DETERMINATION OF WATER IN GLYCERINE
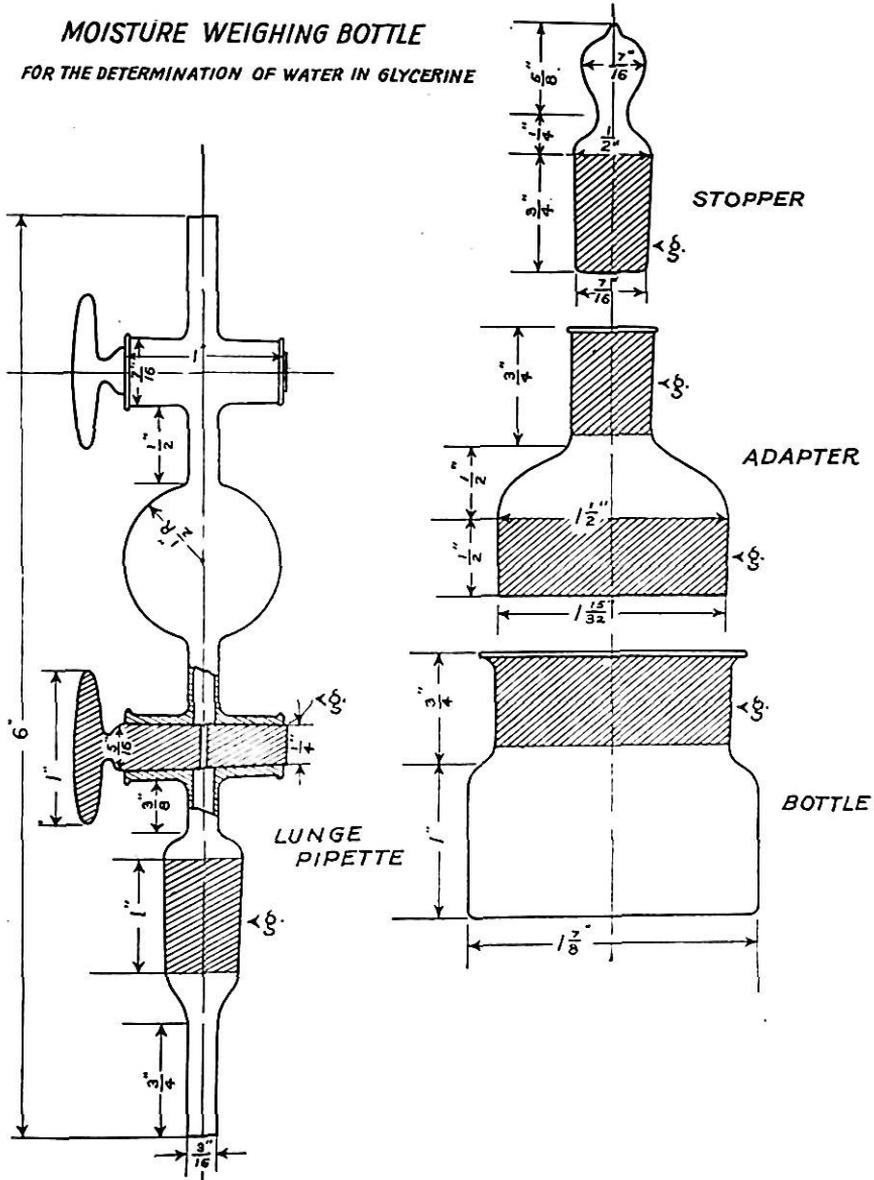
FIG. 20.

Procedure.—Dry the weighing bottle, containing the glass wool, for 1 hour at 120° without the auxiliary pipette and allow it to cool for

1 hour in the vacuum desiccator over phosphorus pentoxide at the working pressure of 12–15 mm. Weigh rapidly and dry to constant weight. Introduce the sample as described above, taking care not to wet the ground joint of the adapter. By rotating the bottle in inclined and vertical positions, distribute 15–18 drops of glycerin (about 1 grm.) evenly over the surface of the glass wool. Reweigh, and place the bottle in the desiccator with the adapter removed but placed in proximity to the bottle. Reduce the pressure in the desiccator to 12–15 mm. and close the exit tube of the desiccator. After 24 hours, test the pressure in the desiccator with a manometer to make sure that it is remaining constant. Allow air to flow in slowly through a long calcium chloride tube. Close the bottle quickly and weigh, the loss in weight representing the moisture in the sample. The drying of all samples in one desiccator must be started at the same time. Before beginning the drying, remove the entire adapter and not merely the stopper.

Calculation:

$$\frac{\text{Loss in wt. of bottle} \times 100}{\text{wt. of sample}} = \% \ H_2O.$$

GLYCERIN FOOTS

Of considerable interest in the distillation of crude glycerin is the residue or foots left in the still. These foots contain the salts and non-volatilisable residue from the crude glycerin as well as any polymerised glycerin produced during the distillation. This polymerised glycerin is usually a direct loss in the process and it is important therefore to know the composition of the residue left on distillation. E. Lewis (*J. Soc. Chem. Ind.*, 41, 97T) has made an investigation to estimate the constituents and to devise means of separating the unchanged glycerin.

The solid hygroscopic residue remaining from the distillation contains about 25% of glycerin and polymerised glycerin together with about 70% of inorganic matter, consisting chiefly of sodium chloride and smaller quantities of sodium carbonate, sulphate and hydroxide. A detailed analysis of an average sample of glycerin residues taken over an extended period gave results as follows: .

Glycerol T. A. V.,[1] 24.52%; acetylisable impurities, 6.52%.

[1] Total acetyl value as 100% glycerol.

Glycerol I. S. M., 18.00%; total residue at 160°, 78.84%; inorganic residue, 62.50%; organic residue at 160°, 16.34%; moisture, 0.35%; sodium chloride, 56.25%; sodium carbonate, 1.73%; sodium hydroxide, 0.12%; sodium sulphate, 3.42%; sodium sulphide, 0.55%; sodium sulphite, 0.48%; sodium thiosulphate, 0.30%; calcium carbonate, 0.25%, ferric oxide, 1.14%; aluminium oxide, 0.029%; albuminoids, 1.28% (calculated from organic nitrogen content); fatty acids, 0.92%; resinous matter, 2.85%; tarry matter, 2.40%; glyceric acid, dihydroxyacetone, acrolein, glyceraldehyde, formic, oxalic, butyric and glycollic acids were also present.

From a consideration of the total hydroxyl content, also that of the organic residue at 160° and of that portion which is volatile at 160° the percentages of glycerol and polyglycerols can be calculated. On this basis the analysis of the residue corrected is:

Glycerol, 10.05%; polyglycerols calculated as diglycerol, 19.56%; inorganic salts, 65.5%; fatty acids, 0.93%; albuminoids, 1.28%; resinous matter, 2.85%; tarry matter, 2.46%; moisture, 0.35%.

The author goes into some detail as to the methods used for making these estimations. They are of interest, but the entire procedure is too tedious for regular plant operations. An occasional check-up on the residues, however, is very important.

POLYGLYCERINS

"D" glycerin or diglycerin is used very extensively in the production of low-freezing dynamites. Hibbert (U. S. Pat. 126467, 1912) gives a method for the production of pure diglycerol by the addition of 0.05% iodine to pure glycerol maintained at a temperature of 210° for 2 hours, with continual agitation. On distillation under reduced pressure, an 85% yield of colourless, very hygroscopic, polymerised glycerol, boiling at 257–260° at 30 mm. pressure is obtained. The sp. gr. at 20°/20° is 1.3215. By analysis it contained C, 43.10%; H, 8.59% ($C_6H_{14}O_5$, diglycerol, requires C. 43.35%, H-8.50%). The b. p. agrees with that found by Nef (*Annalen*, 335, 239) which is 261–262° at 27 mm. Commercially, polymerised glycerol is made by the addition of 0.2% sodium bicarbonate to glycerin of dynamite grade, which is heated under slight vacuum to 260° for several hours until the desired percentage of polymers is obtained. It may be analysed by the methods given

under dynamite or pure glycerin and the amount of polymers is estimated by the spread of the acetin figure and the sp. gr. for the polymerised and dynamite grades of glycerin. For plant purposes it is more convenient to estimate the percentage polymers from a special table of sp. gr. determined from mixtures of pure diglycerol and glycerol. The following table has been developed, taking the sp. gr. at 26.45/26.45°. This temperature was used because of the high viscosity of the polymerised glycerin and the difficulty of getting rid of air bubbles at lower temperatures:

Sp. gr.	Sp. gr. "D" glycerin—per cent. polymers, sp. gr. at 26.45/26.45°										Avg. diff.
	0	1	2	3	4	5	6	7	8	9	
1.259	5.25	5.75	6.50	7.00	7.50	8.00	8.50	9.00	9.75	10.25	0.500
1.260	10.75	11.25	11.75	12.50	13.00	13.50	14.00	14.50	15.00	15.75	0 500
1.261	16.25	16.75	17.25	17.75	18.25	18.75	19.25	20 00	20.50	21.00	0 475
1.262	21.50	22.25	22.75	23.25	23.75	24.25	24.75	25.25	26.00	26.50	0 500
1.263	27.00	27.50	28.00	28.50	29.25	29.75	30.25	30.75	31.25	31.75	0 475
1.264	32.50	33.00	33.50	34.00	34.50	35 00	35.50	36.25	36.75	37.25	0.475
1.265	37.75	38.25	38.75	39.50	40.00	40.50	41.00	41.50	42.00	42.50	0 475
1.266	43.00	43 75	44.25	44.75	45.25	45.75	46.50	47.00	47.50	48.00	0.500
1.267	48.50	49.25	49.75	50.25	50.75	51.25	51.75	52.25	52.75	53.25	0.475
1.268	53.75	54.50	55.00	55.50	56.00	56.50	57.00	57.50	58 00	58.50	0 475
1.269	59.00	59 75	60.25	60.75	61.25	61.75	62.25	62.75	63 25	63.75	0 475
Av. diff.	4.89	4.90	4.89	4.89	4.89	4.89	4.89	4.89	4.86	4.86	0.484

Fermentation Glycerin.—Fermentation glycerin has, in recent years, assumed a very important place. Pasteur (*C. R.*, 46, 857, 47, 1224), in 1858, was the first to observe that glycerin was produced by fermentation, and he found on careful analysis of regular alcohol fermentations that about 3 % of the sugars present in the mash was fermented to glycerin. As glycerin is the basic material for the production of nitroglycerin it was in great demand during the War, and its scarcity was early felt in Germany. Connstein and Lüdecke (*Wochenschrift für Brauerei*, May 10, 1919) following the experimental work of Neuberg, found by the addition of solutions of sodium sulphite to a sugar mash that considerable quantities of glycerin were produced in the presence of a large proportion of yeast. Their method of procedure was to make up a mash in the proportions of 10 parts of water, 1 part of sugar and 0.4 part of anhydrous sodium sulphite, together with ammonium sulphate, sodium phosphate and potassium salts, and to add 0.10 part of yeast, all by weight. With the large proportion of yeast present fermentation proceeded very rapidly and was usually completed within 24 to 48 hours. They claim

yields of 20 parts of glycerol, 27 parts of ethyl alcohol and 3 parts of acetaldehyde based on the weight of sugar used in the mash. This process was undertaken on a very large scale in Germany by the Protol Company in 63 factories; some 1000 tons of glycerin being produced per month. Ger. Patent 298593 (April 13, 1915) and 298594 (April 23, 1916). Other published reports indicate, however, that only 10% of the weight of the sugar in the mash was recovered in the form of dynamite grade glycerin. The theory of the formation of glycerol has been developed by Neuberg (*Ber.*, 1919, **52**, 1677–1703; *Biochem. Zeitsch.*, 1918, **89**, 365–414). During the fermentation there is considerable acetaldehyde produced which unites with the sodium sulphite. The reactions given by Neuberg are as follows:

I. $C_6H_{12}O_6 - 2H_2O \rightarrow C_6H_8O_4$ (aldol of methylglyoxal)

II. $C_6H_8O_4 \rightarrow 2\ CH_2{:}C(OH).CHO$ or $2CH_3.CO.CHO$

III. $CH_2{:}C(OH).CHO + H_2O \quad H_2 \qquad\qquad$ Glycerol +

$$CH_2{:}C(OH).CHO \qquad O \qquad\qquad \text{Pyruvic acid}$$

IV. $CH_3.CO.COOH \qquad \rightarrow \qquad CO_2 + CH_3CHO$

Pyruvic acid $\qquad\qquad\qquad$ Acetaldehyde

V. CH_3COCHO

$$O \qquad\qquad \text{Pyruvic acid} +$$

$$CH_3CHO \quad H_2 \qquad\qquad \text{Ethyl alcohol}$$
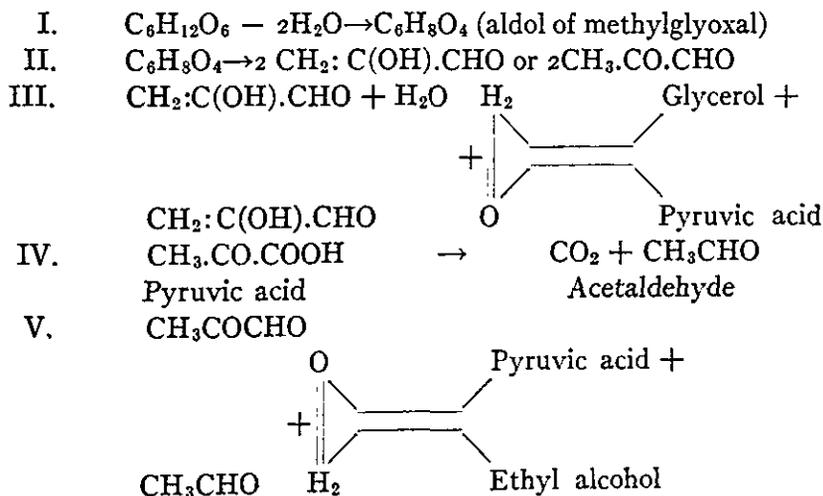
The mechanism of the sodium sulphite reaction is shown as follows (Neuberg, *Biochem. Z.*, 1918, **89**, 365):

(a) $C_6H_{12}O_6 + Na_2SO_3 + H_2O \rightarrow C_6H_{12}O_5(OH).O.SO_2.Na + NaOH.$

(b) $\frac{1}{2}C_6H_{12}O_5(OH).O.SO_2Na = H_2 + CH_3(C(OH)(COOH).O.SO_2Na.$

(c) $CH_3.C(OH)(COOH).O.SO_2Na = CH_3.CH(OH).O.SO_2Na + CO_2.$

(d) $NaOH + CO_2 \rightarrow NaHCO_3$

$$C_6H_{12}O_6 \rightarrow CH_3CHO + CO_2 + \left(\frac{C_6H_{12}O_6}{2}\right) + H_2.$$
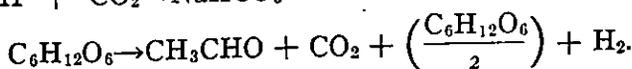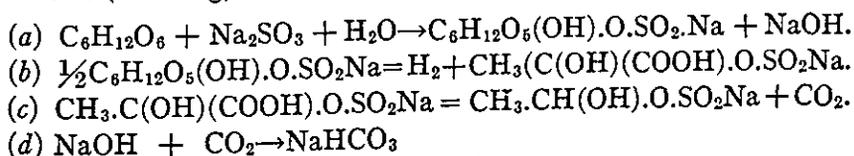
It was also found in the experimental work that the addition to the fermentation mash of different salts, such as sodium hydrogen phosphate, ammonium carbonate, sodium bicarbonate, sodium

carbonate, etc., gave varying percentages of glycerin by fermenta-
tion.   The best results, however, were found to be from the use of
sodium sulphite.   Cocking and Lilley (Br. Pat. 164034–6–30–21)
found that using a neutral mixture of sodium sulphite and sodium
bisulphite as high as 45% of the sugar could be converted into
glycerin.   Eoff was granted a patent in the United States (1,288,
398, 1918) for the use of alkalies, especially sodium carbonate, and
he found, by adding up to 5% of the weight of the mash as sodium
carbonate in several doses so as not completely to stop fermentation,
that he was able to ferment approximately 25% of the sugar to
glycerol and 30% to ethyl alcohol.

The estimation of glycerol produced by the fermentation method
has offered considerable difficulty, because of the presence of large
quantities of salts and organic substances.   Two general method
have been developed which give fair results.   The first method is to
evaporate the beer to a fairly heavy consistence and then mix with
sand to a very stiff paste, which is dried on a water-bath at tem-
peratures not to exceed 80°.   This material is then broken up
into small pieces and extracted in a Soxhlet apparatus with C.P.
dry acetone.   This dissolves the glycerin and leaves the gums and
salts in the extraction thimble.   The acetone is next evaporated
at low temperatures and the glycerin in this form is weighed.   Its
purity is then further determined by the acetin method and correc-
tion made for the weight of the glycerin found.   This method has
given only fair results, but has been made use of very extensively
in Germany.

Fachini and Fortor (*Ind. Chim.*, 10, 3111–4 *Seifenfabr.;* 30, 1205–7,
1233–4,) give a modification of the acetone extraction method of
Schurre Schetevoke, which is based on the solubility of glycerin
in acetone (which has been found to be about 5% at ordinary
temperatures).   Their method is as follows: 5 grm. of the sample
of crude glycerol are mixed with enough anhydrous sodium sulphate
to form a dry mass which can be powdered.   This is transferred to
a 200 c.c. flask, and 100 c.c. of acetone (56–7° b. p.) is added, the
flask connected with a reflux condenser and heated 1 hour over
a water-bath.   It is then cooled and the contents are transferred
to a beaker through a filter.   The residue is again re-ground and
extracted as before.   The combined filtrate is evaporated to 80 c.c.,
transferred to a weighed dish and dried in vacuo over H_2SO_4.

For the analysis of glycerol resulting from the various saponification methods, 50 grm. are taken, diluted with 25 c.c. of water, heated, acidified with dilute sulphuric acid to liberate any fatty acids which are separated by the filtration and extracted with ether in a separating funnel. The filtrate is then neutralised with sodium carbonate and concentrated on a water bath at a temperature not over 80–85°. When a sirupy consistency is reached anhydrous sodium sulphate is added until a dry mass results, and then it is extracted as above, Using 2.7248 grm. of glycerol of 99.4 strength and adding 10 grm. of sodium chloride and 20 grm. of anhydrous sodium sulphate, this method gave a recovery of 2.7316 grm. of pure glycerol. A sample of crude analysing 76.51% by the acetin method gave 76.88 and 76.5% by the extraction method; also a sample showing 6.16% by the acetin method gave 6.47, 6.72 and 6.46% by the extraction method.

