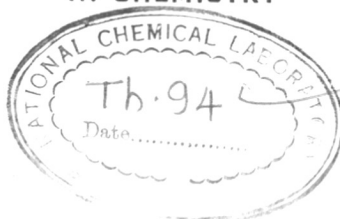


**STUDIES OF NEW STATIONARY PHASES AND
THEIR APPLICATION IN GAS LIQUID
CHROMATOGRAPHY**

A Thesis submitted to
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INTRODUCTION

INTRODUCTION

An organic chemist is often required to separate and characterise the components of a complex mixture. In earlier days, he used to employ methods such as crystallisation and distillation. It was not always possible to separate intricate mixtures by these methods. It was just in the beginning of this century when Tswett¹ developed a new technique called chromatography and used it for the separation of components of plant pigments. This technique, however, remained more or less a laboratory curiosity for the next 25 years. In 1931, Winterstein and Lederer² employed this technique for the isolation of alpha- and beta-carotenes. This technique of chromatography was correctly defined by Keulemans³ in the following manner:

"Chromatography is a physical method of separation in which the components to be separated are distributed between two phases, one of the phases constituting a stationary bed of large surface area, the other being a fluid that percolates through or along the stationary bed".

Martin and Synge⁴ introduced the partition column chromatography in 1941. They had predicted the use of a gas as the moving phase. The technique of gas-liquid chromatography (GLC) was introduced only in 1952 when James and Martin reported the results of their experiments⁵⁻⁸. GLC became a versatile analytical tool with use of gas-density balance as

the detector, together with the development of thermal conductivity detector. The first instrument was manufactured in 1955 and this was followed by many improvements in design. The ionisation detector was introduced in 1957. It was more sensitive than the detectors developed earlier. The capillary columns were developed by Golay⁹, which were very useful for extremely small samples and are more efficient than the packed columns.

Apparatus and techniques for GLC

The apparatus required for GLC is shown in the figure. The important part is column, which is a long tube packed with an inert material coated with the liquid stationary phase. The column is maintained at constant temperature and a current of inert gas is passed through it. A small quantity of the volatile mixture to be separated is introduced into the front end of the column with the help of hypodermic syringe, micro-pipette, capillary tube etc. The components of the mixture are transported in the form of vapour through the column and their separation takes place as they travel through the column at different speeds and finally emerge from it as the individual bands. At the other end of the column is a device, the detector, which detects the individual components as they emerge one by one.

GLC is the most elegant and useful technique for the separation and analysis of the mixtures of volatile compounds. It has been employed for the separations that were, hitherto,

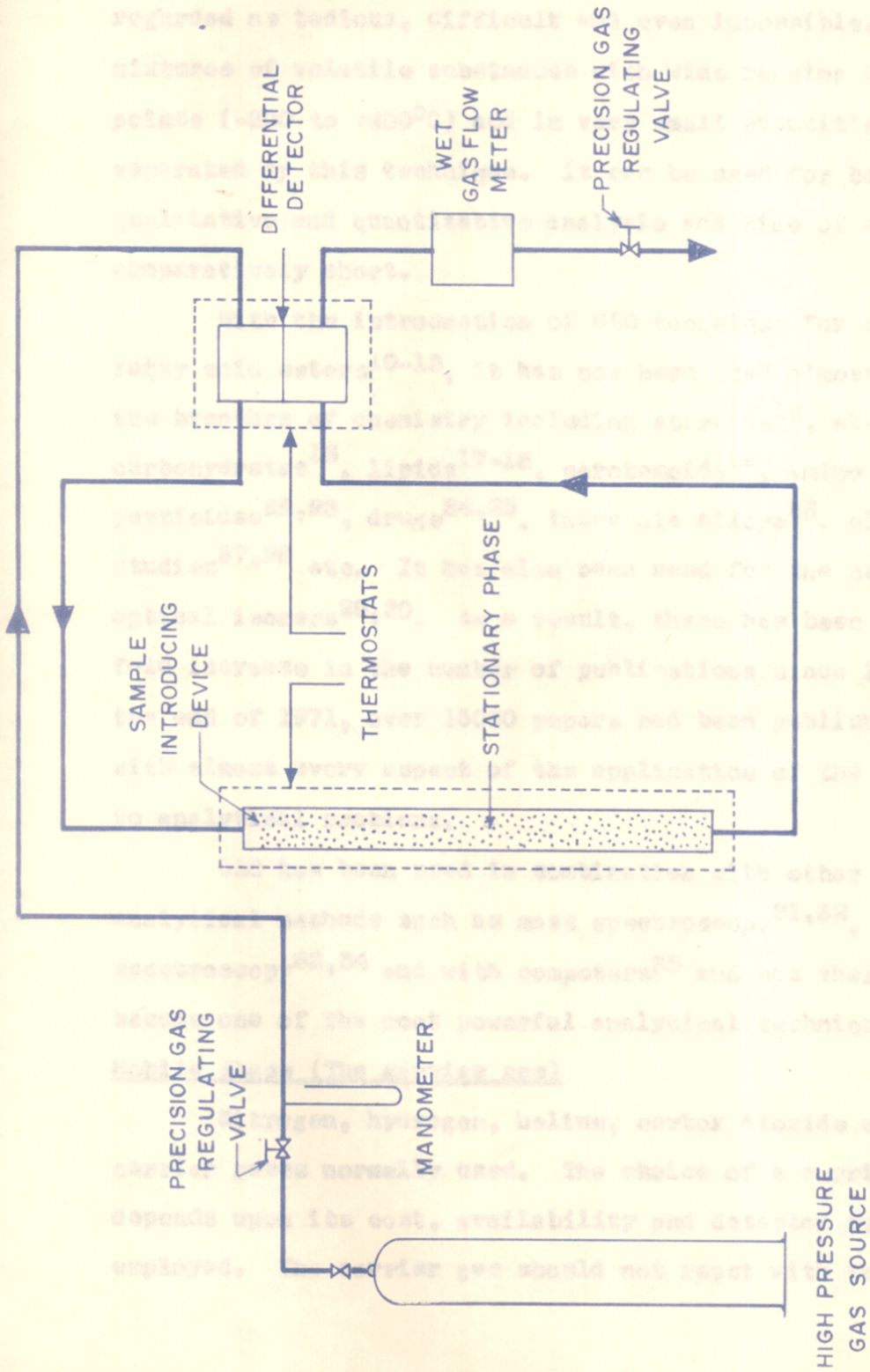


FIG. 1. APPARATUS FOR GAS CHROMATOGRAPHY

(Ref. A.I.M. KEULEMANS, "GAS CHROMATOGRAPHY,"
 REINHOLD PUBLISHING CORPORATION, NEW YORK,
 1957)

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regarded as tedious, difficult and even impossible. Complex mixtures of volatile substances with wide ranging boiling points (-200 to +400°C) and in very small quantities can be separated by this technique. It can be used for both qualitative and quantitative analysis and time of analysis is comparatively short.

With the introduction of GLC technique for separation of fatty acid esters¹⁰⁻¹³, it has now been used almost in all the branches of chemistry including steroids¹⁴, alkaloids¹⁵, carbohydrates¹⁶, lipids¹⁷⁻¹⁸, carotenoids¹⁹, amino acids^{20,21}, pesticides^{22,23}, drugs^{24,25}, inorganic alloys²⁶, clinical studies^{27,28} etc. It has also been used for the separation of optical isomers^{29,30}. As a result, there has been hundred-fold increase in the number of publications since 1952. By the end of 1971, over 15000 papers had been published dealing with almost every aspect of the application of the technique to analytical problems.

GLC has been used in combination with other physical analytical methods such as mass spectroscopy^{31,32}, infra-red spectroscopy^{33,34} and with computers³⁵ and has therefore, become one of the most powerful analytical technique.

Mobile Phase (The carrier gas)

Nitrogen, hydrogen, helium, carbon dioxide etc. are the carrier gases normally used. The choice of a carrier gas depends upon its cost, availability and detector system employed. The carrier gas should not react with the liquid

phase as well as the sample. For good results, it is purified³⁵ by passing through a simple molecular sieve and fine filter to remove the oil.

Hydrogen and helium have lower densities and higher thermal conductivities than nitrogen and therefore increase the sensitivity of the detecting devices employing these properties. Hydrogen has been shown to have lower separations efficiency than nitrogen³⁷.

The column efficiency depends upon the linear gas velocity which has an optimum value for given operating conditions.

The sample and sample introduction devices

GLC columns have high efficiencies, but these can be realised only if the sample after introduction occupies a small section of the column. It is therefore important to employ small samples and for good resolution, the sample should be introduced as quickly as possible.

Liquid sample are normally injected with the help of micrometer syringe and hypodermic needle. The original method suggested by Ray³⁸ has been improved by other workers^{39,40}.

Gas samples can be introduced with a hypodermic syringe, but by-pass gas-pipettes or mercury burettes are commonly employed^{41,42}.

The chromatographic column

Columns of 4-6 mm internal diameter and 1-3 m in length are used for routine analysis. These may be straight, coiled

or U-shaped and are made from glass, copper or stainless steel tubings. Glass columns should be used at higher temperatures as metal tubings would catalyse the decomposition of the sample. For reproducible results, accurate temperature control of the column is necessary.

The liquid stationary phase is coated on a porous solid support. The support should consist of uniformly spherical particles having a large surface area and should be inert as well as mechanically strong over a wide temperature range. The commonly used supports are celite, chromosorb, embacel and celatom or crushed fire-brick.

Small diameter particles increase the efficiency of a packed column. Owing to the difficulty in packing such columns evenly, the efficiency goes down due to increase in eddy diffusion³. The optimum particle size appears to be between 50-80 mesh. As far as possible, small mesh range of support should be used.

Other types of supports such as glass powder^{43,44}, ground silicone rubber⁴⁵, etc. have also been used. Porous supports have been found preferable to non-porous⁴⁶ ones.

Capillary column

The use of columns with very small diameter was predicted by Martin⁴⁷. The liquid stationary phase is coated on the inner surface of a capillary tube and such columns have low resistance to carrier gas flow and hence low-pressure drop along the column length. Such columns, therefore,

provide higher resolution, faster analysis times, but require a highly sensitive detector and extremely small quantity of the sample. The flame ionisation detector was developed almost at the same time for use with capillary columns.

Warren Averill⁴⁸ has discussed the practical difficulties in the preparation of capillary columns and the temperature limitations of liquid phase when used for such columns. By chemical treatment^{49,50}, the inner surface of the capillary can be modified to retain more liquid phase or by depositing a support for the liquid phase on its internal surface^{51,52} and in this way the high permeability of capillary column is combined with larger sample capacity of the packed column.

Detectors

"Titration cell" was first used by James and Martin⁶ in their studies with acidic and basic compounds. "Gas density balance"⁵³ was the first detector which was independent of the chemical properties of the eluted samples. Thermal conductivity^{53a} or flame ionisation detectors⁵⁷ are used in most of the modern chromatographs. For specific analytical purposes many other types of detectors have also been used.

Thermal conductivity detector

Thermal conductivity detector^{53a} employs the difference in the thermal conductivity of the carrier and a mixture of the carrier gas with eluted sample. This detector has been widely

used because of its simple design, low cost, general applicability and good sensitivity. For use at higher temperatures upto 350°C , thermal conductivity cells have been developed^{54,55}.

Scott⁵⁶ introduced hydrogen flame temperature detector in 1955. It was replaced by the flame ionisation detector^{57,58} which is claimed to be extremely sensitive. The introduction of an alkali metal halide probe into the flame ionisation detector increased its response to organo-phosphorus and -halogen compounds^{59,60}. Radioactive source ionisation detectors have been developed in which the carried gas is ionised by radiation from a suitable radio-active source. For semi-specific analysis of organophosphates and organo-sulphur compounds, Brody and Chaney⁶¹ report a modification of the flame ionisation detector.

Development of the theory

The fundamental theories have been developed through the efforts of many workers. Of particular interest in GLC are (i) the plate theory of Martin and Synge⁴, subsequently modified by Glueckauf⁶² (ii) the rate theory of van Deemter et al.⁶³ specially developed for GLC; and (iii) the theory developed by Golay^{9,64} for capillary columns.

By analogy with a distillation column, the chromatographic column can be considered to be made up of a number of theoretical plates. A theoretical plate is defined³ as the length of column required to establish an

equilibrium in which the vapour pressure of the solute in the gas phase equals the vapour pressure of the solute in the liquid phase. The number of theoretical plates is a measure of column efficiency which may, therefore, be increased by increasing the column length. As column length increases, the ratio of inlet to outlet pressure also increases and thus tends to reduce the efficiency.

"Height equivalent to a theoretical plate" (HETP) is a more convenient quantity for comparative purposes and is obtained by dividing length of the column by $\text{\textcircled{N}}$ number of theoretical plates. It is ^{seen} that smaller the value of HETP, better is the column.

van Deemter⁶³ employs a kinetic approach to GLC and explains band broadening in terms of a number of rate factors. The equation is given below:

$$\text{HETP} = 2 \lambda \frac{d_p}{u} + \frac{2\gamma D_0}{u} + \frac{B_2}{\pi} \frac{k'}{(1+k')^2} \frac{d_r^2}{D_L} u$$

(eddy diffusion) (molecular diffusion) Non-equilibrium effect
 Axial diffusion

The simplified form of the equation is:

$$\text{HETP} = A + \frac{B}{u} + Cu,$$

where A = "eddy diffusion" or multiple path term

B = molecular diffusion, and

C = resistance to mass transfer

In theory, A can be reduced by reducing particle size, d_p , but below a certain limit there is an increase in λ (measure of packing irregularities) because of difficulty of packing very fine powders. Since 'B' is proportional to diffusion coefficient of carrier gas, the heavier gases such as carbon dioxide tend to give best performance at low flow-rates, that is smaller values of HETP. The constant "C" comprises the gase phase transfer term, C_G , and the liquid mass transfer term, C_L .

Keulemans⁶⁵ has reviewed the combination of "rate" and "plate" theories which help in better understanding of the numerous parameters operating in GLC. The rate theory adopts a more realistic approach than the plate theory and suggest ways in which the performance of a column can be improved^{66,67}.

Golay's theory⁶⁴ describes performance of a capillary column in terms of plate height (HETP) and the average carrier gas velocity, u , as given below:

$$HETP = \frac{B}{u} + (C_L + C_G)u,$$

where C_L and C_G account for the resistance in the liquid and gas phases (ϕ) respectively. Golay derives another expression which he calls the "performance index" of a column and it measures overall column efficiency.

Factors responsible for separation

The final separation obtained on a GLC column can be broadly related to two factors (1) column efficiency, and

(ii) solvent efficiency. The first factors covers a number of parameters concerning the column such as (a) length (b) diameter (c) inlet and outlet pressure ratio (d) the nature and particle size of the support (e) temperature of the column (f) nature and flow rate of the carrier gas, etc.

The solvent efficiency results from the solute-solvent interaction and determines the relative position of solute bands on a chromatogram i.e. the separation achieved. Significant change in the degree of separation can be obtained by changing the nature of the solvent. The choice of a proper solvent (stationary phase) for a particular separation is, therefore, of great importance.

Importance of stationary phase

In GLC, the liquid stationary phase plays a most important role since the successful resolution of the components of complex mixtures depends upon its solution properties. Throughout the short history of GLC, there has been an almost continuous quest for more efficient and rapid separations, and as a consequence there is now available a bewildering number of stationary phases. The requirements of a stationary phase are given below.

It should be thermally stable and non-volatile at the column temperature. It should have good solvent properties for the sample components. It should be chemically inert towards the solutes of interest at the operating temperature. It should also have good selectivity for the components to be separated.

For good separation of components of a mixture, the choice of a stationary phase is critical. There is, however, no fool-proof method for selecting the stationary phase for a given mixture. The choice depends mainly on experience and by trial and error. Two important points to be considered are (i) chemical nature of the sample to be analysed and (ii) upper and lower temperature limits at which the column can be operated.

Depending upon their chemical structure, stationary phases can be divided into three categories:

- (a) Polar phases: These have a high ratio of polar or polarisable groups per molecule.
- (b) Non-polar phases: These have no polar or polarisable groups.
- (c) Semi-polar phases: These are in between the two extremes.

The polarity of a liquid phase has been defined in terms of its effect on the retention of polar solute relative to that for ^anon-polar solute and polarity is greater if there is a greater difference between their retention volumes. Attempts have been made to define the term more precisely⁶⁸. The polarity of liquid phase has been expressed in terms of polarity index⁶⁹. The non-polar squalane has been assigned the value zero and the polarity index value for polar phase, β, β' -oxydipropionitrile is 100. The difference in the retention volumes for a homologous series of non-polar solutes is greater on a non-polar than on polar columns and this forms the basis of Littlewood's polarity scale⁷⁰. The use of

dielectric constant⁷¹ as a measure of polarity has also been advocated.

The solutes which can form hydrogen bonds with the polar solvents will be retained for a long time. Further, the polar character of a molecule depends upon the fact whether it is electron-donor or electron-acceptor and phases can therefore be classified as electron-excessive and electron-deficient phases. This applies to solutes as well. Brown⁷² tried to define relative polarity as well as electronic character of the stationary phase by using n-decane as the non-polar solute and 1,1,2-trichloroethane and dioxane as the electron-acceptor and donor solutes respectively.

A brief review on various common liquid phases is given below:

1. Paraffins $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$

Liquid paraffin was used by Keulemans⁷³ as the stationary phase for the separation of C_3 - C_4 hydrocarbons. Higher paraffin greases are quite common in use. Separation is more or less by difference in boiling points.

2. Phthalates and halogenated phthalates

Phthalates^{53,73a} have been widely used as liquid phases for different separations. The commonly used esters are dicyclopentylphthalate, dioctylphthalate, dibutylphthalate etc. These phases, though selective in nature, have temperature limitations. Tetrachlorophthalates^{73b} have also been used as selective phases for separation of aromatic isomers, specially

xylene.

3. Tricresylphosphate

Haslam and Jaffe⁷⁴ used this phase for the analysis of monoterpenic hydrocarbons. Herout et al.⁷⁵ separated various terpenic mixtures on tricresylphosphate column. It has also been used as the liquid phase for examination of monoterpenes in the essential oils⁷⁶.

4. Polyglycols

These have been used as stationary phases in the temperature range, 130-170°C. Adlard⁷⁷ has studied these polymers in detail and found that polyethylene glycol is highly selective for aromatic hydrocarbons. Polyethylene glycol (Carbowaxes) are polar phases suitable for general use such as high b.p. alcohols, esters and phenols etc.

5. Liquid phases containing inorganic electrolytes

Solutions of silver nitrate⁷⁸⁻⁸⁰ in ethylene glycol, glycerol, triethyleneglycol and benzyl cyanide have been used as stationary phases for selective separation of olefins. Amines and hydrazines have been separated on polyethylene glycol containing KOH⁸¹. Bighi et al. examined hydrocarbons and alcohols on carbowax 400⁸² containing LiCl, KCl, CsCl and KOH. Thallium (I) nitrate⁸³ in diethylene glycol or polyethylene glycol compares favourably well with silver nitrate containing columns in the separation of aromatic hydrocarbons.

Giess et al.^{84,85} used metal halide, sulfate and nitrate salts dissolved in the liquid phase for separation of aromatic isomers, phenols and aromatic nitro- and bromo-compounds.

6. Bentone-34

Bentone-34 (dimethyldioctadecyl ammonium bentonite) has been used for the separation of aromatic hydrocarbons by several workers^{86,87}. Bentone-34 modified with a phthalate ester or silicone oil⁸⁸ has been used to separate efficiently C₆-C₉ aromatic hydrocarbons.

7. Liquid crystals

Nematic and smectic liquid crystals have been found to be effective for the separation of positional isomers and give better separations than the conventional silicone liquid phase. 4,4'^{-bis}(benzylidenebenzidine), 4,4'-bis (p-methoxybenzylidene)-4,4'-diaminostilbene and bis-phenetidine-tetra-phthalaldehyde are reported to be the suitable phases^{89,90} for the separations of naphthols, condensed aromatics, chlorotoluenes, isomeric benzylpyridines, etc. Kelker and Schivizhoffen⁹¹ have reviewed the use of liquid crystals as stationary phases in GLC.

A. Ono⁹² has recently studied the separation behaviour of positional isomers of alkylbenzenes by GLC with liquid crystals as phases.

8. Silicones

Silicones are widely used as stationary phases because of their excellent thermal stability at temperatures upto

250°C and in some cases 400°C or higher. Silicones are suitable for the analysis of high boiling compounds like fluoroesters of camphoric acid, high molecular weight fatty acid esters, alcohols, amines etc. Previously non-polar methyl- and phenyl-silicones were available only and separations on these phases were based on boiling point differences. New materials such as Dow Corning FS 1265 (a type selective fluoro-silicone), and General Electric XE-1150 (a polar cyano-ethyl-silicone) are now being used by several workers.

Now a days, the trend is to attach silicones directly on the solid support by chemical bonding. Bonding of silicones to diatomaceous earth, silica gel and glass beads by polymerisation and their thermal stability for GC separations was investigated by many workers^{93,94}. Karasek⁹⁵ has reviewed the nature and uses of chemically bonded phases.

9. Polymer substrates

A lot of work⁹⁶⁻⁹⁸ has been done for the development of thermally stable phases. The preparation of porous poly-aromatic copolymers of divinylbenzene, ethyl-vinylbenzene and styrene physically bonded to support (chromosorb, glass beads) is described by Fuller⁹⁹. Poly(vinyl-formal prepionitrile)- a new polar liquid phase, remains stable at temperatures upto 300°C and has been used for separation of polyols, fatty acid esters and multifunctional alcohols¹⁰⁰.

The chromatography of compounds like carboxylic acids, alcohols, phenols, carbohydrates, amines, amino-acids, etc. is often difficult, but can be readily carried out by converting them into their more volatile and usually less polar derivatives. The identification of peaks becomes easier with the formation of derivatives. For example alcohols, phenols, glycols, steroids, carbohydrates, amines, amino-alcohols and amino-acids are converted into their trimethylsilyl derivatives¹⁰¹.

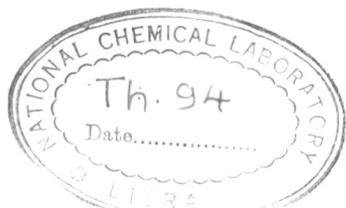
10. Mixed liquid phase

The separation of complex mixtures is often not possible with a single phase. A combination of two or more phases may be effective in such cases. The preparation of mixed phase column has been studied in detail by Mayer et al.¹⁰² and Hildebrand and Reilley¹⁰³.

Mixed phase of Carbowax-400 and silicone oil has been used for the separation of methyl iodide, ethyl iodide, cyclohexene and cyclohexane mixture¹⁰³. Miyake et al.¹⁰⁴ separated C₆-C₁₀ aromatic hydrocarbons in crude oil on a mixed phase column.

11. Polyesters

With the rapid development of huge number of stationary phases, the versatile medium polarity and substantially thermally stable liquid phases are still in great demand. This led to the introduction of polyester type plasticisers as stationary phases. These were found to give excellent



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separations and also possess a number of advantages over other phases.

Polyesters with various chemical structures for different applications can be easily synthesised from a number of dibasic acids and glycols. These have usually low viscosity at the column temperature. Their polarity can be readily varied by introducing various cross-linking agents. The polyesters can be made fairly stable upto 200-240°C by proper purification and can be readily blended with other liquid phases.

Two main drawbacks in the use of polyesters as stationary phases are:

- (a) Slow volatilisation of low molecular weight materials in the polyester resulting in noise in the detector and eventual deterioration of column efficiency.
- (b) Possibility of trans-esterification reaction in the column between the non-volatile polyester and volatile methyl esters (when used for fatty acid esters).

The first defect can be reduced by pre-treatment of the column at the operating temperature¹⁰. The second defect can be minimised by reducing the column temperature.

Polyester stationary phases have been studied by several workers. It will, therefore, be worthwhile to review their findings.

For analysis of fatty acid esters, Apieson L and silicone grease^S were used as liquid phases by many workers.

Peaks were broad and these phases were not suitable for resolution of any acids other than normal saturated acids. Orr and Callen used polyester plasticizer Reoplex 400 as stationary phase and this was found to give excellent separation of methyl esters of fatty acids^{10,105} normally encountered in natural fats, including polyunsaturated esters.

Lipsky et al.^{11,106} examined a number of polyesters of varying compositions as stationary phases to achieve rapid and complete resolution of a wide range of saturated and unsaturated fatty acid esters. They used adipate polyesters of neopentyl glycol, butylene glycol and diethylene glycol for their studies. They introduced additional polarity in the diethylene glycol polyester by partially cross-linking it with about 4% penta-erythritol. By using succinate polyester of diethyleneglycol at 203°C, these workers could resolve the individual components of the mixtures of biochemically important saturated and unsaturated esters ranging from C₁₂ to C₂₆ in approximately 38 minutes. This was remarkable achievement in view of the fact that retention time of esters upto C₂₀ chain length on 'Apiezon' column was of the order of 3-4 hours. Dimick and Chu¹⁰⁷ have used succinate polyesters of butanediol and diethylene glycol for similar separations.

Craig¹⁰⁸ have tested phthalic acid based polyesters as liquid phases for analysis of fatty acid esters. The o-phthalic-ethylene glycol polyester prepared by Fischers' method¹⁰⁹ was found suitable for resolution of methyl esters

of fatty acids and the time of analysis was about 40 minutes. Metcalfe¹² used adipate polyester of diethylene glycol treated with 2%-phosphoric acid on 60/80 mesh acid-washed celite 545 and separated long chain fatty acids upto chain length C₂₂ directly.

Hahti and co-workers¹¹⁰ have used five polyesters neopentyl glycol adipate, neopentyl glycol succinate, ethylene glycol adipate, ethylene glycol succinate and ethylene glycol isophthalate as liquid phases for the separation of steroids.

Lipsky and Landowne¹¹¹ have studied in detail the separation of steroids with GLC technique. They used a number of polyester phases such as succinate, adipate and sebacate polyesters of neopentyl glycol, 1,4-butane-diol, 1,5-pentanediol and 2-ethylhexane-1,3-diol. For comparison they employed a number of non-polar and polar phases like Apiezon L, silicones, polybutene, poly-phenyl ethers and polyalkylene glycols. The non-polar phases showed poor performance as compared with that of polar liquids. The performance of polyalkylene glycol was somewhat better. Extremely good separation was achieved with polyester phases. A complete separation of steroidal ketones, pregnanolone, pregnane-3,20-dione and allopregnane-3,20-dione, was obtained.

Adlard et al.¹¹² have tested 11 polyesters for separation of C₁₆-C₂₀ fatty acid esters and have recommended ethylene-glycol-phthalic acid polyester. A new polyester liquid phase prepared by the condensation of maleic acid with diethylene-glycol has been found to be useful for the separation of methyl

esters of fatty acids,¹¹³ including cis-trans isomers of octadecadienoic acid.

It is therefore clear that the polyester type medium polarity substrates are widely used for the analyses of various complicated mixtures.

Investigation of polyester substrates in this laboratory

Systematic studies for the development of series of polyesters and their proper evaluation were undertaken in this laboratory¹¹⁴⁻¹¹⁷. In continuation of the same work, polyesters based on unsaturated glycols, aromatic- and substituted aromatic-acids have been prepared and their performance as substrates in GLC has been evaluated in detail. The results of these studies are presented in different parts of this thesis.

Before concluding this brief introduction, it is quite justifiable to mention about preparative GLC, temperature-programming and the recently developed high speed liquid chromatography.

Preparative applications of GLC

Scientists are not contented only to find out the analytical method of separation of ingredients of the mixture, but they want actual separation in quantity sufficient to work up further and this quest is now fulfilled to some extent with the development of preparative GLC¹¹⁸⁻¹²⁰. Today, it is possible to separate the components from a complex mixture upto

200-~~200~~³ g¹²¹ with the automatic injection and collection of components.

Four different operations are involved in automatic preparative separation of components from a mixture:

- (a) Injection of the sample by a pneumatic injection system.
- (b) Isothermal or programmed temperature separation of the individual components followed by collection in separate traps.
- (c) Increase in column temperature to remove the residual components rapidly, and
- (d) Decrease in column temperature to the normal operational temperature for further injection and separation.

Temperature programmed gas-chromatography

If the components of a mixture vary widely in their boiling points, no single temperature is optimum for their analysis on a non-polar column. On polar columns, similarly, analysis of components of considerable different polarities is difficult. These difficulties are overcome by using programmed temperature gas chromatography¹²². The column temperature in this technique is gradually increased at a fixed rate so that the more volatile components are eluted first and the strongly retained components are resolved as sharp peaks at higher temperature. The heating rate is usually between 0.5° and 50°C/minute depending upon the initial and final temperatures.

Major drawback of temperature programming is the higher rate of "bleed" of the stationary phase which results in a base-line drift. This difficulty is overcome by using a second column having almost identical characteristics. This practice of using two columns - reference and analytical, however, does not stop column bleeding. Levy et al.¹²³ have suggested as a remedy the use of a short column containing a phase of low volatility to absorb the column bleed.

High speed high performance modern liquid chromatography (LC)

There are some obvious limitations to GLC. It can be used for only about 20% of the known compounds because of their insufficient volatility or thermal instability. GLC cannot be used for the analysis of ionic compounds (amino acids, nucleotides), labile naturally occurring compounds, polymers, and high molecular weight polyfunctional compounds. Liquid chromatography (LC) on the other hand is ideally suited for such applications.

Stainless steel or glass tubes of 2 to 3 mm internal diameter and 50-100 cm length are used as columns which can be connected in series to achieve a large number of theoretical plates. Low dead-volume fittings are used to avoid any loss in column efficiency¹²⁴. Particle size of the packing material and internal diameter of the column have profound influence on the column efficiency¹²⁵.

Dense, spherical, porous-layer bead materials such as Zipax chromatographic support and corasil down to particle

size 20-30 μ can be dry packed into columns efficiently. In modern adsorption and partition liquid chromatography, particle size in the range 20-60 μ is normally used. The liquid flow in modern L.C. is achieved with the use of high-pressure pumps and pressures employed are in the range 500-5000psi. The high carrier velocities permit the elution of complex samples quickly.

Horn et al.¹²⁶ suggested the possibility of use of non-porous supports having thin, uniform surfaces of sorbent for high speed L.C. The development of chemically bonded, thermally and hydrolytically stable polymeric silicone¹²⁷⁻¹³⁰ stationary phases of Permaphase type has made L.C. a versatile technique.

Kirkland¹³¹ has reviewed different column packings for modern liquid chromatography. Several workers^{132,133} have described the applications of Zipax and Corasil porous layer supports for liquid chromatography. Wu et al.¹³⁴ report the successful separation of purine and stychnos alkaloids using high-speed liquid chromatography.

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CHAPTER - I

USE OF UNSATURATED POLYESTERS AS STATIONARY
PHASES IN GAS-LIQUID CHROMATOGRAPHY: THE EFFECT
OF UNSATURATION IN POLYESTERS AS COMPARED WITH
THE SATURATED POLYESTERS

S U M M A R Y

A new series of polyesters has been prepared from 1,4-butanediol and various dicarboxylic acids such as succinic-, adipic-, sebacic-, and 1,16-hexadecane^{dicarboxylic} acids and their suitability as substrates (liquid phases) in gas-liquid chromatography (GLC) for effecting the separation of terpenoids has been investigated. The unsaturation centre in these polyester phases was found to have a profound influence on the value of the retention time. The retention times of hydrocarbons and neutral oxygenated compounds on these phases have been found to vary linearly with the number of methylene groups in the acid fragment upto C₁₆-dicarboxylic acid. The transition in contribution per methylene group in the acidic fragment of the polyesters synthesised has been worked out. It has been found that the gradual change in the cohesive energy is due to the basic structural difference in the glycolic fragment of the polyesters.

I N T R O D U C T I O N

Polyester liquid phases were introduced by Orr and Callen¹ and Lipsky and Landowne² in the separation and quantitative estimation of saturated and unsaturated fatty acid esters by gas-liquid chromatography. The further developments by other workers³⁻⁷ using polyesters as stationary phases has led to the complete analysis of fats and oils on a micro-scale.

Sweeley and Horning⁸ employed polyesters for the separation of steroids. These workers developed a method in which polyester was applied to silane treated⁹ support and this they claimed minimised thermal breakdown of polyesters at high operating temperatures. Rudloff¹⁰⁻¹¹ investigated polyesters for the separation of mixtures of terpenoids by GLC. Melkonyan et al.¹² used poly(ethyleneglycol)-succinate polyester for the separation of free diols and glycerol. James¹³ employed poly-ethylene glycol-adipate and Apiezon L grease for determination of degree of unsaturation and the chain length of unknown fatty acids by GLC. Retention volumes of the methyl esters of fatty acids with special reference to n-odd numbered, iso-, and (+)-Anteisoacids have been determined on Apiezon M and poly-diethylene glycol-succinate¹⁴ phases. Zaman¹⁵ has compiled data on the behaviour of saturated and unsaturated C₁₂-C₂₂ fatty acid methyl esters on four different polyester columns. Vigdergauz et al.¹⁶ have employed polyester resins as the

stationary phases for the separation of C_6 - C_{10} n-paraffins.

Hunter et al.¹⁷ separated volatile organic acids in the presence of water by GLC using an adipate polyester of diethylene glycol as the liquid phase. Janak and Hainova¹⁸ studied the thermal stability and sorption properties of Czechoslovakian polyesters such as poly (ethylene adipate), poly (1,4-butanediyl succinate), etc. and compared these domestic products with foreign ones used as stationary phases in GLC. Acetylated polyesters¹⁹ as liquid phases were examined for the analysis of formaldehyde, methyl alcohol and water.

Gehrke, Zumwalt and Wall²⁰ have shown that by varying the length of carbon chain in a polyester phase, the separation characteristics of a chromatographic column can be markedly influenced. They observed optimum chromatographic performance for neopentylglycol polyester at a carbon chain length of ten and neopentyl-glycol-sebacate polyester was found to exhibit good separation ability for protein amino-acid esters.

