ORGANO-METALLIC COMPOUNDS OF ANALYTICAL IMPORTANCE.

A

THESIS

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by

NAVIN CHANDRA SOGANI,
Government College, Ajmer,
&
National Chemical Laboratory of India,
Poona 8

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PREFACE

In this thesis, a large number of compounds related to cupferron have been examined as possible analytical reagents. Some of these possess excellent qualities, details of which will be available in the text. We have concentrated our efforts more on the analytical aspects of these reagents rather than on the ultimate structure of the complexes formed by them, though that has also not been overlooked.

In naming the azo-compounds of this series, we have adopted the procedure suggested by the Editor, Nomenclature Section, "Chemical Abstracts". The other compounds have been named according to the procedure adopted in "Beilstein".

The valency of an element or an ion has been indicated with roman letters written immediately after it in brackets, a procedure which is followed in "Analytical Chemistry".

In describing the structural formulae, a benzene ring has been usually indicated by a hexagonal ring  without the double bonds. Wherever there was any possibility of ambiguity, the ring has been shown with the double bonds. Relevant references have been given after each part.

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PART I

INTRODUCTION.

SUMMARY

A brief survey of the use of organic reagents in the inorganic analysis has been made, and the scope and the basis of the present work explained.

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INTRODUCTION.

Application of organic reagents for inorganic analysis is now very well established. But this was not so towards the beginning of this century.. Certain organo-metallic compounds, like those derived from mordant dyes and ferrocyanic pigments were not unknown. However, the real development in this field started in 1905 when Tschugacff[1] reported the use of dimethyl glyoxime as a reagent for nickel. Later on, Brunk[2] made extensive use of this reagent and carried out many valuable separations.

Tschugacff's nickel reaction may still be considered as ideal in certain respects. Because of the intense colour and insolubility of the nickel complex, the reaction furnishes a sensitive method for the detection of nickel, its exceptional purity and definite composition making the estimation of nickel possible through direct weighing. Its special merit is that it is extremely specific.

Development of dimethylgyoxime as a nickel reagent very soon attracted the attention of analytical chemists. As a result, extensive work started for the development of other similar reagents. At the initial stage efforts were mostly arbitrary in nature. But it was soon realized that the organic reagents are guided by two fundamental principles.

1. The compound must have a group containing an available hydrogen which is replaceable by a metal. Such groups are :

$-CO_2H$ (carboxyl)

$-SO_2H$ (sulphinic)

$-SO_3H$ (sulphonic)

$-OH$ (hydroxyl)

$-SH$ (mercapto)

$-NOH$ (oxime)

$=NO-OH$ (nitroxyl)

$=NH$ (imine)

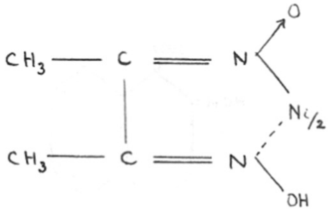
$-As(OH)_2$ (arsinic)

$-AsO(OH)_2$ (arsonic)

2. At the same time, the organic compound must also contain other functional groups like carbonyl ($=CO$), thiocarbonyl ($=CS$), primary amine ($-NH_2$), secondary amine ($-NHR$), tertiary amine ($-NR_2$), nitroso ($-NO$), nitro ($-NO_2$), azo ($-N=N-$) etc. in such a position that it may saturate the residual valency of the metal atom, giving rise to a five or a six membered ring. The structural and stereochemical features of such complexes are basically governed by (i) Werner's co-ordination theory and (ii) Baeyer's strain theory.

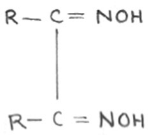
Inner complex forming reagents

During the investigation of various organic reagents, it was found that certain functional groupings react specifically towards certain metallic ions. As a starting point towards these, we may again take up the case of dimethyl-glyoxime. The nickel complex, which is considered to be an inner complex, has the following structure:



I

In an excellent review made by Diehl[3], on the group action provided by 1,2 dioximes, he has stated that other anti-dioximes having the general formula (II) react in a similar way as dimethyl-glyoxime. Thus benzil-dioxime[4] (III), furil dioxime[5] (IV), diaminodioxime[6] (V) etc. form similar nickel complexes.



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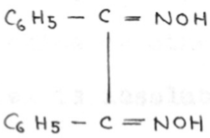
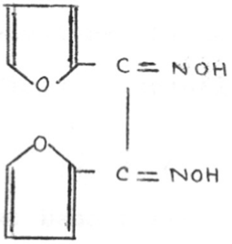
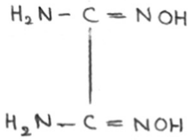


III

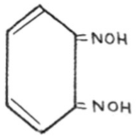


IV

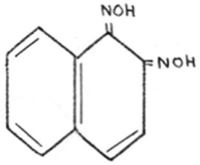


V

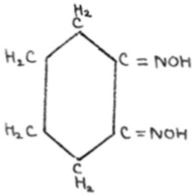
The salt forming ability of the group -C(=NOH)-C(=NOH)-, and its specific action towards nickel salts is also related to the structure of the molecule of which it is a part. As for example 1,2-benzoquinone dioxime (VI) and 1,2-naphthoquinone dioxime (VII) do not exhibit nickel specificity. This is due to the location of dioximes groups on aromatic system which make them stronger acids than ordinary dioximes. These compounds behave as dibasic acids and yield yellowish brown precipitate with most of the metals.



VI



VII



VIII

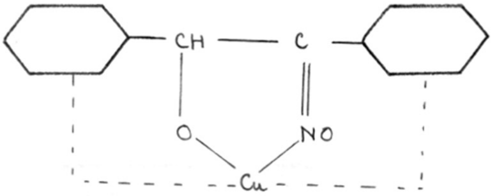
The specificity returns when the aromatic ring is reduced. Thus cyclohexanedionedioxime[7] (VIII) gives usual nickel complex. This dioxime, also shows that the insolubility of the nickel complex is in no way related to the insolubility of the reagent in water, for cyclohexanedionedioxime, in contrast to dimethyl-glyoxime or other dioximes is soluble in water but its nickel complex is insoluble.

The dioximes also behave specifically towards palladium in dilute mineral acids. They form yellow, water-insoluble complexes which are similar in structure to the nickel complexes.

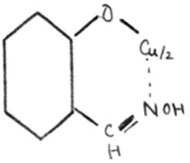
The examples of dioximes also indicate that it is possible to improve the analytical value of a reagent, by incorporating certain changes in the molecule, but keeping the specificially active group intact.

The relation of specificity to certain characteristic groupings is also shown by two copper reagents - namely, α-benzoinoxime[8] and salicylaldoxime[9]. The former is considered to be specific for copper in ammoniacal medium and the latter in acetic acid medium. The complexes are represented by the structures

IX and X respectively.



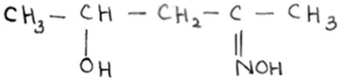
IX



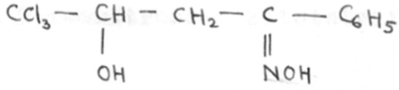
X

Feigl[8] has shown that -C(OH)-C(:NOH)- grouping is responsible for forming green water insoluble copper complex and this is quite independent of the other groups attached to the molecule. The copper complex is, however, stable towards ammonia only if the residual valency of copper can be satisfied by the rest of the molecule. Accordingly, cyclohexanolonoxime, for example, yields a copper complex which is soluble in ammonia, whereas the complex formed by α-benzoin oxime is insoluble in the same medium.

Ephrain[9] has studied the reaction of a number of compounds which contain the same reactive grouping as salicylaldoxime, and has found that they all form characteristic copper complexes in acetic acid solutions. The group $Ho-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}{=}NOH$, which is contained in salicylaldoxime is not in itself sufficient to give a specific copper reaction. Pentanol-2-one-4-oxime (XI) and chloral acetophenone oxime (XII) do not react with copper. From this it appears that the acidity of the hydroxyl group because of its linkage to the aromatic ring was responsible for the copper specific action in salicylaldoxime.

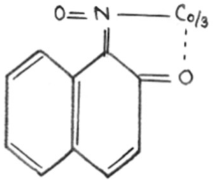

$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{NOH}{\underset{\|}{C}}-CH_3$

XI

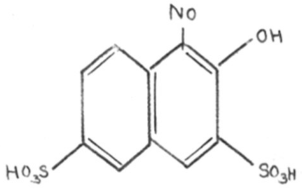

$CCl_3-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{NOH}{\underset{\|}{C}}-C_6H_5$

XII

In describing the specific action, mention must be made of the cobalt reagent α-nitroso β-naphthol, described by Illinsky and v.Knorre[10], which forms a reddish brown complex (XIII) with cobalt salts.



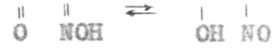
XIII



XIV

The isomeric β-nitroso α-naphthol also forms an inner complex with cobalt, which is indistinguishable from the precipitate obtained from the former isomer. Belluci[11] found that the precipitating action of β-nitroso compound is about 8 times as sensitive as that of α-nitroso compound. The influence of the introduction of sulphonic groups in the α-nitroso compound was explored by Klooster[12], who studied the corresponding disulphonic acid (XIV), commonly known as nitroso R salt. It still retains the cobalt specificity, however, both the reagent and its cobalt complex have been converted into water soluble products. In addition, its selectivity is also enhanced.

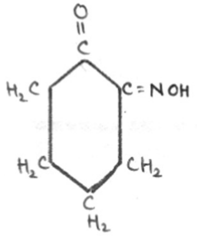
The active functional group present in these compounds is the tautomeric group



$$-\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle NOH}{\|}}{C}- \rightleftarrows -\underset{\underset{\displaystyle OH}{|}}{C}=\underset{\underset{\displaystyle NO}{|}}{C}-$$

Thus isonitrosocyclohexanone (XV), 2-isonitroso-1-ketotetraline[13]

(XVI), isonitrosocamphor[14] (XVII) and other allied compounds form characteristic cobalt complexes.



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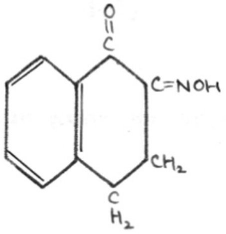
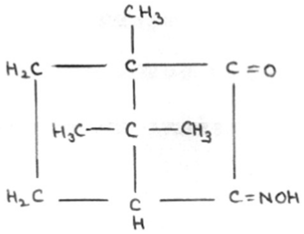
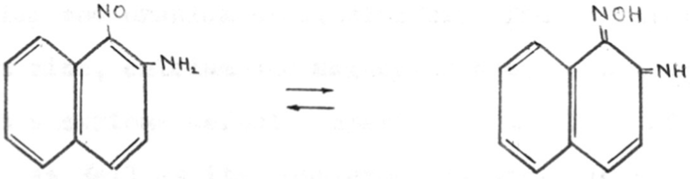


XVI



XVII

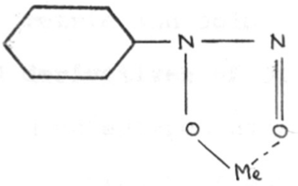
The cobalt specificity is also retained if the oxygen atom of the :CO group is replaced by =S or =NH groups, as both isonitrosothiocamphor and α-nitroso β-naphthylamine[15] (XVIII) (naphthoquinone iminoxime, XIX) form characteristic red complexes with cobalt.



XVIII XIX

Stability of the cobalt complex is, however, dependent on the nature of the ring system. In those cases where the functional group is attached to an aliphatic or alicyclic system, the precipitate is less stable towards mineral acids. Nitroso-naphthols also precipitate iron, palladium and zirconium.

The ammonium salt of nitrosophenylhydroxylamine, was introduced by Baudisch,[16] in 1909. It is more commonly known as "Cupferron" and has been widely used as analytical reagent. Under varying pH conditions, it forms insoluble inner complexes with many metallic elements of the general type, as shown below (XX):



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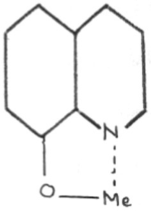


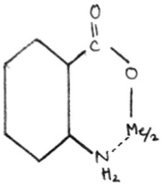
XXI

It has been used for some of the otherwise difficult separations of elements, for example gallium from aluminium, chromium, indium, cerium and uranium etc., zirconium from aluminium and uranium from zinc, calcium and magnesium etc. However, cupferron suffers from a serious defect. Apart from the lack of specificity, the reagent, as well as its complexes are unstable above room temperature and cannot be used for direct weighing. We shall discuss about cupferron in more detail later on, as the work incorporated in the thesis is also directly related to it.

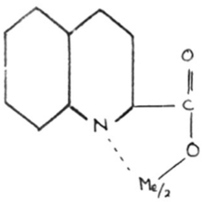
Another organic reagent, which has been very extensively used in analytical chemistry is 8-hydroxyquinoline[17] which is commonly known as "oxine". In this compound the hydroxyl group is so located with respect to the nitrogen atom of the quinoline nucleus that a five membered ring is easily formed with metals. The inner complex with metals has the general formula XXI.

Oxine is not very specific and forms precipitate with many elements. Specificity of the reagent can be, however, increased by proper control of pH of the reaction medium. The complexes formed by oxine are stable towards heat and are often directly weighable. The phenolic nature of the reagent, moreover, makes a volumetric and colorimetric determination possible. Many substituted derivatives of oxine have also been used, which sometimes offer certain advantages over the parent compound. Merrit and Walker[18] first noted that any substitution in the 2 position of 8-hydroxy-quinoline prevents the precipitation of aluminium complex. This effect is probably due to the steric hinderance provided by the group in the 2-position.

Two ortho amino-carboxylic acids, which are able to form inner complexes of analytical importance, are anthranilic and quinaldinic acids. By means of the former, Funk[19] and co-workers have done certain gravimetric estimations of divalent metals. Quinaldinic acid has been developed by the eminent Indian chemist P.R.Ray[20] and his collaborators. It is one of the best copper reagents developed so far. These compounds give inner complexes with metals of the following structure:



XXII



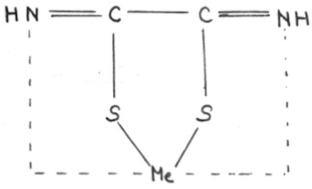
XIII

Of the sulphur containing organic reagents rubeanic acid and dithiozone are more important.

Rubeanic acid, which has also been developed by P.R.Ray[21,22] is the diamide of dithioxalic acid, exists in solution in the following tautomeric forms:

XXIV XXV

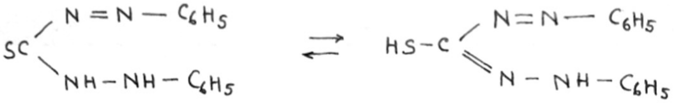
The acid form yields coloured insoluble nickel, cobalt and copper salts of the following structure:



XXVI

Though the complexes are not directly weighable, rubeanic acid has been acclaimed to be the most sensitive copper reagent developed so far.

Dithiozone or diphenylthiocarbazone was investigated by Fischer[23]. It exists in the following two tautomeric forms:



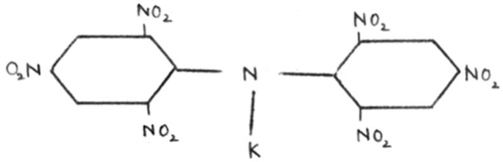
XXVII XXVIII

It gives colour reactions both in keto and enol forms, with a very large number of metals, but by controlling the conditions of the reaction, interference by various metals can largely be eliminated.

In fact, the number of inner complex forming organic compounds are so many that it will need considerable space to describe them. An excellent collection of all these reagents used upto 1945 has been given by Welcher[24] in four volumes of his monumental work 'Organic Analytical Reagents'. An interesting review made by Feigl[25] in his excellent book "Chemistry of specific, selective and sensitive Reactions" is also particularly noteworthy. In this place we are only naming some of the important reagents: thionalide, β-furfuraldoxime, benzotriazol, mercaptobenzthiazole, alizarin, pyrogallol, catechol, sulphosalicylic acid, barbituric acid, nitroquinoline, isonitrosodimidone etc.

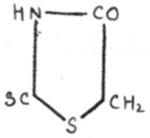
Normal salt forming reagents

Among organic reagents which do not form inner complexes but form insoluble normal salts with metals, mention may be made of (i) mercaptobenzothiozone, (ii) picrolinic acid (iii) phenylarsonic acid, (iv) rhodamine and (v) hexanitrodiphenylamine[26] etc. The last compound is of special interest as it gives an insoluble salt with potassium of the following formula:



XXIX

An interesting example of modifying organic reagents to form derivatives that give highly coloured complexes is furnished by rhodanine (XXX). The reactivity of rhodanine is retained in all its derivatives with an intact imino group. Thus, Feigl[27] has introduced dimethylaminobenzylidene rhodanine (XXXI) as a very sensitive reagent for silver. Whereas the parent compound XXX forms an almost colourless silver salt, that formed by XXXI is deep red in colour.