The second method for the quantitative estimation of fermentation glycerin is the so-called "brass still" distillation. The still unit consists of two parts: the still proper and the heating bath for the still. The still is made either from a solid piece of brass or is cast. Its dimensions and construction are shown in Fig 21. It has two openings, the larger of the two acting as the still body proper and the smaller as the expansion and superheat chamber for the live steam used in the distillation. The top of the still is flanged so as to serve as a cover for the heating bath and an opening is made in the cover for a thermometer. It is the practice to use glycerin as the heating medium in the bath. The apparatus all set up is shown in Fig. 22. Beginning at the left the 16 oz. bottle holds a supply of water for the 1000 c.c. flask. This flask is filled about one-half with water and in operation the water is kept boiling at a uniform rate by the introduction of pumice and glass wool. From this flask a brass or copper tube leads to the steam expansion chamber of the still. As the steam passes through this tube it is superheated by means of a gas flame impinging on a piece of iron pipe about 6 in. long covering the brass pipe. In the still the superheated steam expands and is reheated to the proper temperature for the distillation by means of the glycerin bath. This temperature is from 170–200°, depending on the kind of material from which the glycerin is being distilled. The expanded superheated steam then passes through the small opening at the bottom

of the expansion chamber into the still section, where it picks up the glycerin from the crude material and carries it over to air condensers. Either one or two air condenses (8 or 16 oz. glass bottles) are used, depending on the amount and kind of raw materials used. Most

PLAN OF TOP

CROSS & LONGITUDINAL SECTIONS
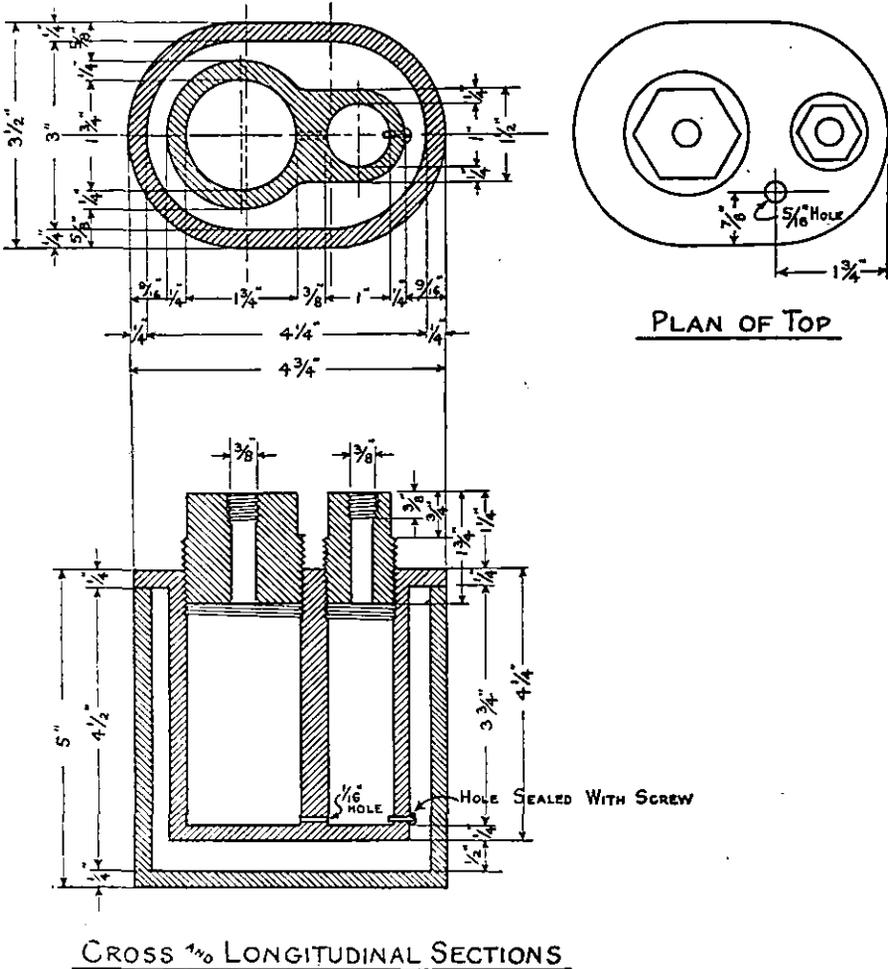
FIG. 21.

of the glycerin condenses out at this place, but a small amount is carried over with the steam which passes through a water-cooled condenser and is collected as sweet waters. The sweet water receiver is connected to two 16 oz. bottles, as shown, which act as safeguards against any run-back from the vacuum pump, and also

FIG. 22.

RUBBER CONN. WITH PINCH

1000 C.C. FLASK

16 OZ.

FLAME SPREADER

½"X6" IRON PIPE

STILL

RUBBER CONN.

THERM

RUBBER CONN.

16 OZ.

RUBBER STOPPERS

16 OZ.

RUBBER WITH PINCH
VACUUM RELEASE

RUB. STOPPER

2-LITER.

INLET

OUTLET

CONDENSER

RUBBER STOPPER

RUBBER CONN.

16 OZ.

RUBBER STOPPER

16 OZ.

RUBBER CONN.

GLASS TEE FOR VACUUM GAUGE.

RUBBER CONN.

VACUUM PUMP
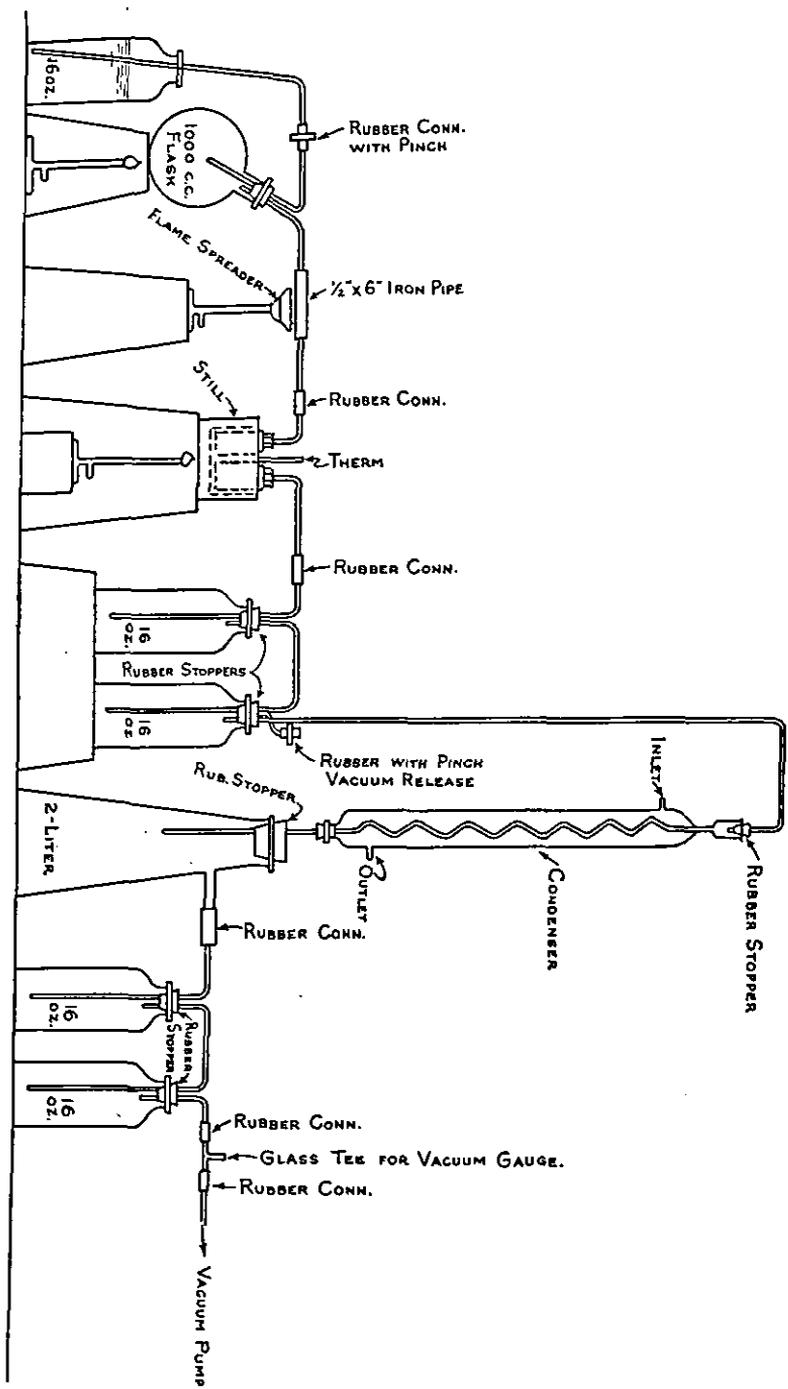
help to collect any uncondensed vapours from the sweet-water receiver.

A weighed sample of material containing glycerin is evaporated, if necessary, to a fairly viscous liquid, keeping the glycerol concentration below 50% so as to avoid loss of glycerol. This heavy liquid is absorbed by asbestos wool and the saturated wool is placed in the large opening of the brass still in which there is already placed a pad of asbestos wool. This wool should be fluffy, free from hard fibers and should be purified if needed by washing with hydrochloric acid, then with water. On top of the saturated wool is placed another pad of dry asbestos wool. The top of the still is then screwed down tightly and the brass pipe is connected with the other apparatus. The vacuum pump is started and the glycerin bath is gradually heated until the thermometer shows 170° when the water in the 1000 c.c. flask is heated and the steam is superheated and goes through the still, etc. The time of actual distillation is usually about 3 hours. The contents of the two air condenser bottles are washed into a 100 c.c. short-neck round-bottom flask, previously tared with its stopper. The condensate in the sweet water receiver is evaporated to a volume of about 20 c.c. and added to the round-bottom flask. This is then heated on a glycerin bath, being connected by a bent glass tube to a small Erlenmeyer flask, cork stoppers being used, and the connection in the Erlenmeyer flask being loose. The glycerin bath is heated gradually to 160° and any glycerol in the sweet waters coming off is retained in the Erlenmeyer flask and the steam free from glycerol escapes. This sweet water is returned to the round-bottom flask and the bath is brought up to 195° at which temperature the glycerin in the flask is 98% strength. The flask is removed from the bath at once, the tared stopper inserted, the flask washed, dried, cooled, and weighed. An acetin estimation can then be made to check the strength of glycerol in the flask. This method has been used for a long period on fermentation glycerin and checked by made-up samples. In the hands of an experienced and careful operator it gives checks within $\frac{1}{10}\%$ to $\frac{1}{2}\%$ of the true glycerol contents and can be used with dilute as well as strong glycerol mixtures. A somewhat similar method, in which glass apparatus is used, has been described by K. Fleischer (*Zeit. anal. Chem.* 1921, **60**, 330). This is shown in Fig. 23. The sample is placed in *C* and enough is run into the flask *B* so that the end of

the steam inlet pipe B is under the liquid. B is a Claussin flask of 500 to 750 c.c. capacity. The apparatus is evacuated to about 15 mm. pressure, the water-bath J is heated to 70°, and water at 70° is run through the partial condenser H. Cold water is run through K. The steam is superheated to 150° as shown at thermometer A, and the air-bath D is heated also to 150°. The remainder of the material is run into B and the dropping funnel washed with a little water. The temperature of the steam and air-bath is now raised to 250°. The glycerin water distillate comes over into F
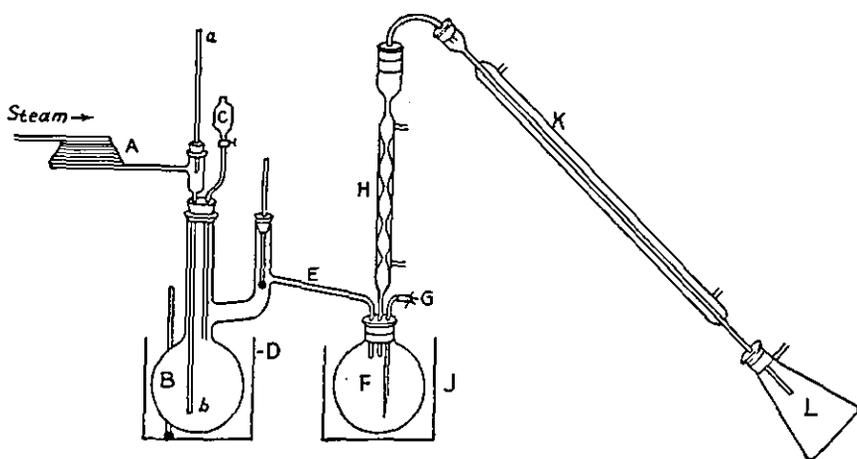
FIG. 23.

where the glycerol is refluxed and the steam goes on through condenser K and is collected in L. The tared flask F is weighed and the gravity of the glycerin is taken in a 5 c.c. pyknometer and correction made for its water content. There are also certain other corrections to be made, depending on the starting material. The apparatus, being made from glass, is easily broken and likely to crack, due to drops of water condensing on the walls, etc.

Other methods for estimating fermentation glycerin have been developed, such as first purifying by precipitating the non-glycerin organic materials with basic lead carbonate, alumina cream, etc., but, as glycerin forms compounds with lead salts, these methods do not give accurate results. In the case of the use of alumina cream, some of the glycerin is carried along with the impurities and it is

practically impossible to wash these out; therefore, the results
are low.

· *Glycerol in Dry Wines (Off. and Tent. Methods of Anal. of the Assoc.
Off. Agr. Chem.* 1919, 1920, p. 174).

Method I.—(By Direct Weighing)—Official.

Evaporate 100 c.c. of the wine in a porcelain dish on the water-
bath to a volume of about 100 c.c. and treat the residue with about
5 grm. of fine sand and 4–5 c.c. of milk of lime (containing about
15% of calcium oxide) for each gm. of extract present and evaporate
almost to dryness. Treat the moist residue with 50 c.c. of 90%
alcohol by volume, remove the substance adhering to the sides of
the dish with a spatula and rub the whole mass to a paste. Heat
the mixture on a water-bath, with constant stirring, to incipient
boiling and decant the liquid through a filter into a small flask.
Wash the residue repeatedly by decantation with 10 c.c. portions of
hot 90% alcohol until the filtrate amounts to about 150 c.c.
Evaporate the filtrate to a syrupy consistency in a porcelain dish
on a hot, but not boiling, water-bath, transfer the residue to a small
glass stoppered, graduated cylinder with 20 c.c. of absolute alcohol
and add 3 portions of 10 c.c. each of anhydrous ether, shaking
thoroughly after each addition. Let it stand until clear, then pour
off through a filter, and wash the cylinder and filter with a mixture
of 2 parts of absolute alcohol to 3 parts of anhydrous ether, also
pouring the wash liquor through the filter. Evaporate the filtrate
to a syrupy consistency, dry for an hour at the temperature of boiling
water, weigh, ignite and weigh again. The loss on ignition gives
the weight of glycerol.

Method II.—(By Oxidation with Dichromate)—Official.

Evaporate 100 c.c. of the wine in a porcelain dish on a water-bath,
the temperature of which is maintained at 85–90° to a volume of
10 c.c. and treat the residue with about 5 grm. of fine sand and 5 c.c.
of lime (containing 15 grm. of calcium oxide per 100 c.c.), and evapo-
rate almost to dryness, with frequent stirring, avoiding the formation
of a dry crust in evaporation to complete dryness. Treat the moist
residue with 5 c.c. of water, rub into a homogeneous paste and then
add slowly 45 c.c. of absolute alcohol, washing down the sides of
the dish to remove adhering paste, and stir thoroughly. Heat the
mixture on a water-bath, with constant stirring, to incipient boiling,
transfer to a suitable vessel and centrifugalise. Decant the clear

liquid into a porcelain dish and wash the residue with several small portions of hot 90% alcohol by volume by aid of the centrifuge. (If a centrifuge is not available, decant the liquid through a folded filter into a porcelain dish. Wash the residue repeatedly with small portions of hot 90% alcohol, twice by decantation, and then by transferring all the material to the filter. Continue the washing until the filtrate amounts to 150 c.c.) Evaporate to a syrupy consistency, add 10 c.c. of absolute alcohol to dissolve this residue, and transfer to a 50 c.c. glass stoppered cylinder, washing the dish with successive small portions of absolute alcohol until the volume of the solution amounts to 20 c.c. Then add 3 portions of 10 c.c. each of anhydrous ether, shaking thoroughly after each addition. Let it stand until clear, then pour off through a filter, and wash the cylinder and filter with a mixture of 2 volumes of absolute alcohol and 3 of anhydrous ether. If a heavy precipitate has formed in the cylinder, centrifuge at low speed, decant the clear liquid and wash 3 times with 20 c.c. portions of the alcohol-ether mixture, shaking the mixture thoroughly each time and separating the precipitate by means of a centrifuge. Wash the paper with the alcohol and ether mixture, and evaporate the filtrate and washings in the water bath to about 5 c.c., add 20 c.c. water and again evaporate to 1 c.c., again add 20 c.c. water and evaporate to 4 c.c.; finally add 50 c.c. of water and evaporate to 5 c.c.

These evaporations are necessary to remove all the ether and alcohol and when conducted at 85–90° result in no loss of glycerol if the concentration of the latter is less than 50%.

Transfer the residue with hot water to a 50 c.c. graduated flask, cool, add the silver carbonate, prepared from 0.1 grm. of silver sulphate, shake, and allow to stand 10 minutes; then add 0.5 c.c. of basic lead acetate solution, shake occasionally and allow to stand 10 minutes, make up to the mark, shake well, filter, rejecting the first portion of the filtrate and pipette 25 c.c. of the clear filtrate into a 250 c.c. volumetric flask.

Add 1 c.c. of concentrated sulphuric acid to precipitate the excess of lead, and then 30 c.c. of the strong potassium dichromate solution. Add carefully 24 c.c. of concentrated sulphuric acid, rotating the flask gently to mix the concentrate and avoid violent ebullition, and then place in a boiling water-bath for exactly 20 minutes. Remove the flask from the bath, dilute, cool and make up to the mark at room

temperature. The amount of strong dichromate solution must be sufficient to leave an excess of about 12.5 c.c. at the end of the oxidation, the amount given above (30 c.c.) being sufficient for ordinary wine containing about 0.35 grm. or less glycerol per 100 c.c.

Standardise the ferrous ammonium sulphate solution against the dilute potassium dichromate solution (5 parts of the strong solution used for the oxidation made up to 100 c.c.), by introducing from the respective burettes approximately 20 c.c. of each of these solutions into a beaker containing 100 c.c. of water. Complete the titration, using the potassium ferricyanide solution as an outside indicator. From this titration calculate the volume (F) of the ferrous ammonium sulphate solution equivalent to 20 c. c. of the dilute and therefore to 1 c.c. of the strong dichromate solution.

In place of the dilute dichromate solution, substitute a burette containing the oxidised glycerol with an excess of the strong dichromate solution and ascertain how many c.c. are equivalent to (F) c.c. of the ferrous ammonium sulphate solution and therefore to 1 c.c. of the strong dichromate solution. Then 250, divided by this last equivalent, equals the number of c.c. of the strong dichromate solution present in excess in the 250 c.c. flask after oxidation of the glycerol.

The number of c.c. of the strong dichromate solution added, minus the excess found after oxidation, multiplied by 0.02, gives the grams of glycerol per 100 c.c. wine.

Glycerol in Sweet Wines—Official.—With those wines whose extract exceeds 5 grm. per 100 c.c. heat 100 c.c. to boiling in a flask and treat with successive small portions of milk of lime until the wine becomes first darker and then lighter in color. Cool, add 200 c.c. of 95% alcohol by volume, allow the precipitate to subside, filter and wash with 95% alcohol. Treat the combined filtrate and washings as in the preceding two methods.

Beys (*Compt. rend.*, 1910, **151**, 80) states that discordant results obtained in estimating glycerol in wine by the usual methods are caused mainly by variations in the quantity of barium hydroxide used to render the sugar insoluble. In a later paper (*Bull. Soc. Chim.*, 1912, **11**, 618) the following process is recommended: The volume of wine taken for analysis is 100 c.c. in the case of dry wines, 50 c.c. in the case of sweet wines and 25 c.c. if the sp. gr. exceed 5° Bé. The wine is neutralised with barium hydroxide

and evaporated to a syrup in a platinum dish at a temperature not exceeding 70°. Some sand is added and the mixture extracted with acetone, such a quantity of the latter being first used that the strength of the acetone is not reduced below 95% by admixture with the syrupy residue; after this extraction, which is carried out at a temperature below 56°, the liquid is cooled and filtered and the residue extracted with successive quantities of 40–50 c.c. of acetone until at least 200 c.c. of the filtrate are obtained. Two aliquot portions of the filtrate are evaporated (without boiling). In one of the residues the invert sugar is estimated by Fehling's solution; the other is dissolved in 5 times its weight of water and a quantity of powdered barium hydroxide added as follows:

(1) If the weight of the sugar is less than 0.05 grm., a few mg. of barium hydroxide in excess of the sugar are added.

(2) If the weight of the sugar is between 0.05 and 0.3 grm., an equal weight of barium hydroxide is used.

(3) If the sugar is between 0.3 and 0.5 grm., $\frac{4}{5}$ of its weight of barium hydroxide is added.