Karpov et al.²¹ investigated some polyesters as stationary phases in GLC and found that the polyesters, poly(ethylene azilate) and poly(ethylene sebacate), have superior thermal stability and diminished volatility at temperatures upto 220°C.

Earlier work in this laboratory

From this brief discussion, it is clear that the polyester stationary phases have been widely used by a number of workers; however, there had been no systematic approach to

evaluate these polyesters. An effort in this direction was initiated by Bapat, Chate and Bhattacharyya^{22,23} in this laboratory, who systematically synthesised polyesters from diethylene glycol and 1, ω -dicarboxylic acids, HOOC-(CH₂)_n-COOH, where "n" varies from 1 to 16, and studied them as substrates in GLC.

They found that if t_R^x is the retention time in minutes and x is the number of methylene groups present in the acidic fragment of the polyester, and if t_R^y be the retention time on another polyester containing 'y' methylene groups, then

$$\frac{t_R^x - t_R^y}{x - y} = C, \text{ where 'C' is a constant for a particular compound}$$

at a particular temperature and is the individual contribution of a single methylene group. This indicates that retention time and structure of the polyester are intimately related and each methylene group makes a distinct contribution in the retention time. They also observed that the molecular weight of the polyester plays a less important role than the number of methylene group present in the acidic fragment of the polyester.

These workers subsequently prepared polyesters derived from different 1, ω -glycols, HOCH₂-(CH₂)_n-CH₂OH (n ranges from 0 to 13) and some fixed acids such as adipic acid, etc. and evaluated them as liquid phases. The similar effect of spacing of methylene groups in the glycolic fragment of the polyester on the retention time was also valid in this series. It was, however, observed by them that this linear relationship of

retention time and number of methylene groups in the polyester starts deviating from 1,10-decanediol.

Present approach

In continuation of the systematic study of the polyester type stationary phases, work on the synthesis and evaluation of several new polyesters was undertaken. Stepwise modification was brought about in the structure of saturated polyesters, normally prepared from glycols and dicarboxylic acids, by introducing unsaturation centre and then aromatic- and substituted aromatic- nuclei in the polyester molecule. An interesting relationship in retention times has been found during these investigations and the detailed results are presented in different parts of this thesis.

Actual investigation

It was felt that the introduction of unsaturation in liquid substrate molecule may be quite interesting to investigate and therefore a new series of polyesters was synthesised from 1,4-butenediol (constant unsaturated glycol fragment) and various dicarboxylic acids like succinic-, adipic-, sebacic-, and 1,16-hexadecane dicarboxylic-acids. The effect of "unsaturation centre" in polyesters in their utility as liquid phases for the separation of various types of compounds was examined.

During this study, it was found that these unsaturated polyesters behave somewhat differently, showing linear rise

in retention time upto C_{16} -dicarboxylic acid polyester and this linearity is valid not only in case of hydrocarbons, but also for neutral oxygenated compounds. Two more polyesters from 1,3-propanediol (constant glycol fragment) and dicarboxylic acids, succinic- and adipic-acids, were further prepared for comparative evaluation of these polyesters. The results are discussed in this part of the thesis.

Instrument and general conditions employed during analysis

Modified MK II model of 'Griffin and George VPC Apparatus' has been used for collection of all the data during the entire investigations.

The carrier gas flow system in the original instrument was working under vacuum. It was modified in this laboratory. The instrument at present works with usual pressurised system employing hydrogen as the carrier gas.

In order to compare the retention time data on one column with that on another column, all the column variables were normalised according to Littlewood²⁴.

1. Column: 2 m long; 6 mm internal dia.
2. Weight of the liquid phase: 2.5 ± 0.005 g.
3. Carrier gas flow-rate (hydrogen): 4 litres/hour.
4. Bridge current: 150 m.A.
5. Sample size: 1 μ l (with the help of Hamilton Syringe, 10 μ l capacity)
6. Inlet pressure: i) 130 ± 4 mm at 96°C
 - ii) 135 ± 4 mm at 100°C
 - iii) 155 ± 5 mm at 120°C
 - iv) 185 ± 5 mm at 164°C
 - v) 200 ± 5 mm at 170°C

Chromatograms

In order to get better separation of peaks in actual chromatogram, in some of the cases, variations in carrier gas flow-rate and/or change in column temperature have been used.

Most of the chromatograms attached in the thesis have been taken on the above-mentioned instrument, while a few chromatograms were taken on another instrument⁶ Mark II Gas Chromatograph Serial No.70020⁷ supplied by M/s. Associated Instrument Manufacturers (India) Pvt.Ltd., Bombay-1.

EXPERIMENTAL

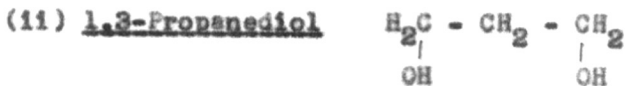
The following polyesters were synthesised from 1,4-butenediol (constant) and various dicarboxylic acids:

1. 1,4-butenediol-succinic acid polyester
2. 1,4-butenediol-adipic acid polyester
3. 1,4-butenediol-sebacic acid polyester and
4. 1,4-butenediol-1,16-hexadecane dicarboxylic acid polyester.

Two more polyesters were prepared from 1,3-propanediol (constant) and succinic- and adipic-acids. The sources of all these compounds are described below:

I Glycols

It was available from the laboratory stock. Its purity was checked by elemental analysis (Found: C, 54.50%; H, 9.12% $\text{C}_4\text{H}_8\text{O}_2$ requires: C, 54.54%; H, 9.09%). The same sample was used throughout the course of this study.



It was available commercially and was purified by fractionation. The purified product gave a single peak on GLC analysis.

II Dicarboxylic acids

Succinic-, adipic-, and sebacic-acids were available from the laboratory. They were initially recrystallised from ethyl alcohol and their purity was checked by melting point determination.

- (i) Succinic acid $\text{HOOC}-(\text{CH}_2)_2-\text{COOH}$
 Melting point: 184-185°C (lit. 185°C)
- (ii) Adipic acid $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$
 Melting point: 149°C (lit. 150°C)
- (iii) Sebacic acid $\text{HOOC}-(\text{CH}_2)_8-\text{COOH}$
 Melting point: 132-133°C (lit. 133°C)
- (iv) 1,16-Hexadecane dicarboxylic acid, $\text{HOOC}-(\text{CH}_2)_{16}-\text{COOH}$

It was prepared by the oxidation of ω -hydroxy -stearic acid, $\text{HOCH}_2-(\text{CH}_2)_{16}-\text{COOH}$, with Jones's reagent. The product was recrystallised from ethyl alcohol, m.p. 123° (lit. 124°C). Its purity was tested by elemental analysis (Found: C, 68.72%; H, 10.86%; $\text{C}_{18}\text{H}_{34}\text{O}_4$ requires C, 68.79%; H, 10.83%).

III Diglycerol

It was prepared by the dehydration of glycerol as described in literature²⁵.

Preparation of the polyester

The polyesters are generally prepared either in the presence of a cross-linking agent or without a cross-linking agent. Diglycerol (2%) has been used as a cross-linking agent in these investigations. The polyesters have been prepared by following basically the method of Craig and Murty²⁶ with some

minor modifications.

1,4-Butenediol and the corresponding dicarboxylic acids were taken in molar proportions in a round-bottomed flask. To this were added p-toluene-sulphonic acid (0.5 g) and the required quantity of diglycerol. The mixture was heated at 100-110°C (bath temperature) for 2 hours and then the temperature was maintained at 135-140°C/2 mm pressure for further 2 hours. The polyester thus formed was dissolved in methylene chloride and washed initially with water, followed by aqueous sodium bicarbonate solution (10%) and finally with water till neutral. Methylene chloride solution was dried over anhydrous sodium sulphate and the solvent was removed. The residue was taken in acetone and the pure polyester was precipitated by the addition of pet.ether b.p. 40-60°C as described in literature⁶. The solvent removed and the residue dried to constant weight under vacuum at room temperature.

All the polyesters were prepared under exactly identical conditions.

Polyesters from succinic- and adipic-acids with 1,4-butenediol were viscous liquids, while those from higher acids were low melting solids. They were light yellowish in colour.

All the polyesters showed molecular weight of the order of 10,000 when determined by end group titrations and the actual results are given in Table I.

Table 1Molecular weights of the polyesters as determined by end group titration

S.No.	<u>Components of the polyester</u>		No. of methylene groups in the acidic fragment	Molecular weights
	Acid	Glycol		
1.	Succinic acid	1,4-butenediol	2	9875; 9902
2.	Adipic acid	1,4-butenediol	4	10,045; 10,038
3.	Sebacic acid	1,4-butenediol	8	9,988; 9970
4.	1,16-hexadecane-dicarboxylic acid	1,4-butenediol	16	10,125; 10,142

Solid support

Indian fire-brick powder (60-100 mesh) was used as the solid support throughout the course of these studies. It was purified by the method described in Chapter V.

Impregnation and filling

The polyester and fire-brick support were weighed separately in required quantities. The polyester was dissolved in chloroform and the solution was applied to the support. Chloroform was carefully removed on a water-bath at 60°C. The resulting material was then dried in an oven at 110°C to a constant weight. The impregnated material was free-flowing.

Column filling

In order to have uniformity, one and the same column was used throughout these studies. The same amount of material was used every time to keep the weight of stationary phase the same in all the cases. On completion of the study with one column filling, the column was carefully cleaned to avoid any contamination of the previous column filling with the next one.

The column was tested for inlet pressure and the flow rate every time. If the inlet pressure was too high, the column was repacked to get the required flow rate at desired inlet pressure.

Column conditioning

It is necessary to stabilise the column before taking actual readings. For this purpose, the column was first conditioned at 100°C for 4 hrs. and then the temperature was maintained about 20°C higher than the required temperature. The flow-rate of carrier gas was nearly 4-5 litres/hour. The column conditioning generally required about 10 hours and within this period, the recorder showed a steady base-line.

Recording the retention time data

Retention times were recorded with the help of a stop-watch. When the air peak reached its maxima, the stop-watch was started and it was stopped when the sample peak reached its maxima. Internal standard samples were reinjected to check their retention times at regular intervals. The

retention time data was collected by taking several concordant readings in each case.

The following chart (chart I) gives the structures and other physical properties of the compounds which are used as standard samples during the present investigation.

Results and discussion

Column temperature (100°C) was used for monoterpenes and $163.5 \pm 0.5^\circ\text{C}$ for sesquiterpenes as well as monoterpene oxygenated compounds. The retention time results are recorded in Table 2 and 3. The behaviour of different classes of compounds on these polyesters is discussed below in detail.

Table 2

Retention time in minutes at 100°C: Glycolic fragment (1:4-butanediol) constant



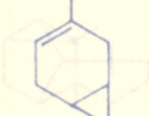
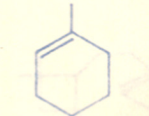
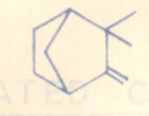

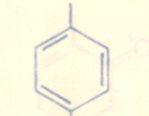
Column	I	II	III	IV
Compound	Number of methylene groups in the acidic fragment of polyester			
	2	4	8	16
α -Pinene	1.70	2.17	4.0	7.57
β -Pinene	2.80	3.7	6.4	11.7
\triangle^3 -Carene	3.50	4.5	8.1	15.3
α -Carene	1.85	2.3	4.8	10.8
Camphene	2.23	3.0	5.0	10.10
Limonene	4.67	6.05	10.0	19.0
1:8-Cineole	5.7	8.0	12.9	21.1
o-Xylene	3.34	4.17	5.8	8.8
p-Cymene	6.67	8.9	13.4	23.65
Cyclohexanone	10.50	13.0	13.0	13.5

Table 3




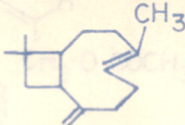
Retention time in minutes at 163.5 ± 0.5°C: Glycolic fragment
(1:4-butenediol) constant

Column :	I	II	III	IV
	Number of methylene groups in the acidic fragment of polyester			
Compound	2	4	8	16
Longifolene	2.5	4.0	7.5	17.0
Longicyclene	2.0	3.1	6.0	13.8
Isolongifolene	2.17	3.4	6.5	14.8
Caryophyllene	2.7	4.2	7.9	17.13
Camphor	2.5	3.9	4.9	6.6
Carvone	5.13	7.7	9.5	11.6
Dihydrocarvone	3.4	5.25	6.7	8.7
Methylheptenone	1.0	1.5	1.75	-
Geraniol	4.75	8.4	10.5	12.13
Geraniolacetate	3.9	6.4	9.1	14.25
Nerol	4.1	7.1	8.95	10.36
Nerolacetate	3.53	5.8	8.1	12.35
Borneol	3.43	5.7	7.46	9.0
Borneolacetate	2.5	4.15	5.8	9.0
Citronellol	3.43	6.2	8.65	10.2
Citronellolacetate	2.85	4.65	6.85	11.2
Carveol	5.83	9.7	11.83	-
α-Terpeniol	3.55	5.8	7.8	10.07
Linalool	1.65	2.8	3.5	4.8

MONOTERPENIC HYDROCARBONS

NO.	NAME OF THE COMPOUND	STRUCTURAL FORMULA	M. P. °C.	B. P. °C.
1	α -PINENE		—	150-156 / 36 mm
2	β -PINENE		—	107-162
3	Δ^3 -CARENE		—	169/70 / 5 mm
4	LIMONENE		—	174
5	CAMPHENE		—	159
6	CARANE		—	169
7	p-CYMENE		—	177

SESQUITERPENIC HYDROCARBONS

NO.	NAME OF THE COMPOUND	STRUCTURAL FORMULA	M. P. °C.	B. P. °C.
1	LONGIFOLENE		—	150-1 / 36 mm
2	ISOLONGIFOLENE		—	107- / 7 mm
3	LONGICYCLENE		—	82 / 2 mm
4	CARYOPHYLLENE		—	113 / 8 mm

OXYGENATED COMPOUNDS

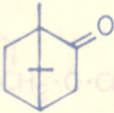
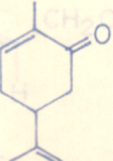
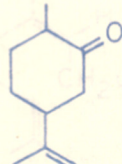
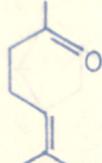
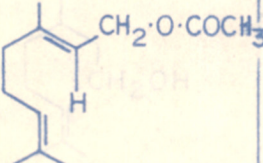
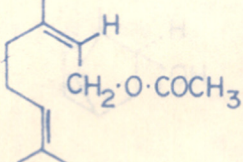
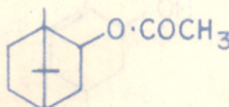
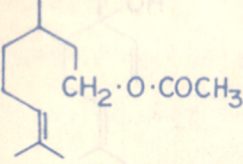
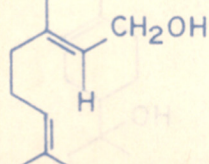
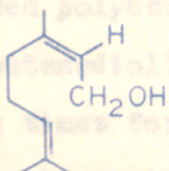
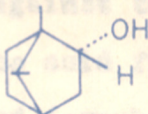
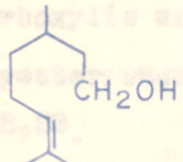
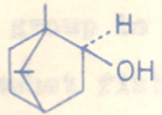
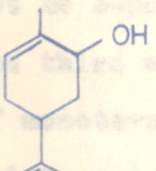
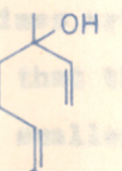
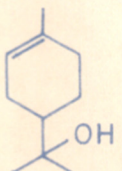
1	CAMPHOR		179	119-2 / 15 mm
2	CARVONE		—	230

CHART - I
OXYGENATED COMPOUNDS

49
49

NO.	NAME OF THE COMPOUND	STRUCTURAL FORMULA	M. P. °C.	B. P. °C.
3	DIHYDROCARVONE		—	75 / 3 mm
4	METHYL HEPTENONE		—	108 / 20 mm
5	GERANYL ACETATE		—	120 / 17 mm
6	NEROL ACETATE		—	125 / 25 mm
7	BORNYL ACETATE		—	106 / 15 mm
8	CITRONELLOL ACETATE		—	119-21 / 15 mm
9	GERANIOL		—	10-230 mm

OXYGENATED COMPOUNDS

NO.	NAME OF THE COMPOUND	STRUCTURAL FORMULA	M. P. °C.	B. P. °C.
10	NEROL		—	125/25 mm
11	BORNEOL		208	—
12	CITRONELLOL		—	222
13	ISOBORNEOL		217	—
14	CARVEOL		—	108/16 mm
15	LINALOOL		—	199
16	α -TERPENEOL		—	104/15 mm

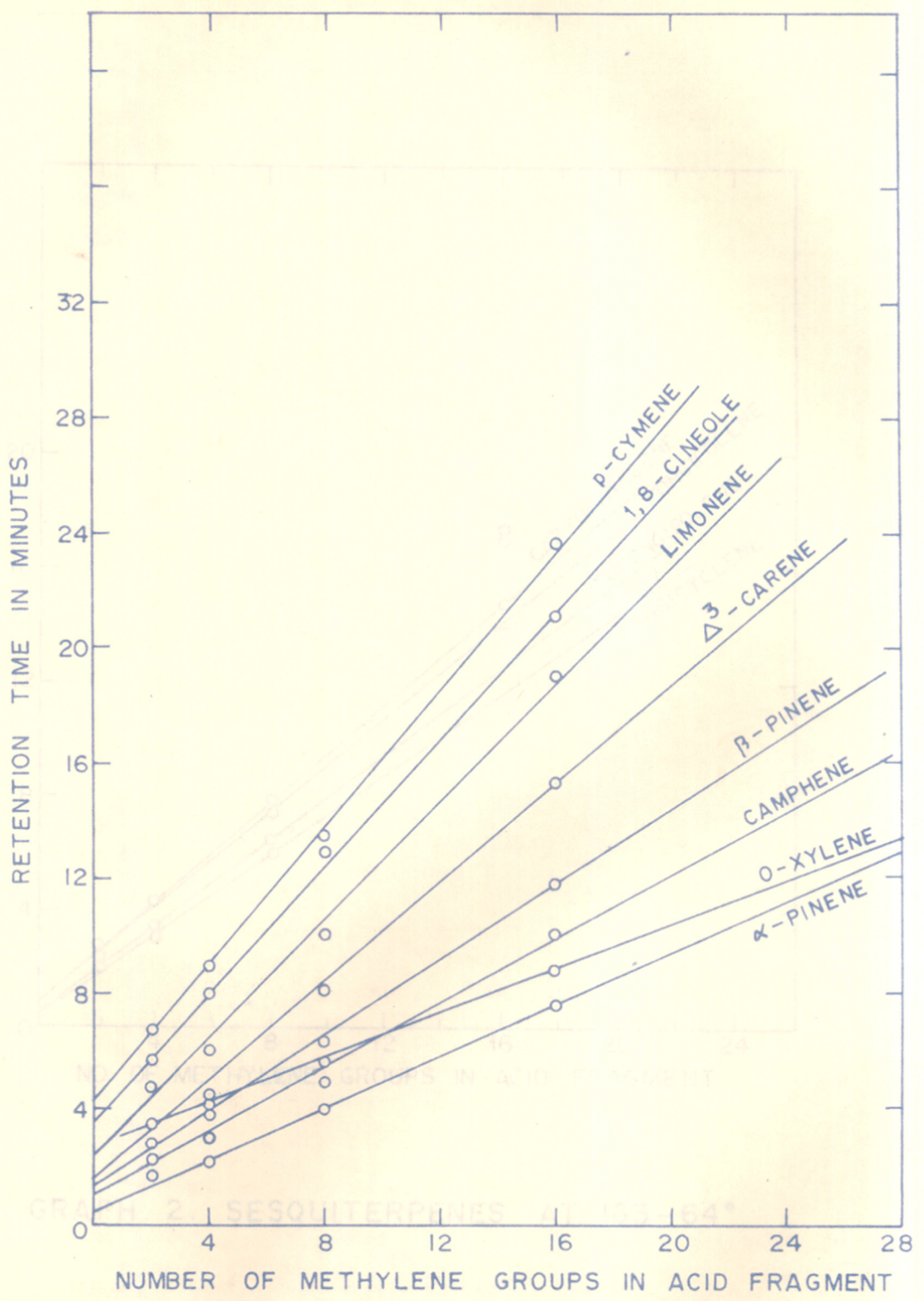
Hydrocarbons

As in earlier investigations on saturated polyesters^{22,23} the unsaturated polyesters, derived from unsaturated glycol (1,4-butenediol), show clear linear relationship in retention times for the hydrocarbons. When the retention times of monoterpenic- and sesquiterpenic-hydrocarbons are plotted against the number of methylene groups (-CH₂-groups) in the acid fragments of the polyesters, straight lines are obtained (graph I and 2).

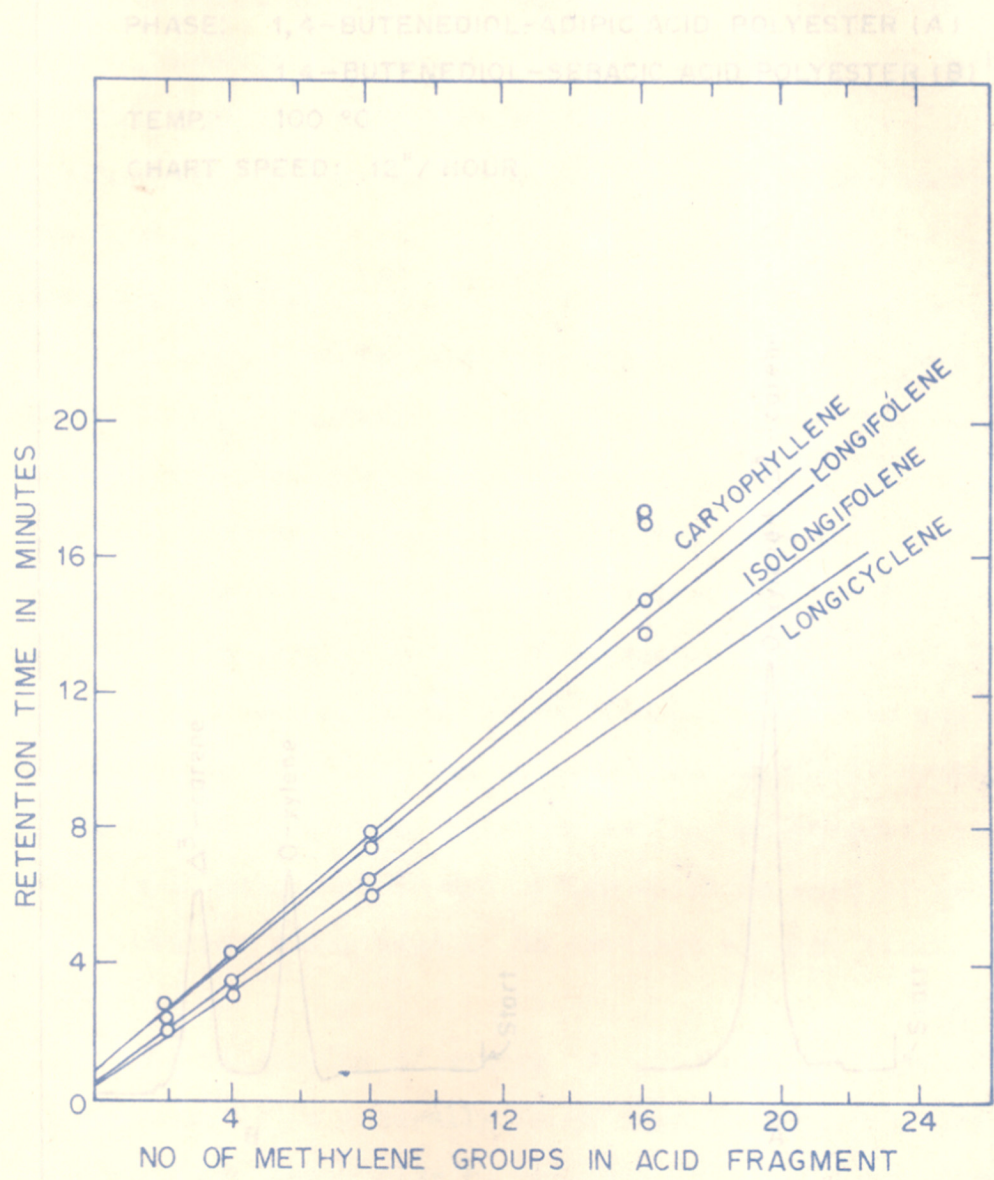
Interesting enough, the linear relationship is valid upto the last 1,16-dicarboxylic acid which is in quite contrast to earlier polyesters wherein the linearity discontinued after C₁₁ carbon-chain^{22,23}.

In case of aromatic hydrocarbon, o-xylene, stretching per intervening methylene group is comparatively less. The linearity graph drops somewhat flat, crossing graphs of other compounds. This gives indication that a mixture of o-xylene and Δ^3 -carene, which cannot be separated on first and second columns, can be resolved on third and fourth columns (Fig. 1).

Actually in case of monoterpenes, the retention times are somewhat lower on succinic acid polyester, while in sesquiterpenes retention times are higher on the last C₁₆-acid polyester. This indicates that the contribution due to unsaturation is greater in smaller acidic fragments of the polyesters and its influence is reduced to some extent in bigger molecules.



GRAPH. I. MONOTERPENES AT 100°C .



GRAPH. 2. SESQUITERPENES AT 163-64°

FIG. 1

PHASE: 1,4-BUTENEDIOL-ADIPIC ACID POLYESTER (A)
1,4-BUTENEDIOL-SEBACIC ACID POLYESTER (B)
TEMP.: 100 °C
CHART SPEED: 12"/ HOUR

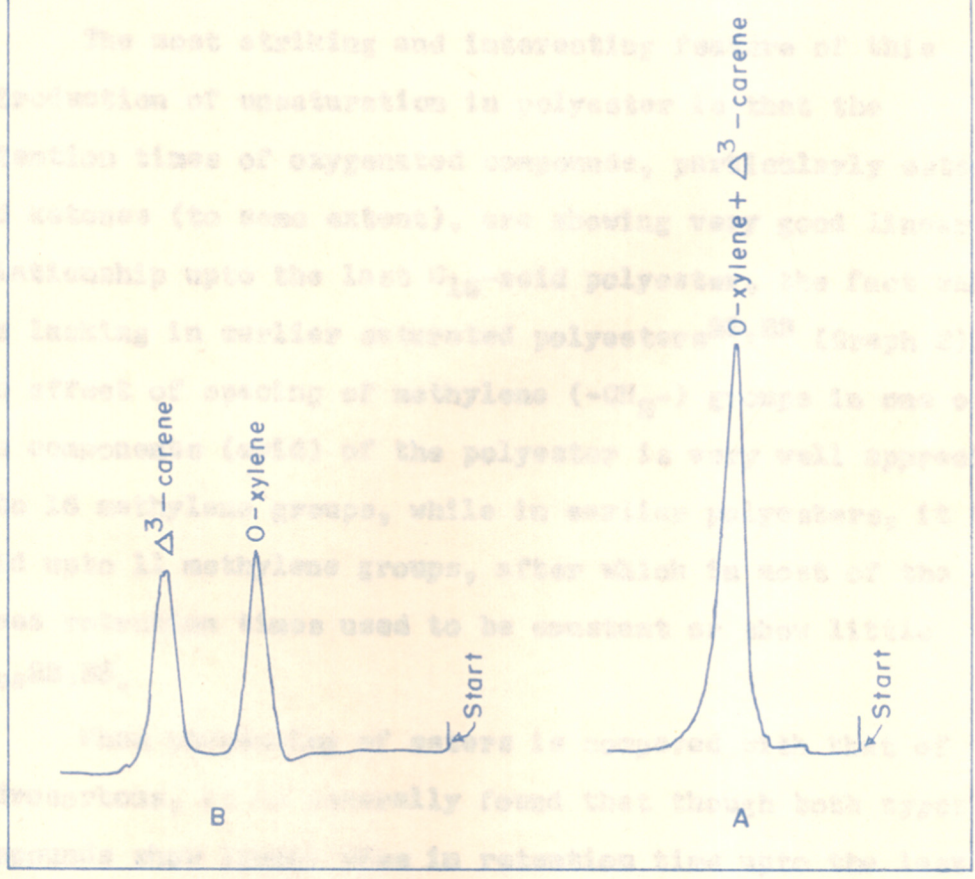


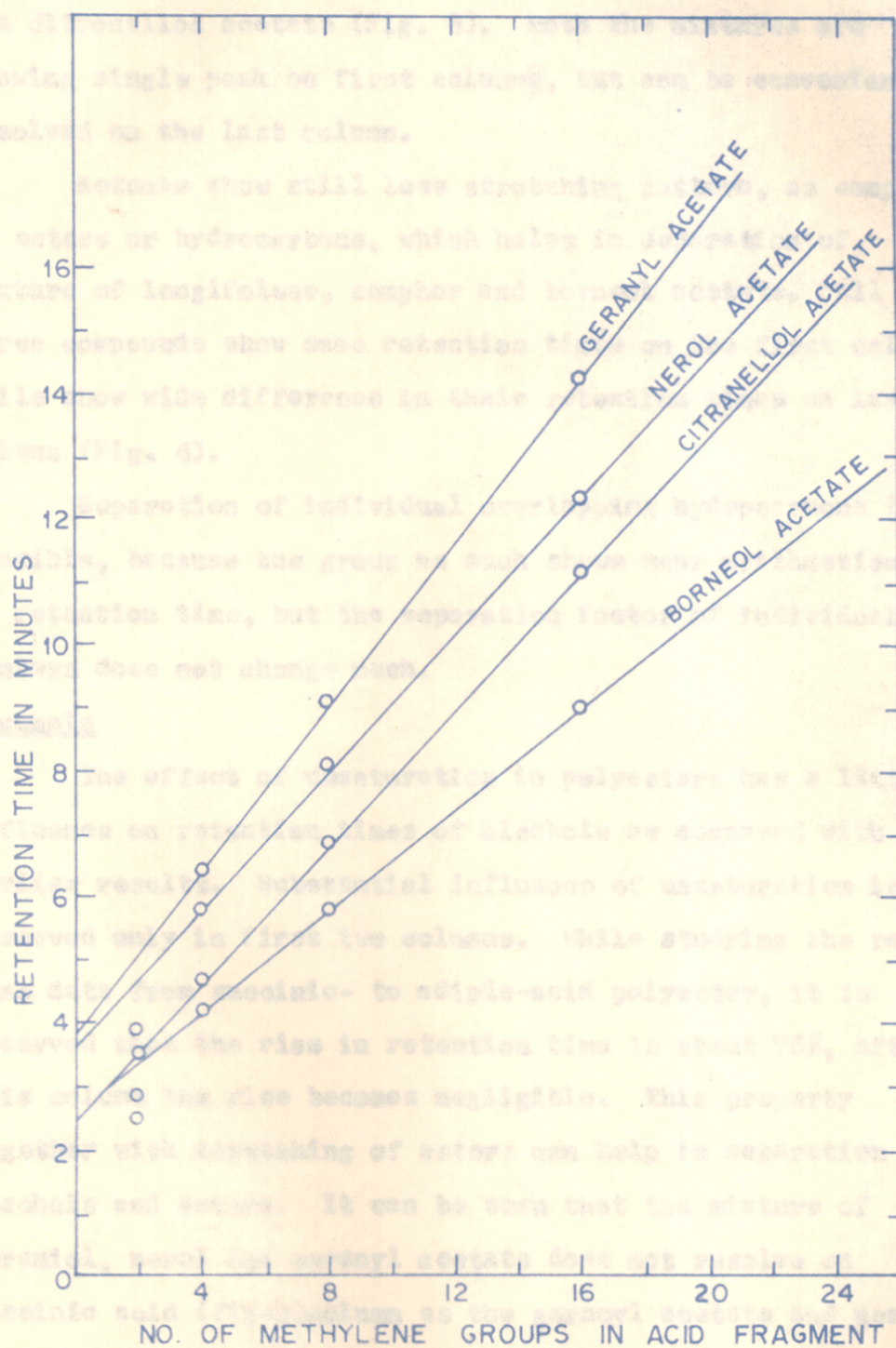
FIG. 1

The exact arithmetical relationship in retention times is, however, not found in these polyesters. In case of sesquiterpenes, the values of retention times are approximately 20% less compared to those on diethyleneglycol polyesters.

Esters and ketones

The most striking and interesting feature of this introduction of unsaturation in polyester is that the retention times of oxygenated compounds, particularly esters and ketones (to some extent), are showing very good linear relationship upto the last C₁₆-acid polyester, the fact which was lacking in earlier saturated polyesters^{22,23} (Graph 3). The effect of spacing of methylene (-CH₂-) groups in one of the components (acid) of the polyester is very well appreciated upto 16 methylene groups, while in earlier polyesters, it is valid upto 11 methylene groups, after which in most of the cases retention times used to be constant or show little rise^{22,23}.

When stretching of esters is compared with that of hydrocarbons, it is generally found that though both types of compounds show linear rise in retention time upto the last column, hydrocarbons are better stretched (about 25% less than arithmetical rise) than esters having considerable less rise in retention time and this fact helps to separate out mixtures of longifolene and borneol acetate (Fig. 2 and 4) and caryophyllene



GRAPH. 3. ESTERS AT 163-164°

and citronellol acetate (Fig. 3). Both the mixtures are showing single peak on first column, but can be conveniently resolved on the last column.

Ketones show still less stretching pattern, as compared to esters or hydrocarbons, which helps in separation of mixture of longifolene, camphor and borneol acetate. All the three compounds show same retention times on the first column, while show wide difference in their retention times on last column (Fig. 4).

Separation of individual overlapping hydrocarbons is not possible, because the group as such shows near arithmetical rise in retention time, but the separation factor of individual members does not change much.