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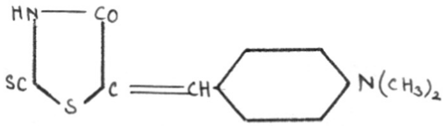
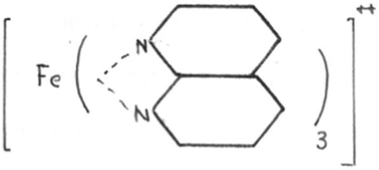


XXXI

All the organic reagents mentioned previously, because of the presence of one or more available hydrogen atoms, form inner complex or normal salts with metals. But there are certain organic compounds which form highly coloured co-ordination complexes which can be used in quantitative analysis. Examples of such compounds are α,α' dipyridyl and 1,10-phenanthioline[28], which form intensely red water soluble complex ions with iron of the type given below:



Formulae is incorrect.

XXXII

Substituted derivatives of these or other similar compounds have also been used for the same purpose.

Masking agents

Before going into the discussion of other matters, it is necessary to make a casual mention of masking agents like sodium potassium tartrate, sodium citrate, glycerol, ethylenediaminetetraacetic acid (E.D.T.A.), sulphosalicylic acid, sodium or potassium fluoride etc. These compounds, when properly used can preferentially mask the precipitation of certain metals and thus making certain separations possible. They are extensively used in analytical chemistry. The detailed description about the mode of reaction of these masking agents is available in the book by Feigl[25], referred to earlier.

Advantages of organic reagents

The organic reagents, especially those which are capable of forming inner complexes have an established position in inorganic analysis. The properties of these compounds differ profoundly, in many respects, from normal salts, thus making their use in analytical chemistry of special significance. The more important of these are:

1. The inner complexes are usually extremely insoluble in water, thus making possible many otherwise difficult quantitative precipitations.

2. These complexes, due to their nonionic nature, are usually soluble in nonpolar solvents, and can be extracted from aqueous solutions or suspensions with immiscible liquids, thus making separations and colorimetric estimations in certain cases possible.

3. The inner complexes are usually highly coloured and are, therefore, suitable for spot test detection of small amounts of metals and for colorimetry.

4. Organic reagents are very often highly specific or selective in their reaction towards inorganic ions.

5. Precipitate formed in many cases is directly weighable and because of high molecular weight of the complex of the metal, it is suitable for micro-quantitative estimations.

Desirable properties of an analytical reagent

From the extensive researches which have already been carried out, it is now possible to enumerate the various properties, which a good analytical reagent should possess. These properties are the guiding factors for further advancement in this field. The properties may be mainly described as follows:

1. The reagent should be stable towards heat, light, air etc.

2. It should be soluble in water, or at least in water-miscible solvents like ethanol,methanol, acetone etc.

3. In contrast to the solubility of the reagent in water or allied solvents, the complex should be insoluble and should also be stable towards heat, light etc.

4. The complex should be granular and of definite composition, so that it can be easily filtered and directly weighed.

5. The ratio between the weight of the metal and its complex should be as high as possible so that small amount of the metal can be accurately estimated.

6. The reagent, under proper pH conditions, should have very high specificity.

7. It should also be possible to prepare the reagent easily from common laboratory chemicals.

Basis and scope of investigation recorded in this thesis

We are now going to give a brief description of the background which prompted us to undertake this investigation, the results of which have been incorporated in this thesis. In the earlier part of the introduction, we have briefly indicated the use of cupferron as an analytical reagent. Along with dimethylglyoxime and 8-hydroxyquinolime, cupferron is one of the most widely used of the organic reagents. Due to the presence of extra-nuclear nitroso group attached to the amino nitrogen atom, cupferron suffers from many serious defects.

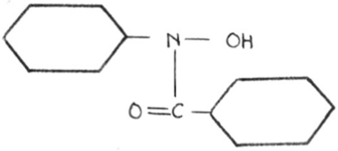
1. The reagent, as well as its ammonium salt, is unstable towards heat, light and air, and even after careful storage under ammonium carbonate, undergoes auto decomposition.

2. The complexes formed by cupferron are also unstable and decompose above room temperature.

3. The complexes are also not of definite composition and consequently cannot be directly weighed.

4. Though the specificity of the reagent can be considerably improved by the adjustment of pH, it is never very conspicuous.

These defects of cupferron were realized by many workers and in an attempt to eliminate these and also to increase the specificity, other derivatives of cupferron-like nitroso-naphthyl hydroxylamine (neo cupferron)-in which the phenyl group was replaced by the naphthyl, has been examined by Baudisch[29]. Such modification is , however, not very useful, as this doesnot introduce any fundamental changes, excepting increasing the bulk of the molecule and its insolubility, the latter itself being a highly undesirable property. The fundamental nature of the cupferron molecule can only be changed when nitroso group is replaced by other negative substituents. The first attempt, in this line of approach, was made by Shome[30], who examined benzoylphenylhydroxyl(XXXIII) amine as an analytical reagent.



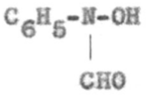
XXXIII

The results were conspicuous, as the reagent as well as the complexes formed by it are stable and are of definite composition and can be directly weighed. It's specificity is also better than that of cupferron. With this reagent Shome has carried out certain interesting estimations and separations. In a preliminary note[31] he has also indicated the possibility of introducing other substituents in place of benzoyl group.

We have examined, this point, now in details. We prepared a large number of substituted phenylhydroxylamine derivatives and have evaluated their possibility as analytical reagents. Some of these possess outstanding qualities, details of which will be available in the subsequent parts of this thesis.

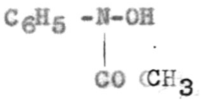
The compounds examined are listed below:

A. Formyl and acetyl derivatives:



$C_6H_5\text{-}N(CHO)\text{-}OH$

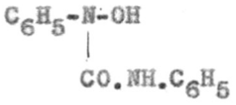
XXXIV



$C_6H_5\text{-}N(CO\,CH_3)\text{-}OH$

XXXV

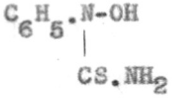
B. Urea derivative



$C_6H_5\text{-}N(CO.NH.C_6H_5)\text{-}OH$

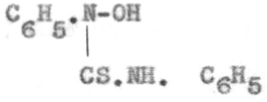
XXXVI

C. Thiourea derivatives



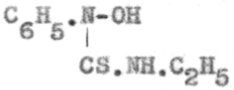
$C_6H_5.N(CS.NH_2)\text{-}OH$

XXXVII



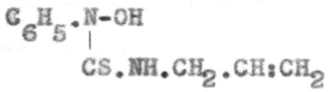
$C_6H_5.N(CS.NH.\;C_6H_5)\text{-}OH$

XXXVIII



$$\begin{array}{l} C_6H_5.N\text{-}OH \\ \qquad | \\ \qquad CS.NH.C_2H_5 \end{array}$$

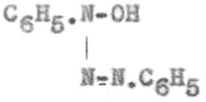
XXXIX



$$\begin{array}{l} C_6H_5.N\text{-}OH \\ \qquad | \\ \qquad CS.NH.CH_2.CH{:}CH_2 \end{array}$$

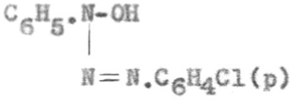
XL

D. Azo derivatives:



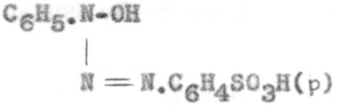
$$\begin{array}{l} C_6H_5.N\text{-}OH \\ \qquad | \\ \qquad N{=}N.C_6H_5 \end{array}$$

XLI



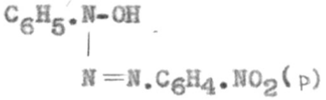
$$\begin{array}{l} C_6H_5.N\text{-}OH \\ \qquad | \\ \qquad N{=}N.C_6H_4Cl(p) \end{array}$$

XLII



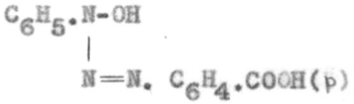
$$\begin{array}{l} C_6H_5.N\text{-}OH \\ \qquad | \\ \qquad N{=}N.C_6H_4SO_3H(p) \end{array}$$

XLIII



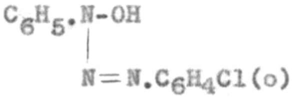
$$\begin{array}{l} C_6H_5.N\text{-}OH \\ \qquad | \\ \qquad N{=}N.C_6H_4.NO_2(p) \end{array}$$

XLIV



$$\begin{array}{l} C_6H_5.N\text{-}OH \\ \qquad | \\ \qquad N{=}N.\ C_6H_4.COOH(p) \end{array}$$

XLV



$$\begin{array}{l} C_6H_5.N\text{-}OH \\ \qquad | \\ \qquad N{=}N.C_6H_4Cl(o) \end{array}$$

XLVI

While examining the above group of compounds, we were guided by the 7 basic properties desirable for an organic reagent, as described earlier on page 14.

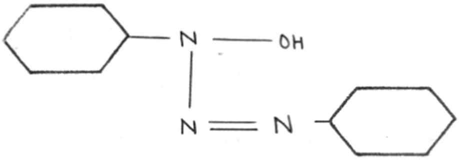
1. Formyl and the acetyl phenyl hydroxylamine (XXXIV and XXXV) are somewhat unstable. It is also difficult to prepare them in quantity. Consequently, they were considered to be unsuitable for analytical purposes, even though they showed interesting colour reactions with certain elements, specially, iron.

2. The urea derivative (XXXVI) has no marked precipitating power, and hence was not further examined.

3. The thio-urea derivatives (XXXVII to XL), excepting the unsubstituted one (XXXVII), could be easily prepared. Most of these derivatives showed precipitating power in the alkaline pH range,

indicating that the iso-thio-urea state of these compounds was active. However, these compounds, apart from the lack of specificity and comparative insolubility in water, suffer from one very serious defect. They were unstable and underwent auto-decomposition, after some time even when carefully stored in a refrigerator. For these reasons, these compounds were not critically examined.

4. Useful group: Finally we found an excellent series of compounds in the azo substituted erivatives (XLI to XLVI), the parent compound of which is 3-hydroxy-1,3-diphenyltriazine (XLVII).



XLVII

This compound could also be named as N-benzenediazophenylhydroxylamine or N-phenyl N-phenylazohydroxylamine. This probably would have brought out the family relationship of this compound with cupferron. However, as the name, as 3-hydroxy-1,3-diphenyltriazine is more in confirmity with the existing procedure now accepted in "Chemical Abstract", we should like to adopt the same.

At low pH, 3-hydroxy-1,3-diphenyltriazine has been found to be an excellent and highly selective reagent for palladium (ref.part IV) and copper (ref.Part V) and can be used for the estimation and separations of these elements through direct weighing. It is superior to all copper and palladium reagents now described in the literature. It possesses most of the desirable properties of a reagent enumerated earlier.

Preliminary examination has indicated that, because of its very favourable factor (0.1303 for copper and 0.2009 for palladium) the reagent is also particularly suitable for the micro-gravimetric estimation of copper and palladium (part X).

At somewhat higher pH, the reagent is also useful for the estimation of nickel and its separation from various elements (part VI).

The corresponding p-chloro derivative (XLII) of the reagent has been found to be very useful for the quantitative estimation of titanium and its separation from other elements including large amounts of aluminium (ref: part VII). Unlike the corresponding titanium complexes of cupferron and N-benzoylphenylhydroxylamine (XXXIII), the titanium complex of 3-hydroxy-1,3-diphenyltriazine is stable towards heat and can be digested on a water bath for an indefinite period.

The corresponding p-sulphonic acid derivative (XLIII) which is soluble in water has also proved to be an excellent colorimetric reagent for the estimation of palladium, as such or in presence of other elements, including the members of the palladium group (part VIII). In many respects, it is superior to p-nitrosodiphenylaniline and other allied compounds, which are now generally recommended for the colorimetric estimation of palladium. It has also proved useful in the colorimetric estimation of molybdenum (part IX).

The other azo derivatives - orthochloro, nitro and carboxylic, though retaining the characteristic precipitating power, had certain undesirable properties, for which their detailed examination was considered to be not useful. The preparative details of various reagents have been described in part II of this thesis and their reactions with various metallic ions are included in part III.

Use of dielectric constant, magnetic suseptibility etc., have been widely used in the investigation of the structure of complex salts. We have not made any attempt to utilize these physico-chemical methods in our investigation. We have rather concentrated our efforts more on the analytical side, where, however, we have tried to use the latest type of equipment including single pan macro, semi-micro and micro balances, Beckman quartz spectrophotometer, automatic pH meter etc.

In colorimetric estimations, we have used a spectrophotometer instead of a colorimeter of the usual type, as it increased the accuracy of estimations and also facilitated a precise adjustment of wave lengths.

<u>Conclusion:</u>

The azo-substitued phenylhydroxylamine derivatives, examined by us, introduce a new group of organic reagents, the type of which has not been described earlier. The common functional group:

$$\begin{array}{lll} -\mathrm{N} & — & \mathrm{OH} \\ \;\;| & & \\ \;\;\mathrm{N} & = & \mathrm{N}- \end{array}$$

present in all these compounds, is a new development for analytical chemistry. The extremely high copper and palladium specificity shown by these compounds, necessitates a modification of the now accepted conception of copper and palladium specificity.

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PART II

PREPARATION AND GENERAL PROPERTIES OF THE REAGENTS

SUMMARY

Preparations of the various reagents have been described. The azo-derivatives form a new group of compounds which have been prepared for the first time.

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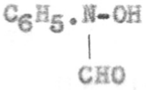
Preparation of the reagents

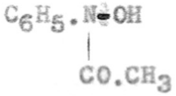
In this part, we have described the preparation of the compounds, listed below. In these compounds the nitroso-group of cupferron has been replaced by other negative substituents.

A. Formyl and acetyl derivatives:



$$C_6H_5.\underset{CHO}{\underset{|}{N}}-OH$$

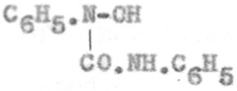
I



$$C_6H_5.\underset{CO.CH_3}{\underset{|}{N}}-OH$$

II

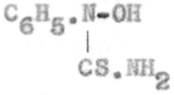
B. Urea derivative:



$$C_6H_5.\underset{CO.NH.C_6H_5}{\underset{|}{N}}-OH$$

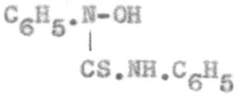
III

C. Thiourea derivatives:



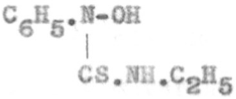
$$C_6H_5.\underset{CS.NH_2}{\underset{|}{N}}-OH$$

IV



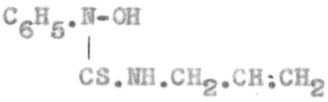
$$C_6H_5.\underset{CS.NH.C_6H_5}{\underset{|}{N}}-OH$$

V



$$C_6H_5.\underset{CS.NH.C_2H_5}{\underset{|}{N}}-OH$$

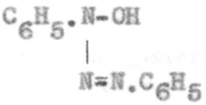
VI



$$C_6H_5.\underset{CS.NH.CH_2.CH{:}CH_2}{\underset{|}{N}}-OH$$

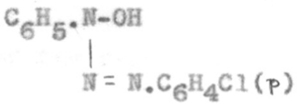
VII

D. Azo-derivatives:



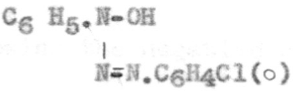
$$C_6H_5.\underset{N=N.C_6H_5}{\underset{|}{N}}-OH$$

VIII



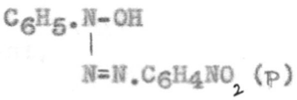
$$C_6H_5.\underset{N=N.C_6H_4Cl(p)}{\underset{|}{N}}-OH$$

IX



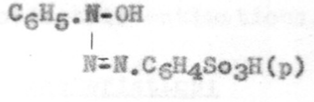
$$C_6H_5.\underset{N=N.C_6H_4Cl(o)}{\underset{|}{N}}-OH$$

X



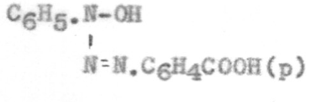
$$C_6H_5.\underset{N=N.C_6H_4NO_2\ (p)}{\underset{|}{N}}-OH$$

XI



$$\begin{array}{l} C_6H_5.N\text{-}OH \\ \quad | \\ \quad N{=}N.C_6H_4So_3H(p) \end{array}$$

XII



$$\begin{array}{l} C_6H_5.N\text{-}OH \\ \quad | \\ \quad N{=}N.C_6H_4COOH(p) \end{array}$$

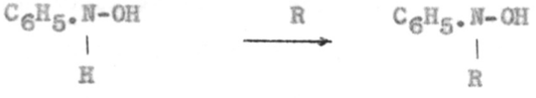
XIII

Of these, the azo-derivatives (VIII to XIII) are an entirely new group of compounds, which have been prepared for the first time by us. Compounds I, II, III, V and VII are known and were prepared according to the procedure described in the literature. The simple unsubstituted thiourea derivative IV and ethylaminothioformyl derivative VI are also unknown compounds. The former was obtained in solution, but considering the ultimate unstability of other thiourea compounds of this series, its isolation was not attempted.