The mixture is frequently shaken and, after about 30 minutes, some sand is added and the glycerol extracted by heating, first with 40 c.c., then 2 or 3 times with 25 c.c. of acetone. The solution after filtration is evaporated at a temperature below 56°, the residue being dried at 60 to 65° and weighed. The glycerin so obtained contains about 5 mg. of impurities, which about compensate for loss in evaporation, etc.

PHYSICAL CONSTANTS

The following physical constants have been determined for glycerol and its solutions in water:

Specific gravity[1–2] .... 1.2653   15°/15°
Specific gravity[3] .... 1.2653   15⁶°/15⁶°
Specific gravity[3] .... 1.2655   15°/15°
Refraction index line C[4] .... 1.471   20°
Refraction index line F[4] .... 1.478   20°
Melting point[5] ....   17.9°
Boiling point[6] .... 760 mm.   290°
Cubical expansion, mean coefficient[7] .... 0.0534   0–100°
Cubical expansion, mean coefficient[8] .... 0.000612   20°
Cubical expansion, mean coefficient[8] .... 0.000617   25°
Cubical expansion, mean coefficient[8] .... 0.000622   30°
Cubical expansion, mean coefficient[9] .... 0.00057   5°
Cubical expansion, mean coefficient[9] .... 0.000587   12.5°
Specific heat [10] .... 0.576   15°–50°

Specific heat [11]................................... $-203°$ to $+26°$
Heat conductivity cal. per sec. per c.c. per deg.[12].   0.000637 $9°-15°$
Specific ind. cap. wave length 1200[13]...........   56.25 $15°$
Magnetic susceptibility[14]...................... -0.81
Capillarity, dynes per cm.[15]....................   65.2 $18°$
Latent heat of vaporization[16] (approximate).....   450 B.t.u.
Vapour pressure[17]............................   760 mm. $290°$
Vapour pressure[17]............................   230 mm. $257.5°$
Vapour pressure[17]............................   139 mm. $240°$
Vapour pressure[17]............................   50 mm. $215°c$
Vapour pressure[1] ....   32 mm. $193°$
Vapour pressure[17]...... . . .   .   10 mm. $177.5°$
Vapour pressure[17]........ . . .   .   9 mm. $166°$
Constant of dielectric dissoc.[18]—OH group 0.7×10^{-13}
Latent heat of fusion[19]—42.50 cals. per grm., 3913.4 per grm. mol.
Entropy of fusion[20]—15.02 cals./degree/mol. or 1.073 cals./degree/gram atom
Energy of liquefaction[21]—1795.219 meg. ergs. per grm.
Surface tension[22]—$L = 3.60$ dynes per cm................... $15°$
Optical rotation—none
Heat of combustion[23]—4323 cals. per grm.
Heat of conductivity[24] $h \times 10^7 = 7251$ C. G. S. units......... $10°$
Dielectric constants[25]
Electrolytic dissoc.[26]—7×10^{-15}....................... $17.5°$
Flash point[27]—glycerol 98.9% open cup..................... $174°$
Fire point[28]—glycerol 98.9% open cup..................... $187°$
Solutions of Glycerol in Water
Specific gravity[29] constant temp........................... $15.6°/15.6°$
Specific gravity[30] varying temp.
Vapour pressure[31].........................   50% glycerol 618 mm. hg. $100°$
                                               60%   565 $100°$
                                               70%   496 $100°$
                                               80%   396 $100°$
                                               90%   247 $100°$
                                              100%   64 $100°$

	DENSITY	VISCOSITY	GLYCEROL, %	
Viscosity mol. C. G. S. units[32]....	1.0098	0.01181	5	$20°$
	1.0217	0.01364	10	
	1.0337	0.01580	15	
	1.0461	0.01846	20	
	1.0590	0.02176	25	
	1.0720	0.02585	30	
	1.0855	0.03115	35	
	1.0989	0.03791	40	
	1.1124	0.04692	45	
	1.1258	0.05908	50	
	1.1393	0.07664	55	
	1.1528	0.0131	60	
	1.1662	0.1451	65	
	1.1797	0.2149	70	
	1.1932	0.3371	75	
	1.2066	0.5534	80	
	1.2201	1.025	85	
	1.2335	2.076	90	
	1.2465	4.801	95	
	1.2620	13.10	98.7	

Osmotic pressure [33]—0.00199 grm. glyc. per c.c. = 367 mm. hg........... $0°$
Coeff. of diffusion[34—35]—$K =$ cm.^{2}/time = unit C. G. S. $\times$ 86,400

Strength glyc. sol. in mols..............   2   1   0.5   0.25   0.125
Coeff. of diff........................ 0.645 0.658 0.676 0.705 0.711
Absorption of gases[36]
Lowering of vapour pressure[37]
Maximum density[38]

	GLYCEROL, %	FREEZING POINT
Freezing points[39]........................	5	$-1°$
	10	$-3°$
	20	$-6°$
	30	$-17°$
	40	$-31°$
	100	$+18°$

Freezing point lowering of water solutions[40]

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WOOL-FAT. WOOL-GREASE
SUINT. DÉGRAS (U. S.)

By AUGUSTUS H. GILL, Ph.D., Sc.D.

Sheep's wool[1] contains a large amount of fatty matter of very peculiar character. It is excreted by all parts of the skin, but is found most abundantly about the breast and shoulders. The crude "yolk," as it is called, is largely soluble in water, and hence is removed by washing the wool, but the wool-fat or suint proper remains, and can be extracted with carbon disulphide, petroleum spirit, or other suitable solvent.

Thus obtained, wool-fat is a yellow or brownish grease, having a peculiar disagreeable smell. It melts between 39 and 43° and has a sp. gr. of about 0.973 at 15°. It possesses the remarkable property of forming a good emulsion with water, which when kept at the ordinary temperature exhibits no tendency to separate. Complete saponification of wool-fat cannot be effected by boiling with alcoholic potassium hydroxide except under pressure. It can, however, be quickly saponified by the method of Kossel-Obermüller, using sodium ethylate prepared by adding 5 grm. of sodium to 110 c.c. absolute alcohol.

Wool-fat has a complex composition; the exact nature of which is still unknown. Cholesterol and isocholesterol are present and potassium salts of several fatty acids, some of them volatile. Contrary to the usually accepted statements, Lewkowitsch (*J. Soc. Chem. Ind.*, 1892, **11**, 136; 1896, **15**, 14) has found that wool-fat is not a mixture of cholesteryl and isocholesteryl stearates, palmitates, and oleates, as is shown by the low iodine absorption of both the fatty acids and the alcohols. The former were found to consist of hydroxy-acids, easily giving off the elements of water at temperatures little above 100°, with formation of inner anhydrides or

[1] "Das Wollfett." Donath and Margosches.
Ahrens—"Sammlung Chemische und Chemische-Technische Vortraege."

lactones. Oleic acid, if present, is in small amount. Besides cholesterol, a considerable proportion of lower saturated alcohols is present. No glyceryl esters have been found in wool-fat.

Darmstädter and Lifschütz (*Ber.*, 1897, **29**, 2890) have reported the isolation of the following substances: *Lanoceric acid*, $C_{30}H_{60}O_4$, insoluble in water, but easily soluble in hot alcohol, from which it crystallises, on cooling, in plates of m. p. 103 to 105°; *lanopalmitic acid*, melting at 87 to 88° and solidifying at 83 to 85°to a lustrous crystalline mass, and having the property of readily forming an emulsion with water; also *carnaübic* and *myristic acids*, an oily acid, apparently *oleic*, and a volatile acid, possibly *caproic*. Among the alcohols, separated by absolute alcohol into several fractions, *ceryl*, *carnaübyl* alcohol (saturated), and *cholesterol* were identified. The investigations of G. de Sanctis (*Chem. Zeit.*, 1895, **19**, 651) point to the presence also of *palmitic* and *cerotic* acids.

The results of Lewkowitsch's inquiries into the nature of wool-fat (*J. Soc. Chem. Ind.*, 1892, **11**, 135; 1896, **15**, 14) led him to conclude that it is a true wax in the strict sense of this generic term. Natural wool-fat resembles beeswax, its closest relative, in that it contains a considerable proportion of free acid and a small amount of free alcohols, besides true waxes, and the term wool-wax should therefore be substituted for wool-fat; but considering the fact that the commercial wool-fat is, as a rule, contaminated with fatty acids derived from the soap used in scouring the wool, it is more convenient to retain the term wool-fat for the commercial product. Lewkowitsch proposes, therefore, that the name wool-wax be given to the neutral portion of the wool-fat. This consists of a mixture of true wax and alcohols, the former predominating considerably. The name wool-wax appears all the more desirable, as this neutral portion is now obtained in large quantities, both in the anhydrous and hydrated state, and confusion with the crude wool-fat is thereby avoided.

Lewkowitsch makes the point that the differences in results obtained by several observers may be due to the fact of the difference in composition of the wool-fats themselves.

Röhmann (*Biochem. Z.*, 1916, **77**, 298–328, thru *Ch. Abs,.* **11**, 711) states that the principal acid is cerotic acid, and that the anhydride of lanoceric acid may also be present. Ceryl alcohol, cholesterol and unknown alcohols are found in the fat; the presence of isocholesterol

is doubtful as a mixture of ceryl alcohol and cholesterol behaves like it.

The following are the results of examinations made by Lewkowitsch, as well as some estimations made in Allen's laboratory by W. Chattaway:

WOOL-WAX (ESTERS AND FREE ALCOHOLS)

	Lewkowitsch	Chattaway
Sp. gr. at 98.5° (water at 15.5° = 1)....	....	0.9017[2]
M. p..	31°–35°[1] 39°–41°	....
Solidifying-point.......................	30°–30.2°[1]	....
Percentage of potassium hydroxide for saponification.......................	10.24[1]	9.83[2]
Saponification-equivalent..............	....	901.7[2]
Iodine absorption.....................	$\begin{Bmatrix} 25.8\text{–}28.9^1 \\ 17.1\text{–}17.6^2 \end{Bmatrix}$	....
Fatty acids, %........................	59.8	....
Alcohols..............................	43.6 51.84[2]	....

	Mixed fatty acids	Mixed alcohols
Solidifying-point.....................	40°	28°[1]
M. p.................................	41.8°	33.5°
Mean molecular weight...............	327.5	239
Iodine absorption....................	17.5	36[1] 26.4[2]

NEUTRAL ESTERS

Potassium hydroxide for saponification, %........................	9.69
Fatty acids, %...	56.66
Alcohols, %...	47.55

[1] From raw wool-fat.   [2] Prepared from "lanolin."

When extracted by means of solvents, wool-fat contains simply the constituents (fatty acids, neutral esters, alcohols, and potassium salts of lower fatty acids) natural to the wool. The following table represents the results of examination of wool-fat extracted by ether (Herbig, *J. Soc. Chem. Ind.*, 1894, **13**, 1069):

Source	Potassium salts in ash, calculated to potassium oleate	Free acid potassium hydroxide required	Percentage of potassium hydroxide for saponification on heating for one hour		Unsaponifiable matter (alcohols)
			Open flask	Closed flask	
New Zealand wool........	4.9	14.3	10 60–10 82	11.05–11.07	43.66–43.94
Australian wool...	4.24	15.5	10.25–10.35	11.27–11.32	....
South American wool.....	9.25	13.2	8.82– 9.14	9.86– 9.89	43.15–43.65
Russian wool	24.4	13.9	7.77– 7 83	9.41– 9.58	38.72–39.10

Wool-fat prepared by acidifying the suds obtained in the wool-scouring process is of irregular composition. Potassium salts of the lower fatty acids are present in but small quantity, since these are removed in the first stage of the process, which consists in steeping the wool in luke-warm water. In addition to the compounds mentioned above as naturally present in the wool, it may contain unsaponified fat and mineral oil which had been added to lubricate the wool and fatty acids derived from the soap used in scouring. The product obtained in this way is called *recovered grease, wool-grease, brown grease,* and *Yorkshire grease.* In the United States it is incorrectly called "dégras." (For a description of true "dégras" see under that head.)

The analysis of wool-fat requires a departure from the usual methods. The potassium and other mineral constituents can be estimated in the ash obtained on ignition. On saponifying the fat and extracting the soap in the manner described below, the *alcohols,* including cholesterol, are dissolved, recovered by evaporation of the solvent, and examined as described under "cholesterol." By treating the soap with acid, the *higher fatty acids* will be obtained, whilst the *lower fatty acids* can be estimated by distillation in the usual way. Foreign saponifiable fats will be indicated by the presence of glycerol in the aqueous liquid separated from the fatty acids, and their amount will be roughly indicated by multiplying the glycerol found by 10.

Free Fatty Acids.—These are measured by treating a weighed portion of the fat with alcohol, and titrating with standard potassium hydroxide in the usual manner; the amount may be calculated from the mean molecular weight. Lewkowitsch (*J. Soc. Chem. Ind.,* 1892, **11,** 136) separates the free fatty acids for the estimation of the molec-

ular weight as follows: The amount of alkali required for neutralisation is first ascertained by titrating a small weighed quantity of the fat. A larger weighed quantity is then dissolved in alcohol and nearly neutralised with the greater part of the alkali required, and the remainder is added cautiously until the solution becomes pink to phenolphthalein. The mixture of neutral fat and unsaponifiable matter, which rises to the surface, is dissolved in ether and separated from the soap solution, which is then repeatedly shaken out with ether. The ethereal extracts are united and washed repeatedly with water to remove all traces of soap. This stage of the process is very tedious on account of the emulsification of the two liquids. There is also formed an intermediate layer, consisting of soap of a higher fatty acid, which is not soluble in water, but dissolves readily in boiling alkaline solution of soap of the other acids. It is separated by filtration. The free fatty acids are thus obtained in 2 parts, those of the dissolved soaps and those of the difficultly soluble soaps. The ether dissolved in the soap solution is distilled off and the fatty acids set free by acidifying with hydrochloric acid. The solid soap on the filter is treated with boiling water and hydrochloric acid for the same purpose.

Cochenhausen (*Ding. Poly. J.*, 1894 292, 91, 112) modifies the above process as follows: The neutralised wool-fat is shaken with 30% alcohol and the soap solution boiled down to dryness, dissolved in 50% alcohol, and exhausted with petroleum spirit. In this process also insoluble soaps of higher fatty acids separate between the two layers as flocculent matter and must be filtered off.

As noted above, wool-fat contains hydroxylated fatty acids, which, on heating to a temperature of 100° and over, lose the elements of water and form inner anhydrides or lactones. These are not completely hydrolysed by aqueous solution of potassium hydroxide, which, if used for ascertaining the molecular weight on a sample which has been heated to dry it, would furnish results in excess of the truth. Error from this source is avoided by boiling the acids with standard alcoholic potassium hydroxide and titrating back the excess of alkali. In this way any anhydride which may be present is effectually hydrolysed.

Saponification-value.—As already noted, wool-fat is not completely saponified by simple boiling with alcoholic potassium hydroxide. Lewkowitsch (*J. Soc. Chem. Ind.*, 1892, 11, 137) found that

complete saponification could be effected by the use of 2N alkali under pressure. The fat and alkali should be contained in a copper flask tightly closed, placed in boiling water, and allowed to remain for from 1 to 2 hours, with occasional shaking. Identical results were obtained without pressure by the use of a freshly prepared solution of sodium ethylate. Herbig's experiments (*Ding. Poly. J.*, 1894, **292**, 42, 66) confirm these results so far as regards the saponification under pressure, but equally satisfactory results were not always secured by the use of sodium ethylate. Herbig found, further, that wool-fat contains esters that are easily saponified by alcoholic potassium hydroxide, and that, working under definite conditions, constant numbers for these are obtained. Heating over the naked flame was found to effect the result much more rapidly than by means of the water-bath, and the action is complete at the end of one hour's heating in a flask provided with a vertical condenser. By reason of its convenience, this method is often employed in the commercial valuation of wool-fats. The table on page 744 shows some results obtained in this way compared with those obtained by saponification under pressure. In the latter estimation, 2N alkali was used and the materials maintained at a temperature of 105 to 106°.

Estimation of Unsaponifiable Matter.—The separation of the ethereal layer from the aqueous solution of saponified wool-fat and recovered grease is troublesome, an intermediate stratum of a very persistent nature being formed. C. Rawson has suggested the following plan:

The sample is saponified in the usual way, and the resultant solution is evaporated in a porcelain basin placed over a small flame. Toward the end of the operation some powdered sodium hydrogen carbonate is stirred in to neutralise the excess of alkali, and some sand also added. The residue is then dried at 100° and exhausted with ether in a Soxhlet tube. The ethereal solution is then evaporated to dryness, the residue boiled with water, and the solution agitated with ether; or the ethereal solution is at once agitated with water containing a little sodium hydroxide to dissolve any soap it may contain, and then evaporated to dryness and the residue weighed.

A more satisfactory method is that of Herbig. (*Dingler Poly. J.*, 1895, **297**, 135.) From 1 to 2.5 grm. of the fat are boiled with N/2 potassium hydroxide for an hour, the excess of alkali neutralised

with standard acid, and the whole washed into a beaker with boiling alcohol. The alcohol is evaporated, the solution heated to 70 to 75°, and the fatty acids precipitated with calcium chloride, the amount of which has been calculated from the saponification-equivalent. The precipitate is filtered off, well washed with dilute alcohol (1 to 20), and dried on the filter *in vacuo*. When dry, it is extracted in a Soxhlet extractor with freshly distilled acetone for 6 hours, after which the acetone is evaporated, the extract washed with ether into a platinum basin, the ether evaporated, and the residue, which consists of the unsaponifiable matter and of the esters which cannot be saponified by the ordinary process of boiling with alcoholic potash, dried at 105° and weighed.

The chief points to be observed are the purity of the acetone—the fraction boiling between 55.5° and 56.5° being used—and the temperature at which the calcium salts are precipitated. If too hot they fuse, and if too cold they become slimy, subsequent filtration being almost impossible in either case.

It is advisable to extract the cork of the extraction apparatus with ether, alcohol, and acetone. Parker's *flat* separatory funnel (*J. Amer. Chem. Soc.*, 35, 295) can also be used.

For the estimation of the alcohols, free and formed by the saponification, it is necessary to saponify under pressure, precipitate with calcium chloride, and extract with acetone as described.

F. Ulzer and H. Seidel propose to ascertain, instead of the saponification-value, the total acidity value, as was recommended by Benedikt and Mangold in the case of wax. This number is the amount of potassium hydroxide (expressed as mg. per grm.) required to neutralise the mixture of fatty acids and fatty alcohols obtained by saponification and decomposition of the soap with acid. 20 grm. of potassium hydroxide are dissolved in 20 c.c. of water in a porcelain basin holding from 350 to 500 c.c., and the solution heated to boiling for about a minute, the heating continued on a water-bath until a thick, uniform soap is obtained, and the basin finally placed for 2 hours in the water-oven to complete the saponification. The soap is dissolved in about 250 c.c. of boiling water and decomposed with 40 c.c. of hydrochloric acid previously diluted with water. The clear fatty layer is repeatedly washed with boiling water until the washings are free from acid, and then dried in the water-oven. From 5 to 6 grm. of the dry mixture of

fatty acids and alcohols are weighed accurately and titrated with *alcoholic* potassium hydroxide with the precautions noted above in the determination of the molecular weight. The authors conclude that for the technical examination of a wool-fat sufficient data are furnished by the estimation of the acid value (*i. e.*, the mg. of potassium hydroxide required to neutralise the free fatty acid of 1 grm.), the total acidity value, the iodine value, and the Reichert-Meissl number, together with a gravimetric determination of the unsaponifiable matter.

Lewkowitsch (*J. Soc. Chem. Ind.*, 1892, **11**, 141, and *Chem. Anal. of Oils, Fats and Waxes*) gives the following data from the analysis of a wool-fat: The volatile acids were estimated by the Reichert process and their mean molecular weight assumed to be 104 ($C_5H_{12}O_2$). The total free and combined fatty acids were well washed to free them from soluble fatty acids, and their molecular weight found to be 332.