Alcohols

The effect of unsaturation in polyesters has a little influence on retention times of alcohols as compared with earlier results. Substantial influence of unsaturation is observed only in first two columns. While studying the retention time data from succinic- to adipic-acid polyester, it is observed that the rise in retention time is about 75%, after this column the rise becomes negligible. This property together with stretching of esters can help in separation of alcohols and esters. It can be seen that the mixture of geraniol, nerol and geranyl acetate does not resolve on succinic acid (first) column as the geranyl acetate and nerol tend to overlap, but the same mixture can be very well resolved

PHASE: 1,4-BUTENEDIOL-SUCCINIC ACID POLYESTER (A-B)
1,4-BUTENEDIOL-SEBACIC ACID POLYESTER (C)

TEMP: 164 °C

CHART SPEED: 12"/ HOUR

TEMP: 164 °C

CHART SPEED: 12"/ HOUR

CHART SPEED: 6"/ HOUR

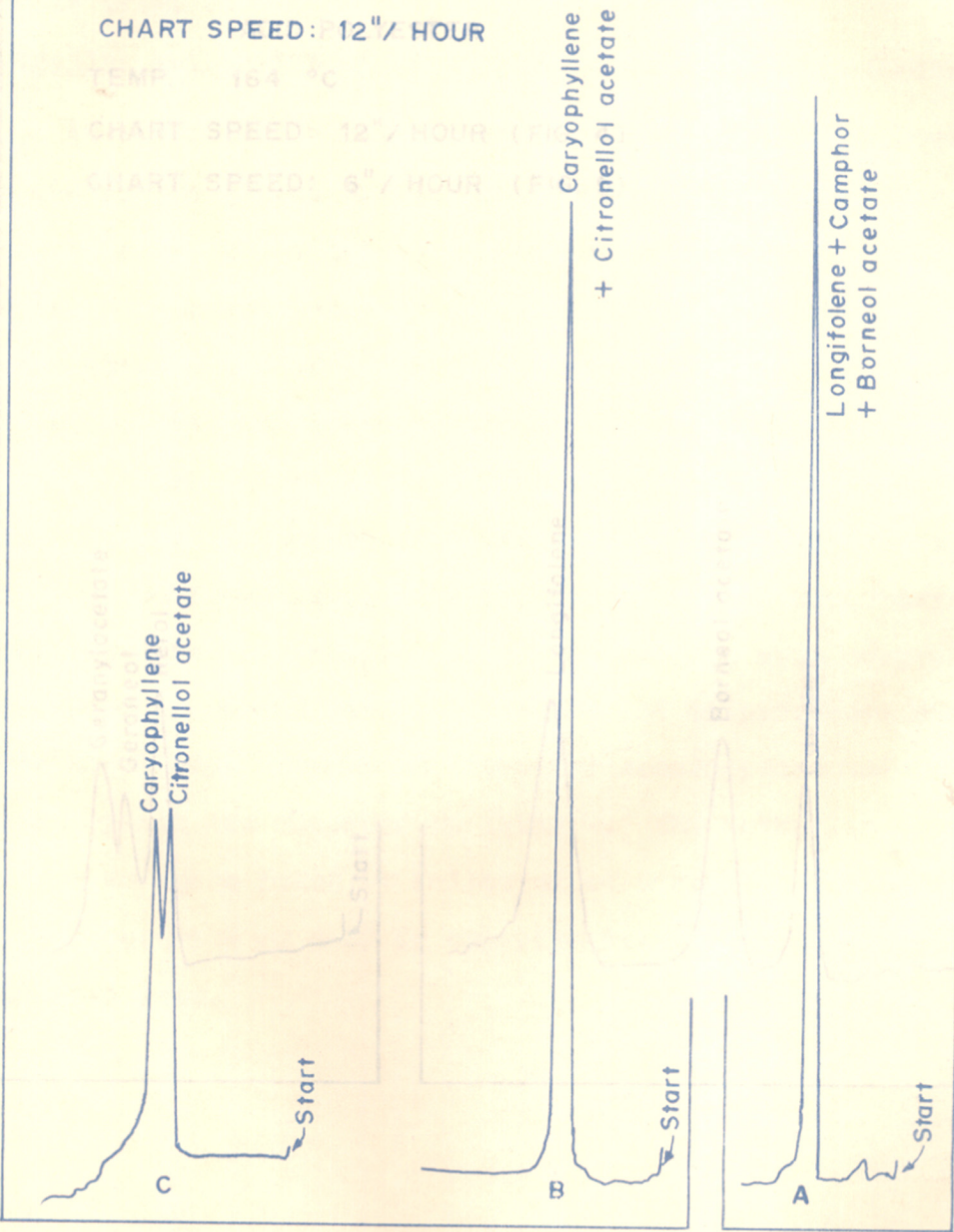


FIG. 5

FIG. 4

FIG. 3

FIG. 2

PHASE: 1,4-BUTENEDIOL-1,16-HEXADECANE DICARBOXYLIC
ACID POLYESTER

TEMP.: 164 °C

CHART SPEED: 12" / HOUR (FIG. 4)

CHART SPEED: 6" / HOUR (FIG. 5)

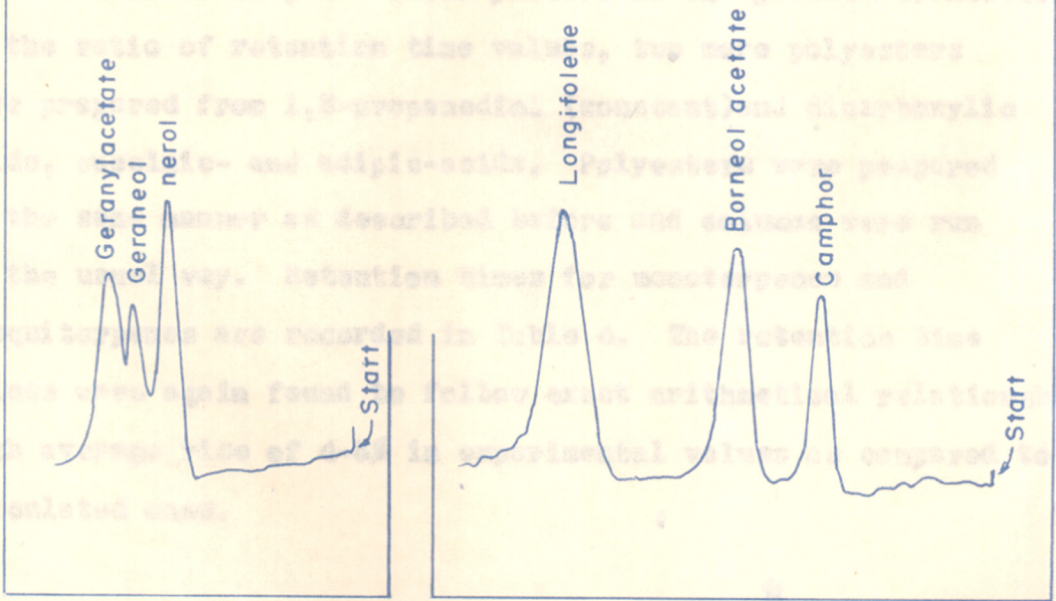


FIG. 5

FIG. 4

on 1,16-dicarboxylic acid column, because geranyl acetate, as a result of better stretching, will emerge after both the alcohols (Fig. 5).

Comparative evaluation of saturated and unsaturated polyesters

It was noted in the earlier studies^{22,23} that polyesters from diethylene glycol and various dicarboxylic acids show exact arithemtical relationship in retention times, while polyesters from ethylene-glycol series give 26% higher experimental values as compared to calculated ones and 1,5-pentane-diol series give 26% lower values of the retention times.

In order to get a clear picture of the gradual^{al} transition in the ratio of retention time values, two more polyesters were prepared from 1,3-propanediol (constant) and dicarboxylic acids, succinic- and adipic-acids. Polyesters were prepared in the same manner as described before and columns were run in the usual way. Retention times for monoterpenes and sesquiterpenes are recorded in Table 4. The retention time values were again found to follow exact arithemtical relationship with average rise of 4-5% in experimental values as compared to calculated ones.

Table 4

Retention time in minutes at 100°C: 1:3 propanediol
(glycolic fragment) constant

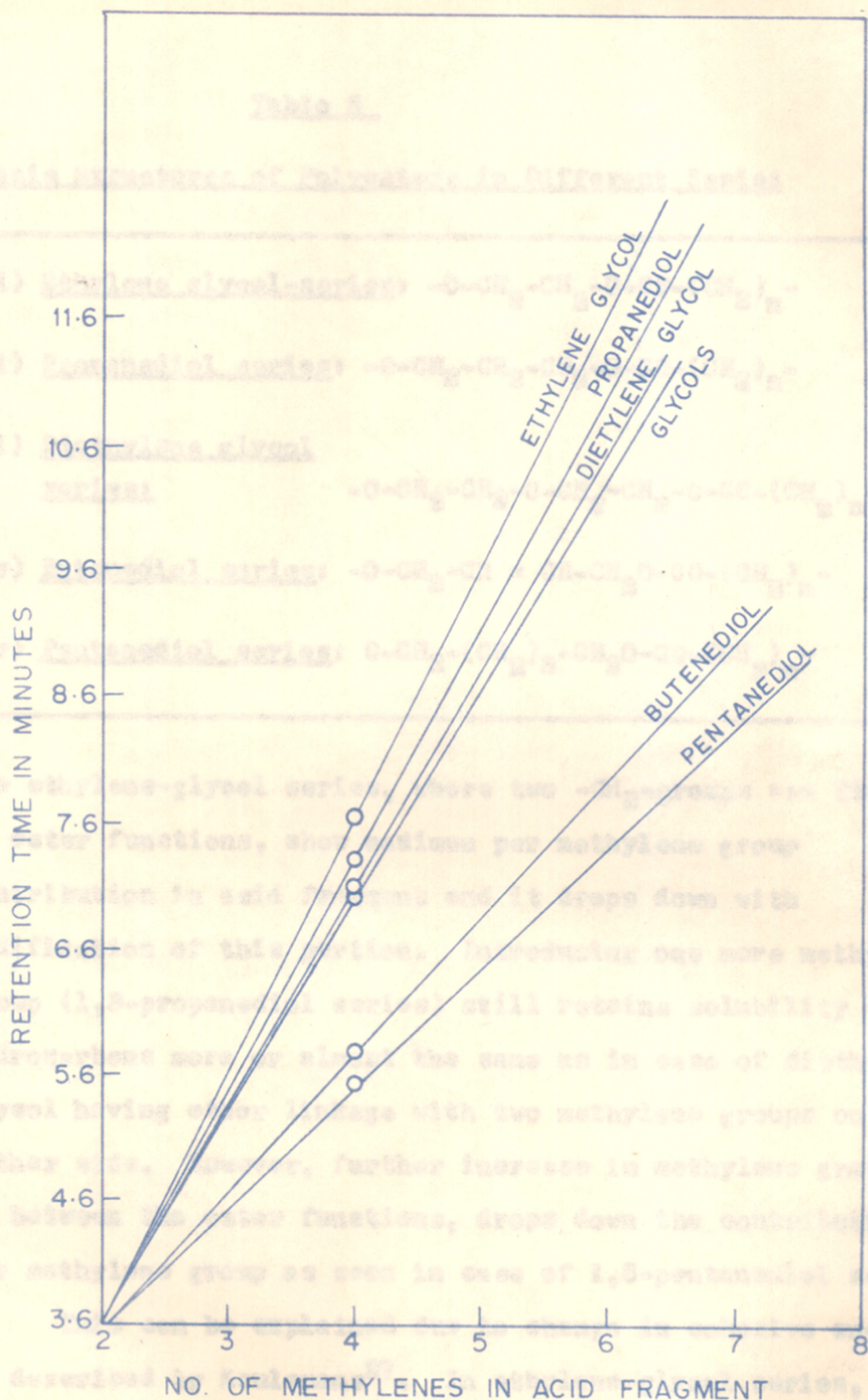
Compound	Acidic fragments	
	Succinic-	Adipic-
α -Pinene	2.90	5.53
β -Pinene	4.41	8.59
Limonene	7.35	13.78
Camphene	3.66	7.43
Δ^3 -Carene	5.50	15.23
p-Cymene	10.15	19.20

Retention time in minutes at 162.5 \pm 0.5°C

Longifolene	5.01	10.50
Longicyclene	3.91	8.83
Isolongifolene	4.33	9.30
Humulene	7.73	15.60
Caryophyllene	5.98	12.75
Carvone	9.50	16.30
Camphor	4.75	8.33
Geraniol	10.75	19.40
Geraniolacetate	9.45	17.73
Nerol	9.66	17.08
Bornylacetate	5.43	10.46
α -Terpeniol	7.03	12.53

Now to trace down the transition from ethylene-glycol to 1,5-pentanediol series, retention times of longifolene (as an example) were normalised to the same value of 3.61 on succinic acid polyesters with the subsequent conversion of retention times on adipic acid polyesters. When these retention times were plotted against intervening methylene groups of the acidic fragments, a gradual change in slopes in various series was observed (Graph 4). Diethylene glycol series, which follow the exact arithmetical relationship, holds the middle position. Ethylene-glycol series having 26% higher experimental values occupies the highest position, followed by the 1,3-propanediol series with 4-5% rise in values. On the lower side of diethylene-glycol series, the first slope is for 1,4-butanediol series with 20% lower values and the lowest one is that of 1,5-pentanediol series with 25% fall in values of retention time. The slope of series of polyesters with change in glycols and constant acid fragment coincides with that of the diethylene glycol series. These variations in experimental values of retention times may be attributed to structural features of the glycol fragments of the various polyesters.

If the basic structures of all these polyester series are considered (Table 5), the relative change in contribution per methylene ($-\text{CH}_2-$) group in retention time value is influenced by structural differences in glycol fragments.



GRAPH. 4. VARIATION IN THE ARITHMETICAL RELATIONSHIP OF POLYESTERS PREPARED FROM DIFFERENT GLYCOLS AND SUCCINIC-ADIPIC-ACIDS

(RETENTION TIMES OF LONGIFOLENE ARE NORMALISED TO 3.61 ON SUCCINIC ACID-GLYCOLS POLYESTERS AND SUBSEQUENT CONVERSION OF RETENTION TIMES ON ADIPIC ACID-GLYCOLS POLYESTER COLUMNS)

Table 5Basic Structures of Polyesters in Different Series

-
- i) Ethylene glycol-series: $-O-CH_2-CH_2-O-CO-(CH_2)_n-$
- ii) Propanediol series: $-O-CH_2-CH_2-CH_2-O-CO-(CH_2)_n-$
- iii) Diethylene glycol series: $-O-CH_2-CH_2-O-CH_2-CH_2-O-CO-(CH_2)_n-$
- iv) Butenediol series: $-O-CH_2-CH=CH-CH_2-O-CO-(CH_2)_n-$
- v) Pentenediol series: $O-CH_2-(CH_2)_3-CH_2-O-CO-(CH_2)_n-$
-

^T
 The ethylene-glycol series, where two $-CH_2$ -groups are flanked by ester functions, show maximum per methylene group contribution in acid fragment and it drops down with modification of this portion. Introducing one more methylene group (1,3-propanediol series) still retains solubility for hydrocarbons more or almost the same as in case of diethylene-glycol having ether linkage with two methylene groups on either side. However, further increase in methylene groups in between the ester functions, drops down the contribution per methylene group as seen in case of 1,5-pentenediol series.

This can be explained due to change in cohesive energy as described by Keulemans²⁷. In ethylene-glycol series, both

the methylene groups are comparatively more active as they are flanked by electron drawing groups (ester groups) and will have maximum cohesive energy. As more methylene groups are introduced in between, activity of end methylene groups is reduced further with consequent decrease in cohesive energy.

When polarity of the polyester phases due to ethereal oxygen and double bond is compared, there is, as expected, greater affinity of unsaturated centres of hydrocarbons towards the lone pair of electrons of ethereal oxygen of polyester than the double bond at its place. The same is true when functions are interchanged in solute and substrate. The neutral oxygenated compounds such as ketones, esters, etc. have more affinity and solubility in unsaturated polyesters than that in polyesters consisting of ethereal functions.

To continue the systematic evaluation of polyester type stationary phases, it was decided to investigate polyesters with aromaticity. The investigations on these are described in the subsequent chapters.

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CHAPTER - II

USE OF AROMATIC ESTERS AS STATIONARY PHASES IN GAS LIQUID-CHROMATOGRAPHY

S U M M A R Y

Esters of phthalic acid from dimethyl phthalate to di-n-nonyl phthalate were prepared and evaluated as liquid substrates for use in GLC. A number of compounds including aromatic hydrocarbons, paraffins, halogenated paraffins, esters, ketones and monoterpenic hydrocarbons were analysed. It was observed that the retention time of these compounds show a linear rise with increase in the number of methylene groups in the alcoholic fragment of the phthalate ester. The rise in retention time, however, does not follow arithmetical relationship observed earlier in case of polyesters (prepared from glycols and aliphatic dibasic acids).

The columns were run at 96°C to avoid any losses due to the evaporation of the stationary phase.

Retention time contributions per intervening methylene group of the liquid phase along with overall total rise in retention time upto the last column have been calculated for all the compounds studied. Some interesting observations have been made regarding the chromatographic behaviour of these compounds on phthalate ester substrates.

A few substituted phthalate esters have also been prepared and their behaviour as stationary phases towards these compounds was compared. It was observed that the solubility of all the compounds is decreased on these esters.

The esters of phthalic acid with various aliphatic alcohols have been widely used as stationary phases in gas-liquid chromatography (GLC). In fact, with the advent of GLC technique, some of these esters were pioneer substrates to be utilised by several workers in this field. It is impossible to cover up the detailed investigations of all the workers here. However, a few interesting applications of these esters as liquid phases have been described in this brief introduction.

As early as in 1954 Ray employed dinonyl phthalate for the separation of hydrocarbons, alcohols, esters, ethers, aldehydes, ketones etc.¹ and also for separation and analysis of gaseous mixtures of propane, propylene, and C₄-hydrocarbons².

Initial work on separation of fluorine compounds was carried by Evans et al.³ using dinonylphthalate liquid substrate. On the same phase Barefoot⁴ studied chloromethanes, chloroethanes and chloroethylenes and compared the separation with that on other substrates.

Separation of lower hydrocarbons along with their isomers have been tried by several workers in the earlier days of development of GLC technique⁵⁻⁸.

James and Martin⁹ employed dioctyl phthalate along with other phases for the separation of methyl esters of lower fatty acids upto n-caproic acid. Fredericks and Brooks¹⁰ used di-isodecylphthalate with dimethyl-sulfolane as liquid phase to analyse gaseous hydrocarbons.

Blom et al.⁶ used dinonylphthalate for determination of aromatic hydrocarbons in wash-oil and simultaneously Brooks et al. tried it for separation of aromatic and paraffinic hydrocarbons¹³.

The presence of chlorotoluenes¹⁴ was detected on dinonylphthalate column in a mixture obtained in the reaction of chlorobenzene with methyl free radicals. Similarly analyses of halogenated hydrocarbons was carried out on such ester phases by Pollard et al.¹⁵ as well as Troupe and Golner¹⁶.

Synthetic mixtures of peroxides, alcohols and water were analysed on dinonylphthalate by Abraham et al.¹⁷ and using the same phase Spencer et al.¹⁸ analysed mercaptans and sulphide compounds. Young plotted¹⁹ a number of family plots for the various ketones on dinonylphthalate between retention volume and the number of carbon atoms.

Studies on separation of low boiling fluorinated hydrocarbons²⁰, deuterio organic compounds²¹, low-boiling²² phenols, xylene isomers²³ and reaction products of hydration of α -pinene²⁴ were carried out by different groups of workers.

Langer et al.²⁵ have investigated tetrachlorophthalates as liquid phases for the separation of meta- and para-xylene. Janak and Harivnac²⁶ have reviewed cases of aromatic selectivity in terms of π -interactions. The investigations of Chen et al.²⁷ have shown that the tetrachlorophthalate esters provide a good means of separating meta- and para-isomers. Littlewood²⁸ has, however, questioned the formation of specific

aromatic π -interactions in some cases. Cooper et al.²⁹ have examined the retention data of substituted anilines, aromatic hydrocarbons and heterocyclic compounds on dinonyl tetrachlorophthalate and conclude that charge-transfer interactions do contribute to the retention of aromatic donors. Ryba³⁰ reports the use of chlorophthalate esters for the separation of C₇-C₁₀ n-mono-olefins.

Evaluation of the individual as well as combination of these ester phases with Bentone-34, tritolylphosphate, etc. has been investigated by several workers in various fields³¹⁻³⁶. Miyake et al.³⁹ separated C₆-C₁₀ aromatic hydrocarbons using mixed stationary phases of dinonylphthalate and 2,4-dinitrochlorobenzene.

Determination of physical constants by GLC

The technique of GLC has been applied for the determination of certain physical constants of some compounds. Kwantes and Rijnders³⁷ have calculated activity coefficients at infinite dilution for a number of halogenated hydrocarbons on dinonyl phthalate from the data of Pollard and Hardy¹⁵. Svered et al.³⁸ measured activity coefficients for the series ethyl- to octyl-nitrate, nitromethane to 1-nitrobutane, and n-pentane to n-nonane on squalane and dinonylphthalate as solvents.

To evaluate the solid support, Dimbat et al.¹¹ used di-isodecylphthalate as substrate, while using the same phase

Porter et al.¹² studied partition coefficients, apparent heats of solutions from GLPC measurements.

A derivatographic study of the thermal stability of 35 substrates such as phthalates, sebacates etc. used in GLC has been carried out by Byl'ev et al.⁴⁰ Gesheva et al.⁴¹ used dinonylphthalate for the separation of the constituents of a mixture of alkyl astatides. Stateczna et al.⁴² showed that diphenylphthalate is selective towards aromatics.

Saha and Giddings⁴³ studied the relative column efficiencies of various chromosorbs using dinonylphthalate as the liquid phase. Relative retention times of 154 hydrocarbons are presented by Csicsery and Pines⁴⁴ on dinonylphthalate, dipropyltetrachlorophthalate and other phases.

From the above discussion, it is evident that although phthalic acid esters have been widely used as stationary phases for quite some time, a systematic study of these esters and their comparative evaluation as GLC solvents has not been carried out. Only recently Bulgarian scientists^{45,46} have tried to investigate phthalic esters as substrates in a systematic way. A brief outline of their work is given below.

Studies by Bulgarian scientists

For a specific analytical application, the selection of a suitable stationary phase is often empirical. The thermodynamic data^{45,46} for solution of organic vapours in high boiling solvents can be obtained from GLC measurements.

Such data is connected with the problem of solute-solvent interactions and provide a basis for the selection of liquid phases in GLC. Petsev and Dimitrov^{45,46} investigated phthalic esters in an attempt to establish some correlation between the structure of stationary phases and their behaviour in GLC from thermodynamic point of view. They found that the structure of the liquid phase has a profound influence on the activity coefficients of the aromatic hydrocarbons. The activity coefficients of paraffins and cyclohexanes was found to decrease with increasing number of methylene groups in the alcohol alkyl chain of the ester. They have also studied the polarity of all these phases^{47,48}.

They have further attempted to study the volatility of phthalic acid esters at the operating conditions⁴⁹ and presented retention time data after applying corrections for the evaporation of stationary phase from the column⁵⁰.

Present Investigations

In this laboratory, in continuation of systematic studies of polyesters⁵¹⁻⁵⁴ as stationary phases ranging from straight chain saturated polyesters, unsaturated polyesters to aromatic polyesters, investigation of simple phthalic acid esters as liquid phases was simultaneously undertaken and the results are incorporated in this Chapter. The approach by the author is to bring about stepwise modification in the structure of the saturated polyesters (normally prepared from glycols and straight-chain dicarboxylic acids) by

introducing unsaturated centre (previous chapter) and then aromatic nuclei (next chapter). In order to study the gradual transition effect from unsaturated centre to aromatic nuclei in polyester stationary phases towards their behaviour in GLC analysis, it was felt that the investigation of phthalic acid esters as liquid substrates is a vital link between these three types of polyesters. Therefore, their GLC behaviour has been examined in detail.

While the investigations in the laboratory were in progress, work by Bulgarian scientists appeared in the literature and as a result certain initiative has been lost. However, approaches by them and the author are different. Studies by Bulgarian workers deal mainly with thermodynamic properties, whereas approach adopted in this laboratory concerns with comparative evaluation laying more stress on organic chemistry and practical separation of various compounds.

The studies revealed that the retention times of all the compounds studied show a linear rise with increase in the number of methylene groups in the alcoholic fragment of the ester. The rise in retention time due to intervening methylene groups does not follow arithmetical relationship observed earlier in the case of saturated polyesters⁵¹⁻⁵⁴. However, the studies of these esters revealed some interesting features which are dealt with in the discussion part.

EXPERIMENTAL

The following phthalic acid esters were synthesised in this laboratory and were examined as liquid substrates: (1) dimethylphthalate (2) diethylphthalate (3) di-n-propylphthalate (4) di-n-^{but}amyl phthalate (5) di-n-amyl phthalate (6) di-n-hexyl-phthalate (7) di-n-octylphthalate (8) di-n-nonylphthalate (9) 4-nitrodiethylphthalate (10) 4-chlorodiethylphthalate and (11) 4-fluoro-diethylphthalate.

Syntheses of esters

The unsubstituted esters were prepared from phthalic acid and the corresponding alcohol by the standard azeotropic procedure generally followed for esterification.

The substituted esters were prepared by following the method of Blicke and Smith⁵⁵ described below.

When phthalic anhydride was nitrated using concentrated nitric acid and concentrated sulphuric acid according to Littmanns' method⁵⁶, a mixture of 3-nitro- and 4-nitro-phthalic acids resulted. The nitro-acid mixture was esterified with ethyl alcohol in the presence of hydrochloric acid gas giving thereby a mixture of 4-nitrodiethylphthalate and mono-ethyl ester of 3-nitro-phthalic acid. The mono-ethyl ester of 3-nitrophthalic acid is then eliminated by treatment with sodium carbonate washing and the remaining 4-nitro-diethylphthalate was worked up in the usual way. Pure product was obtained by fractionation under reduced pressure. The fraction boiling at 210-213°C/21 mm pressure was collected.

The 4-nitrodiethylphthalate was then reduced with hydrogen in the presence of platinum oxide catalyst⁵⁷ under initial pressure of 250 pounds to get 4-amino-diethylphthalate, and subsequently it was converted to 4-chlorodiethylphthalate by diazotisation and treatment with cuprous chloride. After working up in the usual manner, the material was fractionated and the fraction boiling at 185-190°C/25 mm pressure was collected.

4-Fluoro-diethylphthalate was prepared from 4-amino-diethylphthalate by diazotisation and subsequent reaction with hydroborofluoric acid. The mother liquor, after working up, was fractionated^{and} the portion boiling at 165-170°C/25 mm pressure was collected.

The purity of the substituted as well as unsubstituted esters was ascertained by TLC and elemental analysis. For the sake of brevity details are not given.

The following representative compounds were used as the standard samples.

Aromatic hydrocarbons

(i) Benzene (ii) toluene (iii) m-xylene (iv) p-xylene and (v) ethylbenzene.

Halogenated hydrocarbons

(i) Methylene chloride (ii) chloroform and (iii) carbon tetrachloride.

Monoterpene and paraffinic hydrocarbons

(i) α -pinene (ii) β -pinene and (iii) n-hexane.

Ketones

- (1) Acetone

Esters

- (1) Ethyl acetate

All these samples were properly purified and their purity was checked by GLC analyses.

Impregnation and column fitting

The fire-brick was impregnated and filled in the column exactly in the same way as described in the previous chapter.

To have uniformity, only one column was used for this investigation also.

To properly compare the solvent capability of one stationary phase with that of another, the following column parameters were kept constant:

- 1) Inlet pressure: 130 \pm 4 mm
- 11) Column temperature: 96°C

Column conditioning

Initially the column was conditioned at 80°C for about 2 hours and the carrier gas flow rate was 4 litres per hour. The temperature was then raised to 96°C. The column became stable after about 6 hours when the recorder showed a steady base-line.

Results and Discussion

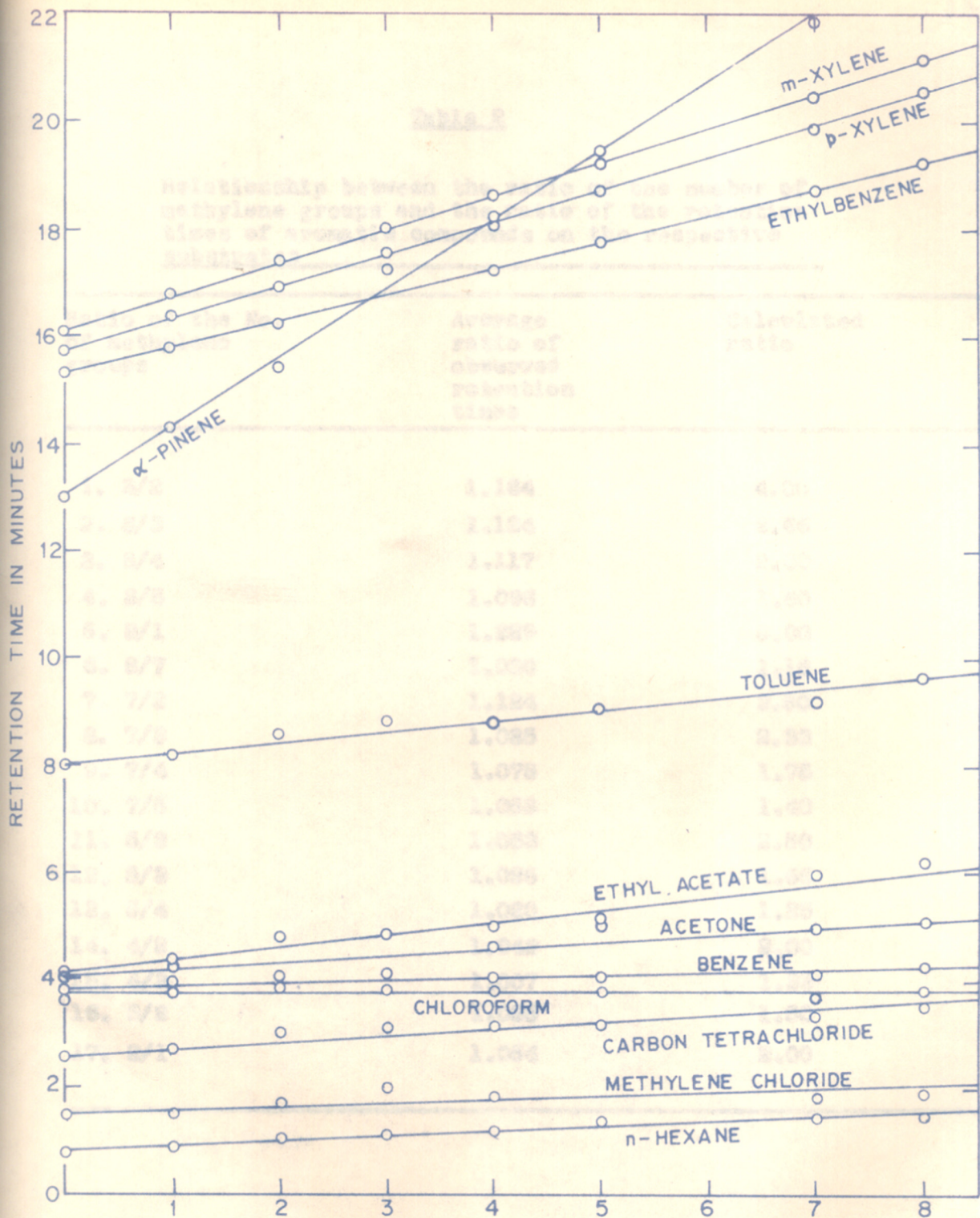
All the columns were run at 96°C and the retention time data for all the compounds investigated is presented in Table 1.

Table I
Retention time in minutes at 96°C

Sl. No.	Compound	Dimethyl phthalate	Diethyl phthalate	Di-n-propyl phthalate	Di-n-butyl phthalate	Di-n-amyl phthalate	Di-n-hexyl phthalate	Di-n-octyl phthalate	Di-n-decyl phthalate	4-Fluorodiphenyl ether	4-Nitrodiphenyl ether
1.	Benzene	3.80	3.88	3.95	4.03	4.03	4.01	4.06	4.31	2.58	2.83
2.	Toluene	8.00	8.20	8.63	8.86	8.83	9.08	9.23	9.68	5.70	6.20
3.	m-Xylene	16.10	16.81	17.40	18.00	18.65	19.25	20.50	21.20	12.33	13.51
4.	p-Xylene	15.75	16.35	16.95	17.55	18.15	18.75	19.91	20.60	11.98	13.28
5.	n-Hexane	0.78	0.88	1.03	1.16	1.15	1.38	1.46	1.48	0.70	0.68
6.	Ethyl acetate	4.20	4.36	4.91	4.88	5.00	5.10	5.98	6.25	3.35	3.80
7.	Acetone	4.04	4.20	4.10	4.10	4.60	5.01	4.98	5.11	2.60	3.50
8.	Chloroform	3.60	3.79	3.86	3.86	3.80	3.73	3.70	3.80	2.26	2.75
9.	Carbontetrachloride	2.60	2.72	3.01	3.11	3.13	3.16	3.36	3.50	1.91	2.15
10.	m-Pinene	13.00	14.30	15.46	17.20	18.20	19.46	22.08	23.73	-	8.83
11.	Ethylbenzene	15.30	15.80	16.25	17.25	17.26	17.73	18.74	19.28	-	13.03
12.	Methylenechloride	1.48	1.50	1.66	1.95	1.83	-	1.81	1.86	-	-

It is observed from these results that the retention times of all the compounds studied show a progressive rise with increase in the number of methylene groups in the alcoholic fragment of the phthalate esters. When retention times of all these compounds are plotted against the number of methylene ($-\text{CH}_2-$) groups in the esterifying alcohol of the esters, good straight lines are obtained. These are shown in graph I. Interesting enough, the linear relationship is valid upto the last ester studied i.e. di-n-nonylphthalate.