The formyl (I) and acetyl (II) derivatives were prepared only in very small quantities, as the former needed 32 days for its preparation and in the case of the latter other undesirable by-products are always formed, which made the isolation of the material in substantial amount, difficult.

In all these preparations, phenylhydroxylamine was the basic raw material. For this reason, though this compound is quite well known, its preparation has been described in details. In most of the preparations pure crystallized phenylhydroxylamine was used.

The general mechanism of the reaction is as follows:



$$\begin{array}{c} C_6H_5.N\text{-}OH \\ | \\ H \end{array} \xrightarrow{R} \begin{array}{c} C_6H_5.N\text{-}OH \\ | \\ R \end{array}$$

R being the negative substituent.

The spectral characteristics of only VIII, IX and XII, which have been found to be useful by us for the gravimetric or the colorimetric estimations, have been incorporated.

Spectral characteristics:

3-Hydroxy-1,3-diphenyltriazine (VIII)

λmax.239, 284, 350 mµ; Log E = 4.0959, 3.6678, 4.2761 respectively.
(figure No: page)

3-Hydroxy-1-p.chlorophenyl-3-phenyltriazine (IX)

λmax.235, 281, 350, mµ; Log E = 3.9911, 3.8743, 4.1833 respectively.
(figure No: page)

3-Hydroxy-1-p.sulphonatophenyl-3-phenyltriazine (XII)

λmax. 235, 345, mµ; Log E = 4.1782, 4.4405 respectively.
(figure No: page).

Apart from other places, all these compounds show peak at about 350 mµ, which may be possibly due to the presence of 'azo' group[1]. Substitution of chloro or sulphonic group in the parent compound did not make any serious difference in the spectral characteristics.

In the spectroscopic examination, a Beckman quartz spectrophotometer, model DU, was used.

Preparation of phenylhydroxylamine[2]

Ammonium chloride (75 g.) was taken in a 6 lit. beaker containing water (2400 ml.). The solution was stirred mechanically and nitrobenzene (125 ml.) was slowly added to it. After the addition of nitrobenzene, zinc dust (200 g.) was added in small amounts in such a way that the temperature of the reaction mixture was between 60 to 65°C. The stirring was continued till the temperature began to fall (about 10 mins.). The reaction mixture was allowed to settle for some time (3 to 4 mins.) and then filtered under suction. The precipitate of zinc hydroxide on the filter funnel was washed with boiling water (3 x 100 ml.). To the filtrate pure sodium chloride (900 g.) was added and the contents cooled in a refrigerator for about two hours. The precipitated phenylhydroxylamine along with certain amount of sodium chloride was filtered. For purification, the precipitate was dissolved in warm benzene (300 ml.) and the accompanying sodium chloride was removed by filteration. To the filtrate, petrol ether (40-60, 300 ml.) was added and the mixture left in refrigerator for overnight. The crystals of phenylhydroxylamine were collected by filtration and dried in vacuum desiccator; yield 81 g; melting point: 81°C.

3-Hydroxy-1,3-diphenyltriazine (VIII)

Freshly prepared crystalline phenyl hydroxylamine (22 g.) was dissolved in warm water (700 ml.) and the solution stirred mechanically with sufficient quantity of crushed ice to bring the temperature to 0°C. A solution of benzenediazonium chloride prepared from aniline (18.6 ml.) hydrochloric acid (60 ml. conc. acid) and sod. nitrite (13.8 g.) was then slowly added under mechanical stirring to this solution. Small portions of a solution of sodium acetate (100 g. in 300 ml. water) were occasionally added to the reaction mixture to prevent it from becoming too acidic. After the addition of diazonium salt was complete, the remaining portion of sodium acetate was added and the reaction mixture stirred for another five minutes, the temperature during the entire course of reaction being kept at about 0°C. The granular, cream-yellow precipitate of 3-hydroxy-1,3-diphenyltriazine was then filtered off under suction, washed thoroughly with water and crystallized two times from alcohol. It was obtained as pale yellow crystals: yield about 20 g., m.p. 119.5-120°C.

Analysis: Found: C, 67.22; H, 4.9; N, 20.16%
$C_{12}H_{11}N_3O$ requires: C, 67.6 ; H, 5.1; N, 19.9 %

Solubility - 0.78 g. per 100 ml. alcohol at 23°C.

0.0044 g. per 100 ml. water at 23°C.

The absorption curve for 4.85 p.p.m. alcoholic solution of the compound is given in figure No: 1 .

Other azo-derivatives:

The other compounds of the azo-group, excepting the sulphonic derivative (XII) were prepared by following, more or less, the same procedure as described above, with only slight modifications as required by the nature of the compound. The quantities of various reagents used were adjusted according to the requirements of the molar proportions. Details have not been included for the sake of brevity.

3-Hydroxy-1-p.chlorophenyl-3-phenyltriazine (IX)

After preparation it was purified by crystallization from alcohol, when it was obtained as light green yellow crystals; melting point 140-140.5°C.

Analysis: Found: C, 58.47; H, 4.15; N, 17.08; Cl, 15.7%

$C_{12}H_{10}N_3OCl$ requires: C, 58.26; H, 4.07; N, 16.97; Cl, 14.32%.

The absorption curve for 2.6 p.p.m. alcoholic solution of the compound is given in figure No: 2 .

3-Hydroxy-1-o.chlorophenyl-3-phenyltriazine (X)

It was also crystallized from alcohol; the compound being fairly soluble in alcohol, only small quantity of the solvent was required. It was obtained as light green crystals; melting point 78-78.5°C.

Analysis; Found: C, 58.08; H, 4.19; N, 17.37; Cl, 13.82%

$C_{12}H_{10}N_3Cl$ requires: C, 58.26; H, 4.07; N, 16.97; Cl, 14.32%.

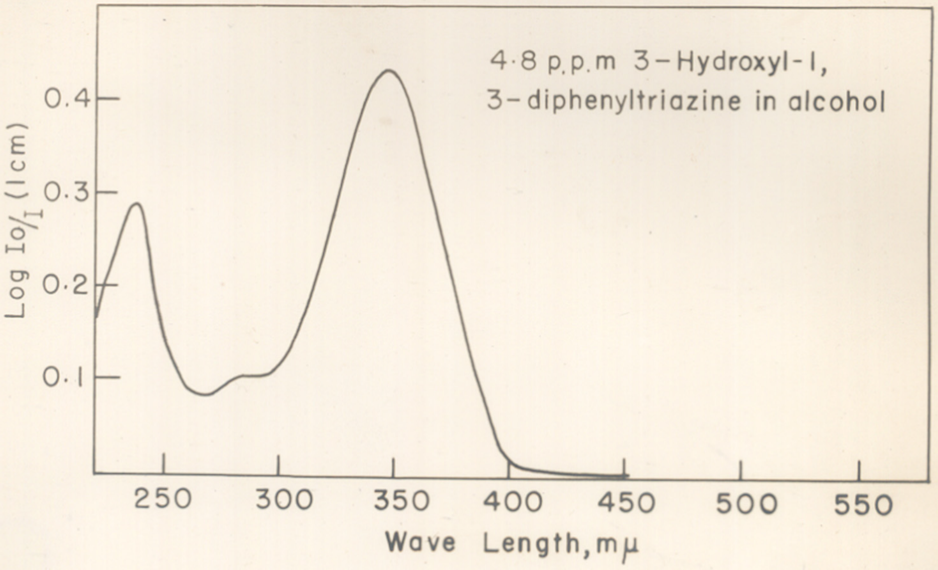


Figure No. 1 . Absorption curve for 4.8 p.p.m. alcoholic solution of 3-hydroxy-1,3-diphenyltriazine.

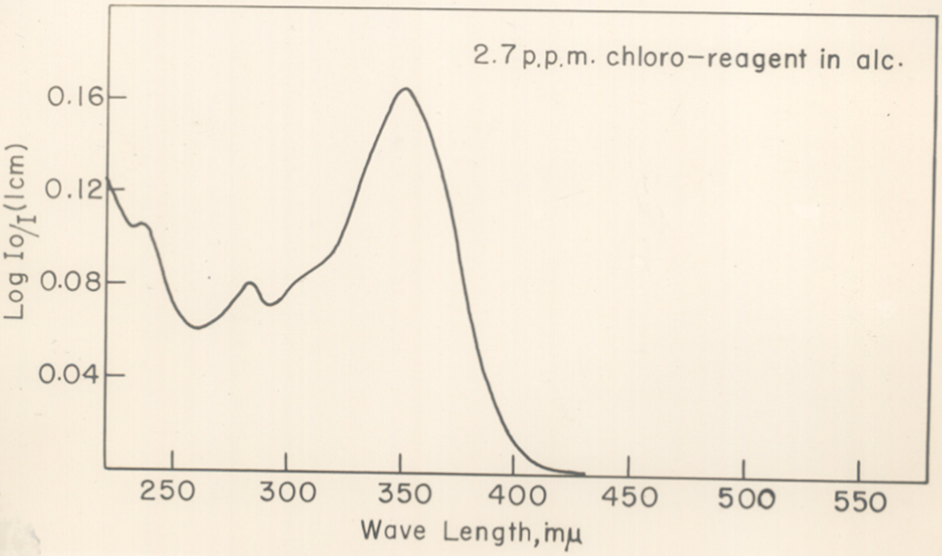


Figure No.2 . Absorption curve for 2.7 p.p.m. alcoholic solution of 3-hydroxy-1-p.chlorophenyl-3-phenyltriazine.

3-Hydroxy-1-p.carboxyphenyl-3-phenyltriazine (XIII)

After preparation it was crystallized from 50:50 alcohol acetone mixture, when it was obtained as pale yellow light fluffy crystals; melting point 184°C.

Analysis: Found: C, 56.66; H, 4.09; N, 15.61 %
$C_{13}H_{11}N_3O_3\ H_2O$ requires: C, 56.72 ; H, 4.72; N, 15.28 %

3-Hydroxy-1-p.nitrophenyl-3-phenyltriazine (XI)

It is a very insoluble compound and could be crystallized with much difficultly from acetone or very large amount of alcohol in the form of greenish yellow crystals; melting point 157°C.

Analysis: found: C, 55.74; H, 3.31; N, 22.04 %
$C_{12}H_{10}N_4O_3$ requires: C, 55.78, H, 3.87; N, 21.70%

3-Hydroxy-1-p.sulphonatophenyl-3-phenyltriazine (XII)

This compound was also prepared basically according to the procedure described for the parent compound. But due to the soluble nature of the compound, caution was necessary to avoid any loss of the same. For this reason its preparation is being described briefly.

Diazotisation of sulphanilic acid was done as follows: Sulphanilic acid (8.6 g.) was dissolved in 5% sodium hydroxide solution (40 ml.) and sodium nitrite (3.5 g.) was added to it. It was cooled by adding crushed ice and then the mixture was slowly poured into conc.hydrochloric acid (20 ml.) also containing crushed ice, with mechanical stirring.

The diazonium salt thus prepared was then added, slowly under mechanical stirring, to phenylhydroxylamine (5.4 g.) dissolved in 20% v/v. alcohol (125 ml.) having sufficient amount of crushed ice. Small portions of sodium acetate (50 g. in 100 ml.

water) were added occasionally to the reaction mixture to prevent it from becoming too acidic. The temperature during the entire course of reaction was kept at about 0°C. The precipitated sulphonic acid derivative was filtered under suction, washed two times with small amount of ice water and crystallized from a large volume of alcohol. It was obtained as bright, light green crystals; yield about 5 g. It was actually the sodium salt of the sulphonic acid derivative; having no sharp melting point. It starts decomposing at 157°C.

Analysis: found: C, 43.8; H, 4.0; N, 12.42; S, 10.48 %
$(C_{12}H_{10}N_3O)SO_3NaO\ H_2O$ requires: C, 43.3; H, 3.9; N, 12.32; S, 9.9 %

Solubility 2.96 g. per 100 ml. water at 23°C.
The absorption of this material was determined in aqueous solution. The full curve, covering both ultra-violet and visible range for 9.3 p.p.m. acqueous solution of the compound is given in figure No: 3.

One of the most common characteristic properties of all these azo-derivatives was that they were hydrolysed on long heating in weakly acidic medium. In this way, the parent azo-compound was initially hydrolysed to phenylhydroxylamine and diazonium salt which were subsequently converted to p.aminophenol and phenol respectively. (also refer p. 54)

These compounds in alkaline medium develop an intense yellow colour. The probable tautomerism taking place is given on page 89

Urea and thiourea derivatives

Substituted urea and thiourea derivatives were prepared by mixing in molecular proportions ethereal or benzene solutions of phenylhydroxylamine and corresponding isocyanate or isothiocyanate.

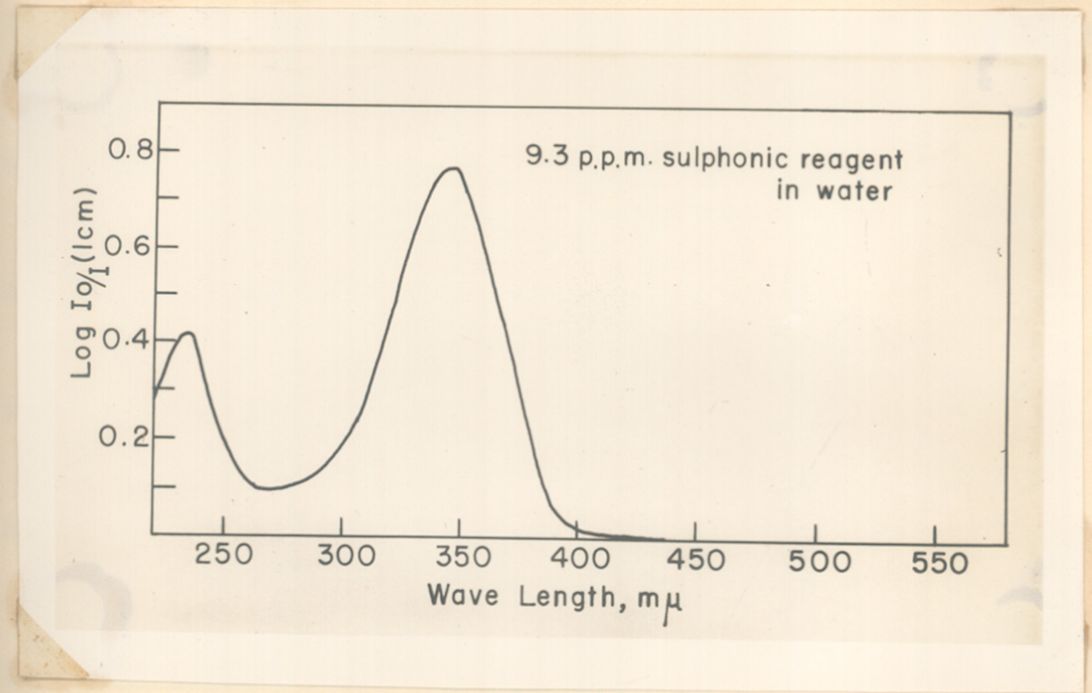
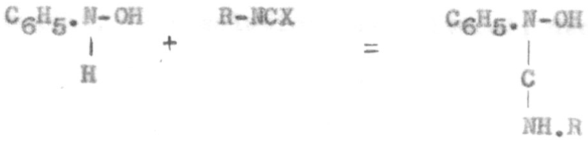


Figure No. 3 . Absorption curve for 9.3 p.p.m. aqueous solution of 3-hydroxy-1-p.sulphonatophenyl-3-phenyltriazine.