Volatile acids from 1 grm. required................. 0.124 c.c. normal KOH.
Free insol. acids from 1 grm. required.............. 0.586 c.c. normal KOH.
Total insol. acids from 1 grm. required............. 2.19 c.c. normal KOH.
Combined insol. acids (by difference)............... 1.48 c.c. normal KOH.
Unsaponifiable matter............................. 36.47 %.

And therefore,

Volatile fatty acids = 0.124 × 10.2 =............... 1.26%
Insoluble free fatty acids = 0.586 × 33.2 =.......... 19.45%
Combined insol. fatty acids (hydrated) = 1.48 × 33.2 = 49.13%
Total unsaponifiable matter....................... 36.47%
_____
106.31%

The excess over 100% is of course due, in part at least, to hydration incident to the saponification.

Lanolin.—On account of its property of forming an emulsion readily with water, wool-fat, purified by various patented processes, has come into extensive use as a basis for ointments and salves. Two preparations are recognised by the British and United States Pharmacopœias—*Adeps Lanæ* and *Adeps Lanæ Hydrosus*. It is commonly known as "lanolin," and consists of about 75 to 80% of wool-wax with 20 to 25% of water. It is usually white or slightly yellow, and of salve-like consistence. It does not turn rancid. According to Liebrich, it should be free from all traces of chlorine,

metals, glycerol or its esters, soaps, saline matters, and mechanically intermixed impurities or colouring matters, and it should not have any disagreeable odour. On rubbing on blue litmus-paper no reddening should occur.

Distilled wool-grease is a product obtained by distilling wool-fat with the aid of steam. When wool fat is distilled (Marcusson and Skopnik, *Z. ang. Chem.*, 25, 2577 thru Ch. Abst., 1913, 7, 1111), with superheated steam at 300-350°, wool-fat olein, semi-solid wool-fat, and wool-fat stearin are obtained. The olein consists of 40-60% liquid fatty acids and 60-40% unsaponifiable matter (see p. 751) and is used as a wool oil. The semi-solid distillate consists of 16-33% unsaponifiable matter and the remainder free fatty acids; its m. p. is below 45° and it is used as a soap-stock. The stearin contains 32-57% unsaponifiable matter and the remainder of fatty acids and is used for stuffing leather, for water-proofing paper and textiles. The lighter portions, "olein," separated by cooling are used for lubricating wool, and the more solid fractions "stearine," in the manufacture of soap and candles. It has also been used to adulterate tallow. According to Lewkowitsch (*J. Soc. Chem. Ind.*, 1892, 11, 142), only a small proportion of the esters originally present in the wool-fat are found in the distilled product, the greater portion being decomposed into fatty acids and hydrocarbons.

$$C_{15}H_{31}COOC_{16}H_{33} = C_{15}H_{31}COOH + C_{16}H_{32},$$

Cetyl palmitate   Palmitic acid   Cetene
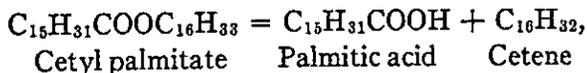
Smith (*Ann. Chim. Phys.*, (3), 1842, 6, 40). The fatty acids, especially the higher members of the series, are further dissociated into hydrocarbons and acids of lower molecular weight. Hydrocarbons are also formed by the decomposition of the free alcohols, a part of which, however, distils unchanged. The nature of these hydrocarbons is not well understood; it is, however, probable that they can be distinguished from hydrocarbons intentionally added, by the estimation of the bromine addition and substitution values, the optical rotation and index of refraction. These constants, obtained on hydrocarbons separated from some distilled grease oleines by Gill and Mason (*J. Amer. Chem. Soc.*, 1904, 26, 665), are shown in the table below:

Oleine	Sp. gr.	Bromine		Optical rotation	Refractive index at 20°
		Addition	Substitution		
A............................	0.896	28.8	14.2	+17° 58′	1.4967
B pure......................	0.902	25.1	14.8	+17° 36′	1.4991
C............................	0.896	21.5	16.8	+15° 13′	1.4948
D (doubtful purity)...........	....	3.8	9.0	+ 2° 56′	1.4921
Mineral oils.......	0.848 to 0.863	4.4 to 5.9	5.6 to 8 4	+ 1° 25′	1.4662 to 1.4750

The extraction of these hydrocarbons is carried out as follows: 200 grm. of the oil are saponified by boiling on a water-bath 2 or 3 hours with an excess of alcoholic potassium hydroxide (120 grm. to the liter) in a 750 c.c. flask, provided with a return flow condenser. When the saponification is complete, the solution is transferred to a liter separatory funnel and shaken several times with 300 to 400 c.c. of redistilled petroleum spirit (gasoline (86° B.)). The soap solution is thrown away. The gasoline solution is concentrated to about ½ its volume and washed with warm water mixed with a little alcohol in the separatory funnel until all the soap is removed. The remainder of the gasoline is distilled off in the water-bath, and the residue heated to 130° in a porcelain dish to drive off the water and last traces of gasoline.

From the saponification values of the different oils, the requisite amount of alcoholic alkali is calculated, and 100% excess employed. After the saponification, when gasoline is first added and the mixture thoroughly shaken, no separation occurs, even after several hours' standing. Salt is without effect. Finally, water is added in small quantities until distinct layers formed. In washing the gasoline solution, water alone was tried, but did not appreciably dissolve the soap. When warm water, mixed with a little alcohol, was used, the soap dissolved readily. In heating the oil to 130° to drive off water, a very small flame or, better, an electric stove should be used, and the oil constantly stirred to prevent bumping. A thermometer serves well as a stirring rod.

The unsaponifiable oil is freed from cholesterol and other higher alcohols by boiling for an hour with 100 c.c. of acetic anhydride in a flask provided with a return flow condenser, and heated over a sand-bath. Water is added, and the solution transferred to a separating funnel where it is washed with water and alcohol until the upper layer is clear and no odour of acetic acid is perceptible.

The cholesterol and higher alcohols are dissolved by the acetic anhydride, leaving the hydrocarbons.

These hydrocarbons have been investigated by Gill and Forrest (*J. Amer. Chem. Soc.*, 1910, 32, 1071) and found to be olefines boiling from 110° to 195° at 1 mm. pressure. They corresponded to eicosylene, $C_{20}H_{40}$, docosylene, $C_{22}H_{44}$, tri-, tetra-, hexa-, hepta-, and nonacosylene, $C_{29}H_{58}$. They were white crystalline substances resembling paraffin wax; some oily lower boiling compounds were also observed.

After submitting the oils to this process, an determination of their saponification number is made, and if more than 0.2 c.c. of alcoholic potash is used up, the treatment with alcoholic potash and acetic anhydride repeated.

Settimi[1] modifies Marcusson's method for detecting mineral oils in wool-fat oleines by shaking 10 c.c. with 40 c.c. amyl alcohol (1 part ethyl alcohol 96%, to 2 parts amyl) mixture in a glass stopped graduate. With pure lanolin at 20° a limpid solution results; 2% mineral oil interferes with the solubility and separates as a layer on standing; 5% may be very readily detected.

The examination of distilled wool-grease is conducted upon the same general lines indicated in the case of wool-fat. Lewkowitsch obtained the following results from a sample obtained by the distillation of recovered grease, the analysis of which is stated on page 748.

Free fatty acids...................................... 54.91%
Combined fatty acids................................. 7.02%
Unsaponifiable.. 38.80%

For other analyses of distilled wool-grease see page 749.

Alcoholic potassium hydroxide should be used in the determination of the molecular weight.

The fatty acids may also be determined with sufficient accuracy by the usual gravimetric method.

SOD OIL. DEGRAS. FRENCH DEGRAS (U. S.)

Dégras is the waste fat obtained in the chamoising process and largely used in dressing leather. The chamoising process consists essentially in oiling the suitably prepared skins with whale or cod

[1] Ann. lab. d. gabelle VI, thru C. Abst., 6, 3535 (1912).

oil (*i. e.,* the lower grades of codliver oil), stamping them in the stocks, and placing them in heaps, so that a fermentative change attended with development of heat is brought about. The process is complete when the skins have acquired the usual yellow colour of chamois leather. Under these conditions, oxidation of the oil takes place, and a portion of it combines with the skin, from which it cannot be removed by the usual solvents. About an equal quantity of uncombined oil is also mechanically enclosed in the skin. After being well scraped with a blunt knife, by which much of the excess of oil is removed, the skins are washed with lye and the emulsion treated with acid; and the fatty matter which rises to the surface is added to the oil already obtained by scraping. The product so obtained constitutes the so-called "sod oil." This is the method largely used in Germany and England. The following process employed in France is also used in England to a considerable extent: The treatment by oiling, stocking, and fermenting is carried out for a shorter period, so that a larger proportion of uncombined oil remains in the skins. This is removed by wringing or hydraulic pressing, and constitutes the "moëllon" or "dégras" of commerce. The remaining uncombined oil is removed by washing with lye and treatment with acid, and is usually added to the product. The moëllon of commerce is said to be invariably mixed with untreated oils. Moëllon contains less fibre, mineral matter, and water than sod oil.

Jean found that dégras (moëllon) contains from 10 to 20% of water, and that the property of forming an emulsion with water depends upon the presence of an oxidation product of the oil formed during the chamoising process. He describes it as a "resinous substance," insoluble in petroleum spirit, but soluble in alcohol and ether. It is saponifiable, but, unlike ordinary fat, the soap formed is not precipitated from alkaline solution by the addition of salt. The m. p. was stated to be 65 to 67°. Simand has given it the name *dégras-former.* According to him it is insoluble in, petroleum spirit benzene, and almost insoluble in ether. It is soluble in alkaline solutions, from which it is precipitated by the addition of acid. It was also found in all animal and marine oils. Fahrion regards it as a mixture of hydroxy-fatty acids and anhydrides. It is an oxidation product, and experience has shown that those marine animal oils which absorb oxygen readily are the most suitable for

the preparation of dégras. Fahrion found an iodine-absorption of 65.9% in dégras-former. Ruhsam found 98.8% in sample No. 1 on page 756. According to Fahrion, dégras-former contains no nitrogen, that found by Eitner being due to impurities.

Dégras-former is said not to exist in the free state in dégras, but forms a part of the saponifiable matter which is readily soluble in petroleum spirit, in which the dégras-former itself is insoluble.

Baron (*Rev. Chim. Ind.*, 1897, **8**, 225) prepares an artificial dégras as follows: 1000 kilos of neutral wool-fat (extracted by petroleum spirit) are placed in a tinned steel vessel with 5000 kilos of cod or whale oil. The liquid is heated by a steam coil, agitated for 3 hours, then allowed to rest and cool for the same period, and the water withdrawn. The water is again heated to 40°, 150 kilos of hydrogen peroxide and 450 kilos of water added, and the whole agitated for 5 hours at a pressure of 2 atmospheres. The resulting product is said to form an excellent moëllon, having a yellow colour and being easily emulsified and absorbed by the skins. It is important that the wool-grease be free from sulphuric acid, lest this should dissolve traces of iron, and so cause darkening of the leather.

Examination of Dégras.—*Water* is ascertained, according to Fahrion's method adopted by the International Association of Leather Trade Chemists, by heating 10 grm. slowly in a platinum crucible, over a small flame, until all the water has been driven off; the end of the operation is recognised by the appearance of a slight evolution of vapours.

French dégras usually contains from 10 to 20% of water; sod oil may contain as much as 40%.

Free Acid.—*Mineral acids* may be detected as described on p. 92. The amount is estimated by boiling a weighed quantity of the sample with water and separating the aqueous solution, which will contain the mineral acids as well as any soluble fatty acids; the estimation of the former is made by adding Methyl-Orange (Methyl-Red) and titrating with standard alkali until the point of neutrality is reached. The *soluble fatty acids* are then estimated by adding phenolphthalein and titrating a second time.

Free fatty acids may be estimated in the residue insoluble in water by dissolving in alcohol and titrating as usual. They are usually calculated to oleic acid.

Ash.—This is estimated in the usual manner. It should be tested for iron. According to Simand, even as low a proportion as 0.05% of ferric oxide has a distinctly injurious effect.

The ash of moëllon is usually less than 0.1%; that of sod oil may amount to several %.

Fragments of hide may be estimated in the residue left from the solution in gasoline (motor spirit), which is dried, weighed, and incinerated. The loss on incineration may be taken to represent, roughly, the hide fragments.

Unsaponifiable matter may be estimated in the usual manner as described on page 90.

Dégras-former.—Simand makes the estimation as follows: 20 to 25 grm. of the sample, according to the amount of water present, are saponified in an Erlenmeyer flask, with a funnel placed in the mouth, using a solution of about 5 to 6 grm. of solid sodium hydroxide in 10 c.c. of water and 50 to 60 c.c. of alcohol. The alcohol is evaporated, the soap dissolved in water, and the fatty acids liberated by hydrochloric acid. The liquid is then warmed until the fatty acids have formed a clear oily layer and the dégras-former has collected in lumps. It is then allowed to cool and the acid water separated from the undissolved portion. This latter is washed several times with boiling water, the washings added to the acid liquid, and the mass remaining in the flask (consisting of the dégras-former, fatty acids, and unsaponifiable matter) is dried at 105°. The acid liquid and washings are neutralised with ammonium hydroxide, evaporated to dryness, redissolved in a small amount of water, the solution feebly acidified with hydrochloric acid and the small amount of dégras-former thus obtained (which had been dissolved in the aqueous liquid) separated by filtration, washed, dried, and added to the contents of the flask. It is then extracted with 100 to 120 c.c. of petroleum spirit, which dissolves the fatty acids and leaves the dégras-former and some albuminous materials. The residue is dissolved in alcohol by warming, the solution filtered, the filtrate evaporated to dryness, and the residue weighed as dégras-former. The process is said to be accurate within 0.5%. The petroleum spirit may be evaporated and the residual fatty acids weighed and examined.

Dégras, according to Simand, is pure and genuine only when it contains at least 12% of dégras-former. It may contain as much as 17%.

Jean ascertains the proportion of "resinous substance" as follows: A weighed quantity of dégras is saponified and the aqueous solution or the soap extracted with ether to remove the unsaponifiable matters. The soap solution is boiled to drive off the ether, and treated while hot with excess of pure sodium chloride. After cooling, the coloured liquid is filtered from the separated soap, the filtrate collected in a flask, and acidified with hydrochloric acid. The "resinous substance" separates in flocks, which on boiling unite and adhere to the sides of the flask. The liquid is cooled, shaken out with ether, the ethereal solution evaporated, and the residue dried and weighed.

Jean considers that a sp. gr. of the oil extracted from dégras of less than 0.920 indicates the presence of foreign fats, e. g., wool-fat, oleic acid, and tallow. The sp. gr. of the oil from dégras made from fish and whale oil is given as 0.949 to 0.955. The presence of tallow is also indicated by the higher m. p. of the fatty acids. In the examination of artificial dégras, Simand takes into consideration, in addition to the ash and water, the following points:

1. The dégras-former, which may be derived from a small quantity of admixed true dégras or from the oils.

2. The wool-fat.

3. Hydrocarbons (vaseline).

4. Colophony.

To determine the dégras-former, Simand proceeds as with genuine dégras, but substitutes ether for the petroleum spirit, since the wool-fat acids are dissolved by the former in the cold.

The estimation of the amount of wool-fat is as yet an unsolved problem. The detection of cholesterol would not, in itself, suffice, as it is a natural constituent of the fish oils used in the manufacture of dégras. Lewkowitsch points out that by the ordinary methods of saponification, a portion of the wool-fat would probably be found in the unsaponifiable portion, and that by again saponifying under pressure a definite saponification value would point to the presence of wool-wax.

Benedikt (*Anal. d. Fette u. Wachsarten*) states that by estimating the amount of cholesteryl acetate (see page 780) a very rough approximation of the amount of wool-fat may be obtained. Wool-fat furnishes percentages of cholesteryl acetate varying from 9.59 to 18.71%.

Rosin may be estimated as on page 94 and hydrocarbons as on page 90.

Jean gives the following example of examinations of dégras:

	1	2	3	4	5	6	7
Water, %	18.90	14.84	12.93	28.90	19.20	5.39	8.90
Ash. %	0.25	0.13	0.55	0.70	0.07	0.25	1.21
Hide-fragments, %	0.30	0.30	0.09	0.58	0.27	....	1.59
Oils, %	69.71	74.65	80.00	66.93	75.66	84.87	72.15
Unsaponifiable matter, %	6.84	6.05	....	....	....	....	....
"Resinous substance." %	4.00	4.05	5.81	3.52	4.80	9.46	16.15

Simand gives the following results:

		Dégras-former, %	M. p. of fatty acids, °	Soap, %	Original dégras	
					Hide fragments, %	Water, %
French dégras (anhydrous)	1	19.14	18.0–28.5	0.73	0.07	16.5
	2	18.43	28.5–29	0.49	0.12	20.5
	3	18.10	31.0–31.5	0.68	0.18	13.0
Sod oil (anhydrous)	1	20.57	33.5–34	3.95	5.7	35.0
	2	18.63	27.5–27	3.45	5.9	28.0
	3	17.84	28.0–28.5	3.00	4.5	30.5

The table on page 760 gives the results of an extended series of examinations of dégras by R. Ruhsam. Samples 1 to 9 are French artificial dégras; No. 10 is a so-called "emulsion fat;" No. 1 is a genuine dégras from the cod oil No. 12.

The iodine absorptions were estimated as usual, the insoluble fatty acids being first freed from dégras-former by solution in petroleum spirit. It will be noted that the figure for genuine dégras is much higher than that of the artificial samples. The acetyl values were estimated by the method of Benedikt and Ulzer, and are of value only for comparison with each other.

The following shows the results of the examination of 12 sod oils found on the American market by Hopkins, Coburn, and Spiller (*J.*

Amer. Chem. Soc., 1899, **21**, 291). The results are calculated on the water-free oil, and the acids in mg. potassium hydroxide per grm. of oil.

	Water	Ash	Mineral acid	Oil, etc., sol. in petroleum ether	Soap, etc., sol. in alcohol	Hide fragments	Unsaponifiable matter	Oxidised acids	Free fatty acids
Minimum....	1.0	0.05	1.1	56.6	0.7	0.15	0.4	1.1	32.3
Maximum....	40.6	1.0	91.5	96.6	8.8	3.0	42.6	26.4	34.6

WOOL OILS.   CLOTH OILS (Eng.)

Cloth oil or wool oil is a trade term for all materials used in lubricating wool before spinning, or rags before grinding and pulling. Since the success of the subsequent dyeing operations is in a great measure dependent upon the thoroughness with which these oils are removed by scouring, mineral oil, or, in general, any unsaponifiable matter is objectionable.

Mineral oils are emulsified by soap solutions and removed in great part, but not completely, by ordinary scouring (Matthews, *J. Soc. Chem. Ind.*, 1905, **24**, 659). With the better grades of goods even a small proportion of these oils is harmful, but with low grades it is permissible to use a strongly alkaline soap by which the mineral oil is to a great extent removed.

According to Horwitz (*Färb. Zeit.*, 1890, No. 11), cholesterol[1] may be present in the cheapest grades of olive oil in sufficient quantity to cause spotting of the dyed fabric. A sample of oil used to lubricate a wool which exhibited this condition was found to contain 3% of cholesterol,[1] and other samples were found to contain as high as 4%.