The linear rise in retention time with increase in the number of methylene groups, however, does not follow the arithmetical relationship observed in earlier studies in this laboratory with saturated polyesters⁵¹⁻⁵⁴. In Table 2, the average ratio of the retention times of the aromatic hydrocarbons on different phthalate esters are given against the expected values. It can be seen from these results that the experimental values are very low as compared with the calculated ones. This indicates that there is a gradual downward change in stretching capacity of the intervening methylene groups, as one can observe ^{from} retention time data on saturated-, unsaturated-polyesters to simple aromatic esters. In previous chapter, it has been shown that introduction of unsaturated centre in polyester molecule has shifted t_R (retention time) values 25-26% lower than the straight arithmetical pattern. Results on simple ester substrates having aromatic ring show still less stretching capacity; t_R data of α -pinene on these types of phases is self/explanatory (Table 3).



GRAPH

FIG. 1. NUMBER OF METHYLENE GROUPS IN THE ALCOHOLIC FRAGMENT OF THE PHTHALATE ESTERS

Table 2

Relationship between the ratio of the number of methylene groups and the ratio of the retention times of aromatic compounds on the respective substrates

Ratio of the No. of methylene groups	Average ratio of observed retention times	Calculated ratio
1. 8/2	1.164	4.00
2. 8/3	1.124	2.66
3. 8/4	1.117	2.00
4. 8/5	1.096	1.60
5. 8/1	1.229	8.00
6. 8/7	1.036	1.16
7. 7/2	1.124	3.50
8. 7/3	1.085	2.33
9. 7/4	1.078	1.75
10. 7/5	1.058	1.40
11. 5/2	1.063	2.50
12. 5/3	1.026	1.66
13. 5/4	1.020	1.25
14. 4/2	1.042	2.00
15. 4/3	1.007	1.33
16. 3/2	1.035	1.50
17. 2/1	1.056	2.00

Table 3Retention times (t_R) of α -pinene on different stationary phases

I Saturated polyesters⁵¹⁻⁵⁴ from diethylene glycol and different dicarboxylic acids - No. of methylene groups in the acidic fragment of the polyester

	1	2	4	8	11
t_R in minutes at 100°C	0.75	1.43	2.75	6.04	8.82

Note: Retention time shows arithmetical rise with increase in the number of methylene groups in the acidic fragment of the polyester

II Unsaturated polyesters (Chapter I) from 1,4-butenediol and different dicarboxylic acids. No. of methylene groups in the acidic fragment of polyester

	2	4	8	16
t_R in minutes at 100°C	1.70	2.17	4.00	7.57

Note: Retention time rise does not show exact arithmetical relationship with increase in the number of methylene groups. The increase is 25-26% less than the arithmetical rise

III Phthalate esters - No. of methylene groups in the alcoholic fragment of the ester

	0	1	2	3	4	5	7	8
t_R in minutes at 96°C	13.00	14.30	15.46	17.20	18.20	19.46	22.08	23.73

Note: The rise in retention time does not follow arithmetical relationship. The total rise in retention time from the first to last column is only 83%.

When retention time data of the various compounds on phthalate esters from dimethylphthalate to dinonylphthalate were examined in detail, it is observed that the total rise in the retention time of paraffinic and alicyclic hydrocarbons is of the order of 100%, whereas in the case of aromatic hydrocarbons, it is only 15-35%. For halogenated hydrocarbons (methylene chloride, chloroform and carbon tetrachloride), the total rise in retention time is very insignificant. It is of the order of 6-30%. The ^{only} ketone (acetone) studied here also shows a negligible rise (25%). Ethyl acetate falls in between paraffins and aromatic hydrocarbons in this respect. This different stretching capacity of intervening methylene groups in these phthalate phases for various types of compounds indicates the possibility of resolving mixtures of components of varied nature. This fact is practically proved and discussed in the latter part of this Chapter.

Studies by Bulgarian scientists

While studies on transition in stationary phase were in progress in this laboratory, there appeared additional papers by Petsev and Dimitrov on aromatic ester phases correcting their earlier results. In earlier communication⁵³, they have shown that the retention volume of aromatic hydrocarbons such as benzene, toluene, ethylbenzene and o-xylene decreased with increase in the number of carbon atoms in the esterifying alcohol. m-Xylene and p-xylene were, however, found to be exceptions by them showing increase in retention volume. On

the other hand, it has been found in this laboratory that retention time (or retention volume) of all the above-mentioned aromatic hydrocarbons show rise with increase in the number of methylene groups in the alcoholic fragment of the phthalate esters.

Later on, these workers, while studying the influence of the structure of phthalic acid esters on their gas chromatographic polarity⁵⁸ have reported the following figures for the retention volume of benzene:

Retention volume at 120°C on

	Dipropyl phthalate	di-n- butyl- phtha- late	di-n- hexyl phtha- late	di-n- octyl phtha- late	di-n- nonyl phtha- late	di-n-decyl phthalate
Benzene	18.0	19.2	20.2	21.3	19.8	22.4

These figures clearly show that the retention volume rises with increase in the number of carbon atoms in the alcoholic fragment of the ester, which is in perfect agreement with the findings in this laboratory. The discrepancy was due to critical temperature for evaporation of ester phases from the column.

Petsev and Dimitrov have investigated the phthalate esters at temperatures 120°, 130° and 140°C. Such temperatures are rather high for these esters and there is tendency of the

stationary phase to evaporate out from the column at a faster rate. These workers have studied the evaporation^{55,56} of stationary phase from the phthalate columns in detail and presented their data duly corrected for the amount of phase evaporated from the chromatographic column.

When higher temperatures were tried, this phenomenon of evaporation of the phthalate esters from the column was observed in this laboratory as well and to minimise the loss of stationary phase on account of evaporation, the studies of phthalate esters as liquid phases have been carried out at a temperature of 96°C. The retention times of all the compounds were recorded a number of times on different columns and no significant difference in these readings was observed indicating negligible column bleeding. Column has a relatively longer life when operated at temperatures not exceeding 100°C.

Actual resolution of various mixtures

(i) Ethylbenzene and α -pinene

π - π Electron interactions between aromatic solutes and these substrates could be illustrated nicely when retention times (t_R) of ethylbenzene and α -pinene are studied. As we go from dimethyl- or diethyl-phthalate phase to di-n-octyl or di-nonyl-phthalate phase, effect on aromatic molecules goes on decreasing and the rise in the number of intervening methylene groups helps in better stretching of non-aromatic, α -pinene, as compared with the aromatic, ethylbenzene. This

is evident from the reversal in order of elution of these compounds on higher esters. On columns upto di-n-propylphthalate, α -pinene is eluted before ethylbenzene, while on di-n-butylphthalate both α -pinene and ethylbenzene show the same retention times and are not separable (Fig. 1 and also see the graph I in which the two lines are crossing each other at this point). The elution order changes from the next ester, di-n-amylphthalate i.e. α -pinene now elutes after ethylbenzene. The difference in their retention times rises with increase in the number of methylene groups in the esterifying alcohol and as a result these compounds can again be separated on di-n-octylphthalate or di-n-nonyl-phthalate column.

(ii) Benzene and acetone

Similar is the case with benzene and acetone mixture. Benzene and acetone curves in graph I show that initially they are not separable on lower ester columns. However, greater stretching of acetone on higher columns could help to separate it from benzene (Fig. 2).

(iii) Benzene and chloroform

The mixture of benzene and chloroform is not separable on ester phases upto di-n-octylphthalate but it can be separated on di-n-nonyl phthalate column (Fig. 3). This can be explained due to the comparative greater rise in the retention time in case of the aromatic hydrocarbons than the chlorinated paraffins.

PHASE: DIMETHYL PHTHALATE
TEMP: 96 °C
CHART SPEED: 12"/HOUR

PHASE: DIBUTYL PHTHALATE
TEMP: 96 °C
CHART SPEED: 6"/HOUR

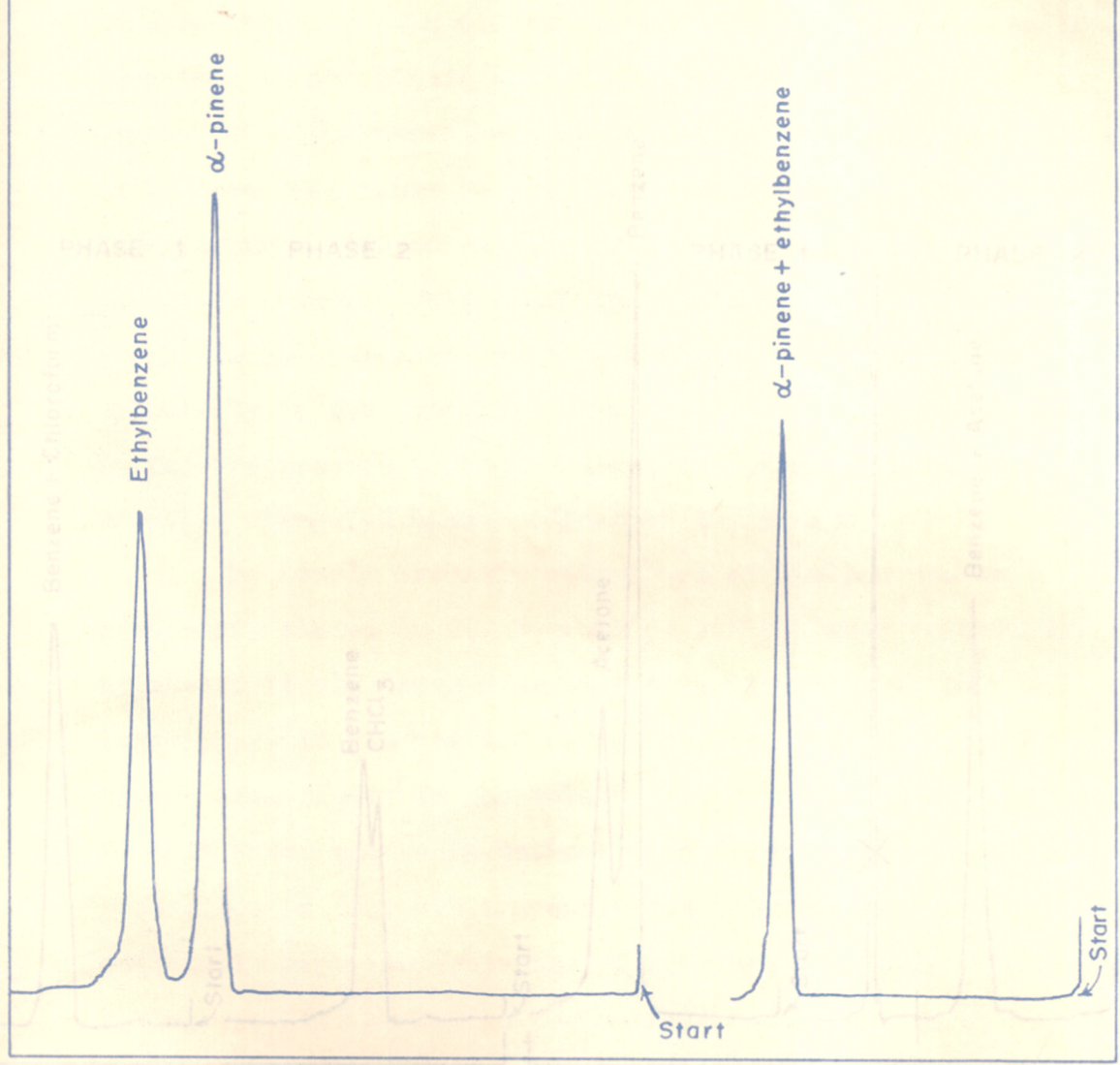


FIG. 3

FIG. 1

FIG. 2

PHASE: 1 DIBUTYL PHTHALATE
2 DINONYL PHTHALATE
TEMP: 96 °C
CHART SPEED: 12"/HOUR

PHASE: 1 DINONYL PHTHALATE
2 DIBUTYL PHTHALATE
TEMP: 96 °C
CHART SPEED: 12"/HOUR

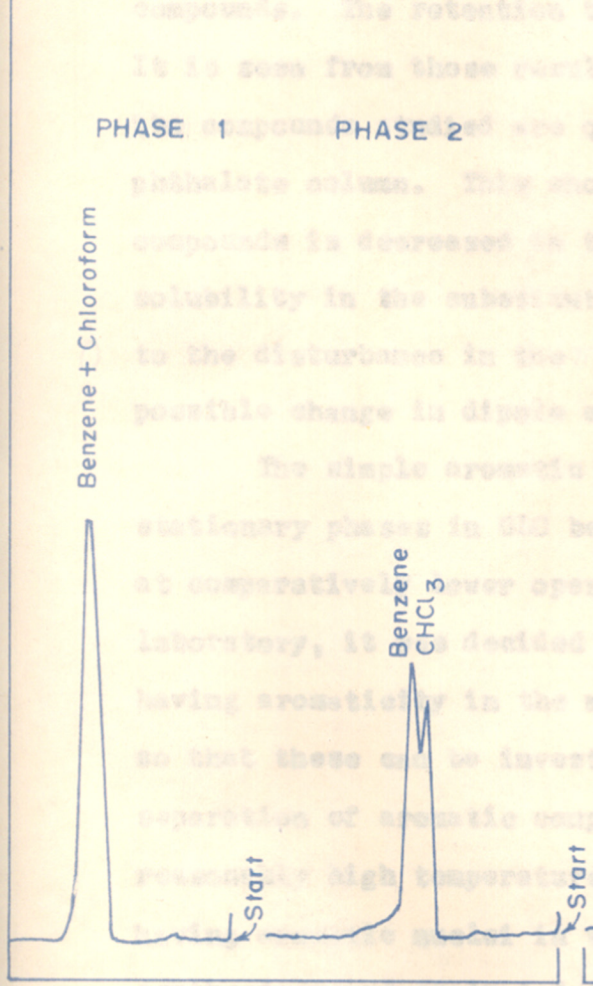


FIG. 3

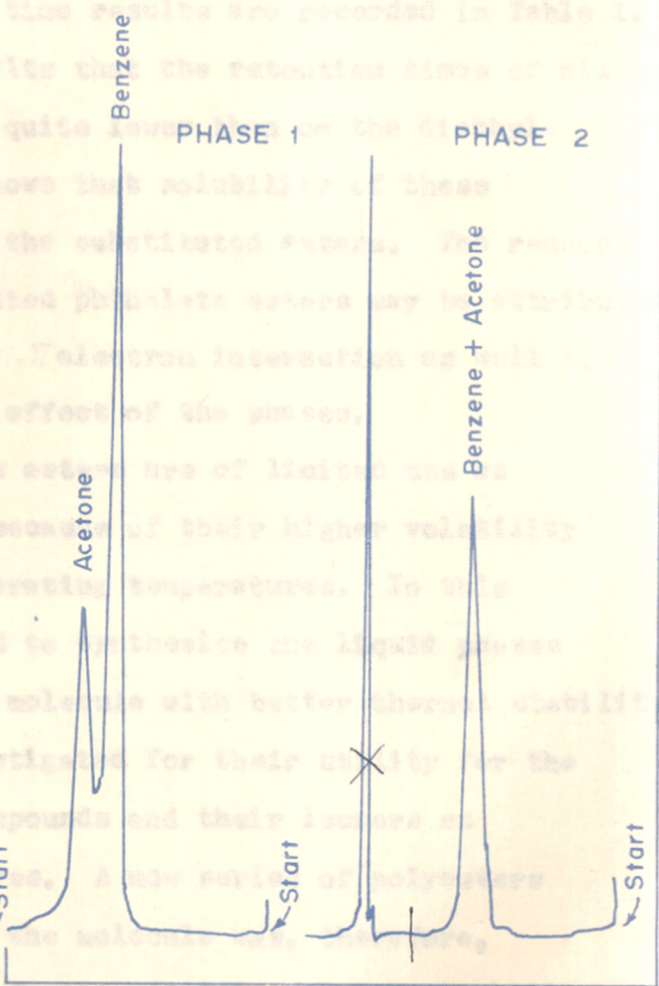


FIG. 2

Substituted phthalic acid esters

During these investigations, some substituted phthalic acid esters such as 4-chloro-, 4-fluoro- and 4-nitro-phthalic acid diethyl esters were prepared and their behaviour as the liquid phases was studied for the same compounds. The retention time results are recorded in Table 1. It is seen from these results that the retention times of all the compounds studied are quite lower than on the diethyl-phthalate column. This shows that solubility of these compounds is decreased in the substituted esters. The reduced solubility in the substituted phthalate esters may be attributed to the disturbance in the π - π electron interaction as well as possible change in dipole effect of the phases.

The simple aromatic esters are of limited use as stationary phases in GLC because of their higher volatility at comparatively lower operating temperatures. In this laboratory, it was decided to synthesise the liquid phases having aromaticity in the molecule with better thermal stability so that these can be investigated for their utility for the separation of aromatic compounds and their isomers at reasonably high temperatures. A new series of polyesters having aromatic nuclei in the molecule was, therefore, synthesised and evaluated for ascertaining their suitability for use as stationary phases in GLC. The details about these polyesters are given in the following Chapter.

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CHAPTER - III

SYNTHESES OF AROMATIC- AND SUBSTITUTED-AROMATIC
POLYESTERS AND THEIR USE AS STATIONARY PHASES
IN GAS-LIQUID CHROMATOGRAPHY

S U M M A R Y

Utility of straight chain phthalic acid esters as stationary phases is restricted due to temperature limitations. In order to introduce aromatic nuclei in the liquid substrates having temperature stability, polyesters from phthalic acid and various glycols, ranging from ethylene glycol to 1,10-decanediol, were synthesised and their performance as liquid phases was systematically studied for the separation of aliphatic, alicyclic and aromatic compounds in detail. The results of these studies are presented in this Chapter.

It was observed that although rise in retention time does not follow arithmetical relationship, percentage rise contributions per methylene group in the series is indicative of their better solvent capability to separate out isomeric compounds.

To test this capability, some substituted phthalic acid polyesters from middle order diols were further synthesised and actual separations of number of isomeric mixtures were effected.

Some of the ^{polyesters} ~~columns~~ are found to be very versatile substrates for the separation of, hitherto, unseparable or poorly separable mixtures.

INTRODUCTION

Craig¹ introduced aromatic polyesters (based on ortho-, meta-, and paraphthalic acid) as stationary phases for the analysis of fatty acid esters. He observed that o-phthalic-ethylene glycol polyester was suitable for this purpose and obtained a separation factor of 1.15 for oleic/stearic esters using this liquid substrate. He further pointed out that the aromatic polyesters have greater thermal stability than the aliphatic polyesters and these should be useful in preparative work. Sweeley and Horning² investigated ethylene glycol-isophthalic acid polyester for the separation of steroids. This polyester was found to be thermally stable at temperatures upto 200-220°C. Rudloff³ employed Craig polyesters (prepared from phthalic acid and ethylene glycol) for the separation of oxygenated terpenes, sesquiterpene alcohols and monophenols at 190-220°C. Vigdergauz et al.⁴ have used phthalic anhydride polyester for the separation of mixture of C₆-C₁₀ n-paraffins.

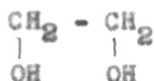
Recently, Sankpal⁵ has prepared polyesters from phthalic acid, isophthalic acid and terephthalic acids with diethylene glycol and evaluated their solvent capability in GLC for several terpenic and some non-terpenic compounds.

As a part of systematic evaluation of polyester type stationary phases, synthesis of aromatic polyesters was undertaken and their behaviour as liquid phases in GLC was

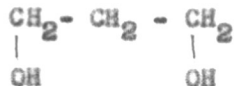
investigated for the separation of aliphatic, alicyclic and aromatic compounds. The introduction of aromatic nuclei in polyester molecule was thought to make the polyester thermally stable and good solvents for aromatic compounds and their substituted isomers. A series of polyesters from phthalic acid and various glycols from ethylene glycol to 1,10-decanediol were, therefore, synthesised and systematically examined for analysis of various types of compounds and the detailed results are presented in this part of the thesis.

EXPERIMENTAL

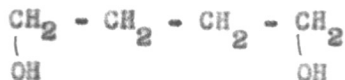
A series of polyesters were synthesised from phthalic acid (constant) and various 1, ω -glycols, HO-CH₂-(CH₂)_n-CH₂-OH, ranging from ethylene glycol (n = 0) to 1,10-decane-diol (n = 8). The sources of all the glycols are described below.

1. Ethylene glycol

It was commercially available. It was purified by careful fractionation and its purity was tested by GLC analysis (single peak).

2. 1,3-Propane-diol

It was available from the laboratory stock. It was purified by distillation and was found to be 95-96% pure as tested by GLC analysis.

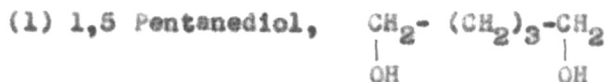
3. 1,4-Butanediol

It was not easily available and was, therefore, synthesised in the laboratory.

Pure succinic acid was esterified to its diethyl ester. The diethyl succinate was carefully distilled under vacuum. This

distilled product was reduced with lithium aluminium hydride as usual. The resulting 1,4-butanediol was distilled under vacuum and the fraction boiling at 118-120°C/10 mm was collected. Its purity was checked by elemental analysis (Found: C, 53.25%; H, 11.12%; $C_4H_{10}O_2$ requires C, 53.33%; H, 11.09%).

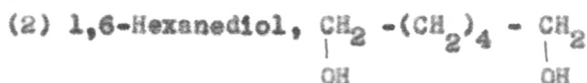
The following diols were similarly prepared from the corresponding diesters by lithium aluminium hydride reduction described above and their purity was tested by b.p., m.p. and elemental analysis.



B.p. 131-133°C/12 mm. Elemental analysis:

Found: C, 57.85% and H, 11.50%

$C_5H_{12}O_2$ requires: C, 57.71% and H, 11.54%



M.p. 41°C (lit. 42°C) Found C, 61.20%; H, 11.82%

$C_6H_{14}O_2$ requires: C, 61.01%; H, 11.87%



M.p. 73°C (lit. 73-75°C). Found: C, 68.92%; H, 12.69%

$C_{10}H_{22}O_2$ requires : C, 68.98%; H, 12.65%

Preparation of the polyesters

The polyesters from phthalic acid and various glycols were prepared in the same manner as described in the previous

Chapter with some modifications.

In the case of unsaturated polyesters, the polymerisation reaction was carried out at 110-120°C for 2 hours and then at 140°C/2 mm pressure for 2 more hours. A few preliminary experiments showed that this range of temperature was rather low. The temperature of polymerisation reaction was, therefore, maintained at 145-150°C throughout. At this temperature, the initial mixture of the phthalic acid and the corresponding glycol at once became homogeneous and the process of polyester formation was found to be satisfactory.

The resulting viscous material was dissolved in chloroform. The solution was washed with dilute sodium bicarbonate solution and then repeatedly with water till neutral. It was dried over anhydrous sodium sulphate and the solvent removed under vacuum at room temperature.

All these polyesters were viscous semi-solids. The approximate molecular weights of the polyesters were determined by the end group titrations in the alcoholic solutions and the results are given in Table 1.

Table 1

Molecular weights of the polyesters as determined by the end group titration

S.No.	Components of the polyester		Molecular weights
	Acid	Glycol	
1.	Phthalic acid	Ethylene glycol	2,124; 2,152
2.	"	1,3-propanediol	3,107; 3,150
3.	"	1,4-butanediol	2,601; 2,575
4.	"	1,5-pentanediol	3,170; 3,192
5.	"	1,6-hexanediol	4,018; 4,050
6.	"	1,10-decanediol	4,047; 4,005

The following compounds were used as the standard samples during this investigation.

Terpenic compounds

(i) α -Pinene, (ii) β -Pinene and (iii) p-Cymene

Aromatic hydrocarbons

(i) Benzene (ii) Toluene (iii) m-Xylene (iv) p-Xylene and (v) Ethylbenzene.

Aliphatic alcohols

(i) Methyl alcohol (ii) n-Propyl alcohol (iii) Isopropyl alcohol (iv) n-Butyl alcohol (v) sec. butyl alcohol and (vi) tert-Butyl alcohol.

Other compounds

(i) n-Hexane (ii) Chloroform (iii) Carbon tetrachloride (iv) Ethyl acetate and (v) Acetone.

All these samples were 96-98% pure as found by GLC analyses.

Impregnation and column filling

This was done according to the procedure given in the previous Chapter.

All the column parameters were maintained constant during this study also.

Inlet pressure: (i) 130 ± 4 mm at 98°C

(ii) 155 ± 5 mm at 120°C

Results and discussion

Stability

The column temperature was raised to 220° to test the stability of the polyester phases. No bleeding of the liquid

phase was observed and even after heating at the same temperature for about 24 hours, the recorder showed a steady base-line. The retention times of a few samples were checked and found to be the same.

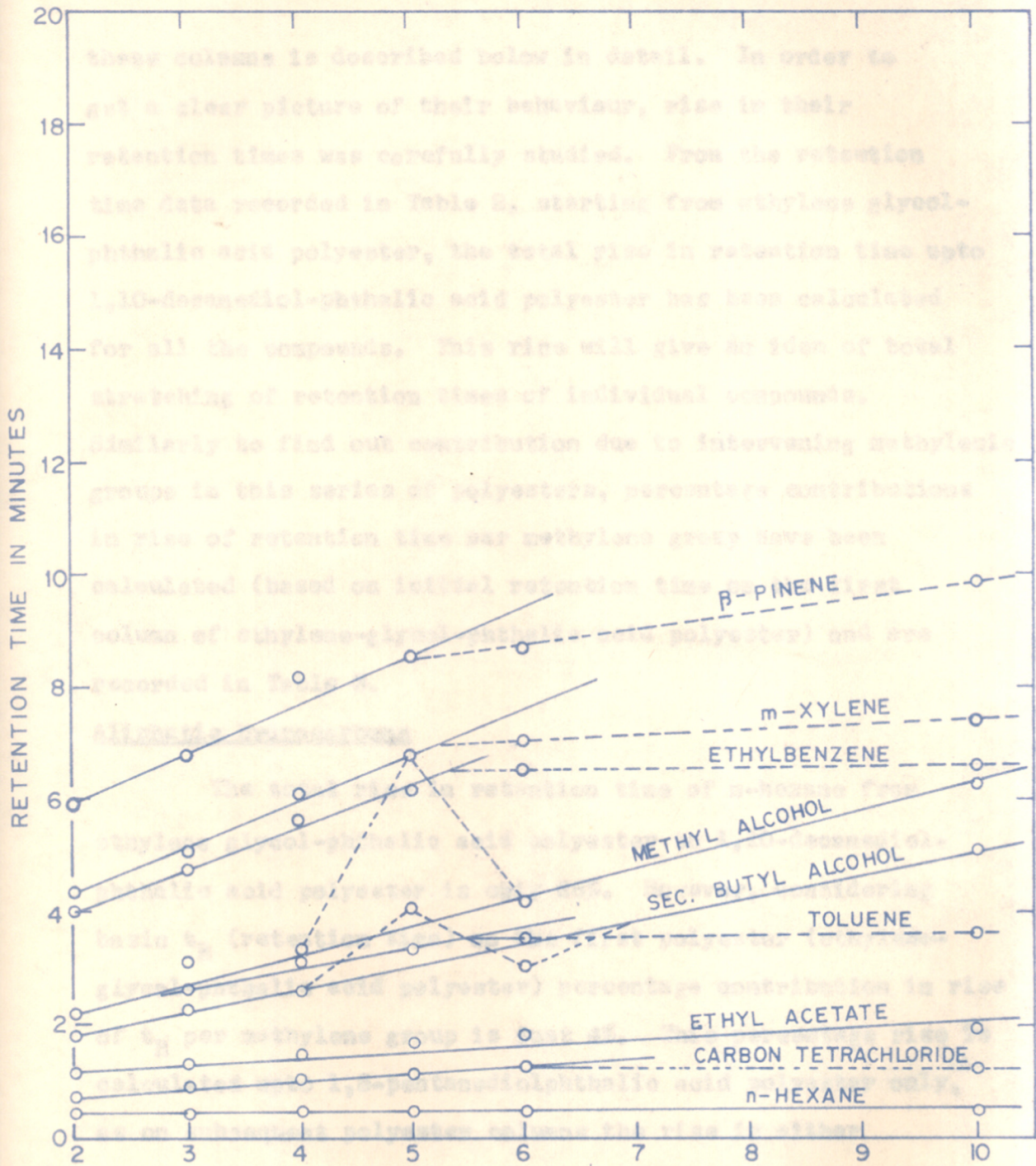
Retention time data

The retention times of all the compounds studied were recorded at temperatures of 98° and 120°C. The results are presented in Table 2.

The behaviour of the aromatic polyesters towards the different classes of compounds is somewhat peculiar (Graph I). In case of aliphatic hydrocarbon (hexane) and the ketone (acetone), linear rise in retention time is observed. The most interesting observation is that alcohols show a linear rise in retention time on polyesters starting from ethylene glycol-phthalic acid polyester upto the last 1,10-decane-diol-phthalic acid polyester investigated. However, the behaviour of middle order polyesters, i.e. 1,5-pentanediol-phthalic acid and 1,6-hexanediol-phthalic acid, is strange. Aromatic hydrocarbons show a linear rise in retention time upto the 1,5-pentanediol-phthalic acid polyester, whereas the aliphatic chlorinated compounds as well as the ester indicate linear rise in retention time upto 1,6-hexanediol-phthalic acid polyester column. Terpenic compounds (α -pinene and β -pinene) show a linear rise in retention time upto 1,4-butanediol-phthalic acid polyester column only. The behaviour of different types of compounds on

Retention time in minutes

S.No. Compounds	Ethylene glycol phthalic acid polyester		1,3-Propane diol-phthalic acid polyester		1,4-Butanediol diol phthalic acid polyester		1,5-pentane-ester		1,6-hexane-diols-phthalic acid polyester		1,10-decane-diols phthalic acid polyester	
	98°C	120°C	98°C	120°C	98°C	120°C	98°C	120°C	98°C	120°C	98°C	120°C
1. Benzene	1.08	0.66	1.30	0.80	1.53	0.87	1.68	1.00	1.80	1.10	1.71	1.10
2. Toluene	2.16	1.26	2.60	1.50	3.15	1.67	3.33	1.83	3.51	2.06	3.61	2.18
3. m-Xylene	4.36	2.33	5.05	2.93	6.08	2.97	6.71	3.41	7.05	3.55	7.41	4.26
4. p-Xylene	4.21	2.25	4.91	2.73	5.95	2.89	6.45	3.40	6.80	3.50	7.16	4.16
5. p-Cymene	-	-	-	-	17.00	7.35	17.75	8.05	18.53	8.40	19.09	10.01
6. Ethylacetate	1.18	0.65	1.28	0.75	1.45	0.79	1.63	1.01	1.80	1.13	1.96	1.10
7. Ethylbenzene	4.00	2.16	4.73	2.53	5.63	2.90	6.13	3.21	6.55	3.33	6.59	3.86
8. α-Pinene	4.08	2.11	4.58	2.46	5.60	2.65	5.55	2.86	5.60	3.20	6.33	3.58
9. β-Pinene	5.90	2.96	6.76	3.60	8.16	3.81	8.48	4.25	8.65	4.41	9.76	5.41
10. Acetone	0.90	0.56	1.03	0.70	1.16	0.80	2.06	0.95	1.36	1.06	1.86	1.21
11. Chloroform	1.06	0.61	1.23	0.76	1.48	0.80	1.61	0.93	1.75	1.03	1.60	1.00
12. Carbontetra-chloride	0.71	0.48	0.90	0.56	1.03	0.63	1.13	0.71	1.23	0.80	1.23	0.83
13. n-Hexane	0.40	0.23	0.41	0.26	0.43	0.27	0.45	0.23	0.46	0.28	0.50	0.31
14. Methyl alcohol	2.16	1.00	3.10	1.43	3.30	1.90	6.78	4.86	4.15	2.16	6.33	-
15. Propyl alcohol	2.15	1.63	2.71	1.50	3.50	1.50	4.83	2.95	4.86	3.21	7.93	4.00
16. Isopropyl alcohol	1.13	0.61	1.31	0.73	1.51	0.81	2.35	1.20	2.50	1.32	3.03	1.81
17. n-Butyl alcohol	-	2.05	5.15	2.50	6.23	2.62	11.50	4.43	7.33	2.65	14.00	6.50
18. sec-Butyl alcohol	1.80	1.06	2.28	1.30	2.60	1.32	4.03	1.78	3.05	1.80	5.03	2.56
19. tert-Butyl alcohol	-	0.60	1.20	0.68	1.26	0.70	1.46	0.83	1.75	0.90	1.90	1.00



GRAPH. I. NO OF METHYLENE GROUPS IN THE GLYCOL FRAGMENT OF THE POLYESTER

these columns is described below in detail. In order to get a clear picture of their behaviour, rise in their retention times was carefully studied. From the retention time data recorded in Table 2, starting from ethylene glycol-phthalic acid polyester, the total rise in retention time upto 1,10-decanediol-phthalic acid polyester has been calculated for all the compounds. This rise will give an idea of total stretching of retention times of individual compounds. Similarly to find out contribution due to intervening methylenic groups in this series of polyesters, percentage contributions in rise of retention time per methylene group have been calculated (based on initial retention time on the first column of ethylene-glycol-phthalic acid polyester) and are recorded in Table 3.