The product was thrown out in crystalline form after keeping for sometime or after partial removal of the solvent. The general mechanism of the reaction is as follows:



$$C_6H_5.\underset{\substack{|\\ H}}{N}\text{-}OH \quad + \quad R\text{-}NCX \quad = \quad C_6H_5.\underset{\substack{|\\ C\\ |\\ NH.R}}{N}\text{-}OH$$

where X is O or S

The products were crystallized again from ether or benzene. The characteristics of various derivatives are given below:

N-anilinoformyl-N-phenylhydroxylamine[3,8] (III),
melting point 125°, literature m.p.125°C.

N-anilino-thioformyl-N-phenylhydroxylamine[4,8] (V)
melting point 110.5°C, literature, m.p.111°C.

N-ethyl-amino-thioformyl-N-phenylhydroxylamine (VI)
melting point 131°C, new compound.

N-allyl-aminothioformyl-N-phenylhydroxylamine[5,8] (VII)
melting point 97°C, literature m.p.98°C.

<u>The unsubstituted thiourea derivative (IV)</u>

It was obtained in solution only. A solution of potassium thiocyanate (9.5 g. in 50 ml.water) was added to phenylhydroxylamine solution (11 g. in 200 ml. warm water). It was cooled and a dilute solution of sulphuric acid (2.5 g. in 25 ml. water) was added to it, with stirring. The mixture was left for about an hour. Solid barium carbonate was then added to neutralise the excess of sulphuric acid. The solution was filtered and a solution of copper acetate (12 g. in 100 ml.) was added to it. The brown copper complex formed was filtered, washed and suspended in 100 ml. warm water. Hydrogen sulphide gas was passed in to decompose the copper complex and to liberate the reagent. The solution was filtered, decolorised with charcoal and concentrated on a water bath. Qualitative testings were carried out with this solution.

N-formyl-N-phenylhydroxylamine[6,8] (I) and N-acetyl-N-phenylhydroxylamine[7,8] (II) were prepared, in very small amounts, by the procedure described in the literature. As these compounds were only preliminarily tested, their preparation is not being described here, for the sake of brevity.

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4. Beckmann, J.Prak.Chemie (2), 56, 89.

5. Beckmann, J.Prak.Chemie (2), 56, 90.

6 Bamberger, Ber., 35, 732.

7. Bamberger and Destraz, Ber., 35, 1883.

8. Beilstein, XV, 8 and 9.

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PART III

Reaction of various reagents with metallic ions.

SUMMARY

Reaction of the various reagents towards different metallic ions under varying pH conditions, has been described.

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Reaction of reagents with various metallic ions

In this part, we have recorded the reactions of the various reagents toward different elements, tested qualitatively. The reactions were carried out by adopting conventional procedures using spot plate, micro test tubes, hand centrifuge etc. pH was determined by using pH paper and also Beckman automatic pH meter, Model H-2. Completeness of precipitation was tested by applying spot test technique and using sensitive reagents like rubeanic acid in case of copper; dimethylglyoxime in case of nickel and palladium; catechol, hydrogen peroxide in case of titanium etc.

Azo-derivatives:

Details of the reactions of parent azo-compound - 3-hydroxy-1,3-diphenyltriazine (VIII, p. 25) towards various elements are recorded in table I (p. 39).

The results recorded in the table were also, more or less, true with the other members of the azo group, so far as the specificity, pH limit etc. were concerned.

The precipitates formed by the p.chloro-derivative (IX, p. 25) were more stable, compared to the complexes formed by the parent reagent. Precipitates formed by the o.chloro-derivative (X.p. 25) were gelatinous in nature and comparatively less stable towards heat; this was presumably due to the steric hinderance created by the ortho-substitution, which prevented the formation of stable complexes.

TABLE I

Reactions of 3-hydroxy-1,3-diphenyltriazine with various elements

Elements	pH for quantitative precipitation.	pH, below which there is no reaction.	Colour of the complex	Remark
Cu(II)	1.9 to 7.0	--	chocolate brown	granular, stable towards heat.
Ni(II)	4.4 to 7.0	3.5	bright yellow	granular, stable towards heat
Co(II)	5.0 to 7.0	4.0	dark brown	granular, slightly soluble in water
Mn(II)	N.Q.	5.5	dirty brown	unstable towards heat
Cd(II)	N.Q.	6.0	light yellow	fine precipitate
Zn(II)	N.Q.	6.0	light yellow	fine precipitate
Pb(II)	N.Q.	7.5	light yellow	fine precipitate
Fe(II)	4.9 to 7.0	upto low pH	bluish black	granular, unstable towards heat
Fe(III)	4.5 to 7.0	upto low pH	bluish black	granular, unstable towards heat.
Hg(II)	5.4 to 7.0	4.0	yellow precipitate	fine, unstable towards heat
Sn(IV)	N.Q.	6.5	yellow precipitate	fine, only very slight precipitation.
Sn(II)	N.Q.	6.5.	""	""
Ti(IV)	2 to 3.5 (at low pH only)	--	orange	unstable towards heat, fairly soluble in alcohol.
Pd(II)	1.6 to 7.0	--	yellowish brown	granular, stable towards heat
V(IV)	at low pH only	--	grassy green	unstable towards heat, fairly soluble in alcohol
Vanadate	""	-	dark green	"" ""
Molybdate	""		deep orange red	"" ""
Ag, Au(III), Os(IV)	--	--	--	Reduced to the metallic state
As(III), Sb(III), Bi(III), Al(III), Be(II), Cr(III) Th(IV), Ge(IV), Ce(IV), U(IV), UO_2(II), Pt(IV), Rh(IV) Ru(III), Ir(III), WO''_4, PO'''_4 alk.& alkaline earth metals				no reaction

N.Q. = not quantitative

The complexes formed by the p.carboxy-derivative (XIII, p 26) were also gelatinous in nature, and not useful for analytical purposes.

The nitro compound (XI, p.25) was very insoluble, its complexes were also, more or less, so. The colour intensities of these complexes were superior than those formed by the remaining azo-compounds.

The complexes formed by the sulphonic acid derivative (XII, p. 26), were, like the reagent itself, soluble in water, otherwise, the colour, pH limit etc., were, more or less, the same as the parent azo-compound.

Formyl and acetyl derivatives:

The formyl (I, p.25) and acetyl (II, p.25) derivatives which were obtained in very small amounts, were tested against only a limited number of common ions. Both of them gave intense red colour with iron (III) and deep green colour with copper. Both of these compounds have excellent possibilities as spot test and colorimetric reagents. This point will be investigated when the method of preparation of these compounds can be improved.

Urea and thiourea derivatives:

The urea derivative (III, p. 25) showed only weak precipitating property. Details of the reactions of these compounds toward various elements are recorded in Table II.

TABLE II

Reactions of urea and thiourea derivatives

Material tested	N-anilinoformyl phenylhydroxylamine (III,p 25)	N-anilinothioformylphenylhydroxylamine (V,p. 25)	N-allylaminothioformylphenylhydroxylamine (VII,p25)	N-ethylaminothioformylphenylhydroxylamine (VI, p 25)
Copper acetate				
pH, 5-6	light greenish turbidity and precipitate	brown, granular precipitate	brown turbidity	brown turbidity
+NH_3; pH 7-8	" "	brown turbidity and precipitate	grey turbidity	grey turbidity
Silver nitrate				
pH, 5-6	immediate black precipitate	immediate black precipitate	pink colour, changes to brown precipitate	pink colour, changes to black ppt.
+NH_3; pH, 7-8	no reaction	granular brown precipitate	dirty brown turbidity	dirty brown turbidity
Hg(II) acetate				
pH, 5-6	no reaction	pinkish turbidity	yellow turbiditiy and ppt.	yellow turbidity
+NH_3-pH,7-8	no reaction	yellowish turbidity	" "	" "
Fe(II)sulphate				
pH, 6-7	light pink colour	violet turbidity	violet turbidity	violet turbidity.
Co(II),Ni(II), Fe(III),Zn(II), Cd(II), Pb(II) Cr(III),Bi(III) Mn(II),As(III), Sb(III),Al(III) Mg(II), alk.& alkaline earth metals	no reaction	no reaction	no reaction	no reaction

Of the various reagents tested in this part, some of the azo-derivatives (VIII, IX and XII, p. 25) have been found to possess excellent qualities as analytical reagents. Their use for this purpose has been described in details in subsequent parts of the thesis. The thiourea derivatives, because of their instability, about which mention has also been made earlier, were not examined in detail.

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PART IV

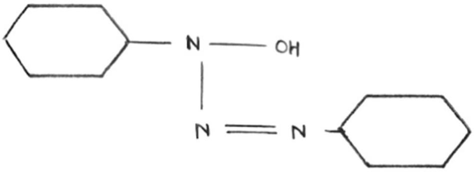
3-HYDROXY-1,3-DIPHENYLTRIAZINE AS A REAGENT FOR GRAVIMETRIC ESTIMATION OF PALLADIUM

*

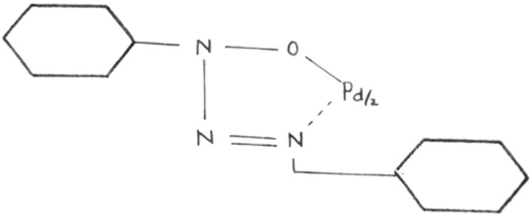
3-Hydroxy-1,3-diphenyltriazine as a reagent for palladium (II).

SUMMARY.

At low pH (2.0 to 3.0) 3-hydroxy-1,3-diphenyltriazine (I) is a highly selective reagent for palladium and forms an inner complex with it, having the following structure (II).



I



II

The palladium complex is of definite composition and is directly weighable. With the help of this reagent palladium can be quantitatively estimated as such, or in presence of nickel(II), zinc (II), manganese (II), cadmium (II), bismuth (III), aluminium (III), chromium (III), mercury (II), arsenic (III), lead (II), magnesium (II), antimony (III), tin (IV), cobalt (II), iron (II), iron (III), beryllium (II), uranyl (II), molybdate, tungstate, phosphate, fluoride, nitrate; platinum metals - platinum (IV), rhodium (IV), ruthenium (III), iridium (III) and alkali and alkaline earth metals.

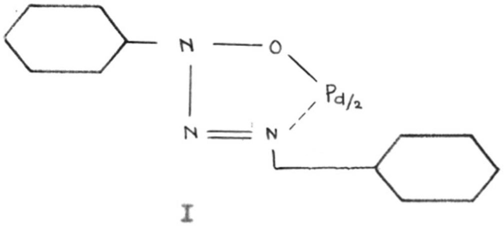
3-hydroxy-1,3-diphenyltriazine is superior to all the palladium reagents now described in the literature including dimethylglyoxime. It is also suitable for micro-gravimetric estimation of palladium.

***

3-hydroxy-1,3-diphenyltriazine as a reagent for palladium

In part III of this thesis, along with other reagents, the general precipitating properties of 3-hydroxy-1,3-diphenyltriazine have been described. At low pH, below 3, the reagent precipitates only palladium (II), copper (II), iron (II), iron (III), vanadate, vanadium (IV), titanium (IV) and molybdate. Excepting the first two complexes, others are decomposed on heating in acidic reaction medium thus making the reagent highly selective for palladium (II) and copper (II). In this part the use of this reagent for gravimetric estimation of palladium and its separation from a very large number of other elements, including the members of the platinum group, has been described.

The palladium complex is yellowish brown in colour, is stable towards heat and dilute mineral acids and does not decompose below its melting point (252°C). It is of definite composition and can be directly weighed. Elemental analysis of the complex indicated the formula $(C_{12}H_{10}N_3O)_2Pd$. It can be represented by the structural formula given below:



I

Palladium is quantitatively precipitated by this reagent between pH 1.6 to 7.0. In order to increase the specificity of this reagent, most of the estimations were carried out at pH between 2.0 to 3.0. Working in this low pH region had another special advantage. Any excess of the reagent present in the reaction medium, on heating, during the usual processing of the complex, was hydrolysed into water soluble products and thus could be easily eliminated. The palladium complex remained unaffected under these conditions. This easy hydrolytic removal of the excess of the reagent imparted to 3-hydroxy-1,3-diphenyltriazine all the advantages inherent in a water-soluble reagent, about which we shall again discuss in details later on.

Estimation and separation of palladium

Palladium can be quantitatively estimated in presence of nickel (II), zinc (II), manganese (II), cadmium (II), bismuth (III), aluminium (III), chromium (III), mercury (II), arsenic (III), lead (II), magnesium (II), antimony (III), tin (IV), cobalt (II), iron (II), iron (III), beryllium (II), titanium (IV), zirconium (IV), cerium (IV) thorium (IV), uranyl (II), platinum (IV), rhodium (IV), iridium (III), ruthenium (III), molybdate, tungstate, phosphate, fluoride, nitrate, alkali and alkaline earth metals.

Only a few ions created interference in palladium estimation. Gold(III), silver and osmium (IV) do not react with the reagent, but interfere, as they are reduced to the metallic state by it. Tin (II) also does not react appreciably with the reagent, but interferes as it reduces palladium to the metallic state. Tin (IV), as it has been indicated, does not create any interference. Palladium, obviously, cannot be separated from copper, as the two complexes have virtually identical properties. It cannot also be quantitatively separated from vanadium (IV) and vanadate because of partial coprecipitation. Cyanide, more or less, completely masks the precipitation.

Superiority over other reagents

Dimethylglyoxime is the conventional reagent for palladium. The present reagent is superior to dimethylglyoxime in many respects. Its palladium complex is very stable towards heat and dilute mineral acid; it is very granular, not voluminous like Dmg-complex and can be filtered quickly in the hot state even through sintered crucible No:2. Its specificity, is in no way less than that of dimethylglyoxime.

Other reagents for palladium

Before going into the details of the various estimations and separations, carried out with 3-hydroxy-1,3-diphenyltriazine, it is worthwhile to discuss about the other reagents, which have been used for the same purpose. Of these, the following are important.

1. Dimethylgyoxime.
2. Benzoylmethyl-glyoxime.
3. β-Furfuraldoxime.
4. 1,2-Cyclohexanedionedioxime.

We shall now briefly discuss the merits and limitations of these reagents.

1. Dimethylgyoxime

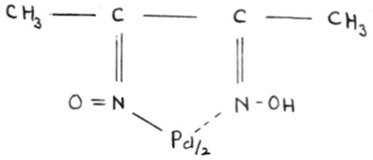
$$CH_3 - \underset{\underset{HON}{\|}}{C} - \underset{\underset{NOH}{\|}}{C} - CH_3$$

I

Dimethylglyoxime was introduced by Tschugaeff[1], as a reagent for nickel and palladium. Later on, it was thoroughly investigated by Wunder and Thuringer[2], for the separation and determination of palladium.

It is well known for its use in estimating nickel, in slightly ammoniacal or acetic acid medium. In dilute mineral acidic medium, it is also a highly selective reagent for palladium, and has been widely used for its estimation and separation from various elements. Currently, it is considered to be the most reliable reagent for this purpose.

Dimethylgyoxime palladium complex is yellow in colour, is of definite composition and can be directly weighed. The complex has the following structure, which is similar to that of the nickel complex:

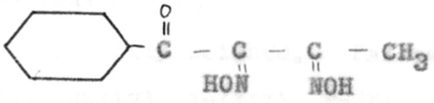


II

Platinum is partially precipitated by dimethylgyoxime, and gold is reduced to the metallic state, hence these elements interfere in the determination of palladium, otherwise it can be separated from all the other elements, though quantitative data in certain cases are not available.

Palladium dimethylglyoxime complex is stable in dilute mineral acid at ordinary temperature but is affected at higher temperatures. For this reason, the estimation of palladium with dimethylglyoxime, is to be done at room temperature alone. The complex formed under such conditions, is very voluminous and gelatinous in nature, and offers great difficulties in filtration, which, obviously, is quite a serious defect.

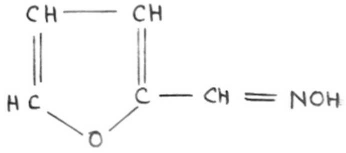
2. Benzoylmethyl-glyoxime:



III

This compound was introduced by Hanus and collaborators[3] as a palladium reagent and later on the work was extended by Grisollet[4] and others. It's palladium complex has the same type of structure as the dimethylglyoxime complex. It also appears to be specific for palladium and has been used for separating palladium from Pt(IV), Ir(III), Os(IV), Rh(IV), Au(III), Sb(III), Bi(III), Cu(II), Hg(II), As(III), Sn(IV), Fe(II), Ni(II), Co(II), Zn(II), molybdate, tungstate and vanadate from dilute hydrochloric acid solution. The palladium complex after precipitation has to be set aside for 12 hours, before it is ready for filteration. This, obviously, is a very serious defect. The reagent is also not very soluble in water. For these reasons, it has not found any extensive use so far.