Olive, lard, and neatsfoot oils and commercial oleic acid ("red oil," "elaine," "oleine"), sulphonated oils, are largely employed, and when of good quality are the most suitable. Besides these, however, wool-grease, distilled grease, and seek oil (the recovered

c This unsaponifiable matter is probably phytosterol, as the researches of Lewkowitsch loc Gill and Tufts (*J. Am. Chem. Soc.*, 1903, **25**, 498) have shown that cholesterol does not nadur in olive and corn oils.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
		Iodine absorption, %			Acid No.	Saponification No.	Ether No. (difference between 6 and 7)	Constant acid No.	Constant saponification No.	Constant ether No. (difference between 9 and 10)	Acetyl acid No.	Acetyl saponification No.	Acetyl No. (difference between 12 and 13)	True acetyl No. (difference between 14 and 11)
No. of sample	Water, %	Dégras (anhydrous)	Insoluble fatty acids	Acetylised fatty acids										
					Mg. of potassium hydroxide per grm. of anhydrous dégras			Mg. of potassium hydroxide per grm. of fatty acids			Mg. of potassium hydroxide per grm. of acetylised fatty acids			
1	19.1	74.7	70.5	73.1	37.7	......	....	185.5	224.3	38.8	181.0	280.0	99.0	60.2
2	12.9	64.2	58.6	52.7	72.7	110.4	37.7	102.8	131.5	28.7	92.6	164.7	72.1	43.4
3	12.4	77.4	75.4	90.4	40.2	110.7	70.5	129.6	172.9	43.4	128.9	196.1	67.2	23.8
4	15.9	78.4	70.2	66.6	50.1	134.8	84.7	162.9	193.7	30.8	157.0	237.0	80.0	49.2
5	16.4	77.8	78.5	76.2	52.7	137.4	84.7	163.5	185.9	22.4	160.9	227.0	66.1	43.7
6	11.5	76.6	76.5	75.7	64.9	108.8	43.9	175.8	229.6	53.8	171.0	282.5	111.5	57.7
7	13.9	96.7	95.9	88.9	......	....	....	182.5	215.6	33.1	178.7	212.4	33.7	0.6
8	17.3	83.7	93.4	102.7	28.9	100.8	71.9	96.7	197.1	100.4	92.8	175.4	82.6	....
9	16.6	80.9	....	....	52.0	141.2	89.2	....	....	....	....	....	....	....
10	5.3	74.4	79.3	73.0	54.1	125.2	71.1	179.5	210.2	30.7	180.1	217.0	36.9	6.2
11	.. ....	127.7	142.3	127.4	......	163.8	....	180.8	212.2	31.4	176.8	228.3	51.5	20.1
12	.. ....	126.7	106.0	101.9	......	186.0	....	159.3	213.2	53.9	158.2	215.7	57.5	3.7
Mean of 1–10	......	78.5	77.6	77.7	50.4	121.2	70.8	160.3 (except No. 8)	195.5 (except No. 8)	35.2 (except No. 8)	149.2	221.3	72.1	....

grease from the scouring of various silk, woolen, and cotton goods) are employed. The cheaper oils in the market consist of one or more of the above, mixed with more or less mineral oil. So-called "emulsion oils," consisting of oil or "olein," held in suspension in a solution of soap, or of borax and Irish moss, and also simple solutions of soap are employed. The latter are prepared from castor oil or ricinolsulphuric acid.

The important factors to be considered in judging of the suitability of an oil for this purpose are: *First, its easy removal.* The success of subsequent dyeing and finishing operations is in a great measure dependent upon the thoroughness with which the oil is removed by scouring. Consequently anything interfering with this process, as the gumming or resinification of the oil, and particularly the presence of unsaponifiable matter, is objectionable. Gumming interferes with the carding and spinning operations. Drying, semidrying oils and acids, rosin and rosin products are consequently to be avoided. Mineral oils, whilst emulsified by soap solutions, are not completely removed by ordinary scouring (Matthews,

FIG. 24.

J. Soc. Chem. Ind., 1905, **24**, 659). With the better grades of goods even a small proportion of these oils is harmful; with low grades they can be practically all washed out by the use of strongly alkaline soaps. It would seem that the hydrocarbons in distilled wool grease, those of the olefine series, can be more readily scoured out than the mineral oils.

Second, its liability to cause spontaneous combustion. All oils that absorb oxygen are dangerous in this respect. Mineral oils, whilst not open to this objection, are still considered dangerous by reason of the facility with which a fire, once started, will spread in their presence. An examination directed to these points is all the more important in view of the higher rate of insurance which may be charged in some countries when oils considered unsafe in this
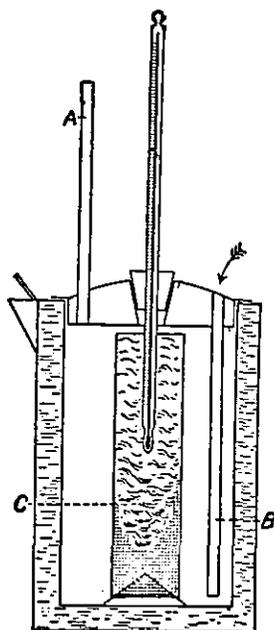
respect are employed. In Great Britain the rating is based upon the nature of the oil, the proportion of unsaponifiable matter, and the flash test. The lowest rate is charged when an olive oil, lard oil, or "oleine" is used containing not more than 10% of unsaponifiable matter, or a fish or manufactured oil containing not more than 30% of unsaponifiable matter and having a flash-point not under 167°. The highest rate is charged in the presence of drying oils or of more than 50% of unsaponifiable matter.

The "flash-point" of an oil intended for this purpose may be easily ascertained by placing 50 c.c. in a porcelain dish or crucible, in a sand-bath, heating with constant churning and noting the temperature at which a flash across the surface is produced when a small flame is brought near.

A satisfactory test of the liability of an oil to inflame spontaneously may be made by Mackey's "Cloth-oil Tester" (J. Soc. Chem. Ind., 1896, 15, 90; also Gill, ibid., 1907, 26, 185). This consists of a cylindrical copper water-bath of the following dimensions: Outside, 8 in. high and 6 in. diam.; inside, 7 in. high and 4 in. diam. The tubes A and B are ½ in. internal diam. and 6 in. long measured from the lid. The depth inside with the lid on is 6¼ in. The lid is packed with asbestos wool, and the tubes serve to maintain a current of air. Care should be taken that the steam from the water jacket is neither drawn down B nor warms A. C is a cylinder of wire gauze (24 meshes to the in.) 5 by 6 in. forming a roll 6 in. long and 1½ in. diam. In it is placed 7 grm. of ordinary bleached cotton-wadding, previously impregnated with 14 grm. of the sample occupying the upper 4½ in. of the cylinder.

The water being brought to the b. p., a thermometer is inserted in the oiled cotton contained in the gauze cylinder, which is then placed in the bath, the thermometer being allowed to protrude through a cork in the opening shown in the lid. The water is kept boiling and the temperature read at the end of an hour. An oil attaining a temperature of 100° or over at the end of this time is to be regarded as dangerous. The following are the results of experiments:

Oil used	Temperature at the end of			Maximum
	One hour	One hour fifteen minutes	One hour thirty minutes	
				H. M.
Cottonseed...............................	125	242	....	242 in 1 15
Cottonseed...............................	121	242	282	284 in 1 35
Cottonseed...............................	128	212	225	225 in 1 30
Cottonseed...............................	124	210	....	248 in 1 35
Cottonseed...............................	116	192	200	200 in 1 30
Cottonseed..	118	191	202	202 in 1 30
Cottonseed...............................	117	190	194	194 in 1 30
Cottonseed...............................	112	177	204	211 in 1 45
Olive, fatty acids......................	114	177	....	196 in 1 25
Olive, fatty acids......................	105	165	....	293 in 1 55
Olive, fatty acids......................	102	135	208	226 in 1 45
White Australian olive................	103	115	191	230 in 1 45
Olive, with 1 % free fatty acid........	98	102	104	241 in 3 25
"Oleine"	98	101	102	110 in 2 8
"97 % oleine"........................	98	100	102	172 in 3 15
Belgian "oleine".	98	99	100	173 in 3 16
Olive, neutral.	98	100	101	235 in 5 15
Olive, neutral	97	100	101	228 in 4 30
Olive, neutral...	97	....	101	235 in 4 55

In applying this test, the fact that small quantities of a metal will catalyse the reaction must not be overlooked. It has long been known that "red oil" behaves anomalously in the mill, some samples heating and others giving no trouble. This has been shown by Swett and Hughes (*J. Ind. Eng. Chem.*, 1917, 9, 623), and also by the writer, to be due to iron salts, as little as 0.1% present as ferric oxide being sufficient to cause a dangerous rise when the spontaneous conbustion test is applied. On the removal of the iron, by shaking with hydrochloric acid, the oil gave no rise of temperature. Iron compounds are, however, not the only exciting causes. Mackey and Ingle (*J. Soc. Chem. Ind.*, 1917, 35, 454; 36, 317) and the writer have found that cobalt, manganese, lead, zinc, chromium, sodium, nickel, iron, magnesium, barium, strontium, tin and copper salts will all catalyse the reaction in about the order given, cobalt being the most, and copper the least active. Aluminium has no effect, as it forms but one oxide; the action of cobalt compounds is quite marked as mixed with olive oil they give a rise to 175° C. in 25 minutes, *ibid.*, 1924, 16.

Chemical examination of wool or cloth oils is by application of principles and methods already given. An estimation of *unsaponifiable matter* is important, and if hydrocarbons are present, the flash-point should be ascertained; this should not be lower than 300° F. The iodine value will aid in the detection of *semi-*

drying or drying oils. The examination of commercial oleic acid is given in detail on page 526; it is to be especially tested for *unsaponifiable matter* and for linolic and linolenic acids (using the iodine value). *Rosin* should be looked for in the fatty acids separated from the saponifiable portion as described on page 94. See also under "Wool-fat" and "Distilled Wool-grease." *Free mineral acid,* which is especially apt to be present in commercial oleic acid, is objectionable on account of its corrosive action on card-teeth. This applies also to elaine or red oils and the very rancid olive oils.

In the case of "emulsion oils" the fatty matter may be separated by treatment with acid and examined as above. *Gelatin* or *gummy matters* used in preparing the emulsion may be separated by addition of alcohol.

THE STEROL ALCOHOLS

By JOHN ADDYMAN GARDNER, M.A., F.I.C.

The sterols constitute a group of alcohols, saturated and un-saturated, of high molecular weight, which appear to belong to the class of polyterpenes, and are widely distributed in the animal and vegetable kingdoms. They appear to be intimately related to the bile acids. For example, Windaus and Neukirschen (*Ber.*, 1920, **52**, 1915) have recently shown that ψ-coprostane, a hydrocarbon derived from the sterol ψ-coprosterol, yields on oxidation the same cholanic acid, $C_{24}H_{40}O_2$, m. p. 159–160, as that obtained by Wieland and Weil from cholic acid (*Zeitsch. physiol. Chem.*, 1912, **80**, 287), and consequently ψ-cholestane and cholic acid possess the same carbon skeleton, and cholic acid and its derivatives only differ from the sterol hydrocarbon by three carbon atoms split off from a side chain.

The best known members of the group are the unsaturated alcohols cholesterol and phytosterol and the saturated alcohols β-cholestanol and coprosterol.

CHOLESTEROL. CHOLESTERYL ALCOHOL

$$C_{27}H_{46}O = C_{27}H_{45}OH$$
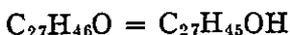
Cholesterol is widely distributed in the animal kingdom both in the free and ester form, but has never been found in the vegetable kingdom. It is present in bile, blood-corpuscles, blood serum, brain, spinal cord, sperm, yolk of egg, perspiration, and skin grease; in the glands—liver, kidney, pancreas, salivary, stomach, and ovaries; in the fat tissues—bone-marrow, under-skin fat, kidney fat, milk fat; in tendons and muscles. It occurs also in the tissues of the lower animals and has been found in various species of sea anemone (*Actinia equina* and *Taclia crassicornis*) (Dorée, *Biochemical Journal*,

1909, 4, 72). It is found in most pathological fluids and tumors, gall-stones often containing as much as 98% of their weight of cholesterol. There can be no doubt that it is a constant constituent of all killed animal protoplasm.

Cholesterol is quite insoluble in water, very slightly soluble in cold dilute alcohol, still less so if the alcohol contains salt in solution. It is easily soluble in 5 to 9 parts of boiling alcohol, in 3.7 parts of ether, 6.6 parts of chloroform, and in acetone, benzene, petroleum spirit carbon disulphide, and turpentine. It is also dissolved by volatile and fatty oils and by aqueous solutions of bile salts. Though insoluble in water, it may be obtained in colloidal suspension by stirring a solution in alcohol (Partington, *Trans. Chem. Soc.*, 1911, 318) or acetone (Porges and Neubauer, *Biochem., Zeitsch.* 1908, 7, 151) in small quantities into water and dialysing the fluid. The solution keeps well and gives precipitates with mineral acids, alkalies, calcium chloride, etc. It appears to be an anodic suspensoid. It crystallises from ether or chloroform in anhydrous silky needles, and from 80 to 90% alcohol in characteristic rhombic plates containing $1H_2O$. It loses this water at 100° or in a vacuum. Anhydrous cholesterol melts at 147° and has a sp. gr. 1.046. It is lævorotatory, and the specific rotatory power appears to be independent of temperature and strength of solution and is not altered even by long standing. In ether solution $(\alpha)_D = -31.12°$, but in chloroform $(\alpha)^{16}_D = -36.16°$. On heating, it sublimes almost without decomposition in delicate laminæ and can be distilled without any decomposition in a vacuum of 1 mm. This constitutes a ready method of purification, particularly in the case of cholesterol isolated from tissues, which often contains traces of pigment difficult to remove by crystallisation.

Cholesterol is not acted on by dilute acids, or by concentrated alkaline solutions even on boiling. Lewkowitsch has noted that when cholesterol is heated with soda-lime no, or at most very small, quantities of fatty acids are formed—an important difference from aliphatic alcohols. Chemically, cholesterol behaves as an unsaturated secondary alcohol.

Cholesterol dibromide, $C_{27}H_{46}Br_2O$, is best prepared by dissolving 50 grm. of cholesterol in 500 c. c. of ether and adding a solution of 25 grm. of bromine in 250 c.c. of glacial acetic acid. After a short time the mixture sets to a mass of crystalline needles of cholesterol

dibromide. These are filtered on the pump, washed with acetic acid and then with water. The dibromide thus prepared is pure, and if the small quantity that remains in solution is precipitated by the addition of water, the yield is quantitative.

The dibromides of the esters of cholesterol may be prepared in a similar manner. Cholesterol dibromide, prepared as above, melts at 123°. It is readily reduced to cholesterol by the action of zinc dust and glacial acetic acid or of sodium amalgam in presence of ether.

The calculated iodine absorption of cholesterol is 68.3. Lewkowitsch obtained figures closely approximating to this, using Hübl's method. Wijs' method, however, gives quite abnormal values.

Cholesteryl Esters.—*Cholesteryl acetate*, $C_{27}H_{45}C_3H_2O_2$, is best prepared by boiling cholesterol for 20 to 30 minutes with an excess of acetic anhydride. It crystallises from benzene in needles. It is fairly soluble in ether and slightly so in cold alcohol, but more readily in hot alcohol. It melts at 113°, and has a specific rotatory power $(\alpha)_D = -29.8°$.

Cholesteryl propionate, $C_{27}H_{45}C_3H_5O_2$, is prepared by heating anhydrous cholesterol with half its weight of propionic anhydride on the water-bath for half an hour. On cooling, the propionate separates as a white mass, and may be purified by repeatedly dissolving in ether and reprecipitating with alcohol. It crystallises in rhombic plates something like cholesterol, and melts at 98°. On cooling from the melted state, a play of colours is seen about the point of solidification—violet, blue, green, orange, copper-red by reflected light and the complementary colours by transmitted light. This is very characteristic.

Cholesteryl benzoate, $C_{27}H_{45}C_7H_5O_2$, is formed by heating cholesterol with benzoyl chloride or benzoic anhydride, but the best way to prepare it is to dissolve cholesterol in dry pyridine and add a moderate excess of benzoyl chloride. The mixture is allowed to stand overnight, and then poured into water. The precipitated cholesteryl benzoate is washed with a little alcohol and recrystallised from ethyl acetate or from boiling alcohol. It is only slightly soluble in absolute alcohol. If crystallised from alcohol, the mother liquors retain at 20° 0.12 grm. per 100 c.c. The crystals are, however, more difficultly soluble. The writer found that on allowing crystals to stand in alcohol at 20° for several hours, with occasional shaking,

only 0.029 grm. dissolved in 100 c.c.   Cholesteryl benzoate melts at 145 to 146° to a turbid liquid, which becomes clear at 178°.   On cooling from 178°, a deep blue colour appears but soon vanishes, and near the point of solidification an azure blue persisting for a few moments is seen.   This behaviour is exceedingly characteristic.

Cholesteryl chloride, $C_{27}H_{45}Cl$, was first obtained by Berthelot by heating cholesterol at 100° with strong hydrochloric acid for 10 hours.   It may also be prepared by the action of phosphorus pentachloride on cholesterol, but, according to Diels and Abderhalden, it is most readily obtained by the action of thionyl chloride.   Cholesterol dissolves in this substance with foaming, and the solution eventually sets to a stiff mass of cholesteryl chloride, which may be purified by crystallisation from ether.   It melts at 96°, and has a specific rotatory power $[\alpha]_D = -26.36°$.   Many other esters of cholesterol have been prepared, but the only ones that need be mentioned here are the oleate and palmitate, as they have been found in blood serum and in some pathological fluids.

Cholesteryl palmitate melts at 78.5° to 79.5° and has specific rotatory power in chloroform $[\alpha]_D = -24°2$.   *Cholesteryl oleate* is easily soluble in ether, chloroform, benzene, and hot acetone, but in alcohol is more difficultly soluble than cholesterol.   It crystallises in needles, melts at 41°, and has specific rotatory power $[\alpha]_D = -18.48°$.

It is insoluble in water, but is said to possess the peculiar property of taking up considerable quantities of water, forming a perfectly homogeneous salve-like, somewhat foamy mass, not unlike lanolin. It gives the cholesteryl colour indications (see later) in a modified manner.

The cholesteryl esters can be easily saponified by boiling with an alcoholic solution of potassium hydroxide, or, at a lower temperature, by the action of an alcoholic solution of sodium ethoxide on the ethereal solutions.

Digitonin-cholesteride, $C_{27}H_{46}O.C_{55}H_{94}O_{28}$, is prepared, according to Windaus (*Ber.*, 1909, **42,** 240), by mixing a hot solution of 1 grm. digitonin in 100 c.c. 90% alcohol with a solution of 0.4 grm. cholesterol in 60 c.c. of 95% alcohol.   The substance is precipitated in the crystalline form and, after standing for 1 hour, is filtered off washed with alcohol and dried at 110°.   It is easily soluble in pyridine, but insoluble in cold water, acetone, ether, ethyl acetate and benzene.   100 c.c. methyl alcohol dissolves at 18° about 0.47

grm.; 100 c.c. 95% ethyl alcohol at 18° only 0.014 grm., and at 78° about 0.16 grm.; 50% boiling alcohol, 0.03 grm. The dry substance is very hygroscopic and gives in a typical manner the Burchardt-Liebermann test for cholesterol. It has no definite m. p., but decomposes gradually at 240°.

Phytosterol, coprosterol, stigmasterol and many alcohols of other series form similar compounds, but *the esters of cholesterol do not interact with digitonin.* (See also p. 783.)

Oxidation.—The carbon skeleton of cholesterol is extremely stable, and though the substance is readily attacked by oxidising agents, the products are usually neutral or acid substances of the same carbon content. Oxidising agents usually attack the double linkage, or both the double link and the carbinol group; but Diels and Abderhalden (*Ber.*, 1904, **37**, 3092) found that when cholesterol is heated with powdered copper oxide to 280 to 300° the CH(O.H.) group is oxidised to CO, the ketone cholestenone being formed.

Cholestenone, $C_{27}H_{44}O$, is, however, more readily prepared by a method devised by Windaus (*Ber.*, 1906, **39**, 518). Cholesterol dibromide is oxidised either by chromic acid in glacial acetic acid solution at 70° or by means of an acid solution of potassium permanganate in the cold. The cholestenone dibromide thus formed is reduced by means of zinc dust and acetic acid, and the cholestenone obtained in a yield of 60%. Cholestenone melts at 81 to 82°, and forms a hydrazone, which crystallises in needles, m. p. 152°; a semi-carbazone, m. p. 234°, and an oxime, m. p. 150°.