Aliphatic hydrocarbons

The total rise in retention time of n-hexane from ethylene glycol-phthalic acid polyester to 1,10-decanediol-phthalic acid polyester is only 25%. However, considering basic t_R (retention time) on the first polyester (ethylene-glycol-phthalic acid polyester) percentage contribution in rise of t_R per methylene group is just 4%. This percentage rise is calculated upto 1,5-pentanediolphthalic acid polyester only, as on subsequent polyester columns the rise is either

Table 3

Calculations of contribution* per methylene group in rise in retention time of compounds on polyester phases upto 1,5-pentanediol-phthalic acid polyester at 98°C

S.No.	Compound	Contribution per -CH ₂ -group in rise in t _R ("c" value)	%Contribution per -CH ₂ -group in rise in t _R %
1.	Benzene	0.24	22.20
2.	Toluene	0.39	18.00
3.	m-Xylene	0.78	17.96
4.	p-Xylene	0.75	17.76
5.	Ethyl acetate	0.15	12.13
6.	Ethylbenzene	0.71	18.00
7.	α-Pinene	0.49	12.00
8.	β-Pinene	0.86	14.00
9.	Acetone	0.38	42.00
10.	Chloroform	0.18	16.00
11.	Carbon tetrachloride	0.14	19.00
12.	n-Hexane	0.17	4.20
13.	Methyl alcohol	1.54	71.00
14.	n-Propyl alcohol	0.90	42.00
15.	Isopropyl alcohol	0.40	35.00

*Note: The figures of contribution are based on the initial retention times recorded on first column i.e. ethylene glycol-phthalic acid polyester

**'c' (Contribution in rise in retention time per -CH₂-group) value

is calculated by the formula, $c = \frac{t_R^x - t_R^y}{x - y}$, where

t_R^x and t_R^y are the retention times on polyesters having x and y methylene groups respectively. The percentage contribution per -CH₂-group in rise in t_R is calculated from the expression

$$\% \text{ contribution} = \frac{\text{"c" value} \times 100}{t_R \text{ on first polyester}}$$

insignificant or negative. The percentage contribution in rise of t_R in case of hydrocarbon, when compared with other polyester phases, is found to be 100% for saturated polyesters²⁹ (arithmetical rise) and 25% for unsaturated polyesters (Chapter I).

Acetone

As in case of hydrocarbon, acetone shows linear rise in t_R throughout. In addition, it has better solubility in these substrates as indicated by the total rise in retention time (t_R) as 100% and percentage contribution in rise per methylene group is 42%.

Chloroparaffins and ethyl acetate

It is observed from the retention time data that these compounds show linear rise in retention time upto the last column, 1,10-decanediol-phthalic acid polyester. The total rise in retention time is of the order of 70-75%. However, their percentage contribution in rise in retention time per methylene group upto 1,5-pentenediol-phthalic acid polyester is 18%.

Aromatic hydrocarbons

This group of compounds show a linear rise in the retention time upto 1,5-pentenediol-phthalic acid polyester column only, while their average total rise upto the last column is of the order of 65-70%. The percentage contribution in rise in retention time per methylene group is 18%, while it was 12% on unsaturated polyester columns (Chapter I) and

59% on saturated polyester columns²⁹.

Ternenic compounds

These compounds show a steep rise in retention time, upto 1,4-butanediol-phthalic acid polyester column and afterwards, the rise changes its pattern. The rise in retention time still shows linearity but of a very reduced order. The total rise in retention time is of the order of 60%. The percentage contribution in rise per methylene group is 14%; while the figures for saturated²⁹ and unsaturated polyesters (Chapter I) are 100% (arithmetical pattern) and 25% respectively.

Alcohols

Alcohols show linear rise in retention time upto the last polyester column. The total rise in retention time is 200%. A peculiar behaviour of alcohols was observed on 1,5-pentanediol-phthalic acid and 1,6-hexanediol-phthalic acid polyester columns. On the former polyester, very sudden rise in retention time was observed for primary alcohols and to a lesser extent for secondary alcohols; whereas on the latter polyester experimental values of retention time showed decrease to but a lesser extent (graph I). This anomalous behaviour on these polyester columns may be due to some unexplainable interactions between these solutes and the ~~structures of~~ middle order aromatic polyester columns. Possible cause for this behaviour is being investigated. The alcohols are the maximum stretched compounds in this series, percentage contribution in rise per methylene group is 70% as against 26% for saturated polyesters²⁹.

This fact indicates the polar nature of these polyesters.

Comparative behaviour of aromatic polyesters, saturated polyesters and unsaturated polyesters

When behaviour of most of these compound was compared on various types of polyesters ranging from saturated-, unsaturated- and aromatic-polyesters, it was evident that percentage contribution in rise in retention time per methylene group varies considerably, as is clear from the Table 4.

Table 4

Comparative data on % contribution in rise in t_R per $-CH_2-$ group for various classes of compounds on different types of polyesters

Sl.No.	Type of polyester	Class of compounds			
		Aliphatic hydrocarbons	Terpenic hydrocarbons	Aromatic hydrocarbons	Alcohols
1.	Saturated polyesters	100%	100%	59%	26%
2.	Un-saturated polyesters	0-12%	25%	12%	-
3.	Aromatic polyesters	4%	14%	18%	70%

*These figures are calculated from t_R data on saturated polyesters investigated earlier in this laboratory²⁰.

**These figures are calculated from t_p data on unsaturated polyesters described in Chapter I of this thesis.

In case of terpenes, aliphatic hydrocarbons and chlorinated compounds, it drops down from 100% (saturated polyesters) to 25% (unsaturated polyesters) and then to 14% (aromatic polyesters). While for the aromatic compounds, though the value of percentage contribution has decreased from 59% (saturated polyesters) to 12% (unsaturated polyesters), it has gone upto 18% in case of aromatic polyesters; showing thereby a better solubility of aromatic compounds on these phases (aromatic polyesters).

The straight-chain saturated polyesters were found to be comparatively more selective for non-aromatic compounds than aromatic hydrocarbons as is indicated by the variation in percentage contribution in rise per methylene group figures, dropping from 100% to 59% (to about half). The relationship is actually reversed in case of aromatic polyesters for terpenes and aromatic hydrocarbons. The stretching capability of the aromatic polyesters is better (18%) for aromatic compounds as compared with 14% for terpenes. Another interesting feature of the aromatic polyesters is the better solubility and stretching capability for alcohols. It was never observed in case of polyesters studied earlier. This is the first time that the alcohols are showing a linear rise in retention time upto the last column, 1,10-decanediol-phthalic acid polyester. Their 70% contribution in rise in retention time per methylene group is approaching nearly to the arithmetical pattern.

Actual separation of different mixtures

(i) Methyl alcohol and toluene

The considerable rise in percentage contribution per methylene group in case of alcohols helped to separate the mixture of toluene and methyl alcohol. Both the compounds are having the same retention time (2.16 minutes) on the first column (ethylene-glycol-phthalic acid polyester), but from the next column onwards because of the comparative better stretching of methyl alcohol, the mixture can be very well separated (Fig. 1). The separation of toluene and n-propyl alcohol can also be explained in a similar way.

(ii) Methyl alcohol and n-propyl alcohol

The mixture of methyl alcohol and n-propyl alcohol, which is not separable on the first column, shows better separation factor from the next column (1,3-propanediol-phthalic acid polyester) as these two compounds have different stretching constants and hence the mixture can be easily resolved (Fig. 2).

(iii) Benzene and ethylacetate

Initially on ethylene-glycol-phthalic acid polyester column, a mixture of benzene and ethylacetate can be resolved, while the separation factor goes on decreasing as the figures of retention time are compared on polyesters from ethylene-glycol-phthalic acid to 1,5-pentanediol-phthalic acid polyester and the mixture cannot be separated. The retention time of ethyl acetate on the first column is higher than that of benzene and these can be separated; but as stretching factor of benzene being

PHASES: A & C ETHYLGLYCOL PHTHALIC ACID POLYESTER
 B 1,5-PENTANEDIOL PHTHALIC ACID POLYESTER
 D 1,10-DECANEDIOL PHTHALIC ACID POLYESTER

TEMP. 98°C
 CHART SPEED: 6"/HOUR (FIG. 2)
 12"/HOUR (FIG. 1)

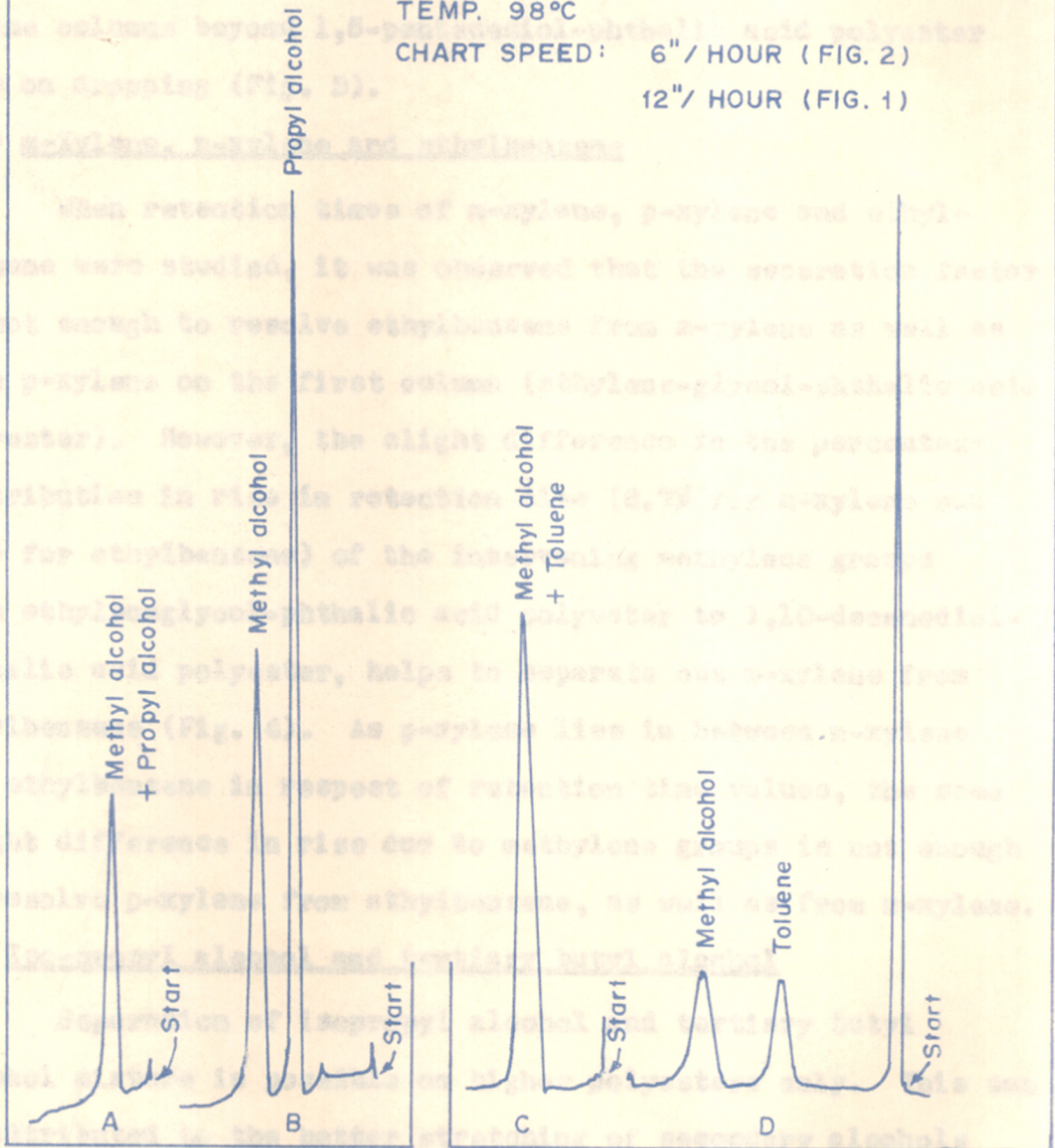


FIG. 2

FIG. 1

more than that of ethylacetate in this series of polyesters, the compound pair starts overlapping. The same pair is again separable on the last column because the stretching capability of the columns beyond 1,5-pentanediol-phthalic acid polyester goes on dropping (Fig. 3).

(iv) m-Xylene, p-xylene and ethylbenzene

When retention times of m-xylene, p-xylene and ethylbenzene were studied, it was observed that the separation factor is not enough to resolve ethylbenzene from m-xylene as well as from p-xylene on the first column (ethylene-glycol-phthalic acid polyester). However, the slight difference in the percentage contribution in rise in retention time (8.7% for m-xylene and 8.1% for ethylbenzene) of the intervening methylene groups from ethyleneglycol-phthalic acid polyester to 1,10-decanediol-phthalic acid polyester, helps to separate out m-xylene from ethylbenzene (Fig. 4). As p-xylene lies in between m-xylene and ethylbenzene in respect of retention time values, the same slight difference in rise due to methylene groups is not enough to resolve p-xylene from ethylbenzene, as well as from m-xylene.

(v) Iso-propyl alcohol and tertiary butyl alcohol

Separation of isopropyl alcohol and tertiary butyl alcohol mixture is possible on higher polyesters only. This can be attributed to the better stretching of secondary alcohols than the tertiary ones.

PHASE: 1,10-DECANEDIOL-PHTHALIC ACID POLYESTER (A)(C)
 1,3-PROPANEDIOL-PHTHALIC ACID POLYESTER (B)
 1,5-PENTANEDIOL-PHTHALIC ACID POLYESTER (D)
 TEMP. 98 °C
 CHART SPEED: 12"/ HOUR

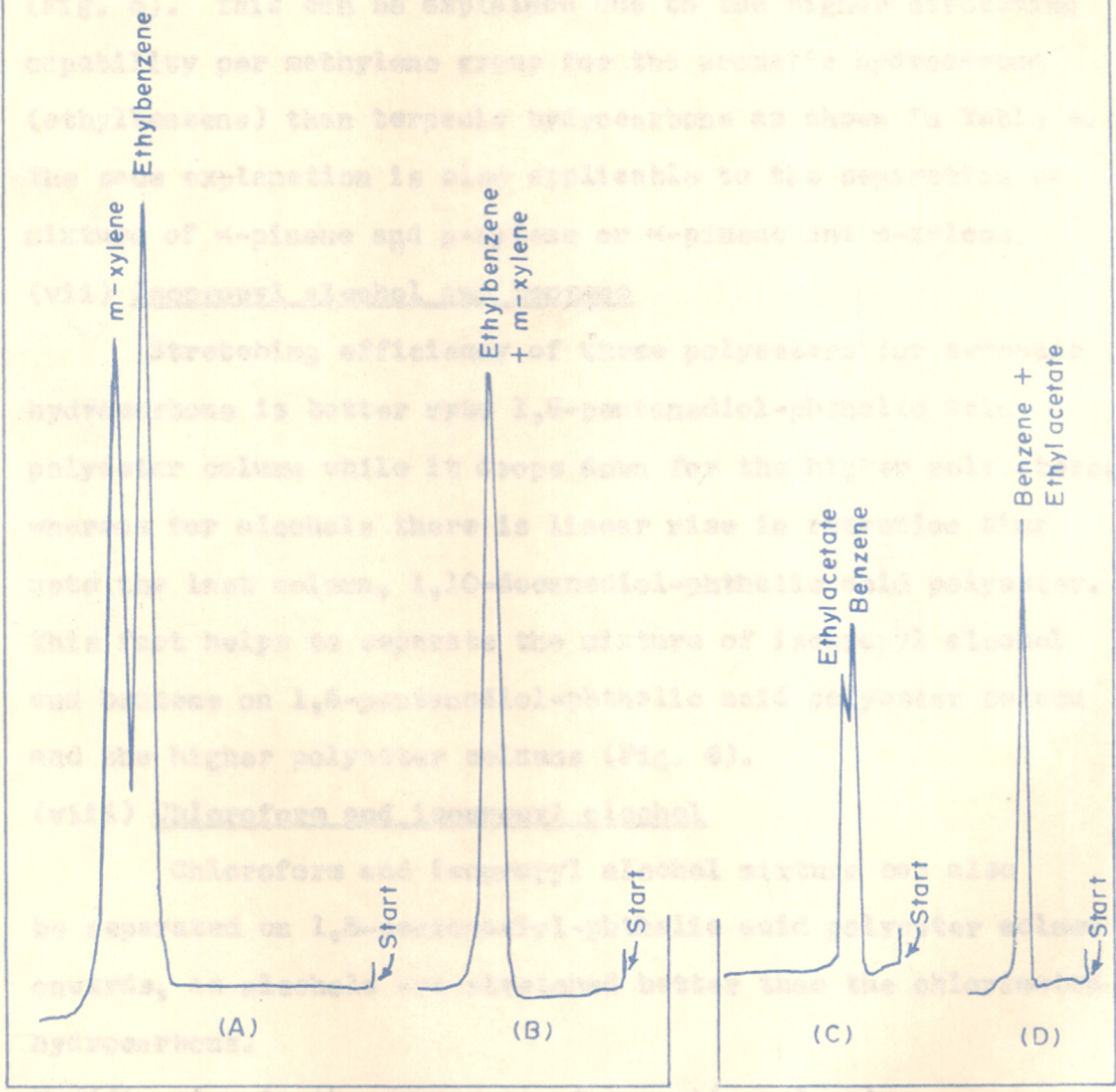


FIG. 4

FIG. 3

(vi) Ethylbenzene and α -pinene

A mixture of ethylbenzene and α -pinene is not separable on lower polyesters. However, it can be separated on 1,5-pentanediol-phthalic acid polyester column on-wards (Fig. 5). This can be explained due to the higher stretching capability per methylene group for the aromatic hydrocarbon (ethylbenzene) than terpenic hydrocarbons as shown in Table 4. The same explanation is also applicable to the separation of mixture of α -pinene and p-xylene or α -pinene and m-xylene.

(vii) Isopropyl alcohol and benzene

Stretching efficiency of these polyesters for aromatic hydrocarbons is better upto 1,5-pentanediol-phthalic acid polyester column while it drops down for the higher polyesters; whereas for alcohols there is linear rise in retention time upto the last column, 1,10-decanediol-phthalic acid polyester. This fact helps to separate the mixture of isopropyl alcohol and benzene on 1,5-pentanediol-phthalic acid polyester column and the higher polyester columns (Fig. 6).

(viii) Chloroform and isopropyl alcohol

Chloroform and isopropyl alcohol mixture can also be separated on 1,5-pentanediol-phthalic acid polyester column onwards, as alcohols are stretched better than the chlorinated hydrocarbons.

Modification in the structure of aromatic polyester

When percentage contributions per methylene group in retention time rise for isomeric compounds such as α -pinene

PHASE: 1,5-PENTANEDIOL-PHTHALIC ACID POLYESTER (A)
1,4-BUTANEDIOL-PHTHALIC ACID POLYESTER (B) (D)
1,6-HEXANEDIOL-PHTHALIC ACID POLYESTER (C)

TEMP. 98 °C.
CHART SPEED: 12"/HOUR

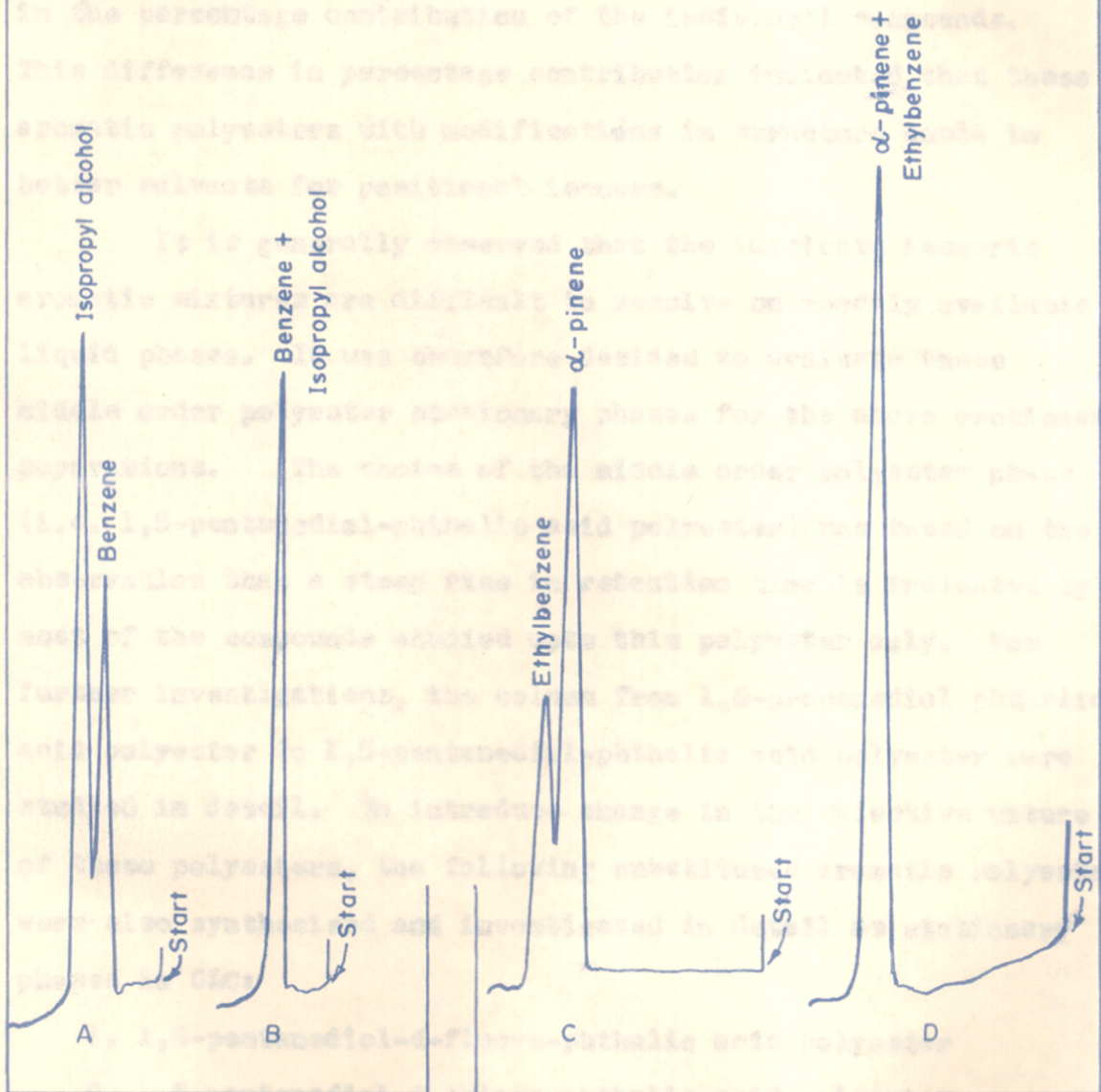


FIG. 6

FIG. 5

and β -pinene as well as m- and p-xylene are carefully studied, it was observed that there is considerable difference in the contribution of the individual compounds of the first pair. In case of xylenes^{also}, there is some difference, though somewhat less, in the percentage contribution of the individual compounds. This difference in percentage contribution indicated that these aromatic polyesters with modifications in structure could be better solvents for positional isomers.

It is generally observed that the intricate isomeric aromatic mixtures are difficult to resolve on readily available liquid phases. It was therefore decided to evaluate these middle order polyester stationary phases for the above mentioned separations. The choice of the middle order polyester phase (i.e. 1,5-pentanediol-phthalic acid polyester) was based on the observation that a steep rise in retention time is indicated by most of the compounds studied upto this polyester only. For further investigations, the column from 1,3-propanediol phthalic acid polyester to 1,5-pentanediol-phthalic acid polyester were studied in detail. To introduce change in the selective nature of these polyesters, the following substituted aromatic polyesters were also synthesised and investigated in detail as stationary phases in GLC:

1. 1,5-pentanediol-4-fluoro-phthalic acid polyester
2. 1,5-pentanediol-4-chloro-phthalic acid polyester
3. 1,5-pentanediol-3,6-dichlorophthalic acid polyester and
4. 1,3-propanediol-4-amino-phthalic acid polyester.

The substituted phthalic acids, 4-fluoro-phthalic acid, 4-chlorophthalic acid and 4-aminophthalic acid were synthesised according to the method of Blicke and Smith⁶. 3,6-Dichlorophthalic acid was prepared by the chlorination of phthalic anhydride in the presence of fuming sulphuric acid and iodine as described in literature⁷. The purity of these compounds was checked by m.p./b.p. and elemental analyses.

The substituted polyesters were prepared ^{by}~~in~~ the same method as described for unsubstituted polyesters from the proper substituted phthalic acid and the respective glycol.

The polyesters, 1,5-pentanediol-4-fluorophthalic acid and 1,5-pentanediol-4-chlorophthalic acid were viscous liquids. The polyester, 1,5-pentanediol-3,6-dichlorophthalic acid was semi-solid; whereas the 1,3-propanediol-4-aminophthalic acid polyester was a low melting solid.

The approximate molecular weights of these polyesters were determined by the end group titration method and the details are given in Table 5.

Table 5

Molecular weights of the polyesters as determined by the end group titrations

S.No.	Components of the polyester		Molecular weights
	Acid	Glycol	
1.	4-Chlorophthalic acid	1,5-pentanediol	1,160; 1178
2.	4-Fluoro-phthalic acid	1,5-pentanediol	1,242; 1225
3.	4-Amino-phthalic acid	1,3-propanediol	2,875; 2893
4.	3,6-Dichlorophthalic acid	1,5-pentanediol	2,108; 2095

The following aromatic isomeric compounds along with other compounds were tried.

(i) Aromatic isomeric compounds

- a) α -Picoline, β -picoline and γ -picoline
- b) Ortho-, para- and meta-toluidine
- c) Ortho-, para- and meta-dichlorobenzene
- d) Ortho-, para- and meta-cresol
- e) Ortho-, para- and meta-chloroaniline
- f) Ortho-, para- and meta-nitro^{-to}luene and
- g) Ortho-, para- and meta-nitrochlorobenzene

(ii) Monoterpene hydrocarbons

- (a) α -Pinene (b) β -pinene (c) Δ^3 -carene (d) limonene
- (e) p-cymene (f) 1,8-cineole and (g) camphene

(iii) Monoterpene oxygenated compounds

- (a) α -Terpeneol (b) linalool (c) geraniol (d) nerol
- (e) borneol (f) citronellol (g) camphor (h) nerylacetate
- (i) geranyl acetate (j) linalool acetate (k) citronellol acetate
- (l) isoborneol (m) l-menthol and (n) menthone.

(iv) Sesquiterpene hydrocarbons

- (a) Longifolene (b) isolongifolene (c) longicyclene
- and (d) caryophyllene.

(v) Other compounds

- (a) Pyridine (b) piperidine (c) aniline (d) nitrobenzene
- (e) ethylbenzene (f) styrene (g) n-butyl alcohol (h) sec-butyl alcohol and (i) tert-butyl alcohol.

The samples of m-dichlorobenzene, m-nitrochlorobenzene and o-m- and p-chloro^{o-}anilines were not readily available in this laboratory. They were therefore prepared for these investigations.

m-Nitroaniline was available in the laboratory stock. It was converted into m-nitrochlorobenzene by diazotisation and subsequent treatment with cuprous chloride by the usual procedure.

m-Chloro-aniline was prepared from m-nitrochlorobenzene by reduction with iron and hydrochloric acid. o-Chloroaniline and p-chloroaniline were similarly prepared from o-nitrochlorobenzene and p-nitrochlorobenzene respectively.

m-Dichlorobenzene was prepared from m-chloroaniline by diazotisation and treatment with cuprous chloride.

All these samples were pure as checked by their m.p./b.p., elemental analysis.

The following chart (Chart 1) gives the structures and other physical properties of the isomeric aromatic compounds which are used as standard samples in the present investigation.

All the column variables were kept constant in order to facilitate the comparison of retention time data from column to column.

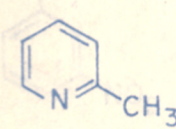
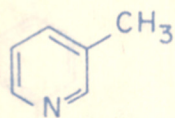
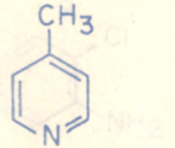
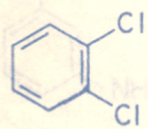
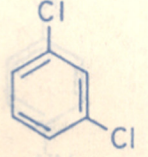
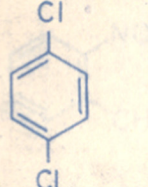
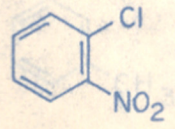
1. Temperature of the column (i) 170°
(ii) 100°C
2. Inlet pressure (i) 200 ± 5 mm at 170°C
(ii) 135 ± 4 mm at 100°C

Results and discussion

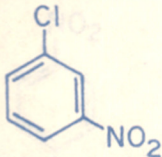
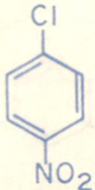
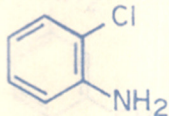
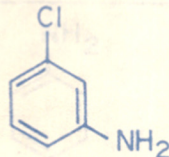
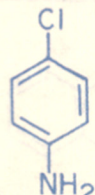
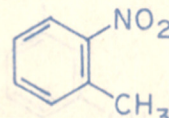
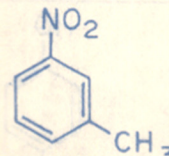
The retention time data of all the compounds is presented in Tables 6 and 7.

CHART - I
POSITIONAL ISOMERS STUDIED

119
119

NO.	NAME OF THE COMPOUND	STRUCTURAL FORMULA	M. P. °C.	B. P. °C.
1	α - PICOLINE		—	129
2	β - PICOLINE		—	143.8
3	γ - PICOLINE		—	143.1
4	o - DICHLOROBENZENE		—	180.3
5	m - DICHLOROBENZENE		—	172
6	p - DICHLOROBENZENE		53	174
7	o - CHLORONITROBENZENE		33	245

POSITIONAL ISOMERS STUDIED

NO.	NAME OF THE COMPOUND	STRUCTURAL FORMULA	M. P. °C.	B. P. °C.
8	m-CHLORONITROBENZENE		46	235
9	p-CHLORONITROBENZENE		83	242
10	o-CHLOROANILINE		—	208.8
11	m-CHLOROANILINE		—	230.5
12	p-CHLOROANILINE		70	232
13	o-NITROTOLUENE		—	222.3
14	m-NITROTOLUENE		—	227.5

POSITIONAL ISOMERS STUDIED

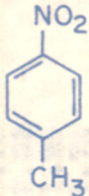
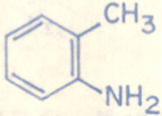
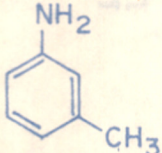

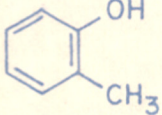
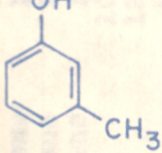

NO.	NAME OF THE COMPOUND	STRUCTURAL FORMULA	M. P. °C.	B. P. °C.
15	p - NITROTOLUENE		54.5	237.7
16	o - TOLUIDINE		—	200.6
17	m - TOLUIDINE		—	203.2
18	p - TOLUIDINE		42	200.3
19	o - CRESOL		30	191
20	m - CRESOL		—	202
21	p - CRESOL		34	202.5

Table 6

Retention time in minutes at 170 + 1°C

S.No.	Compound	1,4-butane- diol-phthalic acid poly- ester	1,5-pentane- ane-diol phthalic acid poly- ester	1,5-pentane- diol-4-flu- oro-phthalic acid polyester	1,5-pentane- diol-4-chlo- ro-phthalic acid poly- ester	1,5-pentane- diol-3,6-di- chloro-phth- alic acid poly ester	1,3-propene- diol 4-amino- phthalic acid polyester
1.α-Picoline		1.05	1.03	1.11	0.95	1.05	2.43
2.β-Picoline		1.81	Ø.58	1.75	1.45	1.18	4.30
3.γ-Picoline		2.10	1.78	1.88	1.55	2.08	5.41
4.o-Nitrotoluene		7.80	8.13	9.60	9.61	7.25	13.26
5.p-Nitrotoluene		11.60	12.00	15.00	14.55	11.88	21.08
6.m-Nitrotoluene		11.83	-	3.28*	-	11.61	13.23
7.p-Toluidine		6.75	-	3.60*	6.91	6.90	10.18
8.m-Toluidine		6.86	-	3.30*	7.50	6.25	11.25
9.o-Toluidine		6.20	-	7.25 ⁵	6.68	5.78	10.00
10.o-Dichlorobenzene		1.90	2.20	2.50	2.63	3.33	3.33
11.p-Dichlorobenzene		1.80	2.16	2.46	2.50	1.98	2.71
12.m-Dichlorobenzene		1.73	-	-	-	1.78	2.40
13.p-Cresol		10.20	12.75	5.66*	11.16	8.61	17.11
14.m-Cresol		12.15	-	5.70*	11.96	8.50	17.50
15.o-Cresol		8.15	-	4.38*	8.50	6.71	12.58
16.p-Chloroaniline		12.30	-	-	-	13.00	24.53
17.o-Chloroaniline		8.83	-	-	-	8.08	13.16
18.m-Chloroaniline		19.25	-	-	-	16.00	28.28
19.o-Nitrochloro- benzene		16.46	-	-	-	15.91	30.08
20.p-Nitrochloro- benzene		14.50	-	-	-	13.50	23.50
21.m-Nitrochloro- benzene		12.00	-	-	-	11.61	20.46

*These values are recorded at temperature of 200°C

Table 7

Retention time in minutes at 170 + 10C

SNo.	Compound	1,4-butene- diol phthalic acid polyester	1,5-pentane- diol phthalic acid poly- ester	1,5-pentane- diol-4-fluoro- phthalic acid polyester	1,5-pen- tane- diol-4- chloro- phthalic acid poly- ester	1,5-pentene- diol-3,6- dichloro- phthalic acid polyester	1,3-propane diol-4-amino- phthalic acid poly- ester
1	Pyridine	1.25	0.85	0.91	0.80	1.05	2.06
2	Piperidine	0.55	0.83	0.83	0.73	-	-
3	Aniline	4.70	-	2.46*	4.70	4.11	7.43
4	Nitrobenzene	6.55	6.33	7.53	7.53	6.05	11.26
5	Ethylbenzene	0.47	0.66	0.75	0.78	0.50	0.76
6	Styrene	0.86	1.00	1.16	1.20	0.95	1.33
7	n-Butyl alcohol	-	-	0.46	0.40	-	-
8	sec-Butyl alcohol	-	-	0.31	0.26	-	-
9	tert-Butyl alcohol	-	-	0.11	0.13	-	-
10	Longifolene	-	5.28	7.08	7.41	5.70	5.70
11	Isolongifolene	-	-	5.50	3.25	-	-
12	Longicyclene	-	4.16	5.56	5.75	-	-
13	Caryophyllene	-	-	7.01	7.38	-	-
14	Geraniol	5.25	7.50	9.41	6.25	6.00	11.00
15	Geranylacetate	4.50	-	8.48	6.45	6.10	-
16	Nerol	4.61	-	8.30	7.21	6.01	-
17	Neryl acetate	4.15	8.50	7.80	3.01	6.21	-
18	Mineral oil	1.63	2.50	3.15	2.80	2.25	-
19	Analyl acetate	-	-	4.25	4.00	3.00	-
20	Citronellol	3.85	6.20	7.20	6.45	4.83	-
21	Citronellyl acetate	3.10	5.40	-	-	-	-

* This value has been recorded at 200°C

Table 7 (continued)

1	2	3	4	5	6	7	8
22.	Camphor	-	-	4.66	4.58	-	-
23.	Borneol	-	-	5.66	5.83	4.83	-
24.	Isoborneol	-	-	4.90	5.08	4.28	-
25.	α -Terpinefol	-	-	6.18	6.45	5.45	-
26.	1-Menthol	-	-	5.36	5.18	4.01	-
27.	Camphor	-	-	4.66	4.58	-	-
28.	Menthone	-	-	3.98	4.08	3.11	5.41
<u>Retention time in minutes at 100°C</u>							
1.	α -Pinene	-	-	3.00	3.75	-	-
2.	β -Pinene	-	-	4.91	6.00	-	-
3.	Δ^3 -Carene	-	-	6.00	7.50	-	-
4.	Limonene	-	-	8.10	10.00	-	-
5.	p-Cyaene	-	-	11.21	13.50	-	-
6.	1,8-Cineol	-	-	10.00	11.53	-	-
7.	Camphene	-	-	4.03	5.00	-	-

From the study of retention data of the various isomeric compounds investigated in this series, it was observed that some of the polyesters are showing selectivity for positional isomers of these compounds. The behaviour of the individual polyesters towards the actual separation of the different isomers is discussed below in detail.