3. β-Furfuraldoxime



IV

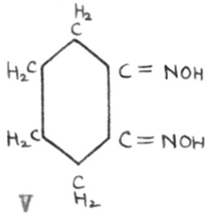
In dilute acidic medium, it forms with palladium chloride, a light yellow complex of the following composition: $Pd(C_4H_3\text{ -O-CH}=NOH)_2\ Cl_2$. It is actually a co-ordination complex and not an inner complex. This reagent was introduced by Hayes and Chandlee[5].

β-Furfuraldoxime appears to be a highly specific reagent for palladium. The palladium complex is of definite composition and can be directly weighed. Palladium has been separated from Pt(IV), Ru(III), Rh(IV), Ir(III), Fe(II), Ce(III), Ni(II), Sb(III), Cd(II), Th(IV), Ti(IV), molybdate, tungstate, vanadate etc. However, gold, silver, mercury (I), lead, and cerium (IV) caused interference.

The palladium complex is unstable at higher temperatures in acidic medium. For drying it also, a temperature not exceeding 110°C. has to be used.

The reagent also suffers from one very peculiar defect. Anions, other than chloride, if present, interfere by changing the composition of the complex. For this reason, in presence of anions like sulphate and nitrate, an extra amount of sodium chloride is added, to keep the precipitate of definite composition.

4. <u>1,2-Cyclohexanedione dioxime</u>



V

This compound has been recently examined, as a palladium reagent, by Voter, Banks and Diehl[6]. Previously, H.Diehl in his book[7] has suggested the possibility of using this reagent for this purpose. The reagent is soluble in water and thus has an advantage over comparatively less soluble dimethylglyoxime. It forms an insoluble yellow complex with palladium, which is similar in structure to other glyoxime complexes. The palladium complex is slightly more stable towards heat than the complexes formed by dimethylglyoxime, benzoylmethyl glyoxime, β-furfuraldoxime etc. However, it also cannot be heated above 60°C. in the acidic reaction medium.

<u>Other less known reagents</u> which have been used for the gravimetric estimation of palladium are:

1. 6-nitroquinoline
2. 8-nitroquinoline
3. 1,10-phenonthroline.

These form insoluble coordination complexes with palladium chloride. However, there is a considerable anomaly as regards the composition and the structure of these complexes, to warrant any serious examination, than a casual survey.

Ogburn and Riesmeyer[8] introduced 6-nitroquinoline for the separation of palladium from other members of the platinum group through direct weighing, and gave the formula of the complex as: Pd $(C_9H_6N.NO_2)_2$ Feigl[9] has elaborately discussed the structure of the complex on the basis of the above formula. Very recently, Ryan[10] has found that the above formula is incorrect. The palladium complex is actually a coordination complex of the usual type, containing about 13.2% chlorine. The reagent, however, has great possibility as it seems to be specific for palladium. However, separations from other metals, except the members of the platinum group, have not been carried out so far. There may be practical difficulties in estimations as the reagent is only slightly soluble in water.

1,10-phenanthroline has been examined by Ryan[11]. Preliminary investigation indicated the possibility of this being useful for the estimation of palladium. Later on[10], it has been reported by the same author that almost all the common anions like sulphate, nitrate, acetate, carbonate, phosphate etc. interfere in the estimation.

After discussing the merits and limitations of various reagents, described in the literature, it is now possible to compare them with 3-hydroxy-1,3-diphenyltriazine, as a palladium reagent.

Comparative characteristics of the reagent

1. 3-hydroxy-1,3-diphenyltriazine is prepared easily from common laboratory chemicals. It is stable towards heat, light and air.

2. As regards specificity, the reagent is as good as any of the reagents described earlier, or is probably superior. With this reagent it is possible to separate one part palladium from ten parts or more of platinum, if the initial precipitation is done in cold. In this respect, it is very much superior to dimethylglyoxime While separating palladium from platinum, using the latter reagent, it has been reported by Thompson, Beamish and Scott[12], that the palladium complex is always contaminated with platinum, giving high results.

Thermal stability of palladium complex

3. Unlike the complexes formed by the other reagents, described earlier, the palladium complex of 3-hydroxy-1,3-diphenyltriazine, is stable towards heat in the acidic reaction medium and can be heated on a water bath for an indefinite period. In the dry state also it is decomposed only when it is heated beyond its melting point, which is as high as 252°C.

In analytical chemistry, heating a complex in the reaction medium is considered to be necessary, because it makes the precipitate granular. This can not be done with dimethylglyoxime or other reagents, described earlier. These reagents suffer from temperature conditioning, so that, the precipitation, processing and filtration etc. have to be carried out at room temperature alone. 3-Hydroxy-1,3-diphenyltriazine palladium complex does not suffer from any of these defects. It is very granular and not at all voluminious like dimethylglyoxime complex, and can be filtered quickly in the hot state, even through sintered crucible No:2. The precipitate can also be dried to a constant weight at 120° to 125°C. in 30 to 45 minutes.

4. 3-hydroxy-1,3-diphenyltriazine also possesses all the advantages of a water-soluble reagent. By itself it is only slightly soluble in water, but in the hot acidic reaction medium, any excess of the reagent present, is completely hydrolysed to water soluble products without affecting the palladium complex and can be easily eliminated by washing with hot water alone. None of other reagents except 1,2 cyclohexanedionedioxime possesses this very desirable property.

5. It's conversion factor 0.2009, is more favourable than all the other reagents, namely dimethylglyoxime (0.3167), 1,2-cyclohexanedionedioxime (0.2743), benzoyl-methylglyoxime (0.2054) and β-furfuraldoxime (0.2669).

Palladium precipitating grouping

Before coming to the experimental part, it will be worthwhile, to have a short discussion about the functional groupings, which are supposed to be specific for palladium.

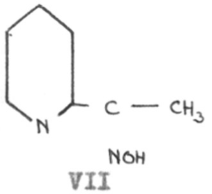
Palladium reagents may be broadly classified as those forming:

1. Inner complexes
2. Coordination complexes.

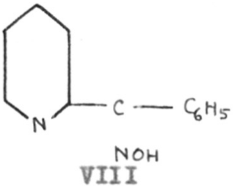
Inner complexes of palladium

Palladium and nickel belong to the same group in the classification of elements. Reagents, which are supposed to be specific for nickel, are also considered to be specific for palladium, though at a different pH.

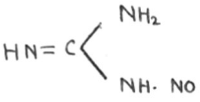
In an excellent review made by H.Diehl in his book[7], he has given that the  $-\underset{\text{HON}}{\underset{\|}{C}} - \underset{\text{NOH}}{\underset{\|}{C}}-$ group, strickly speaking, represents one of the arrangements capable of conferring the property of nickel specificity upon an organic molecule. By taking the examples of 2-pyridyl methylketoxime (VII), 2-pyridylphenylketoxime (VIII) and nitrosoguanidine (IX),



VII

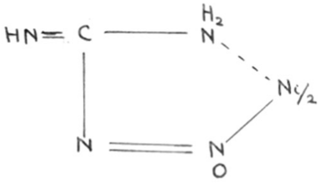


VIII



IX

which also form characteristic nickel complexes, he concludes that the fundamental requirement of a nickel binding group is the union of metal by one principal and one auxiliary valence to two nitrogen atoms, resulting in the development of a five membered ring. Nitroso-quianidine nickel complex has the following structure:



X

These arguments apply equally well in the case of palladium also. The structure of palladium dimethylglyoxime complex (II) has been given earlier (p. 46). It is also a complex where palladium is connected to two nitrogen atoms of the glyoxime molecule through one principal and one auxiliary valence.

Coordination complexes of palladium

Ryan[10] has studied the reaction of many organic compounds containing nitrogen coordinating groups, as possible reagents for platinum metals. The results indicate that tertiary amines containing $=N-C=$ group form insoluble coordination complexes with palladium chloride of the general type-dichlorodiamminepalladium - $Pd(NH_3)_2Cl_2$. Thus, 6-nitroquinoline, 8-nitroquinoline and 1,10-phenanthroline form coordination complexes of the type indicated above. These compounds show possibility as palladium reagents.

3-hydroxy-1,3-diphenyltriazine introduces a new specific functional grouping for palladium, the type of which has not been described earlier.

Industrial possibility of 3-hydroxyl-1,3-diphenyltriazine

It has been pointed out earlier that since 3-hydroxy-1,3-diphenyltriazine is prepared from common laboratory chemicals, like nitrobenzene and aniline etc., its cost of production should be very low. Due to the very high specificity of this reagent towards palladium, it looks probable that this specific, but inexpensive reagent, may possibly be utilised for the industrial isolation of palladium from its ores or for its separation from platinum metals.

The usual procedure for isolation and separation of the platinum metals is very elaborate[13]. These metals are usually obtained as valuable bye-products from nickel refineries. For final purification the concentrate of the platinum metals is dissolved in aqua-regia. The solution contains gold, palladium and platinium along with some silver, from which palladium is recovered, after several stages, as metal. The procedure involved is, also, not very inexpensive.

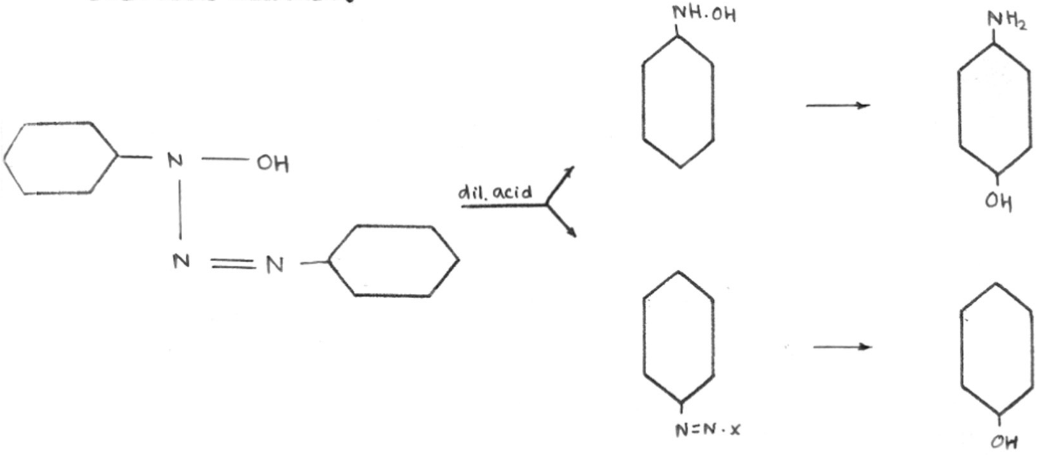
With the help of 3-hydroxy-1,3-diphenyltriazine, palladium could be directly precipitated as an insoluble complex from this solution. Gold and silver are likely to contaminate the

the palladium complex, because of their partial reduction to the metallic state by the reagent. However, this interference could also be easily eliminated by extracting the palladium complex with solvents like chloroform or carbon tetrachloride etc. in which it is very soluble.

Alternatively, gold and silver could be removed as metals by treatment with ferrous sulphate, leaving a mixture of palladium, platinum and iron (III), from which palladium could be directly precipitated in the cold with the help of 3-hydroxy-1,3-diphenyltriazine. Interference by iron (III) could be controlled by using sodium or potassium fluoride as a masking agent.

Mechanism of hydrolysis of 3-hydroxy-1,3-diphenyltriazine

The easy hydrolytic removal of excess of 3-hydroxy-1,3-diphenyltriazine from a reaction mixture is a very interesting phenomenon. We have critically examined the mechanism of this process. The reagent is initially decomposed into phenyl hydroxylamine and benzene diazonium salt, which subsequently form p-aminophenol and phenol respectively. p.Aminophenol remains in solution as its hydrochloride and the amount of phenol formed is so small that it is also completely soluble in the large volume of the reaction mixture.



Iso-merisation of phenylhydroxylamine to p-aminophenol in acidic medium is a well known reaction. While examining this mechanism we have also made another interesting observation, which, though not directly connected with our work, was quite noteworthy. Phenol and p-aminophenol in presence of alkali form a compound which is intense blue in colour. On acidification the colour sharply changes to red. The optimum pH appears to be about 7.0 to 7.5, which is comparable to that of litmus. This compound, if isolated and examined may show possibility as an indicator in acidimetry and alkalimetry. But as it was outside our scope of work, we did not pursue it further.

EXPERIMENTAL.

Standard palladium solution: 1 gram of palladium chloride was dissolved in 6 ml. conc. A.R. hydrochloric acid and the solution diluted to 1000 ml; the content of palladium was estimated by using dimethylglyoxime.

Reagent solution: 1% w/v. solution of the reagent in 95% ethyl alcohol was used.

Metal ion solutions: Reagent grade soluble salts (usually nitrates or acetates, 1% solution) of various metals were used for quantitative separations. Platinic chloride,ceric ammonium sulphate, ferrous ammonium sulphate and ferric alum were used as source of platinium (IV), cerium (IV), iron (II) and iron (III) respectively. Rhodium metal was fused with potassium bisulphate, and thus a soluble double salt-potassium rhodium sulphate was obtained.

Buffering solutions: Normal hydrochloric acid, 10% w/v. sodium acetate and sodium potassium tartrate solutions were used for the adjustment of pH. On a few specially required occasions, 10% acetic acid, normal sulphuric acid or nitric acid were used instead of hydrochloric acid.

Apparatus: All pH measurements were carried out using a Beckman pH meter model H-2. Sintered crucible No:3 was used for collecting precipitates. Ashless filter paper No:40 was used for general filtration and silica crucibles for ignition. A Beckman model DU quartz spectrophotometer was used for determining the spectra of the reagent and the complex. Mettler's single pan macro, semi-micro and micro balances were used for weighing.

Properties of the Pd-complex of N-phenylazophenylhydroxylamine

It is a yellowish brown substance, very soluble in chloroform and benzene, fairly soluble in ether and acetone and only slightly soluble in alcohol. It can be crystallized from acetone in the form of silky needles, m.p.252°. It does not show any sign of decomposition before melting and can be safely heated at 120-130°C. to a constant weight in about forty-five minutes time. Micro analysis of the complex carried under standard conditions showed N, 15.7%; $(C_{12}H_{10}N_3O)_2$ Pd requires: N, 15.82%.

The absorption spectrum of the Pd-complex has been determined in alcoholic solution.

λmax. for the complex 225, 255, 413 m μ; Log E = 4.5847, 4.5847, 4.3835 respectively.

The absorbtion curve of 3.8 p.p.m. Pd-complex in alcohol is given in figure No: 4 .

Effect of pH on the precipitation of palladium (II)

With a view to ascertaining the versatility of this reagent, precipitations of palladium (II) under various pH conditions with varying quantities of the reagent were carried out. Results were checked gravimetrically as well as by spot tests using Dmg and stannous chloride. Palladium (II) was completely precipitated between pH 1.6 to 7.0 with only a slight excess (20-25%) of the reagent. Most of the estimations and separations were, however, carried out between pH 2.0 to 3.0 as it increased the specificity of the reagent and facilitated the removal of the excess of the reagent by hydrolysis. The precipitate formed under these conditions was granular and could be filtered easily.

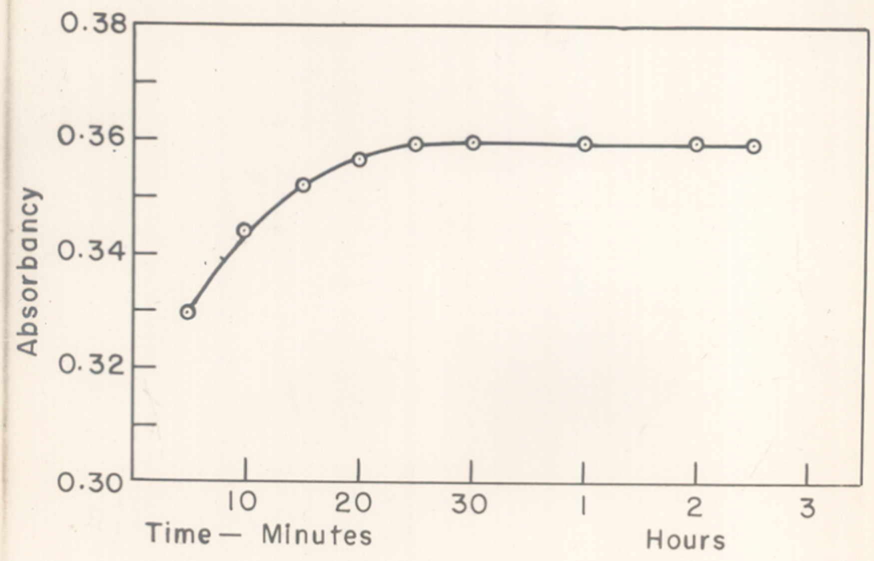


Figure No 4. Absorption curve for 3.8 p.p.m. alcoholic solution of palladium complex.