Detection of Cholesterol.—When moderately pure, cholesterol is easily recognised by its characteristic crystalline form. The substance to be tested should be boiled with 90% alcohol, the solution filtered hot and allowed to cool slowly. Either immediately on cooling, or after previous concentration, the cholesterol will be deposited in crystals, which, viewed under a moderate power appear as thin, very transparent, rhombic plates, the angles of which are well defined and constantly measure 79°30′, and 100°30′.

The most valuable tests are, however, the formation of the acetate, benzoate, dibromide and digitonin compound by the methods already described and the examination of their properties. The esters may be prepared with care from quantities of cholesterol as small as 0.05 grm. and the digitonin-cholesteride from quantities much smaller than this. These derivatives sometimes form a convenient means

of separating cholesterol from other substances. By means of the digitonin compound cholesterol may be distinguished from its esters.

Cholesterol gives a number of well-marked colour indications which are sometimes useful and of which the following are the chief:

Schiff's Test.—Cholesterol is cautiously heated with a drop of concentrated nitric acid, and the pale yellow product treated with ammonia before it has completely cooled. A deep yellowish-red colour is developed which is not essentially altered by fixed alkalies. The indication, however, is not specific, as it is given by turpentine and other substances.

Moleschott's Test.—If a crystal is warmed on a microscope slide with a mixture of 5 volumes of concentrated sulphuric acid and 1 volume of water, cholesterol gives a fine carmine-red coloration; with 4 volumes of acid and 1 of water, it becomes blue without warming; with 3 acid to 1 water, violet, and 2 acid to 1 water, pale lilac.

Hydrochloric Acid Test.—When cholesterol is evaporated with strong hydrochloric and mixed with ⅓ of its volume of a solution of ferric chloride, the residue is coloured a fine red-violet, changing to blue-violet. Gold and platinum chlorides behave similarly to ferric chloride.

Salkowski's Test.—A few mg. of cholesterol are dissolved in about 2 c.c. of chloroform and then shaken with an equal bulk of strong sulphuric acid. The chloroform quickly becomes bood-red and then cherry-red or purple, a colour which it retains for several days. A few drops of this solution poured into a basin become blue, green, and then yellow, owing to the absorption of water. The original colour may be again restored on adding some sulphuric acid. The sulphuric acid which separates from the chloroform presents a distinct fluorescence.

Burchardt-Liebermann Test.—A few mg. of cholesterol are dissolved in 2 c.c. of chloroform, 20 drops acetic anhydride are added, and a single drop of concentrated sulphuric acid. A pink colour is developed, which rapidly changes through violet and blue to a beautiful green. The green colour persists for a considerable time, but gradually changes to a dirty brown. This test is very delicate, but the indication is shared by cholatrienic acid and other bile derivatives. Many resinous substances also give a reddish-brown colour which sometimes develops, on standing, a green tint, or a green fluo-

rescence. More or less similar colour indications are given by many derivatives and isomers of cholesterol, and by other allied substances, though not by all.

Isocholesterol.—This body is isomeric with ordinary cholesterol and, according to E. Schulze (*Ber.*, 1873, 1075), occurs with it in wool-fat. It has not, however, so far as the writer is aware, been found in any of the organs or tissues of the animal body.

To separate cholesterol and isocholesterol, the mixture should be heated for 30 hours in a sealed tube to 200°, with 4 times its weight of benzoic acid or benzoic anhydride. The product is then repeatedly boiled with rectified spirit, when excess of benzoic acid dissolves and the cholesteryl and isocholesteryl benzoates remain. By crystallising from ether, the former is obtained in shining rectangular plates and the latter as a light crystalline powder which may be separated by decantation and elutriation.

Isocholesterol benzoate after recrystallisation from ether is obtained in the form of minute needles melting at 190 to 191°.

Isocholesterol (Schulze, *J. prakt. Chem.* [2], 7, 163) is obtained by saponifying the benzoate with alcoholic solution of potassium hydroxide. It separates from absolute alcohol in flocks when the solution is dilute, but a concentrated solution solidifies as a transparent jelly. From ether it is deposited in needles. It melts at 137° to 138°, and has specific rotatory power $[\alpha]_D = + 60°$, which is independent of the concentration of the solution. Isocholesterol gives the Schiff test (page 768), but shows no colour changes with sulphuric acid and chloroform or with ferric chloride and a mineral acid. With the Burchardt-Liebermann test (page 768) a yellow and afterward a yellowish-red coloration appears, with, at the same time, a green fluorescence. Isocholesteryl acetate is obtained by digesting the alcohol with acetyl chloride until the evolution of hydrogen chloride ceases, and then heating to 100° in a sealed tube. On removing the excess of acetyl chloride by evaporation, isocholesteryl acetate is obtained as an amorphous substance. It is readily soluble in alcohol, and melts below 100°. In the writer's opinion isocholesterol and its derivatives require further investigation.

VEGETABLE STEROLS

Cholesterol is represented in the vegetable kingdom by the various isomeric phytosterols, which appear to be equally widely

TABLE I

Name of chemist	Source of the phytosterol	Name of phytosterol	M. p.	Formula assigned	M. p. of acetate	M. p. of benzoate	References	Remarks
(1) Benecke..........	Seed peas, g r e e n plants, seeds, and blossom parts.	....	136°–137°	....			*Ann.*, 1862, **122**, 249.	
(2) Ritthausen......	Wheat gluten........	....		....			*Jahreshb. d. Fortsch. d. Chem.*, 1863, 544.	
(3) Lindenmeyer.....	Peas, various oils....	....		....			*J. prakt. Chem.*, 1863, 90, 328.	Considered by the writers to be cholesterol.
(4) Hoppe-Seyler.....	Maize, rape oil and almond oil.	....		....			*Med. Chem. Unter-suchung*, 1866.	
(5) Tschirch........	Grass................	....		....			B u r i a n , *Monatsh.*, 1897, **18**, 570.	
(6) Wallerstein.....	Barley	....		....			Cohen, "Ueber Lupeol," Diss., Utrecht. 1906.	
(7) Hesse..........	Calabar beans.......	Phytosterol......	132°–133°	$C_{26}H_{44}O + H_2O(?)$	120°		*Ann.*, 1878, **192**, 175.	
(8) König..........	Meadow hay........	Phytosterol......	134°	....			Cohen's Diss. über Lupeol Tables, 1906.	
(9) R e i n k e a n d Rodewald.	Æthalium septicum....	Paracholesterol...	134°	$C_{26}H_{44}O(?)$	....	127°–128°	*Ann.*, 1881, **207**, 229.	
(10) Lippmann.......	Beet juice (Rüben-saft).	Phytosterol......		....			*Ber.*, 1887, **20**, 3201.	
(11) Arnaud..........	Beets (Rüben).......	Carotol:........	136.5°	$C_{26}H_{44}O(°)$			*Ber.*, 1886, **19**, 105.	Considered identical with Hesse's phytosterol.
(12) Husemann.......	Daucus carota.......	Hydrocarotol....	126.5°				*Ann.*, 1861, **117**, 200.	
(13) Reinitza.......	Roots of carrots......	Hydrocarotol....	137.4°		127.6°	144°	*Monats. Chem.*, 1887, **7**, 597.	
(14) S c h u l z e a n d Barbieri.	Triticum v u l g a r e, folium perenni.	Phytosterol.......	136°	$C_{26}H_{44}O + H_2O(?)$			*J. prakt. Chem.*, 1882, **25**, 159.	
(15) Paschkis.......	Colchicum seeds......	Phytosterol......	133°	$C_{26}H_{44}O + H_2O(?)$			*Zeit. phys. Chem.*, 1884, 8, 356.	
(16) Likiernik........	P i s u m s a t i v u m (Lens esculenta).	Phytosterol......	135°		120°	145°	*Zeit. phys. Chem.*, 1891, **15**, 430.	
(17) Salkowski.......	Adulterated codliver oil.	Phytosterol......	132°–134°				*Zeit. anal. Chem.*, 1887, **26**, 557.	
(18) Bukowsky......	Oil from lycopodium seeds.	Phytosterol......					*Chem. Centralbl.*, 1889, **60**, 156.	About 0.3 %.
(19) Hesse..........	Aristolochia argentina	Phytosterol......		$C_{26}H_{43}OH(?)$			*Archiv. d. Pharm.*, 1895, **233**, 684.	As palmitic ester.
(20) D u n s t a n a n d Chaston.	Roots of s c o p o l i a carniola.	Phytosterol......	137.5°	$C_{26}H_{44}O(?)$		145.5°	Vide Cohen, Diss. über Lupeol.	

(21) Jacobson	Broad beans	Phytosterol	131.5°-132.5°		126°	145°-145.5°	Zeit. physiol. Chem., 1888, 13, 32.	Reckoned cholesterol.
(22) Jacobson	Sweet peas	Phytosterol	134°-135°	$C_{26}H_{44}O+H_2O$	119°-620°	147°		
(23) Jacobson	Peas	Phytosterol	132°-133°		117°-118°	145°-146°		
(24) Jaconson	Lupins	Phytosterol	136.5°		124°-125°	144°-145°		
(25) Bömer	Cottonseed and fatty oils	Phytosterol	136°-137°		123°-126°	142°-143°	Zeit. Nahr. Genuss., 1899, 2, 705.	Phytosterol were also found in various other oils, but not sufficiently investigated.
(26) Bömer	Sesame oil and linseed oil	Phytosterol	137°-137.5°	$C_{27}H_{46}O$	128°-129°	145°-146°	Zeit. Nahr. Genuss., 1901, 4, 865.	
(27) Bömer	Rape oil	Phytosterol	139°-140°		134°-136°			
(28) Villa Vecchia and Fabris	Sesame oil	Phytosterol	137.5°	$C_{26}H_{44}O+H_2O(?)$	....	....	Chem. Centralbl., 1897, Bd. 2, 172.	
(29) Schweissinger	Rape oil	Phytosterol	133°	....	....	....	Chem. Centralbl., 1891, 2, 229.	
(30) Burian	Wheat germ	Sitosterol	137.5°		127°	145°-148.5°	Monatsheft Chem., 1897, 18, 553.	(Pure phytosterol.)
(31) Burian	Mother liquors of above	Parasitosterol	127.5°	$C_{27}H_{46}O+H_2O$	115°-120°		Monatsheft Chem., 1897, 18, 566.	
(32) Ritter	Wheat germ	Sitosterol	136.5°			145.5°	Zeit. phys. Chem., 1902, 34, 461.	Various other esters.
(33) Gérard	Brewer's yeast	Plant cholesterol	135°-136°			Could not purify. 149°	J. pharm. Chim., [6], 1895, 1, 601-608.	
(34) G. Sani	Olive oil	Phytosterol	134°				Chem. Centralbl., 1903, 1, 93.	
(35) Rümpler	Beet root	Betasterol	117°	$C_{25}H_{44}O$			Ber., 1903, 36, 975-976.	
(36) Gill and Tafts	Maize oil	Phytosterol	137.5°-138°				J. Amer. Chem. Soc., 1903, 25, 251.	
(37) Power and Tutin	Eriodictyon californicum	Phytosterol	136°-137°				Pharm. Rev., 1906, 24, 300-304.	Very small and identical with sitosterol.
(38) Windaus and Hauth	Calabar bean	Phytosterol	137°		127°	146°	Ber., 1907, 40, 3681-3686.	
(39) Tarbowa and Hardy	Roots of Echinophora spinosa	Phytosterol	148°		124°-125°	145°	Bull. Sci. Pharm., 1907, 14, 387-392.	
(40) Windaus and Welsch	Rape oil	Phytosterol	142°	$C_{27}H_{26}O$	134°	142°	Ber., 1909, 42, 612.	Authors not quite certain of purity of specimen
(41) Henze	Suberites domuncula	Spongosterol	123°	$C_{27}H_{44}O$	124°	128°	Zeit. physiol. Chem., 1904, 41, 109.	
(42) Dorée	Cliona ciliata	Clionasterol	137°	$C_{27}H_{46}O$	133°	143°	Biochem. J., 1909, 4, 74.	
(43) Power and Moore	Prunus serotina	Phytosterol	135°-136°	$C_{27}H_{46}O$	118°-119°		Trans. Chem. Soc., 1909, 246.	Not identical with sitosterol.
(44) Power and Moore	Bryony seed	Phytosterol	137°	$C_{27}H_{46}O$	155°-157°		Trans. Chem. Soc., 1911, 937.	Optically inactive.
(45) M. T. Ellis	Bean	Phytosterol	142°	$C_{27}H_{46}O$	137°	133°-134°	Biochem. J., 12, 166.	

TABLE II.—SUBSTANCES OF HIGH M. P., ANALOGOUS TO PHYTOSTEROL

Author	Material used	Name of substance and formula given	M. p.	M. p. of acetate	M. p. of benzoate	References	Remarks
Schulze and Barbieri.	Lupins..........	Caulosterol, $C_{26}H_{44}O + H_2O$	158°–159°	......	145°	*J. pr. Chem.*, [2], 1882, 25, 159.	Partly from roots and partly from parts above ground.
Likiernik.........	French beans (Phaseolus vulgare).	Paraphytosterol......	149°–150°	....	142°–143°	*Zeit. physiol. Chem.*, 1891, 15, 427, and *Ber.*, 1891, 24, 187.	
Marino-Zuco.....	Chrysanthemum flowers.	$C_{28}H_{48}O(?)$	183°	223°	246°	*Gazzetta*, 1889, 19, 200.	
Tanret.....	Ergot................	Ergosterol..........	154°	169°–175°	154°	*Compt. rend.*, 1889, 108, 98.	
Likiernik.... ..	Peelings of lupin seeds..	Lupeol, $C_{81}H_{52}OH(?)$.	211°	214°	265°–266°	*Zeit. physiol. Chem.*, 1891, 15, 415.	
Klobb..........	Chamomile (Anthemis nobilis)	Anthesterol, $C_{28}H_{48}O$..	222°–223°	....	284°–286°	*Bull. Soc. Chim.*, 1902, 27, 1229.	
Vesterberg... ...	Gum elemi..........	α-amyrol, $C_{30}H_{50}O$	185°	220°–211°	192°	*Ber.*, 1887, 20, 1242.	
Hesse..........	Coca beans..........	β-amyrin, $\{C_{30}H_{50}O(?)$	195°	235°	230°	*Ann.*, 1892, 271, 214.	
Marck..........	Milky juice of Asclepias syriaci.	$C_{28}H_{48}O(?)$	181°–182°	201°–202°	195°–196°	*J. pr. Chem.*, 1903, 68, 449.	
Bauer..........	Appopunax..........	Chironol, $C_{28}H_{48}O$.....	176°	196°	188°	*Archiv. Pharm.*, 1895, 233, 233.	
Bickern..........	Seeds of Casimiroa edulis.	Casimirol, $C_{27}H_{44}O_2$....	207°	....	....	*Arch. Pharm.*, 1903, 241, 173.	
Sack and Tollius	Brask (Borneo) from sap of Alstonin costulata.	Alstol, $C_{24}H_{38}O(?)$....	158°	· 200°	254°	*Ber.*, 1904, 37, 4110.	
Sack and Tollius.	Bark of Soucheria griffithriana.	Lupeol, $C_{26}H_{42}O$.......	213°	....	262°	*Ber.*, 1904, 37, 4110........	Identical with lupeol of Likiernik.
Ottolenghi.......	Ergot................	Ergosterol, $C_{24}H_{40}O + H_2O(?)$.	....	165°	....	*Centralbl.*, 1906, 1, 541.	
Thoms..........	Ononis roots,........	Onocerol, $C_{28}H_{42}(OH)_2(?)$	232°	224°	178°–190°	*Ber.*, 1896, 29, 2985.	
Klobb..........	Arnica montana........	Arnidiol, $C_{28}H_{44}(OH)_2(?)$	249°–250°	....	223°–228°	*Bull. Soc. Chim.*, 1905, 33, 1075.	
Hinsberg and Roos.	Yeast fat.............	Cholesterol of yeast....	159°	....	....	*Zeit. physiol. Chem.*, 1903, 38, 12.	
Windaus and Hauth.	Calabar beans........	Stigmasterol, $C_{30}H_{48}O$.	170°	141°	160°	*Ber.*, 1907, 40, 3681.......	Along with phytosterol.
Power and Tutin.	Leaves of Olea europæa.	Oleasterol, $C_{30}H_{52}OH$..	174°	....	....	}	
Power and Tutin.	Leaves of Olea europæa.	Olestranol, $C_{28}H_{48}O_2$...	217°–218°	Syrup.	Syrup.	} *Trans.*, 1908, 891........	Colour reactions showed it to be different from casimirol.
Power and Tutin.	Leaves of Olea europæa.	Homo-olestranol, $C_{27}H_{46}O_2$.	210°	....	....	}	
Windaus and Welsch.	Rape oil.............	Brassicasterol........	148°	157°–158°	167°	*Ber.*, 1909, 42, 612.	
Hartwich and Dünnenberger.	Jaborandi bark........	Alcornol, $C_{22}H_{30}O(?)$.	205°	....	....	*Arch. Pharm.*, 1900, 238, 348	$[\alpha]_D + 33.8°$.
T. Henry........	Hyenanche globosa.....	$C_{28}H_{46}O$...	265°	244°	....	*Trans. Chem. Soc.*, 1920....	Lævorotary.

distributed. Since the discovery of vegetable cholesterol by Hesse in calabar beans and peas in 1878, very many plants have been examined by various observers; and a large number of substances all very similar in properties, melting between 130° and 137°, and having the composition $C_{27}H_{46}O$, have been described. A list is given in Table I. The number of possible isomers of the formula $C_{27}H_{46}O$ is of course theoretically very large, but it seems probable from the work of Windaus and Hauth (*Ber.*, 1907, **40**, 3681, 3686), who showed that the original phytosterol of Hesse from calabar beans was really a mixture of sitosterol with another alcohol, stigmasterol, m. p. 170°, that the number occurring in nature will be considerably reduced and many found to consist of one and the same substance in different degrees of purity.

In addition to the true phytosterol, isomeric with cholesterol, a number of substances of different carbon content and usually of higher m. p. have been described. These appear to have the general formula C_nH_{2n-10}, give the sterol colour reactions, and some at any rate, like phytosterol, form insoluble digitonides. As an example, we may mention stigmasterol, $C_{30}H_{50}O$. At least eight kinds have been recognised. A list is given in Table II.

According to Gérard (*Compt. rend.*, 1892, **114**, 1544) the phytosterols of cryptogams quite generally appear to differ from those of phanerogams by having a higher m. p. The best known representative of the first group is the ergosterol of Tanret (*Compt. rend.*, 1908, **147**, 75) isolated from ergot; it melts at 165° and has an unusually high rotation. It undergoes slow decomposition under the influence of light.

Phytosterolins.—In addition to the isolation of phytosterol itself as a constituent of plants, Power and his co-workers in the Welcome research laboratories between 1908 and 1913 made the important discovery that it is often present as a glucoside. In their analyses of plants there often occurred compounds of high m. p., which appeared to be alcoholic in nature, with more than one hydroxyl in the molecule. These gave the sterol colour reactions, but the m. p. and formulae served to differentiate them from true sterols. As an example, ipuranol, $C_{23}H_{38}O_2(OH)_2$, m. p. 285–290°, occurred in the stems of *Ipomœa purpurea*, in olive bark and in nutmeg. In taraxacum root, cluytianol was found, bryonol in bryony root and similar substance in various plant organs. A list

is given in the paper by Power and Salway (*Trans. Chem. Soc.*, 1913, **103**, 402) which describes their identification as phytosterol glucosides. They are unchanged by the usual methods of hydrolysis, but when heated with aqueous hydrochloric acid in amyl alcohol solution, dextrin and a phytosterol are formed. Different phytosterols are obtained from different glucosides, and it seems probable that different sugars may form part of the molecule. Power and Salway succeeded in synthesising sitosterol-d-glucoside. They propose the name *phytosterolins* for this group, and suggest that individuals should not be given special names, but that the future examination of compounds of this type would appear to be most suitably directed to the characterisation of the phytosterols which they yield on hydrolysis and also, when possible, to that of the sugar produced.