Selective separation of the different isomers by the individual polyester columns

1. Picolinas

The retention time data indicates that all the three picolines can be separated on all the columns (Fig.7) except on chloro- and fluoro-substituted polyesters, where β - and γ -picoline mixture show lower separation factor under the normal conditions and both the isomers overlap.

2. Nitrotoluenes

In case of nitrotoluene, the *m*- and *p*-nitrotoluene isomers tend to overlap on all the columns except on 1,3-propanediol-4-aminophthalic acid polyester column. The separation possibility of the two isomers, namely *meta* and *para*, is indicated on the amino-substituted polyester column. However, the *meta*- and *ortho*-isomers overlap on this column, while this pair is easily separable on 1,5-pentenediol-3,6-dichlorophthalic acid polyester column. The separation of all the three isomers of nitrotoluene was therefore tried on a mixed column of amino-substituted polyester and dichloro-substituted polyester. It was found that the mixed column could resolve all the isomers, as is evident from the enclosed chromatogram (Fig. 8).

PHASE: 1,3-PROPANEDIOL-4-AMINOPHTHALIC ACID POLYESTER (A)
 & 1,5-PENTANEDIOL-3,6-DICHLOROPHTHALIC ACID
 POLYESTER (MIXED PHASE) (B)

TEMP.: 170 °C

CHART SPEED: 6"/HOUR

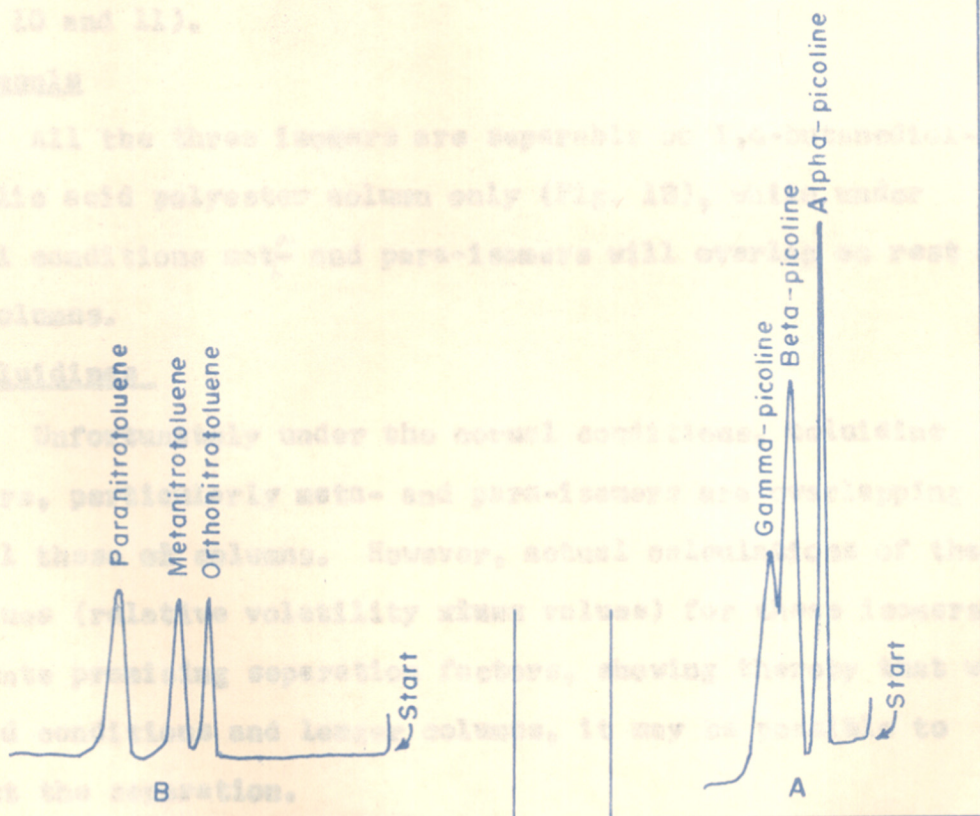


FIG. 8

FIG. 7

3. Dichlorobenzenes

All the three isomeric dichlorobenzenes show separable retention times on amino substituted and dichlorosubstituted polyester columns. The separation of the isomers is comparatively better on amino-substituted polyester column (Fig. 9). On the other columns, ortho- and para-isomers tend to overlap.

4 and 5: Chloroanilines and chloronitrobenzenes

They can be easily resolved on all the columns tried as the retention times of these compounds show wide variations (Fig. 10 and 11).

6. Cresols

All the three isomers are separable on 1,4-butanediol-phthalic acid polyester column only (Fig. 12), while under normal conditions meta- and para-isomers will overlap on rest of the columns.

7. Toluidines

Unfortunately under the normal conditions, toluidine isomers, particularly meta- and para-isomers are overlapping on all these columns. However, actual calculations of the α -values (relative volatility α values) for these isomers indicate promising separation factors, showing thereby that with varied conditions and longer columns, it may be possible to effect the separation.

In order to get a clear picture of selectivity of these polyester columns for all the above isomeric compounds under normal conditions (column temperature 170°C, length 2 metres, carrier flow-rate, hydrogen, 4 litres/hour), relative volatility (α), separation factor (S) and number of theoretical plates required for separation (N) were calculated according to the method of Purnell⁸ and the results are given in Table 8.

PHASE: 1,4-BUTANEDIOL - PHTHALIC ACID POLYESTER (A)

1,3-PROPANEDIOL-4-AMINOPHTHALIC ACID

POLYESTER (B)

TEMP. 150 °C (B) & 170 °C (A)

CHART SPEED: 6" / HOUR

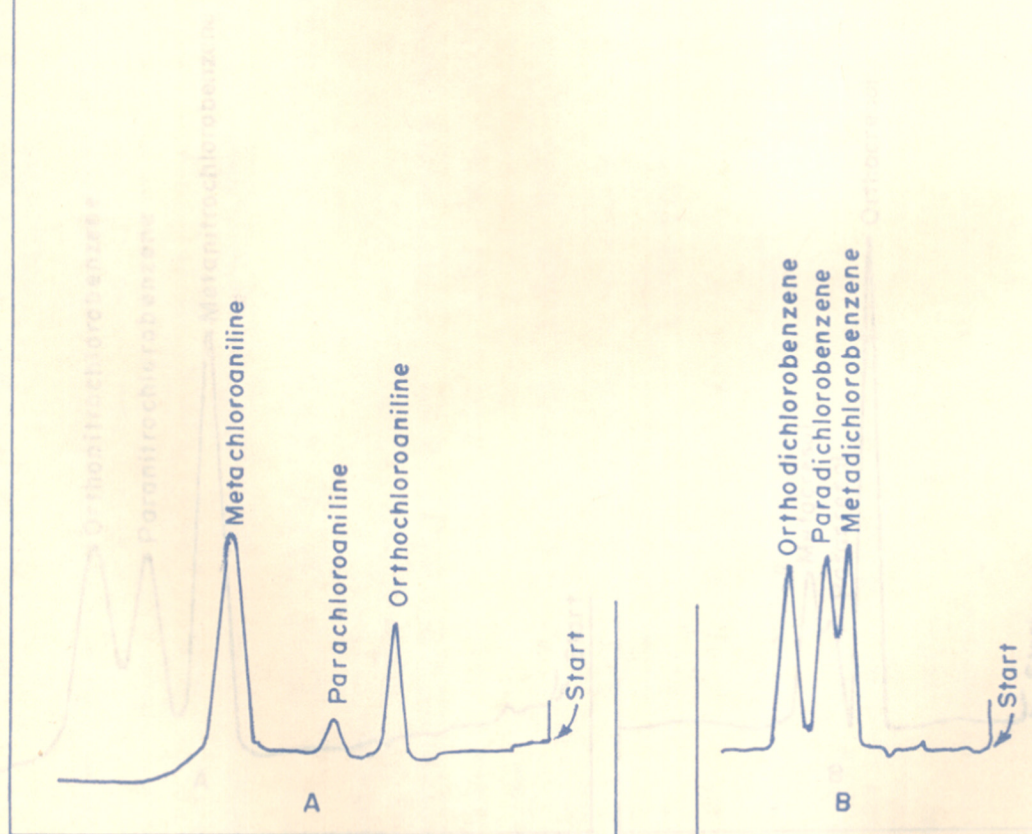


FIG. 10

FIG. 9

PHASE: 1,3-PROPANEDIOL-4-AMINOPHTHALIC ACID POLYESTER (A)

1,4-BUTANEDIOL-PHTHALIC ACID POLYESTER (B)

TEMP. 170 °C

CHART SPEED: 6"/ HOUR

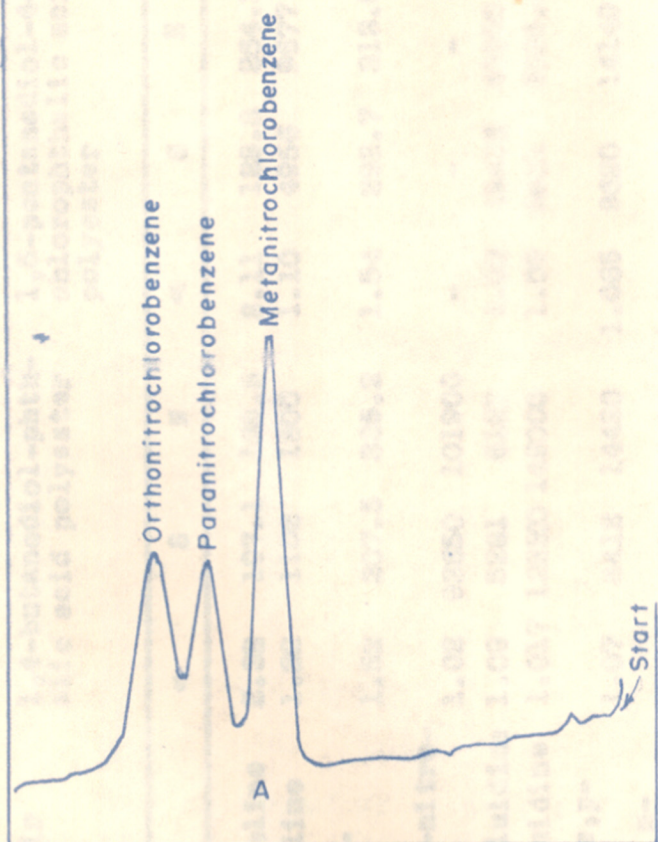


FIG. 11

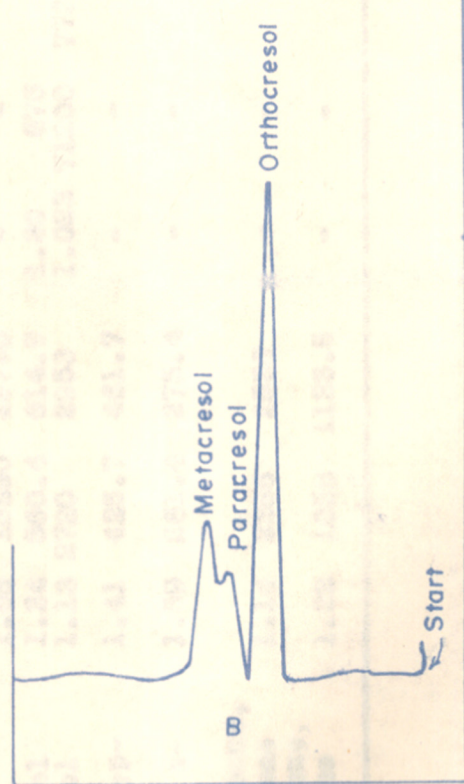


FIG. 12

Table 8

Data on relative volatility (α), separation factor (S) and number of theoretical plates required for separation (N) on different polyesters

S.No.	Compound pair	1,4-butanediol-phthalic acid polyester			1,5-pentanediol-chlorophthalic acid polyester			1,5-pentanediol-4-phthalic acid polyester			1,3-propanediol-4-amino-phthalic acid polyester		
		α	S	N	α	S	N	α	S	N	α	S	N
1.	α -Picoline, β -Picoline	2.36	107.1	188.8	2.11	128.8	264.3	1.23	1030	2545	1.96	150	188.4
	β -Picoline, γ -picoline	1.22	1108	1800	1.10	4956	9677	2.32	121.3	183.1	1.29	712.4	857.4
2.	<i>o</i> -Nitrotoluene, <i>p</i> -nitrotoluene	1.52	207.5	335.2	1.54	292.7	313.5	1.67	223.7	243.4	1.61	250.8	268.6
	<i>p</i> -Nitrotoluene, <i>m</i> -nitrotoluene	1.02	92650	101900	-	-	-	1.024	65540	71310	-	-	-
3.	<i>o</i> -Toluidine, <i>p</i> -toluidine	1.09	5281	6127	1.03	42435	49050	1.02	93650	111000	1.03	115100	12700
	<i>p</i> -Toluidine, <i>m</i> -toluidine	1.017	128300	149000	1.09	5281	6035.4	1.06	11236	13180	1.11	3665	4005
4.	<i>o</i> -Dichlorobenzene, <i>p</i> -dichlorobenzene	1.07	8412	14420	1.065	9620	14140	1.23	1030	1592	1.28	752.1	1020
	<i>p</i> -Dichlorobenzene, <i>m</i> -dichlorobenzene	1.05	15880	28790	-	-	-	1.16	1892.2	3171	1.16	1892.2	2749
5.	<i>o</i> -Cresol, <i>p</i> -Cresol	1.34	560.4	614.9	1.30	676	726	1.30	676	759.3	1.37	493	522.8
	<i>p</i> -Cresol, <i>m</i> -cresol	1.13	2720	2953	1.023	71200	77380	1.014	188300	212100	1.023	71200	75370
6.	<i>o</i> -Chloroaniline, <i>p</i> -chloroaniline	1.41	425.7	461.7	-	-	-	1.64	236.3	285.2	1.88	164.3	171.1
	<i>p</i> -Chloroaniline, <i>m</i> -chloroaniline	1.59	261.4	275.4	-	-	-	1.25	900	1116	1.15	2116	2192
7.	<i>o</i> -Nitrochlorobenzene, <i>p</i> -nitrochlorobenzene	1.14	2386	2536	-	-	-	1.19	1412	1503	1.28	752.1	777.5
	<i>p</i> -Nitrochlorobenzene, <i>m</i> -nitrochlorobenzene	1.22	1058	1133.5	-	-	-	1.17	2147	2312.3	1.15	2116	2208

Comparative evaluation of stationary phases described in literature with those studied by the author for the separation of substituted aromatic isomers

From literature survey, it is observed that separation of some of these isomeric mixtures have been tried by earlier workers on various types of columns. In most of the cases they have used a fairly long column and that too at low temperatures, as a result the analysis time is considerably longer running into hours. Most of the relevant and prominent examples from the literatures for separation of some of these isomers are described in Table 9.

It is evident from Table 9 that cresol isomers are separated by Anwar et al.¹⁹ successfully using 5 feet column of Dispersol CWL. Separation achieved on 1,4-butanediol-phthalic acid polyester column (2 metres) in this laboratory is equally good. 1,3-Propanediol-4-amino-phthalic acid polyester column resolves all the three chloro-nitrobenzenes and comparable separation was reported by Vasaros et al.⁹ and Habboush et al.¹⁶ Anwar et al.^{19,21} has reported separations of ortho- and para-chloroanilines whereas all the three isomers are separated on polyester, 1,5-pentenediol-3,6-dichloro-phthalic acid. Picolines are resolved by Anwar et al.²¹ on a 9 feet column of polyphenylether while 1,3-propanediol-4-aminophthalic acid polyester column (2 metres) indicates comparatively better separation of all the three picolines. The three isomers of dichlorobenzenes have been separated by

Table 9

Relevant and prominent examples from the literature for the attempted separations of positional isomers

S.No.	References	Liquid phase	Column length	Column temp. (°C)	Total time of analysis (in mins.)	α-Value (relative volatility)	
1	2	3	4	5	6	7	
Nitrotoluenes							
	(13)						
1.	R.O.C.Norman	2,4,7-trinitro fluorenone	6 mts.	200	55.5	o.m.= 1.23 m.p.= 1.15	
	(14)						
2.	Courtier et al.	a)Silicone Rhodorshil 47V 300	3 mts.	200	10	om.	m.p. 1.02 1.00
		b)Apiezon L	"	180	13	1.24	1.09
	(15)						
3.	Parsons et al.	Apiezon L	12 ft.	196	-	1.23	1.07
	(12)						
4.	Habboush et al.	a)Dinonyl phthalate	2 mts.	120	65	1.32	1.14
		b)Polyethylene glycol	"	120	141	1.25	1.18
	(16)						
5.	Habboush et al.	a)Polyethylene glycol-succinate				a)1.23	1.15
		b)Polyethylene sorbitan monostearate	2 mts.	140	60	b)1.33	1.18
		c)Polyethylene glycol		120		c)1.4	1.16
		d)Silicone oil				d)1.24	1.09
		e)Squalane				e)1.33	1.16
6.	Author's data	1,3-propane-diol-4-amino-phthalic acid polyester + 1,5-pentane-diol-3,6-dichlorophthalic acid polyester	2 mts.	170	20	1.17	1.29

Table 2 (continued)

1	2	3	4	5	6	7
<u>Chloronitrobenzenes</u>						
	(17)					m.p.
7.K.J. Bombaugh	a)Carbowax	4 mts.	170	-	-	o.p. 1.12 not repro-1.14 rted
	b)Lac 446	2 mts.	150	-	-	
	(18)					
8.Ratusky et al.	1,2,3,4-tetra- kis(2-cyano- ethoxy)-butane	0.83 mts.	180	-	-	1.35 1.06
	(12)					
9.Habboush et al.	a)Dinonyl phth- alate	2 mts.	120	104		m.p. o.p. 1.12 1.08
	b)Tritolyl phosphate	"	145	79		1.15 1.16
	c)Trinitro- fluorenone	"	150	72		1.08 1.20
	(9)					
10.Vasaros et al.	Igepal CO-880	4 mts.	180	32		1.12 1.21
	(16)					
11.Habboush et al.	a)Polyethylene glycol succi- nate	2 mts.	160	-		1.15 1.22
	b)Polyoxyethyl- ene sorbitan monostearate	"	140	-		1.14 1.24
	c)Polyethylene glycol	"	140	-		1.09 1.24
12.Author's data	1,3-propanediol -4-aminophthalic acid polyester	"	170	30		1.23 1.15
<u>Cresols</u>						
13.Anwar et al.	(19) Dispersol CWL	5 ft.	180	15		1.25 1.33
	(20)					
14.Kolsek et al.	a)Apiezon L	1.2 mts.	120	70		1.00 1.08
	b)Dinonyl phth- alate	"				1.00 1.30
	c)2,4-xylene phthalate	"				1.06 1.33
	d)Trimethyl- cyclohexyl- phthalate	"				1.08 1.26
15.Author's data	1,4-butanediol- phthalic acid polyester	2 mts.	170	12.15		1.13 1.34

Table 2 (continued)

1	2	3	4	5	6	7	m.p.	o.p.
<u>Chloroanilines</u>								
	(19)							
16.	Anwar et al.	Carbowax 1500	5 ft.	180	7		not reported	1.75
	(21)							
17.	Anwar et al.	a)Glycerol	"	115	2.5		"	1.66
		b)Diglycerol	"	115	2.5		"	1.66
		c)Polyphenyl ether	9 ft.	178	30		"	1.20
18.	Author's data	1,5-Pentanediol 3,6-dichlorophthalic acid polyester	2 mts.	170	16		1.25	1.64
<u>Toluidines</u>								
	(21)							
19.	Anwar et al.	a)Polyphenyl ether	9 ft.	135	75		not reported	1.07
		b)Diglycerol	5 ft.	90	4		"	1.33
		c)Glycerol	"	90	4		"	1.33
	(22)							
20.	Cooper et al.	a)1,3,5-trinitrobenzene	2 mts.	130	-		1.03	1.13
		b)Silicone oil	"	130	-		1.01	1.03
21.	Author's data	1,5-pentanediol 4-chlorophthalic acid polyester	"	170	8		1.08	1.03
<u>Picolines</u>							<u>BR</u>	<u>BY</u>
	(21)							
22.	Anwar et al.	Polyphenyl ether	9 ft.	110	33		1.76	1.104
23.	Yakerson et al.	(10) a)Polyethylene glycol adipate/diatomite brick	2.6 mts.	150	7		1.43	1.07
		b)Polyethylene glycol/sodium chloride	"				1.47	1.08
	(23)							
24.	Dewar et al.	Liquid crystals	a)4.9 mts.	158	5		not reported	1.30
			b)6.2 mts.	121	16		"	1.16
	(11)							
25.	Kirsten et al.	Tween-20	2 mts.	70	76		1.62	1.11
28.	Author's data	1,3-Propane-diol 4-amino-phthalic acid polyester	"	170	5.5		1.96	1.29

Table 9 (continued)

1	2	3	4	5	6	7	
<u>Dichlorobenzenes</u>						o.p.	m.p.
	(12)						
29.	Habboush et al.	a) Apiezon L	2 mts.	120	66	1.12	1.00
		b) Dinonyl phthalate	"	120	18.5	1.23	1.00
		c) Polyethylene glycol	"	100	125	1.28	1.12
		d) Tritolyl-phosphate	"	100	76	1.27	1.12
		e) Trinitrofluorenone	"	120	26	1.30	1.00
	(24)						
30.	Olah et al.	Polypropylene glycol	4 mts.	150	22	1.32	1.11
	(9)						
31.	Vasaros et al.	Igepal CO-880	"	130	16.63	1.23	1.109
	(23)						
32.	Dewar et al.	Liquid crystals	4.9 mts.	158	4	not reported	1.12
	(25)						
33.	Dewar et al.	"	8.8 mts.	124	23.1	"	1.15
	(26)						
34.	Mortimer et al.	Bentone - 34 + Silicone MS 550	12 ft.	150	35	2.32	1.32
	(27)						
35.	Cowar et al.	Bentone-34	2 mts.	80	55	2.23	-
	(16)						
36.	Habboush et al.	a) Polyethylene glycol succinate	"	80	-	1.29	1.14
		b) Polyoxyethylene sorbitan monostearate		100	-	1.29	1.11
	(28)						
37.	Nadean et al.	Silicone rubber + tribenzylsilyl	4 ft.	75 to 260	15	1.12	Not reported
	(30)	bisphenylether				<u>BY</u>	<u>BY</u>
38.	Murray et al.	Glycerol	"	78	-	1.72	1.21
	(31)						
39.	Fitzgerald	a) Diglycerol	12 ft.	100	-	1.71	1.16
		b) Triethanolamine	"	100	-	1.67	1.14
40.	Author's data	1,3-propanediol 4-aminophthalic acid polyester	2 mts.	170	3.33	1.28	1.16

Habboush et al.¹² on 2 metres column and the total time of analysis was 125 minutes (polyethylene glycol column) and 76 minutes (tritolyl phosphate column). Olah et al.²⁴ have reported the separation of the three isomers on a 4-metre long polypropylene glycol column at 150°C in 33 minutes. Vasaros et al.⁹ employed Igepal CO-880 column (4 metres) at 130°C for this separation. Separation of the three isomers is also reported by Mortimer et al.²⁶ and Habboush et al.¹⁶ By using 2 metres column with 1,3-propanediol-4-aminophthalic acid polyester, all the isomers of dichlorobenzenes have been resolved at 170°C in just 4 minutes.

Versatility of 1,3-propanediol-4-aminophthalic acid polyester

The relative volatility (α -values) values calculated from retention time data described in the literature for dichlorobenzenes was compared with the corresponding values obtained on 1,3-propanediol-4-aminophthalic acid polyester column and the details are given in Table 9. The comparative evaluation of data reveals that amino-substituted polyester is particularly effective for the separation of chlorobenzenes at temperature as high as 170°C with the normal conditions. In most of the earlier investigations, separation is achieved only at low temperatures or with temperature-programming. Low α -values at somewhat higher temperatures (above 130°C) indicate that the isomers may overlap. Some of the liquid phases employed by earlier workers are not thermally stable at elevated temperatures showing thereby limitations in their use. The amino-substituted

polyester is generally quite versatile in its effect as a stationary phase towards the separation of all the isomers investigated and is reasonably thermally stable at elevated temperatures (upto 220°C).

All these considerations are quite indicative that 1,3-propanediol-4-aminophthalic acid polyester can be put into use as a versatile stationary phase for the separation of wide range of compounds. The further investigations are in progress.

The fact that dichlorobenzene isomers are conveniently separated even at a temperature of 170°C on amino-substituted polyester points out that it can find practical application for separation of higher chlorinated benzenes along with the dichlorobenzene. This led^{us} to investigate the possibility of using this polyester as a liquid phase for the separation of all the chlorinated benzenes. The estimation of all the chlorinated benzenes is generally a problem in industrial chlorination processes. The separation and estimation of these different chlorinated benzene isomers by GLC was, therefore, undertaken by using amino-substituted polyester as the stationary phase. The results of this investigation are presented in the following chapter.

Note: The retention time data of terpenoids do not reveal any special characteristics and hence for the sake of brevity, their behaviour is not discussed here.

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CHAPTER - IV

APPLICATION OF AMINO-SUBSTITUTED AROMATIC POLYESTER
AS STATIONARY PHASE FOR THE ANALYSIS OF CHLORINATED
BENZENE ISOMERS BY GLC

S U M M A R Y

The polyester, prepared from 1,3-propanediol and 4-aminophthalic acid, was found to be very good solvent for dichlorobenzene isomers (previous Chapter). This finding was utilised in actual qualitative as well as quantitative analyses of chlorinated benzene isomers in chlorination processes using different catalysts.

Initially most of the common chlorobenzene isomers, normally associated in chlorination processes, were prepared in this laboratory and several synthetic mixtures of varying compositions were made. Actual quantitative estimation of the individual components in these mixtures was carried out by GLC analyses using the amino-substituted polyester as the liquid phase. Normal deviation factors along with the conditions were properly worked out and the method was standardised.

To study the method of chlorination of benzene in detail, the percentage compositions of reaction mixtures at different intervals of time were estimated according to the standardised GLC technique. The results are described in this part of the thesis.

I N T R O D U C T I O N

Chlorinated hydrocarbons, increasingly in news, came dramatically into their own during World War II. Among the many chlorinated hydrocarbons, monochlorobenzene and dichlorobenzenes are in great demand now and their production is steadily increasing¹. Chlorobenzene is produced commercially as the essential intermediate in the manufacture of phenol, aniline, DDT and a host of other organic intermediates. Dichlorobenzene is manufactured on a large scale, the para isomer being used as a larvacide and the ortho-compound as a solvent and heat-exchange medium².

In the manufacture of most of the chlorobenzenes, such as the commercially important p-dichlorobenzene, a complex reaction mixture results³, which contains not only the desired product and hydrochloric acid but also other chlorobenzenes. For example in the manufacture of p-dichlorobenzene, chlorobenzene and some trichloro-benzenes may be produced in addition to the desired main product.

From chemical engineering point of view, the distribution of the various substituted products is of great importance³. In fact the economy of the process depends upon being able to produce in maximum yield the desired product or combination of the desired products and upon knowing the concentration of the by-products. For this purpose, it is necessary to employ a rapid, simple and

accurate method of analysis.

Earlier methods employed for the purpose required the reaction to be stopped at certain density, established through experience³ and analyzing the product by a series of distillations and freezing point determinations⁴. As the ratio of isomers or the product distribution may be affected to varying extents by reaction temperature, rate of chlorination, type of catalyst, catalyst concentration and whether chlorination is in batch or continuous process⁴, the fragmentary density values available in the literature may be misleading⁵. Moreover, analysis by distillation and freezing point determinations require considerable time and excessive handling.

Crude mixtures of chlorinated benzenes have been analysed for sometime by infra-red methods⁶. Infra-red quantitative analysis data for determination of benzene and chlorobenzenes in chlorinated benzene has been reported by Hudson⁷ and Kiley⁸. Kiley suggests that preliminary separation of lowers and highs by distillation with subsequent infra-red analysis of cuts is desirable in the case of more complicated chlorobenzene mixtures. However, it is not always possible to estimate all the components present in these mixtures because of the complexity of the infra-red spectrum resulting from numerous similar compounds and because of a general lack of sensitivity for small concentrations.

Troupe and Colner⁵ employed the GLC technique as a process control method in the chlorination of benzene using

ferric-chloride catalyst at 50°C to produce p-dichlorobenzene (batch process). They employed dinonyl phthalate column at 150°C and samples containing polychlorinated benzenes required approximately 2.5 hours for the last component to appear.

Nadean and Oaks⁹ observed that GLC technique is extremely useful for the separation and analysis of chlorinated organics. The published methods, however, dealt primarily with separations of relatively low-boiling compounds and were not suited for application to complicated mixtures such as the following series of wide boiling range isomeric chlorinated benzenes-benzene, chlorobenzene, ortho-and para-dichlorobenzene, 1,2,4-tri-and 1,2,3-tri-chlorobenzene, sym- and vic-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene.

These workers further pointed out that the wide range in boiling points between isomeric chlorinated benzenes dictated that the GC separation would be more effective if it were performed on a high temperature limit partitioning material and if it were temperature programmed. Temperature programmed separations are most applicable where speed and flexibility of operation are requisite in dealing with compounds possessing a wide spread in boiling points, as in this case. They describe the analysis of synthetic mixtures from monochloro-to hexachloro-benzenes on a temperature programmed gas chromatograph with column temperature range,

75°-260°C and a new liquid phase, tribenzylsilylbisphenyl ether, has been found more useful than the silicone phase.

Schwartz et al.¹⁰ report a method for the analysis of chlorinated benzenes (consisting of 44% 1,2,3,4-tetrachlorobenzene, 33% 1,2,4-trichlorobenzene, 9% penta-chlorobenzene and other chlorinated compounds) in clams and oysters on a silicone gum column (SE-30) at 130° with an electron affinity detector.

Gershtein and co-workers¹¹ investigated the separation of mixtures containing mono-, di- and trichlorobenzenes on various stationary phases and found that best separations were obtained on poly(methyl-phenyl-siloxane), poly(ethylene-adipate) and β,β' -thiodipropionitrile. Quantitative separations of mixtures of chlorobenzenes and chain chlorinated toluenes were achieved at 125-45°C on a hyflosuper cel column¹² with nitrogen as the carrier gas. Hrivnak and Stota¹³ employed poly(propylene adipate) with 2% phosphoric acid as the stationary phase for GC determination of all di-, tri-, and tetra-chlorobenzene isomers in technical trichlorobenzene.

Abe et al.¹⁴ investigated various column packings for the complete separation of chlorobenzene mixtures (benzene, chlorobenzene, ortho-, meta-, and para-dichlorobenzene, and 1,2,4-trichlorobenzene) and found Betone-34 modified with polyethyleneglycol-6000 and di-isodecyl-phthalate are more effective than others for GC analyses of the chlorobenzenes. GC analysis of products formed during chlorobenzene production,

such as benzene, chlorobenzene, ortho- and para-dichlorobenzene was studied by Hudzik and Sokolowska¹⁵ on a 3 m column of polyethyleneglycol-400 at 90°C.

Hrivnak and Michalek¹⁶ separated all positional chloro-substituted derivatives of benzene on open tubular column (0.25 mm i.d., 10 m long) coated with diethylene glycol-succinate with temperature programmed at 4°C/min. from 50° to 150°C.

Present investigation

During the course of present investigation in this laboratory, it was observed that 1,3-propanediol-4-aminophthalic acid polyester (previous Chapter) has a good solvent capability for chlorinated benzenes. It was therefore considered interesting to investigate its application as a stationary phase in GLC analysis of chlorinated isomers from the actual chlorination of benzene. A study was, therefore, undertaken to standardise the GLC method for the quantitative estimation of the products from this process and the detailed results are presented in this part of the thesis.

EXPERIMENTAL

The following chlorobenzene isomers were examined for initial standardisation of the GLC method: (i) Chlorobenzene (ii) m-dichlorobenzene (iii) p-dichlorobenzene (iv) o-dichlorobenzene (v) 1,2,4-trichloro- and 1,3,5-trichlorobenzene (vi) 1,2,4,5-tetrachloro- and 1,2,3,5-tetrachlorobenzene (vii) pentachlorobenzene and (viii) hexachlorobenzene.

Chlorobenzene, ortho- and para-dichlorobenzene were available from the laboratory stock and they were purified by careful fractionation. Their purity was checked by elemental analysis and GLC (single peak).