Determination of palladium

A number of palladium determinations using varying quantities of palladium were carried out according to the following procedure. The final pH measurements were carried out with a glass electrode on the filtrate after removal of the complex.

Procedure for palladium (II) A solution of palladium chloride containing 20-25 mg. of the metal was diluted to about 150 ml. and 1.5 to 3 ml. of 10% w/v. sodium potassium tartrate or sodium acetate added to it. The requisite amount of N-hydrochloric acid (about 2 ml.) was then added to bring the pH between 2-3. pH adjustment could actually be done by adding mineral acid alone, but incorporation of small amount of sodium acetate or sodium potassium tartrate was found to be helpful in stabilizing it. To this solution which may also contain varying quantities of foreign ions, 1% w/v. alcoholic solution of the reagent was added in excess (20-25%) with stirring. The Pd-complex separated out as a light green precipitate. The suspension was heated on a boiling water bath with occasional stirring for 45 to 60 minutes when the complex became granular and its colour gradually changed through yellowish green to yellowish brown. The medium also became clear and free from colloidal suspension. The complex was then filtered hot through a weighed sintered glass crucible No:3 and washed with hot water a few times. The hydrolysed reagent in the filtrate, when tested on a spot plate with a drop of alkali solution develops a blue to bluish violet colour due to the presence of p-aminophenol and phenol. The complex was dried to a constant weight at 120-125°c for 30-45 minutes and weighed. The weight of the complex multiplied by 0.2009 gave the weight of Pd. The results are recorded in table No:I

TABLE I

Determination of palladium.

	Pd. taken G	Foreign ion G	Pd.complex G	Pd. found G	Error G
1	0.02700		0.1344	0.02700	0.00000
2	0.01080		0.0537	0.01078	- 0.00002
3	0.01080		0.0538	0.01080	0.00000
4	0.01080		0.0537	0.01078	- 0.00002
5	0.01754		0.0874	0.01755	+ 0.00001
6	0.01754		0.0875	0.01757	+ 0.00003
7	0.01754		0.0875	0.01757	+ 0.00003

Separation of palladium from cobalt and nickel

We have already observed earlier, under the general precipitating properties of 3-hydroxy-1,3-diphenyltriazine (Part III, p. 39) that there is no precipitation of cobalt below pH 4.0 and nickel below 3.5, hence there was no interference by these elements, at the pH range (2.0 to 3.0) used by us for the estimation of palladium.

Cobalt and nickel salts solutions were added separately to a known volume of standard palladium solution, from which palladium was determined by the same procedure described earlier. The results are recorded in Table II.

TABLE II

Determination of palladium in presence of cobalt (II) and nickel (II).

	Pd.taken G	Foreign ion G	Pd.complex G	Pd.found G	Error G
1	0.01080	0.02 Co(II)	0.0540	0.01084	+ .00004
2	0.01554	0.02 Co(II)	0.0773	0.01553	– .00001
3	0.01554	0.02 Co(II)	0.0775	0.01556	+ .00002
4	0.01080	0.02 Ni(II)	0.0537	0.01079	– .00001
5	0.01080	0.02 Ni(II)	0.0540	0.01084	+ .00004
6	0.01080	0.02 Ni(II)	0.0539	0.01082	+ .00002

Separation of palladium from zinc, manganese and cadmium

Though in neutral or very slightly acidic medium, zinc manganese and cadmium are partially precipitated by 3-hydroxy-1,3-diphenyltriazine, at lower pH, they do not react at all. Palladium was determined in presence of these elements, following the procedure for palladium, described earlier. The results are recorded in table III

TABLE III

Determination of palladium in presence of zinc, manganese(II) and cadmium

	Pd.taken G	Foreign ion G	Pd.complex G	Pd.found G	Error G
1	0.01080	0.02 Zn(II)	0.0537	0.01078	- .00002
2	0.01080	0.02 Zn(II)	0.0538	0.01080	.00000
3	0.01080	0.02 Mn(II)	0.0537	0.01078	- .00002
4	0.01080	0.02 Mn(II)	0.0540	0.01084	+ .00004
5	0.01080	0.02 Cd(II)	0.0536	0.01076	- .00004
6	0.01080	0.02 Cd(II)	0.0539	0.01082	+ .00002

Determination of palladium in presence of nitrate, fluoride and phosphate

Palladium is quantitatively precipitated in presence of large concentration of nitrate, fluoride and phosphate. For this reason, specially in these cases, where chloride and sulphate ions interfere e.g. lead etc., pH adjustments can be done by using N-nitric acid.

Fluoride can be very advantageously used for masking the precipitation of iron (II), iron (III), titanium (IV) and molybdate etc. by 3-hydroxy-1,3-diphenyltriazine and for the prevention of any hydrolysis of zirconium (IV) and tin (IV) salts.

Palladium was determined in presence of these anions by following the procedure described earlier. The results are recorded in table IV.

TABLE IV.

Determination of palladium in presence of nitrate, fluoride, and phosphate.

	Pd.taken G	Foreign ion G	Pd.complex G	Pd.found G	Error G
1	0.01169	0.10 NO_3'	0.0584	0.01172	+ .00003
2	0.01169	0.20 NO'_3	0.0580	0.01164	- .00005
3	0.01169	0.50 NO_3'	0.0583	0.01170	+ .00001
4	0.02427	0.05 F'	0.1205	0.02422	- .00005
5	0.02427	0.20 F'	0.1205	0.02422	- .00005
6	0.02427	0.3 F'	0.1209	0.02429	+ .00002
7	0.02427	0.05 PO_4^{3-}	0.1205	0.02422	- .00005
8	0.02427	0.10 PO_4^{3-}	0.1207	0.02425	- .00002

Separation of palladium from iron (II) and iron (III)

Iron (II) and iron (III) are precipitated by 3-hydroxy-1,3-diphenyltriazine at low pH in the form of bluish black complexes. These complexes, however, are unstable towards heat and are decomposed completely when the reaction mixture is heated on a water bath, thus making the quantitative separation of palladium from iron possible. The procedure followed was the same as the general procedure proposed by us, except, that the time of digestion on the water bath in this case was about 60-70 minutes, instead of the usual 45-60 minutes, employed in other cases. At the end of this digestion period, the bluish black colour of the iron complex disappears completely leaving the palladium complex in a pure state. Alternatively, iron could be masked completely by adding about 0.5 gm of sodium or potassium fluoride, before the addition of the reagent. In that case no special processing was necessary. The results are recorded in table V.

TABLE V.

Determination of palladium in presence of iron (II) and iron (III).

	Pd.taken G.	Foreign ion G.	Pd.complex G.	Pd.found G.	Error G
1	0.01080	0.02 Fe(II)	0.0539	0.01082	+.00002
2	0.01080	0.02 Fe(II)	0.0536	0.01076	-.00004
3	0.01080	0.05 Fe(II)	0.0540	0.01084	+.00004
4	0.01080	0.02 Fe(III)	0.0540	0.01084	+.00004
5	0.01080	0.02 Fe(III)	0.0537	0.01078	-.00002
6	0.01080	0.05 Fe(III)	0.0539	0.01082	+.00002

Separation of palladium from bismuth (III) and antimony (III)

To prevent the hydrolysis of bismuth and antimony salts, 10 ml. of 10% sodium potassium tartrate was used. To it about 10 ml. of N-hydrochloric acid was added to bring the pH between 2.0 to 3.0. The remaining procedure was essentially the same, except that the initial washings of the complex were done with a solution containing 1 g. sodium-potassium tartrate and 0.5 ml. conc.hydrochloric acid per 100 ml. of water. The results are recorded in table VI.

TABLE VI

Determination of palladium in presence of bismuth(III) and antimony(III).

	Pd.taken G	Foreign ion G	Pd.complex G	Pd.found G	Error G
1	0.01080	0.02 Bi(III)	0.0535	0.01075	- .00005
2	0.01080	0.02 Bi(III)	0.0538	0.01081	+ .00001
3	0.01080	0.02 Sb(III)	0.0539	0.01083	+ .00003
4	0.01080	0.02 Sb(III)	0.0537	0.01079	- .00001

Separation of palladium from aluminium, beryllium, chromium, and magnesium

No special precautions were taken in the determination of palladium in presence of aluminium, beryllium, chromium and magnesium as none of these elements react with 3-hydroxy-1,3-diphenyltriazine. The usual procedure for palladium was adopted. The results are recorded in table VII.

TABLE VII

Determination of palladium in presence of aluminium, beryllium, chromium and magnesium

	Pd.taken G	Foreign ion G	Pd.complex G	Pd.found G	Error G
1	0.01080	0.02 Al(III)	0.0539	0.01083	+.00003
2	0.01080	0.02 Al(III)	0.0536	0.01077	-.00003
3	0.01080	0.02 Be(II)	0.0536	0.01077	-.00003
4	0.01080	0.02 Be(II)	0.0537	0.01079	-.00001
5	0.01080	0.02 Cr(III)	0.0538	0.01081	+.00001
6	0.01080	0.02 Cr(III)	0.0540	0.01084	+.00004
7	0.01080	0.02 Mg(II)	0.0537	0.01079	-.00001
8	0.01080	0.02 Mg(II)	0.0536	0.01077	-.00003

Separation of palladium from cerium (IV), zirconium (IV) and tin (IV)

It was observed that cerium and zirconium salts hydrolyse when heated in presence of sodium acetate or sodium potassium tartrate. Hence the pH was adjusted by adding N-hydrochloric acid alone. The hydrolysis of cerium (IV) was further prevented by adding a small amount of solid ammonium sulphate. The hydrolysis of zirconium could also be completely prevented by using about 5 ml. of 5% sodium or potassium fluoride solution. Initial washings of the complex, in the case of cerium were done with 1% ammonium sulphate solution.

Tin (IV) salts, on being heated, also hydrolyse and to prevent it 5 ml. of 5% sodium fluoride or potassium fluoride solution were used.

Palladium could not be determined in presence of tin (II), as it reduces palladium to the metallic state.

Excepting for these special precautions for the hydrolysis of these elements, the usual procedure for the determination of palladium was followed. The results are recorded in table VIII.

TABLE VIII

Determination of palladium in presence of cerium (IV), zirconium(IV) and tin (IV).

	Pd.taken G	Foreign ion G	Pd.complex G	Pd.found G	Error G
1	0.01169	0.02 Ce(IV)	0.0580	0.01164	-.00005
2	0.01169	0.02 Ce(IV)	0.0583	0.01170	+.00001
3	0.01169	0.02 Zr(IV)	0.0584	0.01172	+.00003
4	0.01169	0.02 Zr(IV)	0.0582	0.01169	.00000
5	0.01554	0.02 Sn(IV)	0.0777	0.01561	+.00007
6	0.01554	0.02 Sn(IV)	0.0775	0.01556	+.00002

Separation of palladium from thorium(IV), uranyl(II) and tungstate

Thorium, uranyl and tungstate ions do not react with 3-hydroxy-1,3-diphenyltriazine, hence caused no interference in the determination of palladium by the usual procedure. The results are recorded in table IX.

TABLE IX

Determination of palladium in presence of thorium(IV), uranyl(II) and tungstate

	Pd.taken G	Foreign ion G	Pd.complex G	Pd.found G	Error G
1	0.02427	0.02 Th(IV)	0.1209	0.02429	+.00002
2	0.02427	0.02 Th(IV)	0.1205	0.02422	-.00005
3	0.01080	0.02 UO_2(II)	0.0539	0.01082	+.00002
4	0.01080	0.02 UO_2(II)	0.0536	0.01076	-.00004
5	0.01554	0.02 WO_4''	0.0775	0.01556	+.00002
6	0.01554	0.02 WO_4''	0.0777	0.01561	+.00007

Separation of palladium from titanium (IV) and molybdate

As has already been observed earlier, under the general precipitating properties of 3-hydroxy-1,3-diphenyltriazine (part III, p. 39), that titanium (IV) and molybdate react with the reagent, at low pH, to give orange and orange red precipitates respectively. These complexes are unstable towards heat but do not decompose quantitatively as the unstable iron complexes did, making the separation of palladium possible. The interference of titanium (IV) and molybdate can be completely eliminated by masking these elements by fluoride. 0.5 g of sodium or potassium fluoride was used before the addition of the reagent. The remaining procedure was the same as described earlier. The results are recorded in table X.

TABLE X

Determination of palladium in presence of titanium (IV) and molybdate

	Pd.taken G	Foreign ion G	Pd.complex G	Pd.found G	Error G
1	0.01554	0.02 Ti(IV)	0.0770	0.01547	-.00007
2	0.01554	0.02 Ti(IV)	0.0775	0.01556	+.00002
3	0.01154	0.02 Ti(IV)	0.0776	0.01557	+.00003
4	0.01554	0.02 molybdate	0.0773	0.01553	-.00001
5	0.01554	0.02 molybdate	0.0775	0.01556	+.00002
6	0.01554	0.02 molybdate	0.0772	0.01552	-.00002

Separation of palladium from arsenic (III) and mercury (II)

Arsenic does not react with 3-hydroxy-1,3-diphenyltriazine. Mercury (II) gives a fine yellow precipitate at higher pH, but below 4.0 there is no reaction. Mercury (I), however, is partially precipitated even upto low pH and cannot be separated.

Palladium was separated from arsenic and mercury (II) by following the usual procedure. The results are recorded in table XI.

TABLE XI

Determination of palladium in presence of arsenic (III) and mercury(II

	Pd.taken G	Foreign ion G	Pd.complex G	Pd.found G	Error G
1	0.01080	0.02 As(III)	0.0538	0.01080	.00000
2	0.01080	0.02 As(III)	0.0536	0.01076	-.00004
3	0.01554	0.02 Hg(II)	0.0775	0.01556	+.00002
4	0.01554	0.02 Hg(II)	0.0777	0.01561	+.00007

Separation of palladium from lead.

Lead does not react with 3-hydroxy-1,3-diphenyl triazine in the acidic medium, however, insoluble lead chloride is precipitated with palladium chloride. For this reason palladium nitrate was used. Hydrated oxide of palladium was precipitated by using sodium bromate and sodium bicarbonate[14]. It was thoroughly washed and then dissolved in dilute nitric acid.

Palladium was determined in presence of lead using the above solution following the usual procedure where pH was adjusted with N-nitric or 10% acetic acid instead of hydrochloric acid. The results are recorded in table XII.

TABLE XII

Determination of palladium in presence of lead(II)

	Pd.taken G	Foreign ion G	Pd.complex G	Pd.found G	Error G
1	0.01054	0.02 Pb(II)	0.0523	0.01051	-.00003
2	0.01054	0.02 Pb(II)	0.0525	0.01054	.00000
3	0.01054	0.02 Pb(II)	0.0522	0.01052	-.00002

Separation of palladium from other members of platinum group.

Among the members of the platinum group only palladium forms an insoluble complex with 3-hydroxy-1,3-diphenyltriazine. It, therefore, can be used for the separation of palladium from all the other members of the platinum group, excepting osmium which, however, though not forming any complex with the reagent, interferes, as it is reduced to the metallic state. Initially the separation of palladium from rhodium, ruthenium and iridium is being described. Separation from platinum which requires certain modifications will be described separately.

Separation of palladium from rhodium (IV), ruthenium (III) and iridum (III)

The usual procedure was adopted and the results are recorded in table XIII.

TABLE XIII

Determination of palladium in presence of rhodium(IV), ruthenium (III) and irridium.

	Pd. taken G	Foreign ion G	Pd. complex G	Pd. found G	Error G
1	0.02427	0.03 Rh(IV)	0.1212	0.02434	+.00007
2	0.02427	0.03 Rh(IV)	0.1209	0.02429	+.00002
3	0.02427	0.03 Rh(IV)	0.1208	0.02426	-.00001
4	0.02427	0.03 Ru(III)	0.1211	0.02432	+.00004
5	0.02427	0.03 Ru(III)	0.1205	0.02422	-.00005
6	0.02427	0.03 Ru(III)	0.1207	0.02425	-.00002
7	0.02427	0.03 Ir(III)	0.1210	0.02431	+.00004
8	0.02427	0.03 Ir(III)	0.1209	0.02429	+.00002
9	0.02427	0.03 Ir(III)	0.1207	0.02425	-.00002

Separation of palladium from platinum

Platinum does not form any precipitate with 3-hydroxy-1,3-diphenyltriazine. It also does not react with the reagent in any other way in the cold. When a platinum salt is heated in presence of the reagent, initially there is no perceptible change. After 15 to 20 minutes, the yellow colour of platinum salt changes to orange, and then on further heating, to reddish brown and finally in about two hours, metallic platinum is thrown out. It is likely that at first qudrivalent platnium is reduced to the bivalent state, which then forms a, more or less, water-soluble complex with the reagent, analogous to the palladium complex, thus explaining the deepening of the colour observed at the initial stage. The platinum complex may then be further reduced to the metallic state, either by the reagent or its hydrolysed products, or both.