Phytosterol (**sitosterol of Burian**), $C_{27}H_{46}O$, is easily soluble in ether, chloroform, benzene, and carbon disulphide, sparingly soluble in cold alcohol, but readily in hot. Like cholesterol, it crystallises from 90% alcohol with $1H_2O$. It crystallises from alcohol in fascicular well-formed fairly broad crystals, and when the crystallisation is slow the crystals assume the form of 6-sided tablets. It melts at $137°$, and in ether solution has specific rotatory power $(\alpha)_D = -26.71°$.

Phytosteryl acetate, $C_{27}H_{45}.C_2H_3O_2$, is prepared in a similar manner to cholesteryl acetate. It melts at $127°$.

Phytosteryl propionate, $C_{27}H_{45}.C_2H_3O_2$, melts at $108°$.

Phytosteryl benzoate is prepared by heating phytosterol with benzoic anhydride or benzoyl chloride, but is not readily obtained by the action of benzoyl chloride on a pyridine solution of the alcohol. It crystallises in oblong rectangular leaves and melts to a clear liquid at $146°$. When the melted substance cools, a play of colours at that point of solidification is observed—yellowish-green, blue, and faint red. An account of the esters formed by phytosterol with the higher fatty acids will be found in a paper by Ritter (*Zeit. physiol. Chem.*, 1902, **34**, 430). Gill and Tufts (*J. Amer. Chem. Soc.*, 1903, **25**, 251, 498), and also Schulze and Winterstein (*Zeit. physiol. Chem.*, 1905, **43**, 316) found that phytosterol undergoes a change on standing in the air, which causes a lowering of m. p. According to Polenske and also C. Virchow (*Chem. Centr.*, 1897, **II**, 395), if animals are fed with phytosterol or foods containing phytosterol, no

phytosterol is found in their fat, nor, in the writer's experience. in other tissues or organs.

THE BIHYDROCHOLESTEROLS, $C_{27}H_{48}O(C_{27}H_{47}OH)$

β-Cholestanol.—The reduction of cholesterol to β-cholestanol was first carried out by Willstätter and Meyer in 1908 (*Ber.*, 41, 2199) by the use of hydrogen and platinum black in ethereal suspension. Ellis and Gardner in 1918 (*Biochem. J.*, 12, 72) described a somewhat modified procedure and an apparatus for conveniently carrying out the process.

β-Cholestanol crystallises from 90% alcohol in six-sided leaves containing 1 mol. of water of crystallisation. It is less soluble in alcohol than cholesterol, 100 parts of alcohol at 18° dissolving 1.6 parts. It is sparingly soluble in methyl alcohol and petroleum spirit in the cold, but readily on warming. It is moderately soluble in cold benzene and glacial acetic acid, and readily in chloroform and carbon disulphide. It melts at 141.5°–142° and is dextrorotary ($-[\alpha]_D = +28° - 8$). The esters are easily made in the usual manner. The acetate forms lustrous leaves, of m. p. 110–111°; the chloracetate separates from a mixture of chloroform and ethyl alcohol in glistening plates, m. p. 178–179°; the benzoate is readily form by the pyridine method, and may be crystallised from a mixture of benzene and acetone, or from boiling alcohol, in which it is sparingly soluble. It melts about 155°, exhibiting a most characteristic colour display. On gently heating it in a m. p. tube it assumes, at 138°–139°, a reddish tinge, and at 140° it begins to soften and run together to an opaque opalescent mass of red tinge with flashes of green. At 145° it is still opaque and the play of colours becomes more intense, red or emerald green predominating according to the point of vision. This fluorescence becomes brighter as the temperature rises, until at 155° the colours suddenly vanish and the substance appears as a colourless transparent fluid. On cooling, the fluid becomes opaque at 155° and the colour display is given in reverse order. The colours do not vanish until some degrees below the solidifying-point. The play of colours is so intense that it is difficult to determine the exact m. p.

The stearate is nearly insoluble in alcohol, m. p. 128°–129°, and $[\alpha]^{20}_D = +18.4$.

β-Cholestanol gives *no colour reaction* with acetic anhydride and sulphuric acid, but is precipitated from alcohol solution by digitonin as an insoluble digitonide. It is a saturated secondary alcohol and, on oxidation with chromic acid in glacial acetic acid solution, yields a ketone—β-cholestanone—of m. p. 128–129°, in almost quantitative yield.

It has been found by the writer in human fæces.

Coprosterol is also a bihydrocholesterol and was first isolated by Flint from human fæces and named stercorine. It is the form in which cholesterol is always excreted in adult man. It is also present in the fæces of the dog and cat under certain dietetic conditions. It is said to be formed by bacterial reduction of cholesterol in the human intestines, but, as far as the writer is aware, this bacterial reduction has not yet been effected *in vitro*. It is readily obtained from the unsaponifiable portion of the ether extract of dry human fæces by crystallisation from 80% alcohol or acetone. It may be conveniently purified by distillation at a pressure of 1 mm., when it distils at 210–220°. As ordinarily obtained, it melts at 99–100°, but by distillation or repeated crystallisation the m. p. may be raised to 104–105°. It crystallises in flat needles, and is dextrorotatory ($[\alpha]_D = +24°$). It is a saturated secondary alcohol. The esters crystallise well and are obtained in the usual manner. Acetate, m. p. 85°; propionate (characteristic), 92°; benzoate, m. p. 114–115° without play of colours; chloracetate, 145–146°; stearate, m. p. 65°; palmitate, 62°. The ketone coprostanone crystallises in thin plates, generally squares, with one or all of the corners slightly truncated, m. p. 62–63°. The semicarbazone has m. p. 192°, and the amorphous oxeine 71°.

It gives the Burchardt-Liebermann reaction in a somewhat similar manner to cholosterol, but the changes in colour proceed at different rates. It forms a digitonin compound insoluble in ether and petroleum spirit, but slightly more soluble in alcohol than cholesterol-digitonide.

Ψ-*Coprosterol*.—When coprosterol is boiled with sodium amylate in amyl-alcohol sol. (Dorée and Gardner, *Trans. Chem. Soc.*, 93, 1628), it is partially converted into the isomer Ψ-coprosterol. The action is reversible.

Ψ-Coprosterol crystallises from acetone in needles, m. p. 119°, but by distillation under a pressure of 1 mm. the m. p. can be

raised to 125–126°. The acetate crystallises in prisms, m. p. 83–84°, the benzoate in needles, m. p. 85–86°.

On oxidation it yields the same ketone coprostanone as coprosterol. It forms no compound with digitonin and gives the Burchardt-Liebermann reaction in a less intense manner than coprosterol.

ε-Cholestanol.—When β-cholestanol is boiled with sodium amylate it undergoes intra-molecular change and is partially converted into ε-cholestanol (Windaus and Uibrig, Ber., 46, 2487; 47, 2384). The action is reversible. ε-Cholestanol melts at 184°, and on oxidation gives the same ketone as β-cholestanol. When cholesterol was reduced by hydrogen in the presence of reduced nickel at 200° Windaus (Ber., 1916, 49, 1728) obtained a γ-cholestanol, which crystallised from alcohol in large tables having m. p. 146° and specific rotation $[\alpha]_0 = +29.9°$. Windaus found that this apparently single substance consisted of a mixture of β-cholestanol, ε-cholestanol and ψ-coprosterol. For the method of separation the original paper must be consulted. β-cholestanol and ψ-coprosterol—two isomers which are not mirror isomers—crystallise together to form a beautifully crystalline double compound which melts at a higher temperature than either compound. The union is molecule to molecule and belongs apparently to the so-called class of partial racemates. It crystallises as a single substance, and its constituents cannot be separated by physical means, though the separation can be effected quantitatively by means of digitonin (Windaus and Uibrig, Ber., 1915, 48, 861).

Amorphous Sterols.—The sterols precipitable by digitonin constitute only a portion of the "unsaponifiable matter" of the fat of tissues and organs. This was first pointed out by L. Wacker (Zeitsch. physiol. Chem., 1912, 80, 6, 404), who designated the substances obtained from human depot fat as "Begleitsubstanzen des Cholesterins." He found that, on an average, the under skin fat contains 65.8 and mesenterial fat 61.39% of this substance. He describes it as a wax-like substance, melting at 25–32° and possessing properties analogous to those of cholesterol. It emulsifies easily with water. It is easily extracted from these emulsions by ether, but otherwise they persist a long time. It is soluble in most organic solvents, but cannot be made to crystallise. It is unchanged by acetic anhydride, is not precipitated by digitonin, and gives with

the Burchardt-Liebermann reagent a brownish red colour. It is unstable to alkalies. This description the writer is fully able to confirm. On distillation in superheated steam this substance volatilises readily, condensing in the condenser as a solid emulsion.

The writer has also found (*Biochem. J.*, 15, 244) that the unsaponifiable residue of human fæcal fat contains, in addition to crystalline sterols, a considerable quantity of non-crystallisable oil, often considerably in excess of the crystalline matter. These oils can be distilled in superheated steam or in a vacuum of 1 mm. without apparent decomposition. In superheated steam the material passes over into the condenser in the form of a solid emulsion, which is forced from the condenser by the combined action of the condensed water and the pressure of the steam in solid white candles. This solid emulsion persists a long time, but eventually separates into oil and water. By fractionation in a high vacuum a colourless oil is obtained, distilling at 200–230° according to the pressure. This oil sets, on cooling, to a glass-like substance melting at 16–17°. Though probably not a single substance, it was found by combustion to have a similar composition to that of cholesterol.

When it is treated in chloroform solution with acetic anhydride and sulphuric acid a deep reddish brown colour first appears, very similar to the colour of ferric acetate. In a few minutes this becomes a dusky sage green, which finally changes to a bright green. This stage persists for a long time, but after some hours the green fades and gives place to brown. All attempts to prepare crystalline esters failed, though some indications that the substance was of an alcoholic nature—possibly tertiary—were obtained.

EXTRACTION OF STEROLS AND THEIR ESTERS FROM TISSUES, ETC.

Various methods have been proposed in recent years for the accurate estimation of cholesterol and its esters in tissue extracts, but whatever the method adopted for this purpose, the accuracy of the estimation in the tissue itself must depend ultimately on the thoroughness with which the fats and lipoid substances are extracted from the tissue.

Pflüger (*Archiv f. d. ges. Physiol.*, 1892, 51, 277) long ago showed that it was impossible to extract the whole of the fat from a dried

tissue by simply extracting with ether in a Soxhlet apparatus, and Dormeyer (*Arch. f. d. ges. Physiol.*, 61, 341 and 65, 90) proposed to get over the difficulty by digesting the tissue with pepsin and hydrochloric acid prior to the extraction with ether.

Kumagawa and Suto (*Biochem. Zeitschr.*, 1904, 4, 186) and Schimidzu (*Biochem. Zeitschr.*, 1910, 28, 237-273) find that the most certain method of extracting the whole of the fatty and unsaponifiable matter contained in a tissue is to destroy the tissue completely by heating with an alkali. Grigaut (*Le Cycle de la Cholestérinémie*, Paris, 1913) carries this out in the following manner: 20 c.c. of blood serum are mixed with 20 c.c. of a solution of sodium hydroxide, containing 400 grms. NaOH per litre, and heated in an autoclave at 110° for 1 hour. In the case of solid tissues 5 to 10 grms. of the fresh tissue are heated in a similar manner with 40 c.c. of the sodium hydroxide solution diluted to half the strength.

One of the many disadvantages of this method is that the cholesterol esters are saponified and therefore cannot be estimated. Kumagawa and Suto have, however, shown that the whole of the fats, etc., can be extracted from a tissue by boiling with absolute alcohol and they describe in their paper a convenient apparatus for the purpose.

For some years the writer adopted the following method and obtained, on the whole, satisfactory results, so far as cholesterol is concerned. The *fresh* tissue is minced and ground to a fine pulp with fine sand. It is then mixed with 3 or 4 times its weight of plaster of Paris and allowed to set. The dry mass is then ground up again and extracted with ether in a Soxhlet for 2 or 3 weeks. The writer now finds it more advantageous to extract the pulped tissue with hot alcohol and then with ether. Liquids such as serum, ascitic fluids and the like are mixed with excess of alcohol and filtered. The filtrate is evaporated to approximate dryness, mixed with the residue on the filter and exhausted in a suitable extractor with hot alcohol. The extracted material is then reground and extracted with ether. The alcohol is next distilled off from the alcoholic extract and the residue thoroughly exhausted with dry ether. This ethereal extract is then added to the above ether extract. The ether is distilled off and the residue dried at 100°. Before weighing it is often advisable to take the residue up in petroleum spirit, in order to get rid of traces of other substances than

"fat." In the case of animal tissues, which often contain enzymes which hydrolyse cholesterol esters, the tissue should be extracted as soon as possible after removal from the body, or else treated in such a way as to destroy the enzyme.

Recently J. Fex (*Biochem. Zeit.*, 1920, **104,** 82) has recommended the following procedures: the tissue is minced and allowed to digest at room temperature for several hours with twice its weight of a 2% solution of sodium hydroxide, until the material has swollen up to a gelatinous transparent condition. It is then put on the boiling water bath and heated until all matter has gone into solution—usually about half an hour. The brownish red, moderately clear fluid is then placed in a separator and shaken with ether. After standing over night the ether is separated and the fluid again shaken with ether and allowed to stand. This extraction is repeated two or three times. The ethereal extracts are then united and the ether distilled. This process, according to Fex, gives a very perfect extraction, and sodium hydroxide solution of this strength, and under the conditions discribed does not affect any hydrolysis of the cholesteryl esters.

The writer can fully confirm Fex's statements, and the method has yielded excellent result in his laboratory.

Estimation of Cholesterol and Cholesterol Esters in an Extract

In recent years two methods, quite different in type, have come into common use for the estimation of cholesterol and its esters: a gravimetric method based on the formation of the highly insoluble molecular compound of cholesterol with digitonin,

$$C_{55}H_{94}O_{28} + C_{27}H_{46}O = C_{82}H_{140}O_{29}$$
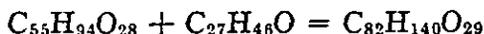
and a colorimetric method based on the Burchardt-Liebermann reaction with acetic anhydride and sulphuric acid.

Both methods give good results when pure cholesterol is in question, but difficulties arise when mixtures of different sterols, or mixtures of cholesterol and oils, or, for example, the ether extracts of tissues, fæces, etc., have to be dealt with.

Gravimetric Methods

Procedure of Windaus (*Zeit. physiol. Chem.*, 1910, **65, 110**).—The ethereal or other extract of a tissue is evaporated and the residue

taken up in 30 times its volume of hot 95% alcohol. This solution is treated with a 1% solution of digitonin in hot 90% alcohol so long as a precipitate is produced, care being taken to leave the digitonin in slight excess. After several hours the precipitate is filtered off on a Gooch crucible, and washed first with alcohol and then with ether. It is then dried at 100°–110° and weighed. Care should be taken in weighing, as the compound is somewhat hygroscopic.

The filtrate from the digitonin-cholesteride is concentrated and, after the addition of water, is shaken out with petroleum spirit or ether. The excess of digitonin remains in the aqueous alcoholic solution, whereas cholesterol esters, fats and other lipoids dissolve in the ethers. The petroleum spirit or ether solution is divided into 2 parts, one serving for the isolation of the esters and the other for their quantitative estimation. For the latter purpose the petroleum spirit or ether is distilled off, and the residue saponified by warming with alcoholic potassium hydroxide. The cholesterol set free is then shaken out with petroleum spirit and estimated as above. This second precipitate gives the amount of combined cholesterol which was originally present as ester.

Digitonin-cholesteride readily dissociates on heating in the vapour of boiling xylene. The compound is placed in a paper thimble and suspended in a flask containing boiling xylene. After heating for 15 hours the dissociation is usually complete. The cholesterol dissolves in the xylene and the insoluble digitonin remains in the thimble and can be used again. The cholesterol is readily recovered by distilling off the xylene in steam.

Procedure of Fraser and Gardner.—This process (Fraser and Gardner, *Proc. Roy. Soc.*, 1910, B, 82, 560) was worked out before the appearance of Windaus' later paper and differs in detail from that recommended by him.

After treating the alcoholic solution of the extract with a slight excess of digitonin in 95% alcohol, the mixture after standing some hours is evaporated to dryness in a vacuum desiccator. The precipitate is then washed by decantation with ether onto a Gooch crucible or a previously tared filter paper until the ethereal washings give no residue on evaporation. Care should be taken to use the minimum volume of ether possible. The excess of digitonin is then washed away by warm water. In most cases the filtration is tedious

and it was often found more satisfactory to use a tared paper rather than a Gooch crucible, care being taken to subject the tare to exactly the same treatment as the filter paper which received the precipitate. The washing with water is continued until there is no residue on evaporation, or until the washings cease to froth on shaking. The precipitate is then dried in an air-oven at 110° and weighed in a stoppered bottle. In order to estimate the esters the ethereal washings containing the fat and esters may be saponified with sodium ethoxide in the manner described below. It was found preferable, however, when the amount of material available was sufficient, to divide the original extract into two halves. In one-half the free cholesterol is estimated as above, and the other half is saponified and the total free and combined cholesterol again estimated. To saponify the esters the extract is dissolved in ether and a large excess of an alcoholic solution of sodium ethoxide added. The saponification of the esters is usually complete on 24 hours' standing in the cold, but it is safer to heat for several hours under a reflux condenser on a warm water-bath. The precipitated soaps are filtered off and well washed with ether. The filtrate, containing the total cholesterol, is thoroughly washed by repeated shaking in a separator with water. The ethereal solution thus obtained is evaporated and the cholesterol estimated as above. Should it happen that the quantity of soap produced is large, it is necessary to allow the ether adherent to evaporate, grind the soap up with excess of salt and extract in a Soxhlet with ether. With small quantities of soap this is unnecessary.

The weight of digitonin-cholesteride $\times$ 0.243 gives the weight of cholesterol. For most purposes it is sufficient to take $\frac{1}{4}$ the weight of the compound.

Both the methods of procedure described have given excellent results in the writer's laboratory. The digitonin method has been adversly criticised by various writers. It has been pointed out that errors are introduced owing to the slight solubility of the compound in ether or petroleum spirit, and that this solubility may be increased if the ether already contains fat or other lipoid substances. When a fair quantity of the compound is weighed such errors are negligible, but become more serious as the quantity dealt with becomes smaller. Such errors are, however, inherent in every gravimetric method of analysis when the quantities to be estimated fall below a

certain limit. When the quantity of cholesterol to be estimated is very small the writer measures the volume of ether used and makes a correction for the compound dissolved. It is better to make this correction by means of a control experiment with digitonin-cholesteride, keeping the conditions as similar as possible to those in the actual estimation. Thaysen, who published in 1914 a detailed critique of the method, emphasised the necessity of using $1\frac{1}{2}$ to $2\frac{1}{2}\%$ excess of digitonin in order to obtain accurate results. This the writer can fully confirm.

Similar insoluble digitonin compounds are formed by other members of the sterol group, and these alcohols may be divided into two classes according as they form insoluble digitonides or not, though, as yet, reliable data are wanting to complete the groups.

Group I. Insoluble digitonides.

The unsaturated alcohols—cholesterol, sitosterol and probably other phytosterols, stigmasterol; the saturated alcohols—β-cholestanol, coprosterol.

Group II. No insoluble digitonides.

The unsaturated alcohol—ψ-cholesterol (Windaus and Resan, *Ber.*, 48, 851); the saturated alcohols—ψ-coprosterol and ε-cholestanol, also α-cholestanol, though this has been shown by Windaus and Uibrig (*Ber.*, 46, 2487) to be an amyl derivative of cholesterol. The amorphous substances which accompany coprosterol in fæces (*Biochem. J.*, 15, 244), if these really belong to the sterol group.