The remaining chlorinated benzenes were not available and therefore had to be prepared.

m-Dichlorobenzene was prepared by the method described in the previous Chapter.

1,2,4-Trichlorobenzene was synthesised from p-dichlorobenzene by the action of chlorinating agent prepared from anhydrous aluminium chloride, sulfuryl chloride, sulphur monochloride and thionyl chloride by following the method of Silberrad¹⁷.

By using the Silberrad's chlorinating agent, 1,2,4,5-tetrachloro, 1,2,3,5-tetrachlorobenzene and hexachlorobenzene were also prepared in this laboratory.

1,3,5-Trichlorobenzene can be synthesised from 2,4,6-trichloroaniline by diazotisation and subsequent knocking off the diazo group. 2,4,6-trichloroaniline was prepared by the chlorination of aniline hydrochloride by the method of Chattaway and Irving¹⁸.

It was converted to 1,3,5-trichlorobenzene by diazotisation in the presence of concentrated sulphuric acid as described in literature¹⁹.

Pentachlorobenzene was synthesised from pentachloronitrobenzene (available from the laboratory stock) by reduction with iron powder and hydrochloric acid and subsequent treatment with sodium nitrite in the presence of concentrated sulphuric acid¹⁹.

The purity of all the chlorinated benzene isomers^{was} checked by melting point/boiling point determination, elemental analysis and GLC (single peak). Since these compounds were required for standardisation of the GLC methods, it was ensured all these samples are above 99% purity.

Stationary phase

1,3-Propanediol-4-aminophthalic acid polyester was used as the liquid phase throughout in this study.

Impregnation, column filling and conditioning

The procedure described earlier was followed in this case also.

Results and discussion

Standardisation of the GLC method

(1) Synthetic mixtures of dichlorobenzenes: To start with, synthetic mixtures of three dichlorobenzenes in different

proportions were prepared on weight basis (Table 1).

Table 1
Analysis of standard mixtures of
dichlorobenzenes

S.No. Component	Mixture No.1		Mixture No.2		Mixture No. 3	
	%Calcd.	% Found	%Calcd.	%Found	%Calcd.	%Found
1.m-Dichloro- benzene	25.89	25.74	47.18	47.23	29.18	29.35
2.p-Dichloro- benzene	33.45	32.70	27.20	27.29	33.50	33.64
3.o-Dichloro- benzene	40.66	41.56	25.62	25.47	37.32	36.98

Response Factors

S.No. Component	Mixture No.1	Mixture No.2	Mixture No.3	Average response factor
1.m-Dichloro- benzene	1.006	0.9988	0.9945	0.9994
2.p-Dichloro- benzene	1.023	0.9994	0.9992	1.0072
3.o-Dichloro- benzene	0.9783	1.006	1.009	0.9978

The mixtures were analysed on amino-substituted polyester at various temperatures such as 130°, 150° and 170°C. It was observed that at 130°C, three good peaks corresponding to the three isomers are obtained (see chromatogram in Figure 1).

FIG. 1 DICHLORO-BENZENES - SYNTHETIC MIXTURE

FIG. 2 DICHLORO- AND TRICHLORO-BENZENES - SYNTHETIC MIXTURE

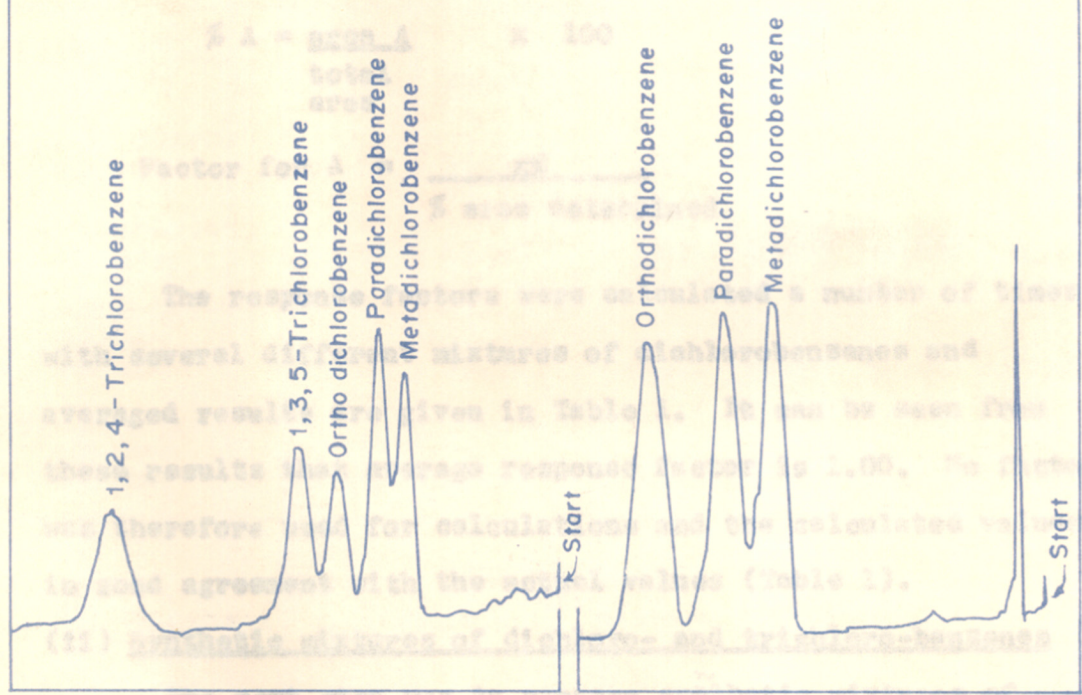


FIG. 2

FIG. 1

The detector response factors were calculated according to the method of Nadean and Oaks⁹. This consists in obtaining chromatograms of the standard mixtures under experimental conditions, calculating percentage composition by direct internal normalisation and solving for the factor relating this calculated value to the true value. For example, if :

Some solution contains x% A + y% B + z% C, etc.

Total area of chromatogram = area A + area B + area C

By direct internal normalisation

$$\% A = \frac{\text{area A}}{\text{total area}} \times 100$$

$$\text{Factor for A} = \frac{x\%}{\% \text{ area determined}}$$

The response factors were calculated a number of times with several different mixtures of dichlorobenzenes and averaged results are given in Table 1. It can be seen from these results that average response factor is 1.00. No factor was therefore used for calculations and the calculated values were in good agreement with the actual values (Table 1).

(11) Synthetic mixtures of dichloro- and trichloro-benzenes

The next step was to prepare synthetic mixtures of three dichlorobenzenes and two trichlorobenzenes in varying proportions on weight basis (details in Table 3) and calculate their response factors. In this case also, the response factors averaged 1.00 (Table 2) and so no factor was used

for calculation of the percentage compositions of the mixtures. The actual values were found to agree well with the calculated ones. The chromatogram showing the analysis of a dichloro- and trichlorobenzene mixture is given in Figure 2.

Table 2

Analysis of standard mixtures of dichloro-
benzenes and trichlorobenzenes

S.No. Component	Mixture No.1		Mixture No.2		Mixture No.3	
	%Calcd.	%Found	%Calcd.	%Found	%Calcd.	%Found
1.m-Dichloro- benzene	17.20	16.89	32.86	33.32	7.75	7.84
2.p-Dichloro- benzene	25.25	24.34	23.65	24.01	20.05	20.58
3.o-Dichloro- benzene	13.87	14.22	7.06	6.80	12.50	12.64
4.1,3,5-Tri- chloro- benzene	23.30	23.60	8.48	8.25	20.30	20.55
5.1,2,4-Tri- chloro- benzene	20.38	20.80	27.89	27.62	39.39	38.63

Response Factors

S.No. Component	Mixture No.1	Mixture No.2	Mixture No.3	Average respon- se factors
1.m-Dichlorobenzene	1.0180	0.9863	0.9886	0.9970
2.p-Dichlorobenzene	1.0380	0.9849	0.9786	1.0005
3.o-Dichlorobenzene	0.9718	1.039	0.9888	1.0030 0.9998
4.1,3,5-Trichloro- benzene	0.9874	1.028	0.9926	1.0030
5.1,2,4-Trichloro- benzene	0.9797	1.009	1.020	1.0029

(iii) Synthetic mixtures of all the chlorobenzenes

Finally, a mixture of all the chlorobenzenes from monochlorobenzene to hexachlorobenzene was prepared. To dissolve the solid components, a little quantity of benzene was added to the mixture. The peak representing benzene in the chromatogram was therefore ignored for computing the percentage composition of the mixture. The hexachlorobenzene peak, however, did not appear within reasonable time even at a column temperature of 170°C. It was therefore dropped and fresh standard mixtures were prepared with different proportions of chlorobenzenes upto pentachlorobenzene only (details given in Table 3). The mixtures were analysed at a column temperature of 170°C. A typical chromatogram showing the analysis of such mixtures is presented in Figure 3. At column temperature of 170°C, m-dichlorobenzene and p-dichlorobenzene peaks as well as o-dichlorobenzene and 1,3,5-trichlorobenzene peaks were not completely resolved. To calculate the areas of these peaks, it was decided to employ the method suggested by Bartlet and Smith²⁰. This method, however, did not prove to be of much use.

As an alternative, the column was run at two different temperatures, namely at 170°C for higher chlorinated benzenes and subsequently at 130°C for lower chlorinated benzenes. Partially resolved peaks at 170°C for m-dichlorobenzene and p-dichlorobenzene as well as o-dichlorobenzene and 1,3,5-trichlorobenzene respectively were taken as single peaks for

Table 3

Analysis of standard mixtures of dichlorobenzenes, trichlorobenzenes, tetrachlorobenzenes and pentachlorobenzenes

S.No. Component	<u>Mixture No.1</u>		<u>Mixture No.2</u>		<u>Mixture No.3</u>	
	%Calcd.	%Found	%Calcd.	%Found	%Calcd.	%Found
1.Chlorobenzene	10.30	10.24	15.38	15.45	5.11	5.01
2.m-Dichlorobenzene	20.47	20.52	12.69	12.78	15.75	15.61
3.p-Dichlorobenzene	25.36	25.42	18.53	18.49	10.32	10.41
4.o-Dichlorobenzene	5.82	5.71	10.21	10.27	16.26	16.34
5.1,3,5-Trichlorobenzene	10.69	10.82	14.12	13.94	6.85	6.79
6.1,2,4-Trichlorobenzene	7.38	7.29	11.25	11.13	20.92	21.07
7.1,2,4,5-Tetrachlorobenzene	15.68	15.75	7.72	7.63	9.34	9.22
8.1,2,3,5-Tetrachlorobenzene						
9.Pentachlorobenzene	4.37	4.28	10.42	10.35	15.40	15.52

Response Factors

S.No. Component	Mixture No.1	Mixture No.2	Mixture No.3	Average value of response factor
1.Chlorobenzene	1.009	0.9954	1.020	1.0081
2.m-Dichlorobenzene	0.9974	0.9956	1.009	1.007
3.p-Dichlorobenzene	0.9977	1.0140	0.9913	1.001
4.o-Dichlorobenzene	1.020	0.9944	0.9949	0.9971
5.1,3,5-Trichlorobenzene	0.9881	1.0130	1.009	1.0034
6.1,2,4-Trichlorobenzene	1.013	1.011	0.9928	1.0056
7.Tetrachlorobenzene	0.9954	1.012	1.013	1.0068
8.Pentachlorobenzene	1.021	1.007	0.9922	1.0067

CHLOROBENZENES-SYNTHETIC MIXTURE

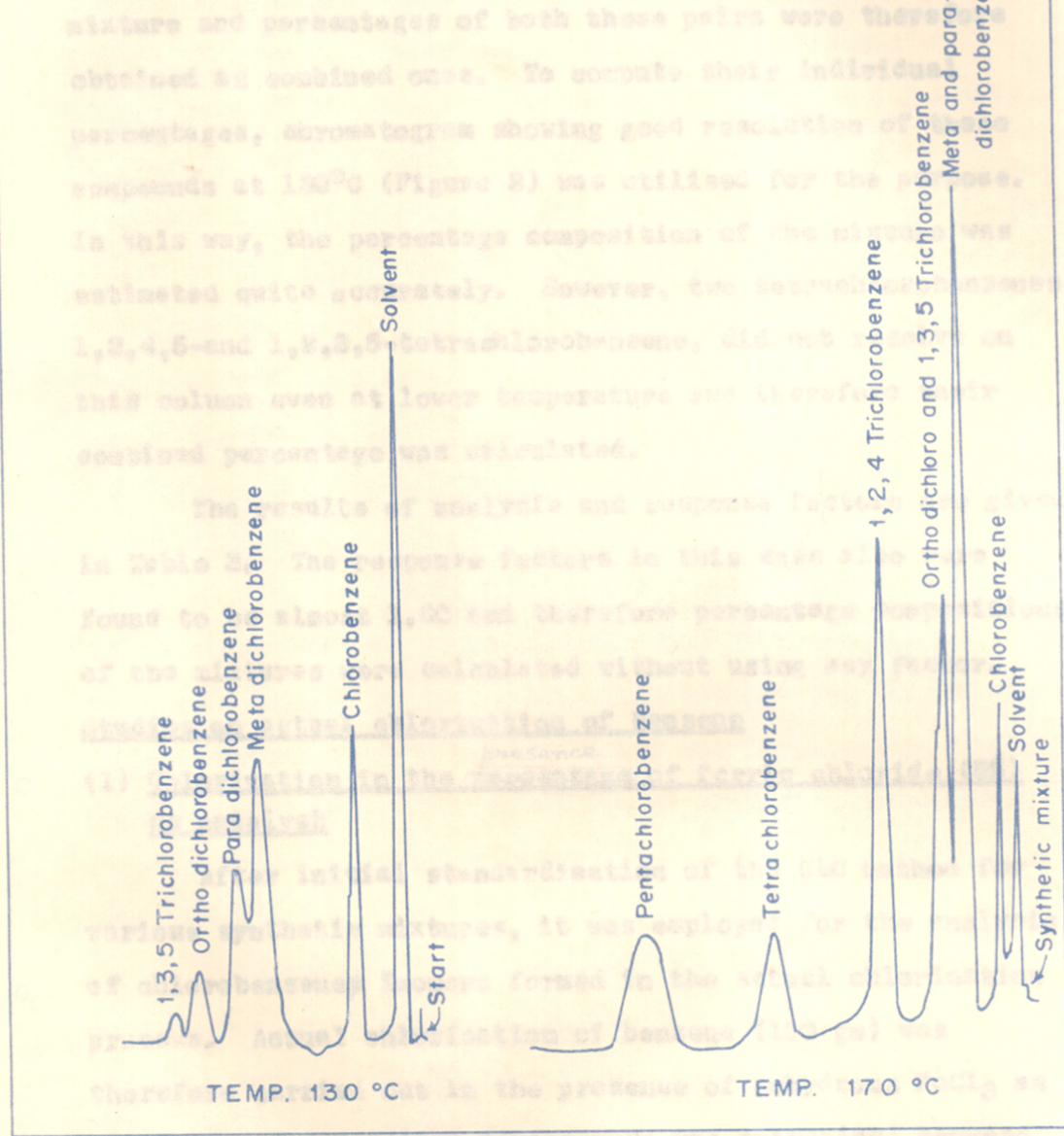


FIG. 3

initial calculation of the percentage composition of the mixture and percentages of both these pairs were therefore obtained as combined ones. To compute their individual percentages, chromatogram showing good resolution of these compounds at 130°C (Figure 3) was utilised for the purpose. In this way, the percentage composition of the mixture was estimated quite accurately. However, two tetrachlorobenzenes, 1,2,4,5- and 1,2,3,5-tetrachlorobenzene, did not resolve on this column even at lower temperature and therefore their combined percentage was calculated.

The results of analysis and response factors are given in Table 3. The response factors in this case also were found to be almost 1.00 and therefore percentage compositions of the mixtures were calculated without using any factor.

Studies on actual chlorination of benzene

(1) Chlorination in the ^{presence} ~~percentage~~ of ferric chloride (5%) as catalyst

After initial standardisation of the GLC method for various synthetic mixtures, it was employed for the analysis of chlorobenzene isomers formed in the actual chlorination process. Actual chlorination of benzene (100 gm) was therefore carried out in the presence of anhydrous FeCl₃ as catalyst. The reaction temperature was maintained between 60-70°C and the rate of passing chlorine gas was about 1.25 litres per hour. The reaction was continued for 12 hrs. The first sample was withdrawn after 6 hrs. and next after every 2 hours to study the progress of the reaction.

The samples were dissolved in ether, washed with water and dried over anhydrous sodium sulphate. The results of analysis of the samples withdrawn at different intervals of time as well as final percentage composition are presented in Table 4 and the final chromatogram as Figure 4. A part of the final chlorinated product was carefully fractionated and each of the fractions thus collected was also analysed to check the composition of the final product. The results agree fairly well (Table 4).

(2) Chlorination in the presence of ferric chloride (10%) as catalyst

As the chlorination of benzene has proceeded mainly upto dichlorobenzene stage with the formation of little trichlorobenzene, it was decided to increase the percentage of catalyst to 10% and also to raise the temperature from 60-70°C to 70-80°C. The formation of higher chlorinated-benzenes would thus be possible under these experimental conditions.

Chlorine gas at the rate of about 1.25 litres/hour was passed into the mixture of benzene (100 gm) and anhydrous ferric chloride (10 gm), maintained at 70-80°C on a water-bath for a period of 18 hours. To study the kinetics of the reactions, samples were withdrawn after 2 hours (first sample withdrawn after 6 hours) and their percentage compositions were estimated by the GLC method standardised. Results are recorded in Table 5. The final product was analysed as such,

Table 4

Analysis of chlorinated benzenes - chlorination with 5% FeCl₃ as catalyst at 60-70°C

S.No. Component	Sample withdrawn after a			Percentage composition of final product after 12 hours by GLC	Percentage composition of final product by fractionation and subsequent GLC analysis	
	Period of	6 hrs.	8 hrs.			10 hrs.
1. Benzene		64.81%	50.13%	45.11%	39.56%	38.18%
2. Chlorobenzene		35.19%	49.87%	47.55%	49.45%	18.92%
3. p-Dichlorobenzene		-	-	3.86%	6.51%	6.60%
4. o-Dichlorobenzene		-	-	3.47%	3.52%	3.24%
5. 1,2,4-Trichlorobenzene		-	-	-	0.94%	1.00%
6. Residue		-	-	-	-	2.12%

CHLORINATION OF BENZENE -

10 % FeCl₃ (FIG. 5)

5 % FeCl₃ (FIG. 4)

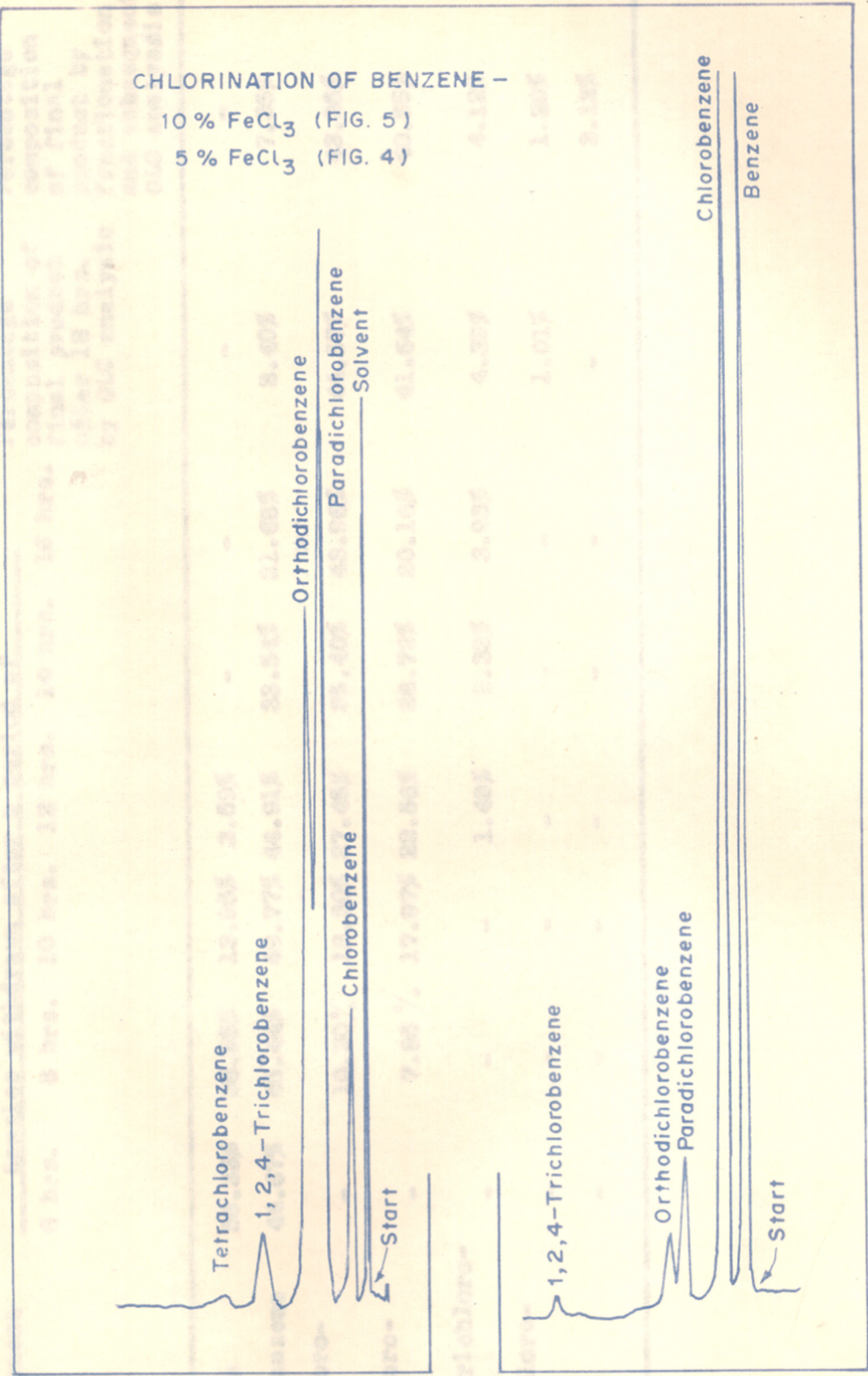


FIG. 5

FIG. 4

Table 5

Analysis of chlorinated-benzenes - Chlorination with 10% FeCl₃ as catalyst at 70-80°C

S.No. Component	Samples withdrawn after a period of						Percentage composition of final product after 18 hrs. by GLC analysis	Percentage composition of final product by fractionation and subsequent GLC analysis
	6 hrs.	8 hrs.	10 hrs.	12 hrs.	14 hrs.	16 hrs.		
1. Benzene	55.33%	36.25%	13.95%	3.59%	-	-	-	-
2. Chlorobenzene	44.67%	45.44%	49.77%	44.91%	33.54%	21.68%	8.40%	7.35%
3. p-Dichloro-benzene	-	10.30%	18.30%	27.45%	35.40%	43.96%	44.57%	43.35%
4. o-Dichloro-benzene	-	7.95%	17.97%	22.56%	28.72%	20.16%	41.64%	40.85%
5. 1,2,4-Trichloro-benzene	-	-	-	1.49%	2.33%	3.93%	4.39%	4.12%
6. Tetrachloro-benzene	-	-	-	-	-	-	1.01%	1.20%
7. Residue	-	-	-	-	-	-	-	3.12%

as well as after fractionation and the results are incorporated in the same Table 5 and chromatogram ^S Figure 5. Direct chromatography analysis results are in well agreement with k fractionation plus GLC technique results.

(3) Chlorination in the presence of aluminium chloride as catalyst

To study the effect of catalyst on the chlorination of benzene, another ^r reaction was carried out with 10% anhydrous aluminium chloride as the catalyst. The other experimental conditions were the same as mentioned above. Samples taken after 2 hours, as well as the final product were analysed by GLC method and the results of their percentage compositions are given in Table 6. The fractionation of the final product was carried out carefully and the results of analysis of the various fractions are also presented in Table 6. It is observed that the chlorination rate is faster in case of aluminium chloride than ^a ferric chloride as catalyst, since the chlorination proceeds upto pentachlorobenzene stage in this case. The chromatogram showing analysis of final product is enclosed as Figure 6. It is observed that one additional peak appears after the peak for 1,2,4-trichlorobenzene. It was, however, not possible to identify the compound representing this peak. Most probably, the compound may be 1,2,3-trichlorobenzene.

Table 6

Analysis of chlorinated benzenes - chlorination with 10% $AlCl_3$ as catalyst at 70-80°C

S.No. Component	Samples withdrawn after a period of				Percentage composition of final product after 18 hrs by GLC analysis	Percentage composition of final product by fractionation and subsequent GLC analysis
	6 hrs.	8 hrs.	10 hrs.	12 hrs. 14 hrs. 16 hrs.		
1. Benzene	57.29%	36.09%	10.13%	-	-	-
2. Chlorobenzene	42.71%	52.86%	53.86%	44.73%	40.96%	31.00%
3. <i>p</i> -Dichlorobenzene	-	5.96%	16.54%	28.14%	29.03%	24.56%
4. <i>o</i> -Dichlorobenzene	-	5.06%	13.55%	18.72%	10.37%	14.17%
5. 1,2,4-Trichlorobenzene	-	-	6.25%	8.36%	11.34%	14.48%
6. Tetrachlorobenzene	-	-	-	-	4.69%	7.93%
7. Pentachlorobenzene	-	-	-	-	3.63%	7.87%
8. Residue	-	-	-	-	-	-

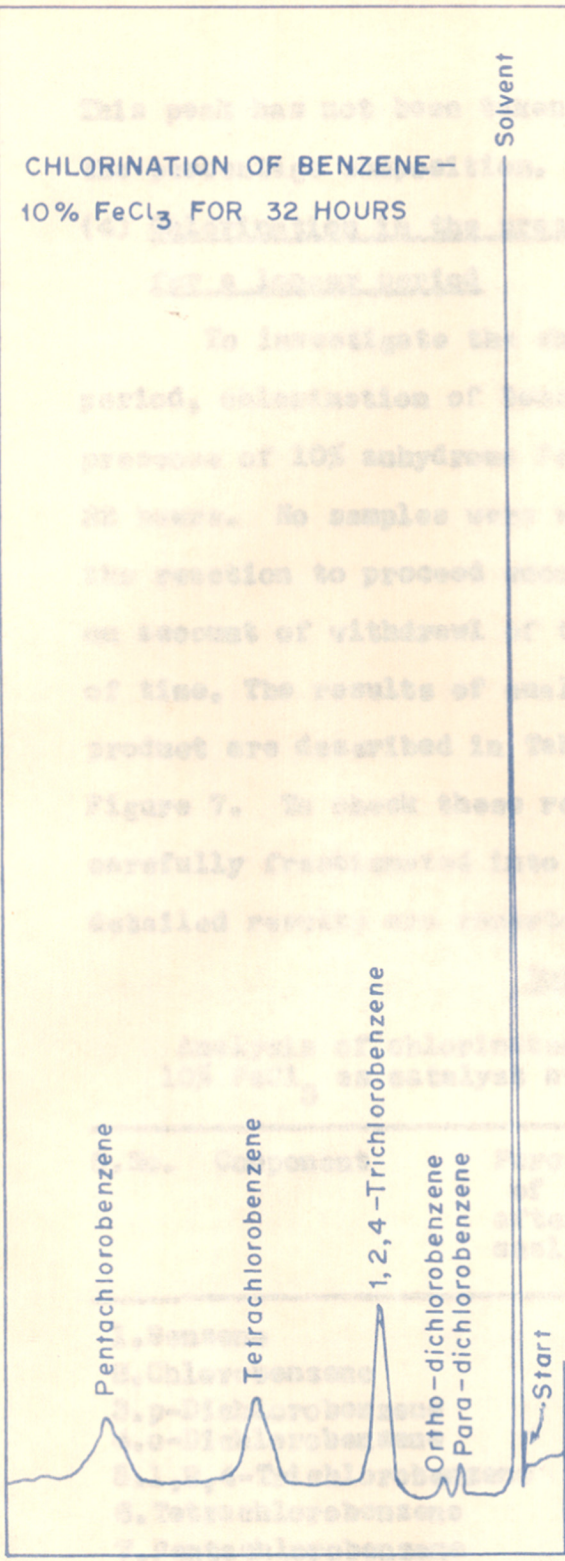


FIG. 7

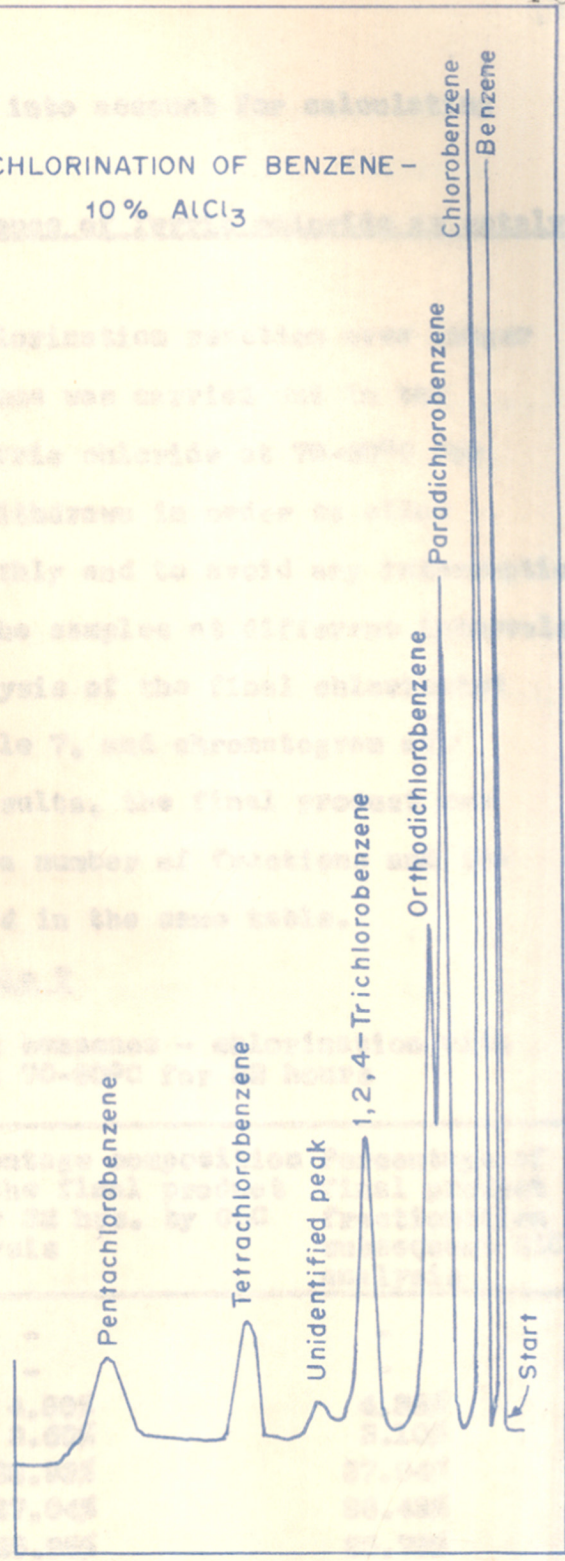


FIG. 6

This peak has not been taken into account for calculating the percentage composition.

(4) Chlorination in the presence of ferric chloride as catalyst for a longer period

To investigate the chlorination reaction over longer period, chlorination of benzene was carried out in the presence of 10% anhydrous ferric chloride at 70-80°C for 32 hours. No samples were withdrawn in order to allow the reaction to proceed smoothly and to avoid any interruption on account of withdrawal of the samples at different intervals of time. The results of analysis of the final chlorinated product are described in Table 7, and chromatogram ^se Figure 7. To check these results, the final product was carefully fractionated into a number of fractions and the detailed results are reported in the same table.

Table 7

Analysis of chlorinated benzenes - chlorination with 10% FeCl₃ as catalyst at 70-80°C for 32 hours

S.No.	Component	Percentage composition of the final product after 32 hrs. by GLC analysis	Percentage of the final product by fractionation and subsequent GLC analysis
1.	Benzene	-	-
2.	Chlorobenzene	-	-
3.	p-Dichlorobenzene	4.50%	4.36%
4.	o-Dichlorobenzene	3.60%	3.10%
5.	1,2,4-Trichlorobenzene	38.93%	37.94%
6.	Tetrachlorobenzene	27.04%	26.48%
7.	Pentachlorobenzene	25.95%	25.75%
8.	Residue	-	2.33%

The residue left after fractionation in all the cases was found to be mainly charred material, insoluble in common organic solvents.

General comments on chlorination by both the methods

In ferric chloride method (18 hrs.), the final analysis shows that the mixture contains basically dichlorobenzenes comprising about 80% of the total product, while in case of aluminium chloride method, distribution of all the chlorobenzenes is well balanced. All the products are formed during that period. Benzene is found upto 10 hrs. chlorination in about the same proportion in both the cases. In ferric chloride method, reaction does not go beyond trichloro-stage even after 16 hours and finally after 18 hours, a little tetrachlorobenzene is formed. While in the case of aluminium chloride, reaction proceeds upto pentachlorobenzene stage after 13 hours and the proportion of higher chlorinated products goes on increasing on further chlorination.

In exhaustive chlorination (32 hrs.) in the presence of ferric chloride catalyst, mostly tri-, tetra-, and pentachlorobenzenes are formed with very little dichlorobenzenes.

The versatility of this phase, 1,3-propanediol-4-aminophthalic acid polyester, is satisfactorily proved by the results obtained in this Chapter as well as in the previous Chapter.

Further investigations on the reaction kinetics of the different chlorination processes are in progress and will be reported separately.