Due to these reducing reactions, platinum creates interference, if the usual procedure is followed, which therefore, had to be modified depending upon the amount of platinum present.

Separation of palladium from platinum (upto two times)

The procedure for the determination of palladium in presence of upto two times its own weight of platinum was the same as described earlier; the only difference was that the period of digestion on the water bath was restricted to 15 to 20 minutes only instead of 45 to 60 minutes. Buffering with sodium potassium tartrate gave slightly more concordant results. It was filtered hot and washed 2 to 3 times with 0.5% v/v. hydrochloric acid. It was found that almost all of the excess of the reagent was removed during the above operation. Any excess, if left, was washed with 20% hot alcohol. The results are recorded in table XIV.

TABLE XIV

Determination of palladium in presence of upto two times of platinum.

	Pd.taken G	Pt.added G	Pd.complex G	Pd.found G	Error G
1	0.01080	0.010	0.0537	0.01078	- .00002
2	0.01080	0.010	0.0539	0.01082	+ .00002
3	0.01080	0.015	0.0538	0.01080	.00000
4	0.01080	0.015	0.0536	0.01076	- .00004
5	0.01080	0.020	0.0539	0.01082	+ .00002
6	0.01080	0.020	0.0537	0.01078	- .00002
7	0.01169	0.020	0.0583	0.01170	+ .00001
8	0.01169	0.020	0.0582	0.01168	- .00001

Separation of palladium from upto ten times of platinum

When the quantity of platinum was more than two times that of palladium, it was found that the results were slightly higher if the above procedure was employed. This contamination of platinum can be completely eliminated by carrying out the initial precipitation of palladium in cold. The details are given in modified procedure I. Alternatively, recourse to reprecipitation of palladium could also be adopted. It is described in modified procedure II. Both the procedures gave excellent results. But for the sake of convenience and speed the modified procedure I was found to be much superior.

Modified procedure I: Palladium, as described earlier, was precipitated in the cold at pH 2.5 by addition of 20% excess of the reagent. After five minutes the dirty green Pd-complex was filtered through a sintered glass crucible (No:3) and washed five to six times with cold dilute hydrochloric acid solution (1%, V/V) for complete removal of platinum. From the combined filtrates platinum was estimated in the conventional way, using ammonium chloride.

The Pd-complex which still contained an excess of the reagent was transferred from the sintered crucible to a beaker with a jet of water (50-70 ml. water); hydrochloric acid (2 c.c. 2N) was added and the mixture heated on the water bath for one hour to destroy the excess of the reagent. The Pd-complex changed colour, as previously, from dirty green to yellowish brown and became granular. It was filtered through the same sintered crucible, washed well with hot water, dried at 120°C. and weighed. The results are recorded in table XV.

TABLE XV

Determination of palladium and platinum

	Pd. taken G	Pt. taken G	Pd-complex G	Pd. found G	Error G	Pt. found G	Error G
1	0.01221	0.0410	0.0609	0.01223	+.00002	0.0414	+ .0004
2	0.01221	0.0410	0.0608	0.01221	.00000	0.0408	- 0.0002
3	0.01221	0.1023	0.0605	0.01215	-.00006	0.1017	- 0.0006
4	0.01221	0.0878	0.0x610	0.01225	+.00004	0.0872	- 0.0006
5	0.01221	0.0878	0.0611	0.01227	+.00006	0.0880	+ 0.0002
6	0.01221	0.1250	0.0609	0.01223	+.00002	0.1245	- 0.0005

<u>The modifed procedure II</u>: According to this, the palladium complex was precipitated as usual by the addition of about 20% excess of the reagent, heated on the water bath for 15-20 minutes, filtered on an ashless filter paper, washed thoroughly with hot water, dried and carefully ignited with usual precautions necessary to avoid any loss of palladium. The residue was then dissolved by heating in 4 ml. concentrated sulphuric acid and 1 ml. concentrated nitric acid, till copious fumes of sulphuric acid began to evolve. This ensured the

complete removal of nitric acid. The residue was then carefully transferred to a beaker by washing with water, the volume made up to 200 ml. and neutralised with AR sodium carbonate. Finally, hydrochloric acid (5-7 ml. N.HCl) was added to bring the pH between 2-3. Palladium was then precipitated in the usual way by the addition of the reagent and estimated by direct weighing. The results are recorded in Table XVI.

TABLE XVI.

Determination of palladium in presence of upto ten times of platinum.

	Pd.taken G	Pt.added G	Pd.complex G	Pd.found G	Error G
1	0.01169	0.030	0.0580	0.01164	-.00005
2	0.01169	0.030	0.0579	0.01163	-.00007
3	0.01169	0.050	0.0582	0.01168	-.00001
4	0.01169	0.050	0.0585	0.01174	+.00005
5	0.01169	0.100	0.0583	0.01170	+.00001
6	0.01169	0.100	0.0582	0.01168	-.00001

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* * *

PART V

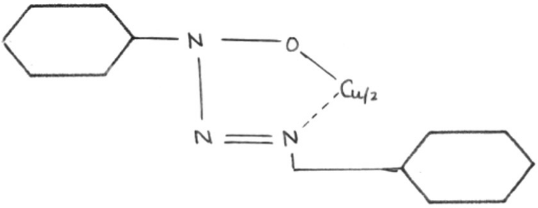
3-HYDROXY-1,3-DIPHENYLTRIAZINE AS A REAGENT FOR GRAVIMETRIC ESTIMATION OF COPPER.

***

3-Hydroxy-1,3-diphenyltriazine as a reagent for copper.

SUMMARY.

At low pH (2.3 to 3.0) 3-hydroxy-1,3-diphenyltriazine is a highly selective reagent for copper, and forms an inner complex with it having the following structure:



The copper complex is of definite composition and is directly weighable. With the help of this reagent, copper can be quantitatively estimated as such, or in presence of cobalt (II), nickel (II), zinc (II), manganese (II), cadmium (II), bismuth (III), aluminium (III), chromium (III), mercury (II), arsenic (III), lead (II), magnesium (II), antimony (III), tin (IV), iron (II), iron (III), beryllium (II), titanium (IV), zirconium (IV), cerium(IV), thorium (IV), uranyl (II), molybdate, tungstate, phosphate, fluoride, nitrate and alkali and alkaline earth metals. The separation from platinum metals - platinum (IV), rhodium (IV), ruthenium (III), iridium (III) though, also possible, was not actually carried out to avoid unnecessary loss of valuable chemicals.

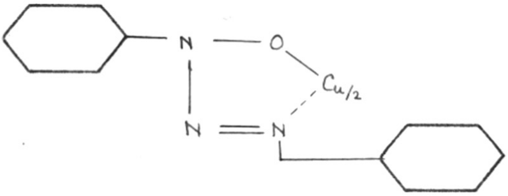
3-hydroxy-1,3-diphenyltriazine is superior to all the copper reagents, now described in the literature, including α-benzoinoxime, salicylaldomime and quinaldinic acid. It is also suitable for micro-gravimetric estimation of copper.

***

3-Hydroxyl-1,3-diphenyltriazine as a reagent for copper

In part IV of this thesis, the use of 3-hydroxyl-1,3-diphenyltriazine as a reagent for palladium has been described. It has also been pointed out that at low pH (2 to 3), this compound is a highly selective reagent for copper. In this part, the use of this reagent for gravimetric estimation of copper and its separation from a very large number of other elements has been described.

The copper complex is light chocolate-brown in colour. It is stable towards heat, dilute mineral acid and does not decompose below its melting point (193°C). It is of definite composition and can be directly weighed. Elemental analysis of the complex indicated the molecular formula $(C_{12}H_{10}N_3O)_2$ Cu. It can be represented by the structural formula given below:



I

Copper is completely precipitated by this reagent between pH, 1.9 to 7.0. In order to increase the specificity of the reagent and to facilitate the hydrolytic removal of the same, most of the estimations were carried out at pH between 2.3 to 3.0. Completeness of precipitation has been tested gravimetrically as well as by spot test with rubeanic acid, which is supposed to be the most sensitive reagents, developed for the detection of copper.

As in the case of palladium, the excess of the reagent added during the precipitation of copper can be completely eliminated by heating the acidic reaction mixture on a water-bath for about 45 to 60 minutes. The copper complex remained unaffected under these conditions. This hydrolytic removal of the excess of the reagent, imparted to 3-hydroxyl-1,3-diphenyltriazine all the advantages inherent in a water soluble reagent.

Estimation and separation of copper

Copper can be quantitatively estimated in the presence of nickel (II), zinc (II), manganese (II), cadmium (II), bismuth (III), aluminium (III), chromium (III), mercury (II), arsenic (III), lead (II), antimony (III), tin (II), cobalt (II), iron (II), iron (III), beryllium (II), titanium (IV), zirconium (IV), cerium (IV), thorium (IV), uranyl (II), molybdate, tungstate, phosphate, fluoride, nitrate, alkali and alkaline earth metals. Copper cannot be separated from those elements which interfere in the case of palladium.

Superiority over other reagents

Regarding the reproducibility of the results, the specificity of the reagent, the stability of the copper complex towards heat and mineral acid, its insolubility in water and fairly concentrated solution of alcohol, the reagent, in our opinion, is superior to all the copper reagents now described in the literature, including salicylaldoxime and α-benzoinoxime.

Other reagents for copper

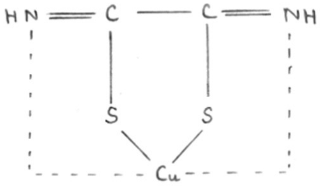
For a comparative evaluation of the qualities of this new reagent, it is necessary to make a short survey of the other copper-reagents which have been used for the gravimetric estimation of copper.

So far the power of forming an insoluble complex is concerned, copper is one of the most versatile amongst the metals. Almost any organic compound, which has the capacity of forming a derivative with a metal, usually forms a precipitate with copper. In fact, the number of such compounds, may exceed several hundreds. However, many of these organic compounds, for various reasons, which need not be discussed in details, do not deserve any serious scrutiny. Only those reagents which have found some reasonable use in analytical chemistry will be taken up for consideration. Of these, the following are important:

1. Rubeanic acid
2. Benzotriazole
3. Isonitroso-3-phenylpyrazolone
4. α-nitroso- β-naphthol.
5. α-nitroso- β-naphthylamine
6. 8-Hydroxyquinoline
7. α-Benzoinoxime
8. Salicylaldoxime
9. N-Benzoylphenylhydroxylamine
10. Quinaldinic acid

1. Rubeanic acid

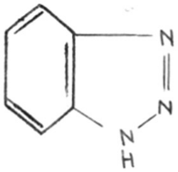
Rubeanic acid, examined by the eminent Indian chemist, P.R.Ray and his collaborators[1,2], is the most sensitive reagent for copper so far known. It is widely used as a spot test reagent for the detection of copper. In alkaline pH, along with other metals like cobalt, nickel etc., it also precipitates copper quantitatively as an olive green to black complex which has the following structure:



II

The complex, due to the presence of certain adhering impurities, cannot be directly weighed. It also lacks specificity. Consequently, inspite of its extreme sensitivity, reabeanic acid has not found any extensive use in the gravimetric estimation and separation of copper.

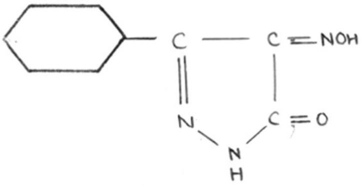
2. Benzotriazole



III

This compound has been examined by Curtis[3]. It forms a directly weighable copper complex between pH 7.0 to 8.5 in presence of tartrate. However, though, copper can be separated from a few other elements, due to the precipitation on alkaline side, the reagent lacks specificity. The direct weighing of the complex also is not always dependable. Consequently, it has been found more desirable to ignite it to CuO.

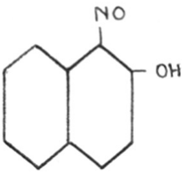
3. Isonitroso-3-phenylpyrazolone



IV

This compound examined by Hovorka and Vorisek[4] is, even less convincing than benzotriazole described above. It forms a brownish green copper complex in presence of sodium potassium tartrate or sodium acetate which, however, is not directly weighable and has to be ignited to CuO. Moreover, in this case the complex is to be set aside for 12 hours, before it can be filtered.

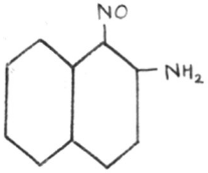
4. α-nitroso- β-naphthol



V

α-nitroso- β-naphthol is a well known reagent for cobalt. It also forms an insoluble complex with copper in slightly acidic medium. With the help of this reagent copper can be separated from a few elements like cadmium, magnesium, manganese, zinc and mercury[5]. However, due to the difficulty in removing the excess of the reagent and possibly for other reasons, the precipitate is not directly weighable and has to be ignited to CuO.

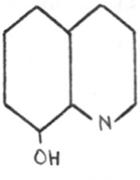
5. α-nitroso- β-naphthylamine



VI

This reagent[6] is comparatively more specific than the parent compound- α-nitroso- β-naphthol, which has been described earlier. In presence of tartrate or acetate, it forms a chocolate brown complex, which is directly weighable. With this reagent copper can be separated from cadmium, zinc, manganese, aluminium, chromium and antimony. However, due to the precipitation on the alkaline side, the reagent has limited specificity. The reagent is also not so stable towards heat and light (personal communication from Dr.S.C.Bhattacharyya).

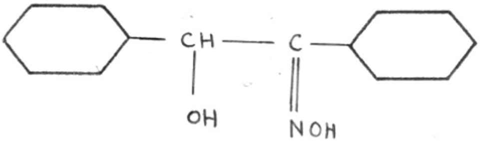
6. 8-hydroxyquinoline



VII

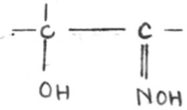
8-hydroxyquinoline is one of the most versatile of the reagents so far discovered. It gives precipitate with a large number of elements. Under varying pH conditions, and also using proper masking agents, its specificity towards certain elements can be improved, but even then, it is not very conspicuous. Literally, several hundred papers have been published on the use of 8-hydroxyquinoline as an analytical reagent. It forms a green complex with copper in acetic acid, ammoniacal, or alkaline tartrate medium between pH 5.3 to 14.0. The complex is represented by the formula $Cu(C_9H_6ON)_2$. With the help of this reagent, copper can be separated from aluminium, magnesium, beryllium, manganese zinc, cadmium and small amount of iron[7]. 8-hydroxyquinoline is, however, not a very specific reagent for copper, and though certain interesting separations can be carried out with it, it has so far not found any extensive use as an analytical reagent for copper.

7. α-Benzoinoxime

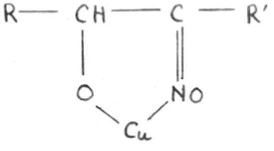


VIII

Feigl[8] has shown that α-acyloinoxime



react towards copper (II) as a dibasic acid forming green water-insoluble complex of the formula:



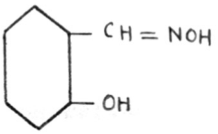
IX

The variation of R and R' produces no change in the colour and water insolubility of the complex, hence the above grouping has been regarded as "copper specific".

Copper is quantitatively precipitated by α-benzoinoxime from a boiling, slightly ammoniacal, or tartrated ammoniacal solution, containing little or preferably no ammonium salts[9]. Interference due to the presence of other metallic salts, which are precipitated by ammonia is prevented by the addition of sodium potassium tartrate. However, large quantities of sodium potassium tartrate and ammonium salts prevent the precipitation of copper complex, which, obviously is a very serious defect.

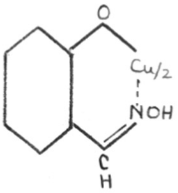
Azzalin[10] has reported that the excess of the reagent is very difficult to wash completely. The ignition of the complex is also to be done very slowly to avoid the formation of graphite. Shik[11] has reported that the method is unsatisfactory due to the precipitation of CuO before the addition of reagent. Even in presence of sodium potassium tartrate, the determinations of copper in presence of iron and zinc are unsatisfactory. Moreover, the reagent itself is photo sensitive and darkens on exposure to light.