The esters of Group I are not precipitated by digitonin. Sitosterol digitonide is quantitatively precipitated in crystalline needles and has similar properties to cholesterol digitonide. The stigmasterol compound is still more insoluble. β-cholestanol, according to Windaus, forms a slightly more soluble digitonide, 100 c.c. of 95% alcohol dissolving 0.21 grm. The writer found by digesting β-cholestanol digitonide for several days with ethyl alcohol of 96% by weight, at temperatures ranging from 10°–18°, with occasional shaking, values of 0.034 to 0.067 per 100 grm. of solvent. At the boiling point 0.27 grm. was dissolved. By working in a similar manner the solubility in commercial ether at 10°–17° was found, as an average of three estimations, to be 0.0084 grm. and in light petroleum spirit 0.018 grm. per 100 grm. of solvent.

Coprosterol digitonide was found to be more soluble in alcohol than the digitonides of other members of the group, 100 grm. of 96%

alcohol (by weight) dissolving, at 10°, 0.143 grm., at 15°, 0.24 grm., and at 78°, 0.83 grm.

In ether at 10–17° the average of three determinations was 0.0077 and in petroleum spirit 0.0025 grm. per 100 grms. of solvent. In applying Windaus' procedure for the estimation of any of these sterols a correction may be introduced for the solubility in alcohol. This becomes the more desirable the smaller the quantity of digitonide to be weighed. It is always necessary, however, in the case of coprosterol. In this case also a considerable excess of digitonin should be used. In the procedure of Fraser and Gardner such a correction is obviated, since the alcohol is evaporated at a low temperature before washing the precipitated digitonide. In this case any accompanying oils should be washed away with ether or petroleum spirit and the excess of digitonin by warm water, but the precipitate should not be washed with alcohol. In both methods a very slight error will be introduced by the ether or petroleum spirit washing, owing to the slight solubility of the compounds in these solvents, but in most cases the error is negligible. As the compound weighed is about four times the weight of the sterol, accurate results are attainable with very small quantities of sterol.

COLORIMETRIC METHODS

The colour methods usually employed depend either on the Salkowski reaction (page 768), as developed by Weston and Kent (*J. Med. Research*, 1912, 26, 531) or on the Liebermann reaction (page 785) as originally proposed by Grigaut (*Compt. Rend. Soc. Biol.*, 1910, 68, 791).

Grigaut's method of procedure in the case of blood serum is as follows: 2 c.c. of serum are placed in a small tap funnel with graduation marks at 15 c.c. and 30 c.c., alcoholic sodium hydroxide (1 in 200) are then added up to the 15 c.c. mark and, finally, ether to the 30 c.c. mark. The funnel is now stoppered and inverted several times to mix the contents thoroughly. After standing until the ethereal layer separates, the aqueous lower layer is run off and the ethereal solution washed twice by shaking each time with 20 c.c. of water. After draining off the wash water the ethereal solution is transferred to a porcelain dish and evaporated to dryness. The fatty residue is dissolved in 5 c.c. of chloroform and transferred to a

graduated test tube of 10 c.c. capacity. To this are now added 2 c.c. of pure acetic anhydride and 3 drops of a solution of sulphuric acid of 66° Bé. At the same time are introduced into a similar graduated tube 5 c.c. of a standard chloroform solution of cholesterol (containing 0.06 grm. per 100), 2 c.c. of acetic anhydride and 3 drops of acid. The tubes are allowed to stand for half an hour for the colour change to become stationary (green). 5 c.c. of the two coloured solutions are poured into the two tubes of a colorimeter, and the one with the deeper tint diluted with a mixture of chloroform, acetic anhydride and sulphuric acid in the above proportions until the tints in the two tubes are equal. If, then, n is the number of c.c. of the diluted solution, the amount of cholesterol P contained in a litre of serum is given by the following formula:

(1) In the case in which the solution to be estimated is diluted

$$P = 0.30 \times n \text{ grm.}$$

(2) In the case in which the standard solution is diluted

$$P = \frac{7.50}{n} \text{ grm.}$$

In order to estimate the cholesterol in a solid tissue, 0.2 to 1 grm. of the tissue, according to its cholesterol content, is put into a 90 c.c. flask with 30 c.c. of alcoholic sodium hydroxide (1 in 100) and heated on a water-bath until the tissue is dissolved and the volume of the mixture reduced to 15 c.c. The 15 c.c. of liquid are then introduced into the tap funnel described above, and the flask washed with 15 c.c. of ether which are also added to the liquid;. The subsequent procedure is exactly the same as in the case of serum.

The weight, P, of cholesterol contained in 1 kilo. of tissue will be obtained by the preceding formula in which the variable weight p of the tissue taken is introduced.

(1) In the case in which the solution to be estimated is diluted

$$P = \frac{0.6n}{p} \text{ grm.}$$

(2) In the case in which the contents of the tube containing standard solution are diluted

$$P = \frac{15}{n \times p} \text{ grm.}$$

Method of Weston and Kent.—This method was devised mainly for the examination of blood and serum.

The serum is extracted with 10 volumes of 95% alcohol and left at 60° for 24 hours. The alcohol is filtered off, the residue washed twice with boiling alcohol, and then extracted for a further 24 hours with ether. The alcohol and ether extracts are then combined and boiled with a few grains of potassium hydroxide for 2 hours, at the end of which time the fluid should have evaporated to a very small bulk. A saturated solution of calcium hydroxide is now added, and the precipitate collected on a filter. The precipitate is washed with calcium hydroxide solution, dried and extracted with chloroform.

From the chloroform solution obtained dilutions are made representing 0.075, 0.1 and 0.125 c.c. of serum and placed in small tubes, 100 × 10 cm. and of exactly the same diameter. The contents of each tube are brought to 1 c.c. by addition of chloroform. In another set of similar tubes are placed quantities of cholesterol varying from 0.0001 to 0.0003 grm. in 1 c.c. chloroform, increasing by 0.000025 grm. Sulphuric acid (0.1 c.c.) is added to each tube and the tube thoroughly shaken. All tubes are placed in a dark chamber for 30 minutes, after which 1 c.c. of chloroform is added to each, and they are again placed in the dark for 15 minutes. Comparisons of colour of the sera with the standards are then made and the amount of cholesterol determined. Alternatively, sets of extract are made up as above, but the standard is made up in 6 c.c. of chloroform. Comparisons are then made in an Autenrieth-Königsberger colorimeter.

Both methods of comparison give the same results.

In recent years a number of variations of the Grigaut method as applied to sera have been described by Autenrieth and Funk (*Münch. Med. Woch.*, 1913, 9, 1243), Henes (*Proc. New York Path. Soc.*, 1913, 13, 155), Csonka (*J. Biol. Chem.*, 1916, 24, 431), Bloor (*J. Biol. Chem.*, 1916, 24, 227), Gettler and Baker (*J. Biol. Chem.*, 1916, 25, 211), Luden (*J. Biol. Chem.*, 1917, 29, 463). Each author uses a somewhat different method of extraction and some carry out the Liebermann reaction at ordinary temperatures; others, *e. g.*, Autenrieth and Funk, at 35°. They differ in their recommendations as to time of induction and whether the reaction should be conducted in the light or in the dark. In 1916 Weston (*J. Biol. Chem.*, 27, 28, 383) made comparative estimations by the various methods, and came to the conclusion that the extraction methods of Autenrieth and Funk, Weston and Kent, Csonka, Gettler and Baker showed

consistent results, but that Bloor's method gave erroneous results. In 1921 the writer and M. Williams (*Biochem. J.*, 1921, 15, 363) published a critical study of the methods of estimating cholesterol and allied substances, and subjected the Burchardt-Liebermann reaction to a closer study. They found that the rate of production of the various colours, and even the order of sequence and the quality of shade, was markedly influenced by the relative mass of sulphuric acid used and by the temperature, whilst the mass of acetic anhydride (always in large excess) had little influence. The behaviour of other sterols was also investigated.

Coprosterol gives a somewhat similar sequence of colours to cholesterol, and the green shade is the same. The rate of induction is also markedly affected by the mass of sulphuric acid and the temperature. Under similar conditions the rate of colour induction is, however, much slower than in the case of cholesterol, so that in comparing the behaviour of a solution of cholesterol and of coprosterol, if the rate of induction of the green stage is slow, when equivalent of tint has been attained the cholesterol solution will have very appreciably faded. Consequently, in the comparison of cholesterol with coprosterol or mixtures of cholesterol and coprosterol sufficient sulphuric acid should be added to get the maximum colour development in each as rapidly as possible, certainly within 30 minutes. If these conditions are fulfilled accurate estimations can be made.

φ-Coprosterol gives, eventually, a green colour with the Burchardt-Liebermann reagent, but the final shade in corresponding solutions is never really comparable in quality with that of cholesterol, and certainly not in depth, so that this substance cannot be estimated colorimetrically either against a cholesterol or coprosterol standard, and, if present in a mixture of either of these sterols, would vitiate any colour estimations of the latter.

β-Cholestanol gives no colours.

The amorphous sterols obtained by the writer from fæces appear to give a depth of colour under optimum conditions intermediate between coprosterol and φ-coprosterol.

EXAMINATION OF THE ETHER EXTRACTS OF TISSUES

With the ether extracts of tissues, animal fluids, such as milk, serum, etc., according to the writer's long experience and that of many other workers, the digitonin method gives accurate results, and

has the important advantage that both cholesterol and its esters can be estimated, though when the esters are relatively small in quantity experimental errors are correspondingly large.

The colorimetric methods give satisfactory results, on the whole, with blood or serum, but with other tissue extracts the estimations are much less trustworthy, owing to greater or less differences in quality between the shades obtained with such tissues and the cholesterol standard used, which render comparison of the colour intensities less precise. When the cholesterol is completely precipitated from the unsaponifiable matter of the fat of a tissue, such as muscle, liver, milk, etc., by digitonin, the unprecipitated portion of the unsaponifiable matter in chloroform solution always gives with acetic anhydride and sulphuric acid a marked brownish-red coloration, which often changes on standing through a dusky green to a yellowish green and even, in some instances, a grass green. Also, it has been shown by Gardner and Fox (*Biochem. J.*, 15, 376) that when ordinary alcohol is boiled with alkalies, diluted and extracted with ether, some substance is yielded to the ether, which in chloroform solution gives with acetic anhydride and sulphuric acid a brown colour, which sometimes becomes more or less green. Whether the green colour observed with the cholesterol-free unsaponifiable matter is due to the inherent properties of the substance, or to traces of cholesterol digitonide remaining in solution, or to the outside cause referred to has not yet been decided. Nevertheless, the production of this brown colour introduces a more or less serious error into the colorimetric results, by modifying the quality of the shade of colour due to the cholesterol compared with that of the standard.

The digitonin method necessitates the use of a certain minimum quantity of material to give an amount of digitionide sufficient for reliable weighing: in the case of blood this means at least 25–30 c.c. The colour method, on the other hand, is of the nature of a micromethod, and in case of serum can be carried out on 2 c.c. or less. This, of course, is a very great advantage in the study of the living animal and the human subject. Very fair agreement between the digitonin and colour methods has been recorded by Klinkert (*Med. Tijdsch. von Genusk.*, Amst. 720, and *Berl. klin. Woch.*, 1, 820) in the case of serum; Fex, on the other hand, finds colour methods unreliable.

In the case of blood, milk, ascitic fluids, etc., accurate comparative results can, the writer believes, be obtained in a series of experiments, provided *rigidly* comparable conditions are adopted. The results should, at some stage, be checked by the digitonin method. Unless these precautions are observed serious errors may arise.

Examination of ether extracts of complex compositions such as "fat" of fæces, etc. In the application of these methods to the analysis of the unsaponifiable matter of fæces, which contains coprosterol, β-cholestanol, cholesterol and, possibly, phytosterols of vegetable food, amorphous sterols, and alcohols such as cetyl alcohols, the digitonin method permits of the quantitative separation of the total coprosterol, β-cholestanol, cholesterol and phytosterol from the amorphous sterols and non-sterol alcohols.

The precipitated sterols may be recovered from the digitonides by heating in the vapour of boiling xylene, as recommended by Windaus. *There is, however, no simple method by which small quantities of these recovered sterols can be analysed.* If sufficient quantity of the material is available, the cholesterol, and perhaps any phytosterol, can be approximately separated from the coprosterol and β-cholestanol by precipitating the cholesterol dibromide from an ethereal solution of the sterols by means of a suitable solution of bromine in glacial acetic acid at a low temperature. The cholesterol may be recovered from the dibromide by reduction with zinc dust and glacial acetic acid.

The coprosterol may also be separated, after the bulk has been isolated by fractional crystallisation, from β-cholestanol by conversion into ψ-coprosterol and precipitation of the β-cholestanol by digitonin, according to the plan adopted by Windaus in the separation of the bihydro-cholesterols obtained in the reduction of cholesterol by hydrogen in presence of nickel, for details of which the original paper must be consulted (*Ber.* 1916, 49, 1724).

A rough approximation of the amount of β-cholestanol in the mixture may also be obtained by the colorimetric method, as β-cholstanol gives no colour reaction.

Colour methods, as applied directly to the unsaponifiable matter of fæces, are quite useless, as it is impossible to make any accurate comparison of the colour obtained with the unsaponifiable matter with that of a coprosterol standard, owing to the quite different quality of the green shades obtained. Even if this could be got over, it would be difficult to assign any meaning to the results, since,

though cholesterol and coprosterol give comparable colour reactions, β-cholestanol gives no colours, and the amorphous sterols give not only a yellower green, but also a colour of a lower order of intensity.

Separation of Phytosterol from Cholesterol.—Pure cholesterol can easily be distinguished from phytosterol by the form and grouping of the crystals. If both substances are present, the mixture crystallises in one form only, the crystals either approximating to the form of phytosterol, or if cholesterol is present in the greater quantity, differing from the pure crystals of either body. The presence of phytosterol mixed with cholesterol may be detected by the examination of the acetate. Cholesteryl acetate melts at 113°; phytosteryl acetate, at 128°; both acetates form isomorphous mixtures and, through the addition of phytosteryl acetate to cholesteryl acetate, the m. p. of the latter is raised.

A good method of separating cholesterol and phytosterol has been given by Windaus (*Chem. Zeit.*, 1906, **30**, 1011) depending on the different solubilities of the dibromides in a mixture of ether and glacial acetic acid. The best way of treating any given mixture will be gathered from the following description taken from his paper:

(1) A mixture of 4 grm. of cholesterol and 4 grm. of phytosterol was dissolved in 80 c.c. ether, and 80 c.c. of a solution of 5 grm. of bromine in 100 c.c. glacial acetic acid were added, and the whole allowed to stand at 0° for 1 hour. The crystalline precipitate (A) which formed was filtered off and washed with 4 c.c. of glacial acetic acid and then with 4 c.c. of 50% acetic acid. The washings were added to the main filtrate, when another precipitate (B) was obtained. A and B, after washing with water and drying, weighed, respectively, 3.7 and 1.4 grm. These precipitates were mixed and heated under a reflux condenser with 100 c.c. of glacial acetic acid and 5 grm. of zinc dust for 2 hours; the excess of zinc was filtered off and the solution treated with a large quantity of water. The precipitate was boiled for 2 hours with 100 c.c. of 10% alcoholic potassium hydroxide, and the cholesterol thrown out of solution by the cautious addition of water. After recrystallisation from alcohol, 2.7 grm. of cholesterol, melting at 146°, were recovered. The filtrate from B, which contained the phytosterol dibromide, was also heated for 2 hours with zinc dust, and the product treated in the same way as cholesterol. The yield of phytosterol was 2.8 grm. It melted at 134 to 136°, and its acetate at 126 to 127°.

2. In this experiment a mixture of 8 grm. of cholesterol with 0.8 grm. of phytosterol was taken. The precipitate (A) weighed 8.1 grms., (B) weighing 1.82 grm. The solution, which contained the phytosterol dibromide and a little cholesterol dibromide, was treated as follows: zinc dust was added, the ether distilled and the remaining solution was boiled for 2 hours. The organic matter was thrown out of solution by the addition of water and taken up in ether. The ethereal solution was freed from acid by shaking with potassium hydroxide, evaporated, the residue acetylated by boiling with acetic anhydride, and the acetate twice recrystallised from alcohol. It melted at 125 to 127° and weighed 0.31 grm.

3. In this experiment a mixture of 4 grms. phytosterol and 0.4 grm. cholesterol was taken and treated as before. On the addition of the solution of bromine in acetic acid no precipitate was formed, but a precipitate (A) settled out on the further addition of 11 c.c. of 50% acetic acid. This weighed 0.14 grm. and consisted of pure cholesterol dibromide. It was washed with 2.2 c.c. of glacial acetic and 11 c.c. of 50% acetic acid. On the addition of the wash liquor to the main solution a precipitate (B) was thrown down weighing 0.24 grm. This was not quite pure. From the filtrate about 3 grm. of phytosteryl acetate was prepared.

The methods of separation of phytosterol from allied substances of higher m. p. and from the aliphatic alcohols have not as yet been thoroughly worked out. Windaus and Hauth have, however, recently made an important advance in this direction by their separation of the phytosterol obtained by Hesse from calabar beans into its constituents. (Hauth, Inaugural Dissertation, Freiburg, 1907.) Hesse's phytosterol melted at 132 to 133° and, under the microscope, appeared to be perfectly homogeneous. This substance was converted into the acetate. 20 grm. of this acetate were dissolved in 300 c.c. of ether, 250 c.c. of a 5% solution of bromine in glacial acetic acid added, and the whole allowed to stand. A copious deposit of small hard crystals separated which was washed successively with glacial acetic, dilute acetic acid, and water. After recrystallisation from alcohol the material melted at 211 to 212°, and had the composition $C_{30}H_{50}O_2Br_4$. On reduction with zinc dust and glacial acetic acid an acetate was obtained which, after recrystallisation from alcohol, melted at 141°. This acetate on saponification with potassium hydroxide gave an alcohol of the formula $C_{30}H_{48}O$, which

was named *stigmasterol*. This melted at 170°, and was sparingly soluble in most solvents, with the exception of ether and chloroform. In ether solution it had specific rotatory power $\alpha_D = -44.67°$. The crystals were very similar to those of phytosterol and showed the typical colour reactions of the cholesterol group.

The *propionate* melted at 122°, and the *benzoate* at 160°.

The filtrate from the tetrabromide contained phytosterol acetate dibromide. This, after reduction and saponification, yielded pure phytosterol. The percentage of stigmasterol in the original material was 20%.

The two alcohols, stigmasterol and phytosterol, are isomorphous and scarcely differ crystallographically.

From this work it would seem probable that the so-called isomers of true phytosterol which differ from it slightly in m. p. consist of phytosterol mixed with stigmasterol or similar substances. In the one other case examined—the phytosterol of rape oil—this inference proved correct (Windaus and Welsch, *Ber.*, 1909, **42**, 612). When the distribution of stigmasterol and like substances in the vegetable world has been more carefully studied, their presence or absence may form a useful test for the adulteration of one vegetable oil with another.

For the approximate separation of the constituents of a complex ether residue, such as that yielded by "recovered grease" or the crude oleic acid obtained by the distillation of such products, Schulze (*J. prakt. Chem.*, 1873, N. F., **7**, 163) has given the following method: The ether residue is boiled for an hour or two with an equal weight of acetic anhydride. The hydrocarbons, such as petroleum, vaseline, ceresin, and paraffin wax, are not dissolved, but form an oily layer on the surface of the acetic anhydride, and may be separated whilst the liquid is still hot. The acetic anhydride solution is boiled several times with water to decompose the excess of anhydride. The residue consists of acetates of the solid alcohols, and, if boiled with sufficient alcohol, will dissolve entirely, but, on cooling the solution, the cholesteryl acetate will crystallise out almost completely. The acetates of the alcohol radicals form sperm oil and the waxes remain in solution, and are precipitated as an oily layer by pouring the liquid into hot water For the identification of wax alcohols, see article on Waxes.

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