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CHAPTER - V

EVALUATION OF INDIAN FIRE-BRICK AS SOLID SUPPORT
FOR GAS-LIQUID CHROMATOGRAPHY: COMPARATIVE STUDY
WITH CHROMOSORB

S U M M A R Y

Throughout the entire investigation, Indian fire-brick powder has been used as the solid support. It was, therefore, felt necessary to compare its behaviour as solid support with that of chromosorb, which is an internationally recognized supporting material. The values of "S", "q", "R" and "H.E.T.P." were calculated for both types of the support for comparison. "R" values of fire-brick columns were also found to coincide with that of chromosorb columns. It was observed that fire-brick support is quite comparable to chromosorb. It is possible to construct efficient columns with this material as the support after proper adjustment of the weight of the liquid phase.

The column has been described as the "heart of the gas chromatograph" and in its efficient performance the solid support plays a critical part¹. The solid support serves to hold the stationary phase and at the same time exposes a large inert surface area for rapid equilibrium between the solute and solvent. Diatomaceous earth has been widely used as the solid support since the early stages of development of GLC.

The degree of inertness of the support is of prime importance in GLC. When polar compounds are chromatographed on columns containing diatomaceous earth supports, peak tailing usually occurs. This is caused by the adsorption of the solute on the support. The practical efficiency of the column is considerably reduced by peak tailing. Peak tailing is particularly troublesome in columns with low loading of a non-polar liquid phase and also when small samples are chromatographed. It is caused by "active sites" of the support surface and much work (discussed below) has been done by several workers to eliminate these sites.

It is generally agreed that the active centres consist of hydroxyl groups associated with silicon, aluminium and iron². T. Johns³ reduced the tail of polar compounds on a column of silicone 550 oil on fire-brick by adding 2% of a polar substrate, polyethylene glycol-600, which forms hydrogen bonding with these surface groups. Other workers have used acid-washing treatments to deactivate the surface of the

diatomaceous earth⁴. For amines, James and Martin⁵, among others have treated the acid-washed support with alkali. Fales and Pisano⁶, however, observe that tailing would still persist if the compounds being analysed contain -OH or -NH groups. These techniques are described in detail by Burchfield and Storrs⁷. Omerod and Scott⁸ covered the surface of the solid support with an inorganic deactivating agent such as silver.

An alternative technique which has been widely used for deactivating diatomaceous earth supports is the modification of the surface -OH groups by reacting with a silanising agent. A procedure for this, using dimethyldichlorosilane (DMCS), was reported by Horning et al.^{9,10} and a detailed study of this technique was carried out by others^{11,12}. Procedures for silanisation have also been described by several workers^{13,14,15}. The silanisation however changes the surface character of the support from hydrophillic to hydrophobic and it becomes difficult to coat with polar phases because of the poor wetting of the surface¹. In an attempt to overcome this difficulty, Vanden Heuvel et al.¹⁶ used a coating of poly-(vinyl pyrrolidone) which they claim acts as a satisfactory support deactivator for use with polar compounds.

Many workers have chemically bonded silicones to chromatographic supports^{17,18} and observed comparable behaviour of "support-bonded" and "regular" GLC phases in terms of column efficiency and overall performance with chromatographic

problem compounds^{19,20}.

The fluorine polymers have been employed as inert solid supports in various applications. Kirkland²¹ has studied fluoro-polymers as support materials in detail. Sawyer and Barr²² in a comparative study of support materials observed that the fluorocarbon support produced very poor plate heights. Ottenstein²³ reported low efficiencies produced with this material as the solid support.

Onaka and Okamoto²⁴ found ^d diatomaceous earth supports coated with PTFE useful for the analysis of polar materials. Kirkland²⁵ compared the performance of these supports with Teflon-6 and found comparatively more tailing, indicating thereby incomplete coating of the support surface.

Dimbat et al.²⁶ have compared crushed diatomaceous earth fire-brick (Johns-Manville C-22) with celite 545 and found higher resolving power ~~am~~ per unit length than celite under comparable conditions. A fire-brick, which has comparable properties and is marketed in Germany under the name of "sterchamol", has been successfully used as a column support by Keulemans and Kwantes²⁷. Nigam and Gupta²⁸ have evaluated Indian fire-bricks as solid supports in terms of their physical and chemical characteristics, adsorption and catalyst activities.

Present investigation

In this laboratory the technique of GLC has been in use for quite a long time for the analysis of terpenes and allied products. Polyester type stationary phases²⁹ and Indian fire-

brick support³⁰ have been systematically studied. The present investigation is in continuation of the same.

Due to non-availability of the imported supports such as celite and chromosorbs, the investigations were carried out using locally available fire-brick powder as the solid support. It was therefore considered necessary to carry out comparative evaluation of this material as column support. Chromosorb has been used all along for comparison and the results are described in this part of the thesis.

EXPERIMENTAL

For a proper comparison of the fire-brick powder with chromosorb W, the following parameters were kept constant:

- i) Column temperature: $170^{\circ} \pm 1^{\circ}\text{C}$ (no injection port heating)
- ii) Flow rate of the carrier gas (hydrogen): 4 litres/hr.
- iii) Column length: 2 metres.

Stationary phase

Polyester, from 1,3-propanediol and 4-aminophthalic acid (described in Chapter III) was used as the liquid phase.

Preparation and properties of the fire-brick powder

Different fire-brick powders available locally were examined and a variety having surface area of about 2 sq.m./g. was used for these investigations. The crushed fire-brick powder was sieved and the fraction passing through 60 mesh sieve and retained on 100 mesh- sieve was collected. The sieved material was taken in a round-bottomed flask and it was washed several times with tap water to remove the fine particles. This material was then treated with concentrated hydrochloric acid and allowed to stand for 24 hrs. After this period, it was washed with water till free from the acid. It was then treated with hot concentrated sodium hydroxide solution and allowed to stand overnight as such. The material was subsequently washed repeatedly with distilled water until ^{free} from alkali. It was allowed to drain and then air-dry. The air-dried material was

ignited at about 600°C for several hours and then transferred to a pyrex glass container, when its temperature came down to about 150°C. The material was stored in an air-tight container. Its storage in air-tight container has proved very useful. Supina et al.³¹ have reported a similar observation earlier. The fire-brick powder thus prepared is light brown in colour and has enough mechanical strength to withstand handling during impregnation or filling in the column.

Packing density of the fire-brick powder

Fire-brick powder (size 60-100 mesh) was filled in 25 ml burette in the same way as it is packed in the chromatographic column. A number of readings gave its density as 0.75 g/ml.

Impregnation and column filling

The impregnation of the support with the liquid phase was carried out as described in the previous chapters of this thesis. 1,3-Propane-diol-4-aminophthalic acid polyester was employed all along as the stationary phase. The liquid phase was used in the following percentages: (i) 3% (ii) 5% (iii) 7% and 10% (w/w).

For comparison, chromosorb W (60/100 mesh) was used as the solid support. It was purified in the same way as described for fire-brick. The following percentages of the liquid substrate (w/w) were employed (i) 15%, and (ii) 20%.

The packing material was carefully filled into the column with gentle tapping by a rubber hammer. The two ends

of the column were closed with glass wool plugs. The weight of the stationary phase was estimated from the weight of column packing filled actually.

The following compounds which were used in the earlier work (Chapter I to III) were chosen as the samples for comparative evaluation of the packing material.

Terpenic compounds

(i) p-Cymene (ii) linalool (iii) citronellol (iv) geraniol (v) menthone (vi) longifolene (vii) isolongifolene (viii) geranyl acetate and (ix) α -terpeneol.

Aromatic and other compounds

(i) o-Cresol (ii) m-cresol (iii) p-cresol (iv) o-toluidine (v) m-toluidine (vi) p-toluidine (vii) pyridine (viii) α -picoline (ix) β -picoline (x) γ -picoline (xi) chlorobenzene (xii) o-dichlorobenzene (xiii) p-dichlorobenzene (xiv) m-dichlorobenzene and (xv), 1,2,4,-trichlorobenzene.

Results and discussion

Retention time data was recorded at $170 \pm 1^\circ\text{C}$. The retention distances (t_R) and peak widths were measured from chart (in mm) and the results are given in Table 1. The last two columns of the Table 1 represent the data collected for columns filled with impregnated chromosorb W solid support.

For direct comparison of the two types of supports, values of relative peak separation (S_{12}), relative peak sharpness (Q) and resolution (R) have been calculated for various compound pairs according to the method of Jones et al.³² and are presented

Table 1
 Effect of liquid loading on retention time and band broadening
 Temperature: 170 ± 1°C

S.No.	Stationary phase	Fire-brick: 60-100 mesh						Chromosorb					
		3%		5%		7%		10%		15%		20%	
Compound	t _R (mm)	Peak width (mm)	t _R (mm)	Peak width (mm)	t _R (mm)	Peak width (mm)	t _R (mm)	Peak width (mm)	t _R (mm)	Peak width (mm)	t _R (mm)	Peak width (mm)	
1. o-Cresol	25.00	5.00	42.00	7.00	72.00	12.10	85.50	14.40	32.50	5.30	47.50	8.00	
2. m-Cresol	36.00	6.75	61.50	9.75	85.50	13.50	127.00	20.5	46.5	7.10	67.5	10.50	
3. p-Cresol	35.00	6.50	58.50	8.75	81.30	12.50	115.00	18.00	46.25	7.00	70.00	10.80	
4. o-Toluidine	19.00	4.25	31.80	6.75	43.50	9.50	62.00	13.60	25.00	5.30	33.25	7.10	
5. m-Toluidine	21.50	4.75	36.50	7.00	48.50	9.75	72.50	14.75	28.00	5.50	39.00	7.90	
6. p-Toluidine	21.00	4.75	22.50	6.50	46.00	9.25	69.00	14.00	26.75	5.30	37.50	7.50	
7. Pyridine	8.50	0.80	4.75	1.00	8.00	1.75	10.25	2.25	4.24	0.90	9.25	2.00	
8. α-Picoline	3.50	0.90	4.75	1.10	8.75	2.10	11.00	2.75	5.50	1.30	9.00	2.10	
9. β-Picoline	6.00	1.50	8.00	1.90	11.50	2.75	18.50	4.50	8.90	2.10	11.50	2.75	
10. γ-Picoline	6.10	1.60	8.50	2.00	13.25	3.25	19.00	4.75	13.00	3.10	15.5	3.75	
11. Chlorobenzene	2.5	0.50	3.6	0.70	4.60	0.90	8.10	1.60	3.30	0.65	3.75	0.75	
12. o-Dichloro-benzene	6.00	1.50	11.00	2.50	16.10	3.75	22.50	5.25	7.90	1.80	12.00	2.80	
13. p-Dichloro-benzene	5.75	1.50	9.00	2.20	13.25	3.25	18.00	4.5	7.25	1.75	9.00	2.20	
14. m-Dichloro-benzene	5.10	1.25	7.00	1.50	11.1	2.50	16.00	3.80	6.00	1.25	8.00	1.80	
15. 1,2,4-trichlorobenzene	12.50	3.00	20.00	4.50	29.00	6.60	39.5	9.00	15.75	3.50	20.80	4.70	
16. p-Cymene	4.00	1.00	5.50	1.25	6.50	1.50	11.00	2.70	5.20	1.20	6.00	1.40	
17. Linalool	8.00	2.00	12.50	2.75	18.50	4.10	27.00	6.00	10.00	2.20	14.00	3.10	
18. Citronellol	13.50	3.10	21.00	4.00	31.50	6.25	42.50	8.50	15.25	2.90	23.50	4.60	
19. Geraniol	27.50	6.50	44.00	9.00	64.00	13.25	69.00	14.50	33.00	6.75	46.50	9.60	
20. Menthone	15.00	3.70	21.75	4.50	31.50	6.75	45.00	10.20	16.50	3.40	23.00	5.00	
21. Longifolene	15.00	3.75	22.75	5.00	30.60	6.75	42.50	9.50	16.00	3.50	21.00	4.70	
22. Isolongifolene	12.70	3.00	18.00	3.90	25.25	5.50	32.50	7.25	12.80	2.60	16.00	3.50	
23. Geranylacetate	13.50	3.50	20.50	6.50	43.50	9.25	58.00	12.75	15.50	3.30	22.25	4.75	
24. α-Terpeneol	17.00	4.00	28.50	5.50	41.50	8.20	58.50	12.00	22.00	4.25	30.10	6.00	

in Table 2.

It is observed that the values of S_{12} , Q and R obtained for the 5% column of the fire-brick support are comparable to the corresponding values on 15% chromosorb column.

The HETP (height equivalent to theoretical plate) values have also been calculated for all the compounds investigated and the results are recorded in Table 3. The HETP values for 5% and 7% columns of fire-brick support are also found to be comparable to those obtained on the chromosorb columns, 15% and 20% respectively. These values appear to be rather high. This may be due to the fact that injection port heaters have not been used and the sample size used was high. These parameters have a pronounced effect on HETP³³.

Many workers have observed that an ideal solid support should be sufficiently porous and hard and it should not have any catalytic effect. Physical characteristics of various Chromosorbs and their effect on column efficiencies have been studied in detail by Saha and Giddings³⁴. These workers showed that the comparison of two supports having different density at equal percentage of substrate does not furnish the real picture of the performance. A more realistic comparison is obtained for equal " β " values³⁴. The β -value may be defined as the ratio of free gas space to liquid phase volume in a typical GLC column.

Table 2

Comparison of column performance: Values of 'S₁₂', 'Q' and 'R' for various compound pairs
 Percentage of stationary phase on fire-brick support

S.No. Compound pair	3%			5%			7%			10%		
	S ₁₂	Q	R	S ₁₂	Q	R	S ₁₂	Q	R	S ₁₂	Q	R
1. o-Cresol and m-cresol	0.440	5.333	2.347	0.464	6.302	2.924	0.183	6.334	1.191	0.486	6.194	3.010
2. o-Toluidine and m-toluidine	0.132	4.526	0.5974	0.116	5.071	0.5834	0.115	4.974	0.5720	0.169	4.915	0.8307
3. α-Picoline and β-Picoline	0.741	4.000	2.964	0.685	4.210	2.884	0.314	4.132	1.313	0.632	4.111	2.804
4. Menthoue and geraniol	0.833	4.231	3.524	1.093	4.890	5.356	1.558	4.831	7.525	0.624	4.757	3.038
5. p-Dichlorobenzene and o-dichlorobenzene	0.043	4.000	0.172	0.222	4.400	0.9790	0.215	4.293	0.9230	0.250	4.289	1.073
6. Minalool and citronellol	0.687	4.354	2.991	0.680	5.250	3.571	0.702	5.040	3.536	0.574	3.972	2.280
7. Geraniol acetate and α-terpeneol	0.259	4.250	1.101	0.070	4.692	0.3484	0.048	4.703	0.2257	0.010	4.628	0.0462
8. Longifolene and isolongifolene	0.131	4.000	0.724	0.264	4.550	1.201	0.212	4.533	0.9612	0.203	4.474	1.378

Table 2 (continued)

Percentage of stationary phase on chromosorb

S.No. Compound pair	15%			20%		
	S ₁₂	Q	R	S ₁₂	Q	R
1. o-Cresol and m-cresol	0.431	6.549	2.823	0.421	6.428	2.707
2. o-Toluidine and m-toluidine	0.120	5.091	0.6109	0.173	4.938	0.8541
3. α-Picoline and β-picoline	0.618	4.238	2.619	0.277	4.173	1.155
4. Menthone and gersniol	1.000	4.888	4.838	1.022	4.844	4.950
5. p-Dichlorobenzene and o-dichlorobenzene	0.090	4.388	0.6249	0.383	4.285	1.427
6. Linalool and citronello	0.525	5.858	2.761	0.679	5.109	3.469
7. Geraniol acetate and α-terpeneol	0.419	5.176	2.169	0.351	5.016	1.760
8. Longifolene and isolongifolene	0.311	4.571	1.422	0.312	4.468	1.394

Table 3

Effect of liquid loading on HETP values (mm): Temperature 170± 1°C

S.No. Compound	Fire-brick 60-100 mesh			Chromosorb		
	3%	5%	7%	10%	15%	20%
1. o-Cresol	5.000	3.473	3.531	3.544	3.324	3.546
2. m-Cresol	4.394	2.986	3.116	3.258	2.914	3.025
3. p-Cresol	4.310	2.796	2.900	3.063	2.864	2.975
4.o-Toluidine	6.253	5.632	5.961	6.013	5.618	5.703
5.m-Toluidine	6.102	4.850	5.053	5.175	4.822	5.123
6.p-Toluidine	6.396	5.088	5.052	5.147	4.908	5.001
7.Pyridine	6.530	5.540	5.980	6.024	5.806	5.845
8.α-Picoline	8.264	6.704	7.199	7.811	6.963	6.982
9.β-Picoline	7.812	7.050	7.147	7.394	6.958	7.145
10.γ-Picoline	8.567	7.082	7.521	7.812	7.108	7.316
11.Chloro- benzene	4.999	4.726	4.784	4.876	4.850	5.001
12.o-Dichloro- benzene	8.012	6.457	6.781	6.806	6.430	6.806
13.p-Dichloro- benzene	8.506	7.467	7.521	7.811	7.231	7.467
14.m-Dichloro- benzene	7.491	5.740	6.342	7.052	5.425	6.327
15.1,2,4-Tri- chlorobenzene	7.199	6.327	6.473	6.489	6.173	6.841
16.p-Cymene	7.812	6.455	6.658	7.532	6.658	6.806
17.Linalool	7.812	6.049	6.139	6.172	6.047	6.112
18.Citronellol	6.594	4.535	4.921	4.999	4.522	4.789
19. Geraniol	6.984	5.229	5.359	5.471	5.230	5.327
20.Menthone	7.605	5.350	5.873	6.422	5.344	5.907
21.Longifolene	7.811	6.037	6.082	6.244	6.006	6.253
22.Isolongi- folene	6.974	5.868	5.930	6.219	5.676	5.982
23.Geranyl- acetate	8.405	5.676	5.650	5.835	5.666	5.697
24.α-Terpeneol	6.921	4.657	4.881	5.259	4.666	4.966

Dal Nogare and Chiu³⁵ demonstrated the relationship between " β " values and resolution. In order to obtain optimum resolution, it is desirable to employ the most efficient column possible, since efficiency enters into the expression for resolution. According to these workers the smallest possible β , consistent with optimum efficiency also leads to best resolution.

For calculations of " β " values, it is necessary to know the density of the stationary phase at the column temperature. For the sake of simplicity, the value of density has been taken as "one" and the " β " values calculated for all the columns. The values are presented in Table 4. This assumption of the density value will not effect the conclusions because the same liquid phase and the same temperature have been employed for

Table 4

Effect of liquid loading on pressure gradient
and β -values

	Percentage of stationary phase on fire-brick support				Percentage of stationary phase on chromosorb	
	3%	5%	7%	10%	15%	20%
β -values	25.73	16.29	10.98	7.70	17.16	11.31
$\frac{P_i}{P_o}$	1.292	1.319	1.294	1.299	1.301	1.293

where P_i = inlet pressure of the carrier gas
and P_o = outlet pressure of the carrier gas

*Calculated according to the method of
S. Dal Nogare and J. Chiu, Anal.Chem. 34, 890 (1962).

for all the columns studied. It is evident from Table 4 that the "β" values of fire-brick support compare very well with that for chromosorb support. Interesting enough, the resolution, "R" values also coincide for both types of the support.

To ascertain usefulness and limitations of fire-brick support, the effect of change of flow-rate of carrier gas was investigated. Columns, with 5% and 7% liquid phase on fire-brick support were employed for this study. Retention time distances and peak widths were calculated from the charts and are given in Table 5. The HETP values at different flow-rates of the carrier gas were also determined and the results are presented in Table 6. The values of flow-rate were plotted against the HETP values and typical hyperbolic curves were obtained as shown in Figures I and II. Even at high flow-rate, the HETP values are found to be sufficiently low. This fact may be utilised in reducing time of analysis without any loss in efficiency of the column.

A graph of HETP values was plotted against the percentage of stationary phase (Figure III). It is observed that, even when stationary phase percentage is increased from 5 to 8, the HETP values do not change much.

It is clear from the above observations that the fire-brick support is quite porous and can be employed efficiently. It may, therefore, be concluded that a solid support with somewhat high packing density with sufficient porosity can be effectively used, if the weight of the stationary phase is properly adjusted.

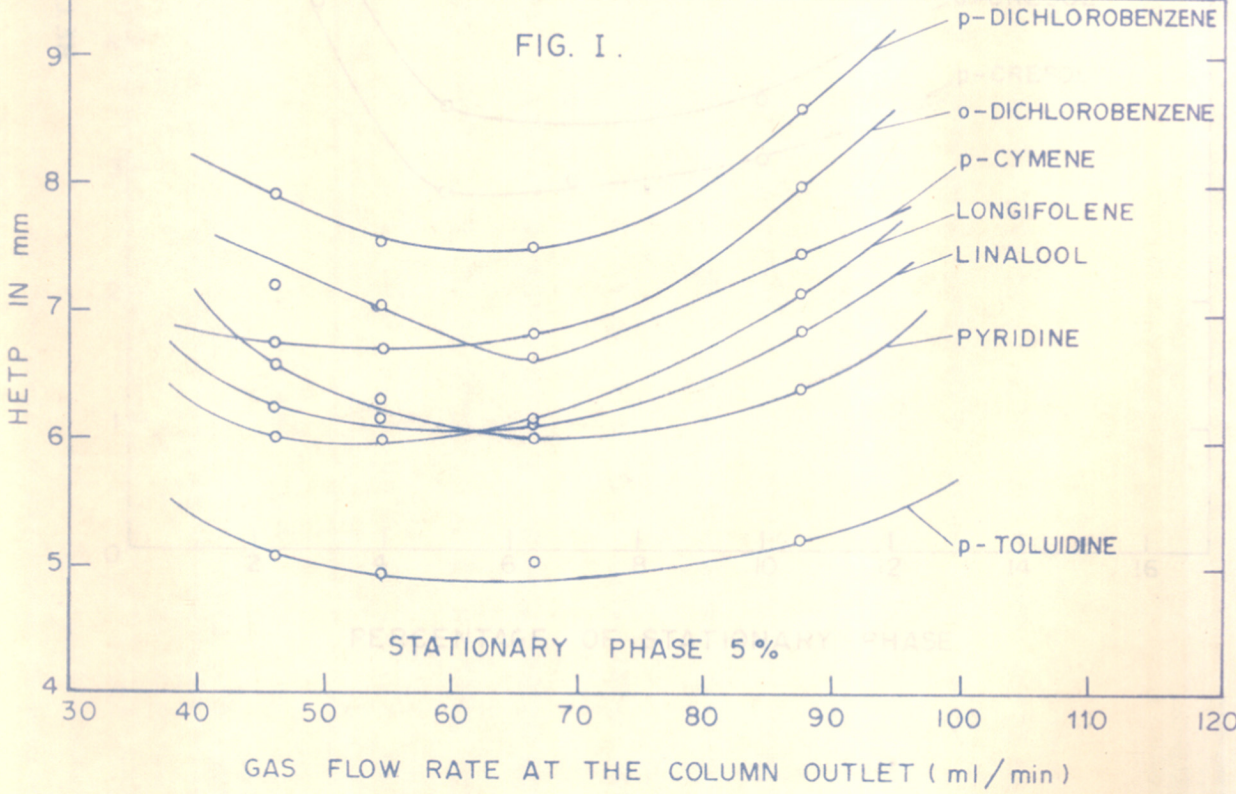
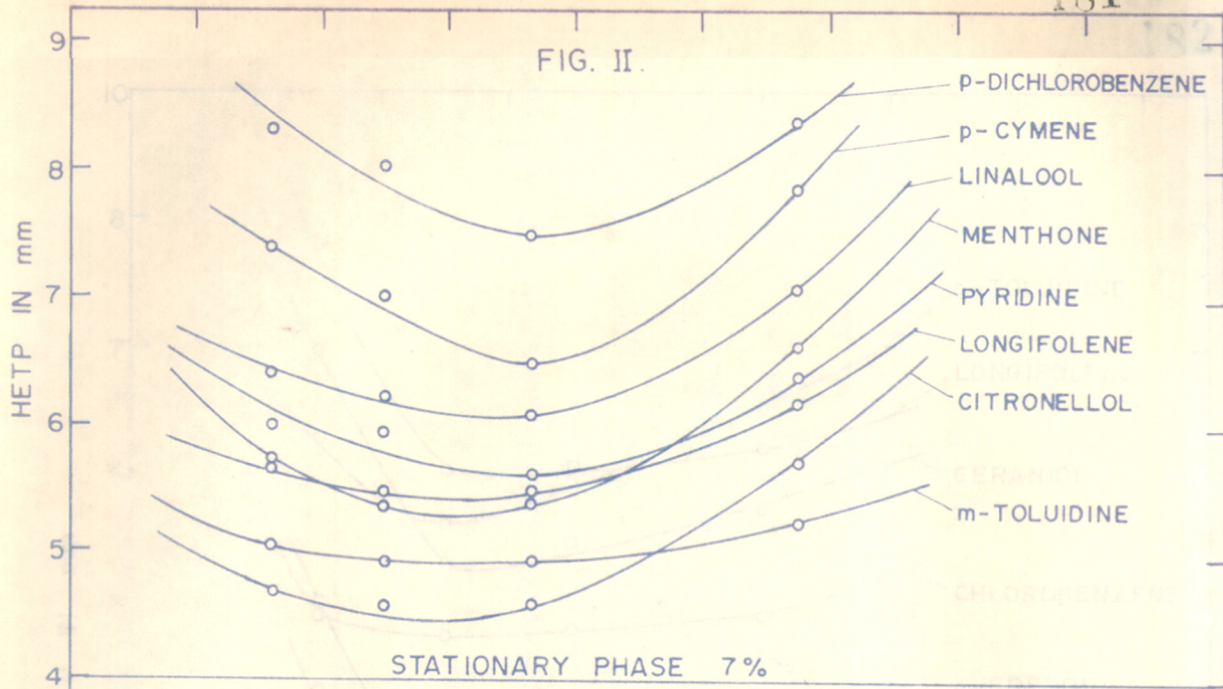


FIG. III.

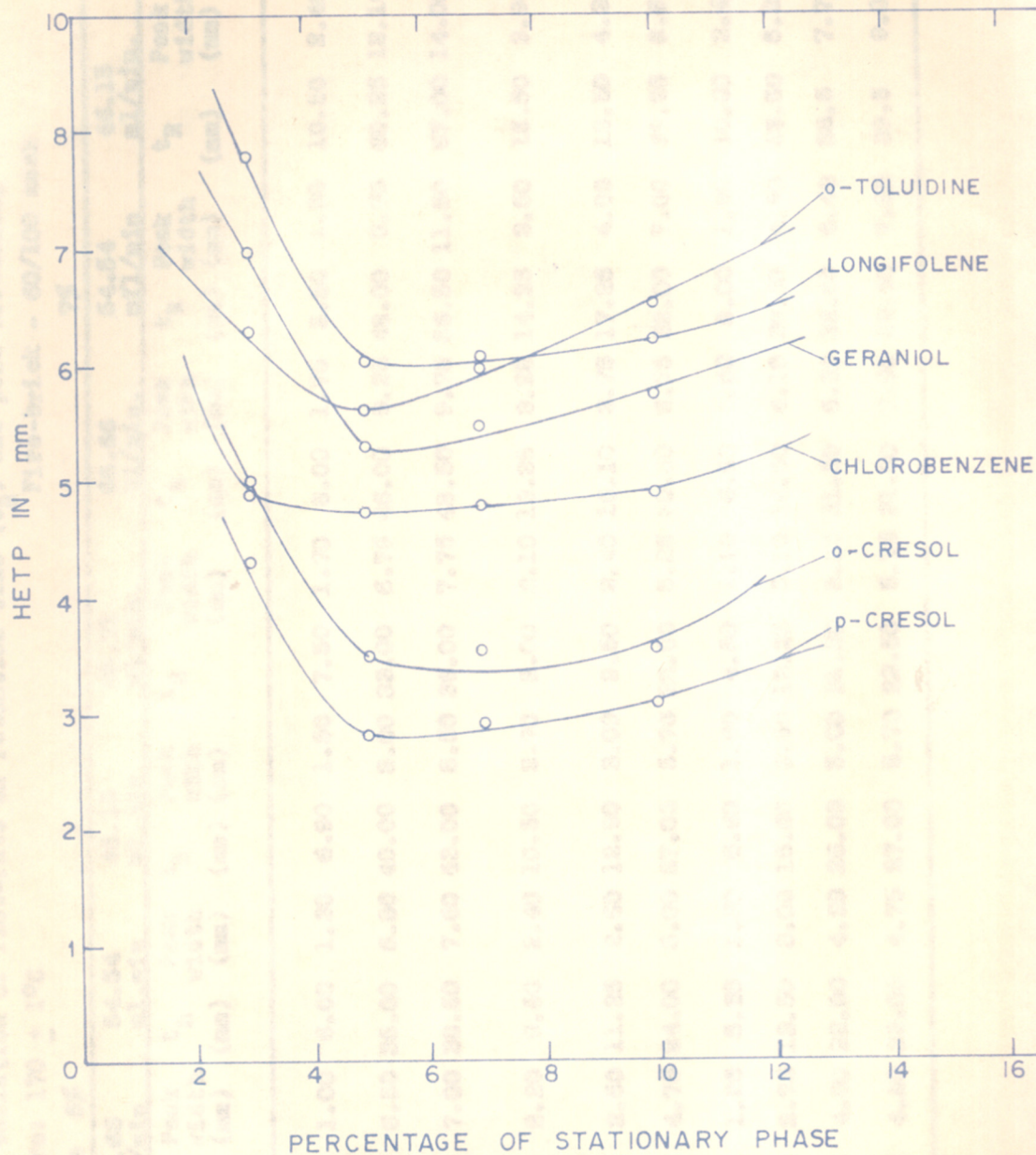


FIG. III .

Table 5

Effect of variation of flow-rate on retention time (t_R) and peak broadening
 Temperature: $170 \pm 1^\circ\text{C}$
 Fire-brick - 60/100 mesh

Stationary phase	5%						7%									
	Flow rate ml/min	Peak t_R (mm)	Peak width (mm)	ml/min	Peak t_R (mm)	Peak width (mm)	Flow rate ml/min	Peak t_R (mm)	Peak width (mm)	ml/min	Peak t_R (mm)	Peak width (mm)				
1. Pyridine	4.00	0.90	4.75	1.00	6.00	1.30	6.90	1.50	7.50	1.70	8.00	1.75	8.50	1.90	10.50	2.40
2. p-Toluidine	25.00	5.25	32.50	6.50	35.00	6.80	40.00	8.00	33.00	6.75	46.00	9.25	48.00	9.75	60.25	12.10
3. n-Toluidine	27.00	5.50	35.50	7.00	38.50	7.60	43.00	8.50	36.00	7.75	48.50	9.75	56.50	11.50	67.00	14.00
4. p-Dichlorobenzene	7.75	2.00	9.00	2.20	9.50	2.40	10.50	2.70	8.00	2.10	13.25	3.25	14.25	3.50	15.50	3.90
5. o-Dichlorobenzene	9.50	2.25	11.00	2.50	11.25	2.60	12.90	3.00	9.50	2.40	16.10	3.75	17.25	4.00	18.50	4.30
6. Longifolene	18.00	4.00	22.75	4.75	24.00	5.00	27.00	5.75	22.00	5.25	30.60	6.75	32.00	7.00	39.25	8.60
7. p-Cymene	4.00	1.00	5.50	1.25	5.60	1.30	6.60	1.60	4.50	1.10	6.50	1.50	8.00	1.90	10.00	2.40
8. Menthyl	9.50	2.25	12.50	2.75	13.50	3.00	15.50	3.50	13.25	3.10	18.50	4.10	20.25	4.50	23.50	5.25
9. Citronellol	16.5	3.5	21.00	4.00	22.00	4.20	26.00	5.00	21.50	5.00	31.50	6.30	32.00	6.40	38.5	7.75
10. Menthone	17.00	3.90	21.75	4.50	23.00	4.75	27.00	5.70	23.50	5.75	31.50	7.00	32.50	7.25	39.5	9.0

Table 6

Temperature 170 ± 1°C

"HETP" values at different flow rates

Support: Fire brick 60-100 mesh

Stationary phase	HETP values in mm					Flow rate						
	5%					7%						
S.No. compounds	87.51 ml/min.	66.66 ml/min.	54.54 ml/min.	46.15 ml/min.	87.51 ml/min.	66.66 ml/min.	54.54 ml/min.	46.15 ml/min.	87.51 ml/min.	66.66 ml/min.	54.54 ml/min.	46.15 ml/min.
1. Pyridine	6.323	5.540	5.863	5.909	6.405	5.930	6.291	6.530	6.405	5.930	6.291	6.530
2. p-Toluidine	5.513	4.976	4.718	5.00	5.230	5.053	4.949	5.041	5.230	5.053	4.949	5.041
3. m-Toluidine	5.137	4.861	4.870	4.833	5.790	5.054	5.130	5.420	5.790	5.054	5.130	5.420
4. p-Dichloro- benzene	3.322	7.467	7.973	8.266	8.612	7.525	7.543	7.915	8.612	7.525	7.543	7.915
5. o-Dichloro- benzene	7.013	6.457	6.675	6.759	7.979	6.783	6.723	6.753	7.979	6.783	6.723	6.753
6. Longifolene	6.173	5.449	5.425	5.679	7.120	6.122	5.952	6.002	7.120	6.122	5.952	6.002
7. p-Cymene	7.812	6.455	6.893	7.347	7.469	6.658	7.050	7.199	7.469	6.658	7.050	7.199
8. Linalool	7.013	6.049	6.173	6.375	6.344	6.129	6.170	6.233	6.344	6.129	6.170	6.233
9. Citronellol	5.624	4.535	4.555	4.622	6.761	4.999	5.001	5.063	6.761	4.999	5.001	5.063
10. Menthone	6.532	5.350	5.332	5.571	7.501	6.173	6.219	6.459	7.501	6.173	6.219	6.459

Efficiency of the fire-brick support

The maximum efficiency of the fire-brick support can be obtained by using the following parameters:

- i) Mesh size : 60/100
- ii) Liquid loading: 5-8%
- iii) Gas flow-rate: 55-65 ml/min.

For the investigations described in this thesis, nearly the same parameters were used.

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