8. **Salicylaldoxime**



X

This reagent was developed by Ephraim[12]. It gives a characteristic green complex with copper having the formula $(C_7H_6NO_2)_2Cu$ and is represented as:



XI

The copper complex is directly weighable and has a factor 0.1895. The estimation of copper with this reagent cannot be carried out in presence of mineral acid. Any mineral acid present initially, is neutralised with ammonium hydroxide, ammonium acetate is then added, followed by specially prepared aqueous-alcoholic solution of the reagent. Reif[13] has reported that only palladium, gold and vanadate interfere in acetic acid solution. Other metallic elements give precipitate only in neutral or alkaline medium, but this has not been so far substantiated by actual quantitative separations.

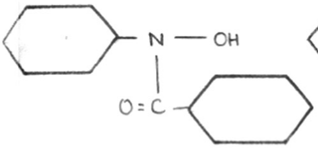
Shik[14] has reported that even by using tartaric acid, only small amounts of iron can be separated from copper. He has further reported that the results in presence of zinc, nickel and cobalt are also not very reliable.

Biefeld and Howe[15] have recommended glacial acetic acid to bring down the pH between 2.6 to 3.1, as nickel precipitate does not begin to form untill pH is 3.3. Chambers[16], however, has reported that cobalt and titanium interfered in the procedure.

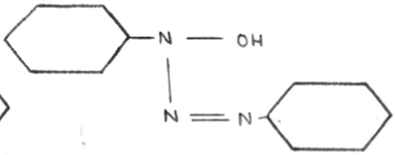
The reagent also suffers from a serious defect. Precipitation with it has to be carried out at room temperature. When heated beyond 80°C in the reaction medium, it gives rise to decomposition products, which are difficult to remove from the copper complex.

9. N-Benzoylphenylhydroxylamine

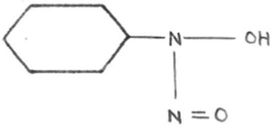
N-Benzoylphenylhydroxylamine (XII), which has been examined by Shome[17], is some what similar to 3-hydroxy-1,3-diphenyltriazine (XIII), as both are related to cupferron (XIV).



XII



XIII

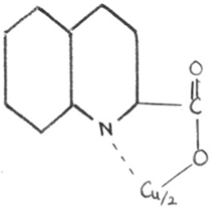


XIV

Incidentally, both XII and XIII have the same factor (0.1303) for copper. With N-benzoylphenylhydroxylamine copper is quantitatively precipitated between pH 3.6 to 6.0; in most of the estimations pH 4.0 was used. Copper has been separated from a few elements like zinc (II), manganese (II), lead (II), cobalt (II), nickel (II), beryllium (II), uranium (VI), phosphate and tartrate. Vanadate, molybdate, tungstate, tin (IV), titanium (IV), zirconium (IV) interfered. Obviously, to avoid the solubility of the complex in dilute alcohol, the volume of the reaction mixture is made upto 400 ml. Due to the fine nature of the complex, the filtration has to be carried out through sintered crucible No:4.

10. Quinaldinic acid - sodium salt

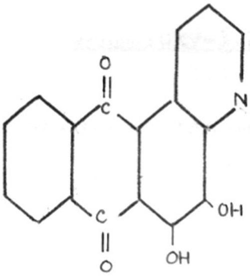
Ray and collaborators[18,19] and later on Majumdar[20,21] have examined quinaldinic acid as an analytical reagent. It reacts with a number of metallic ions to form chelate compounds of the type indicated by the copper quinaldinate, as shown below:



XV

This reagent has been used for the quantitative precipitation of cadmium, copper, zinc and uranium. At low pH, between 1.2 to 2.0, copper has been separated from cadmium, lead, manganese, nickel, cobalt, arsenic, and phosphate; however, iron and zinc interfere. The copper complex is stable towards heat and reasonable amounts of mineral acid. It is precipitated with a molecule of water, and can be dried to a constant weight at 125°C and has a factor 0.1496. Quinaldinic acid has been found to be one of the best copper reagents developed so far, though, it also suffers from limitations like comparative lack of specificity, slight solubility of the complex in acetic acid medium at low pH[21] etc.

Incidentally, we may also mention of alizarin blue which has been recently examined by Feigl[22] as a copper reagent. The structure of the reagent is not well established but is probably represented by the structure given below:



XVI

It forms an insoluble copper complex through the 'hydroxy-quinoline moiety' of the molecule. The copper complex is precipitated even in presence of cyanide, which is rather very unusual. However, inspite of this, the reagent is unlikely to have any bright future, as during the processing of the copper complex, unusual operations like digestion with acetic-anhydride, washing with pyridine etc. have to be adopted.

Another method, which is reasonably well established as a standard procedure for copper, is the "pyridine-thiocyanate" method. In presence of pyridine and thioyanate, copper forms an insoluble coordination complex $(CuPy_2)(SCN)_2$, which is directly weighable. However, the method suffers from many serious defects. The processing of the precipitate is rather tedious, involving washing with ammonium thiocyanat-pyridine solution, absolute alcohol, ether etc. It has to be initially dried over phosphorous pentoxide and finally at 40-45°C for some time. The copper pyridine thiocyanate is not a pure organo-metallic complex of the usual type, but, since it is also partly organic in nature, we considered it desirable to mention it in this connection.

Comparative qualities of 3-hydroxy-1,3-diphenyltriazine as a copper reagent

Having discussed the merits and limitations of the more well known reagents which have been used for the gravimetric estimation of copper, it is now possible for us to assess the comparative qualities of 3-hydroxy-1,3-diphenyltriazine, as a copper reagent.

1. In specificity, it is, without doubt, superior to all the reagents described earlier. This superiority is partly due to the fact that unlike most of the other copper reagents, precipitation of copper with 3-hydroxy-1,3-diphenyltriazine is carried out in acidic medium where pH can be adjusted with mineral acid.

2. The copper complex of 3-hydroxy-1,3-diphenyltriazine is of definite composition, stable towards heat and dilute mineral acid. Consequently, it can be digested on a water bath in the acidic reaction medium for a long time without any effect.

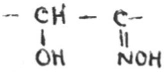
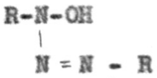
3. Because of the easy hydrolysability of the reagent in the acidic reaction medium, any excess of the same, added during the precipitation is easily eliminated as water soluble products, thus imparting to it all the advantages of a water-soluble reagent. Digestion on water-bath, for hydrolysing the excess of the reagent, is also useful in another way. It helps to make the precipitate very granular, so much so, that it can be filtered even through sintered crucible No:2.

4. It may be broadly said that unlike the other reagents, it does not suffer from any procedural limitations, like solubility, instability, temperature conditioning, lack of

specificity etc. In this respect, quinaldinic acid and N-benzoylphenylhydroxylamine are some what comparable to 3-hydroxy-1,3-diphenyltriazine, though the former two compounds have much less specificity.

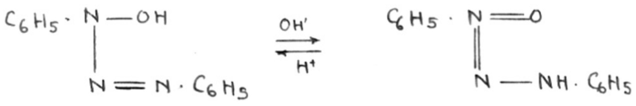
5. Survey of the literature indicates that no other reagent has been used for the separation of copper from so many different elements as in the present case.

6. Its factor (0.1303) for copper is also more favourable than salicylaldoxime (0.1895), α-benzoinoxime (0.2202), quinaldinic acid (0.1496) and 8-hydroxyquinoline (0.1808).

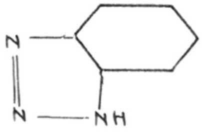
Though α-acyloinoxime  $-\underset{OH}{CH}-\underset{NOH}{C}-$ has been described to be copper specific group by Feigl[9], the present reagent containing the functional grouping  $R-\underset{N=N-R}{N}-OH$ is no less specific and should therefore, also be considered, as a copper specific group.

We expect that this reagent and other allied compounds are likely to be very fruitful in estimation and separation of copper.

Incidentally, we may point out certain similarity of 3-hydroxy-1,3-diphenyltriazine with benzotriazole (ref: p. 79.). As indicated by its colour reaction with alkali, 3-hydroxy-1,3-diphenyltriazine (XVII) can also exist in a tautomeric form (XVIII), the functional part of which has certain similarity with the corresponding part of benzotriazole (XIX)



XVII XVIII



XIX

EXPERIMENTAL

Standard copper (II) solution was prepared by dissolving copper sulphate analytical reagent, in special cases where the sulphate ions interfered with the separation, copper acetate and nitrate was used. Amount of copper in the solution was determined by adopting standard methods.

1. Precipitation as oxide and followed by ignition
2. Iodometric titration.

Reagent solution: 1% w/v. solution of the reagent in 95% ethyl alcohol was used.

Other solutions and apparatus: The same reagent grade soluble salts of various foreign ions, buffering reagents and apparatus as described in part IV on palladium, were used in the present case also.

Effect of pH on the precipitation of copper

Copper was completely precipitated between pH 1.9 to 7.0 by using only a slight excess of the reagent. At higher pH, the complex was found to be slightly soluble.

The pH range was established after carrying out a large number of qualitative and quantitative experiments. pH was adjusted by using N-hydrochloric or N-sulphuric acid, 10% w/v. sodium acetate or sodium potassium tartrate solutions.

While checking the precipitation quantitatively, the copper complex after adequate processing, was ignited to cupric oxide and weighed as such. The results are recorded in Table I.

In qualitative experiments, after the processing, the filtrate was tested with rubeanic acid for copper. The conclusions arrived through both the routes, agreed for the same pH range.

TABLE I

Determination of copper, at different pH, by ignition and spot test with rubeanic acid to establish the pH-limit.

	CuO G	pH	CuO G	Error G	Remark
1	0.0321	1.7	0.0310	-0.0011	N.Q
2	0.0321	1.9	0.0320	-0.0001	Q
3	0.0321	2.3	0.0324	+0.0003	Q
4	0.0321	3.8	0.0322	+0.0001	Q
5	0.0321	6.5	0.0318	-0.0003	Q
6	0.0321	7.8	0.0313	-0.0008	N.Q.

Q	means quantitative
N.Q.	means not quantitative

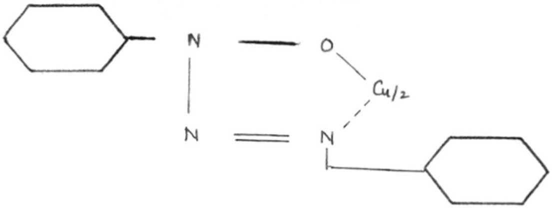
Though copper was completely precipitated between pH 1.9 to 7.0, most of our experiments were carried out between pH 2.3 to 3.0, as it increased the specificity of the reagent and also helped the hydrolytic removal of the same. Results of a few estimations through direct weighing, carried out at some-what higher pH (3.5 to 6.5), have also been included (p. 95) to emphasise the reliability of this reagent in that range of pH. At higher pH, however, the hydrolytic removal of the excess of the reagent was not possible and it had to be eliminated by washing with 30% hot alcohol, in which the complex is insoluble.

Amount of reagent for complete precipitation

The effect of varying the amount of reagent on the precipitation of copper was examined in a similar way, as described above. It was found that about 10 to 15% excess of the reagent was sufficient for the complete precipitation of copper. However, as a precautionary measure, we considered it desirable to use about 20 to 25% excess of the reagent, in our estimations. 1 ml. of 1% w/v. alcoholic solution of the reagent should be added for every mg. of copper to be precipitated. Unnecessary excess of the reagent above this, should be avoided as in that case longer time of heating on a water-bath will be necessary for its hydrolytic removal in the acidic reaction medium.

Properties of copper-complex

It is a chocolate-brown substance, very stable towards heat and moderate concentrations of acid. It is very granular and can be filtered very easily even in the hot state through sintered crucible, No:2. It is very soluble in chloroform, benzene, carbon tetrachloride; fairly soluble in ether and acetone and only very slightly soluble in alcohol. It can be crystallised from acetone in the form of silky brown needles melting point 193°C. It does not show any sign of decomposition before melting. The complex can be dried to a constant weight at 120-130°C. in about 30 minutes. It corresponds to the formula $(C_{12}H_{10}N_3O)_2Cu$ and can be represented as a possible chelate as shown below:



Analysis: Found: N, 17.76%

$(C_{12}H_{10}N_{3}O)_{2}Cu$ requires N, 17.21%.

The copper complex, in aldehyde free alcoholic solution, showed the following spectral characteristics:

λ max. 247, 283, 362 mμ; log E = 4.5634, 4.1324, 4.5720 respectively.

The complete absorption curve covering both the ultra-violet and the visible range, of 5.3 p.p.m. alcoholic solution of the copper complex is given in figure No: 5.

Determination of copper through direct weighing at pH between 3.5 to 6.0

25 ml. of standard copper solution containing 10 to 25 mg. of the metal was taken in a 250 ml. beaker. Varying amounts of N-hydrochloric acid and 10% sodium acetate or sodium potassium tartrate solution was added to it, so that the pH of the final solution, after dilution etc. was between 3.5 to 7.0. To this solution, 10 ml. of alcohol and requisite amounts of 1% w/v. alcoholic solution of the reagent was added with stirring, when light chocolate-brown copper complex was thrown out. Finally about 100 ml. of hot water was added and the mixture was heated on a water bath for 15 to 20 minutes, with occasional stirring, when the complex became granular, deepened in colour and the medium also

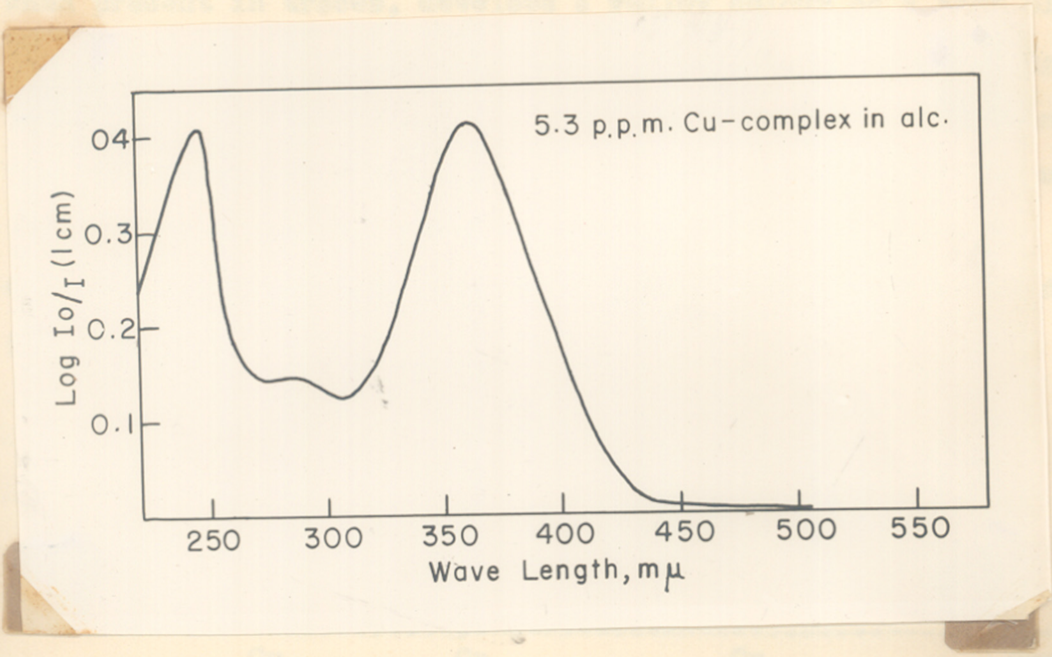


Figure No. 5. Absorption curve for 5.3 p.p.m. alcoholic solution of copper complex.

became clear. The complex was filtered hot through a weighed sintered crucible No:2 or 3. Most of the excess of the reagent, which is fairly soluble in hot reaction medium, was eliminated. It was washed with 30% hot alcohol, till the filtrate gave no test for the reagent, when tested on a spot plate with a drop of alkali. The reagent, as has already been mentioned earlier, even when present in traces, develops a yellow colour on a spot plate with a drop of an alkali solution. Usually, 6 to 8 washings were found to be sufficient for the complete removal of the reagent. The complex was then dried at 120 to 125°C. for 30 to 45 minutes to a constant weight. The weight of complex multiplied by 0.1303 gives the weight of copper. The results are recorded in Table II.

TABLE II

Determination of copper through direct weighing
pH - 3.5 to 6.0

	Cu taken G	Cu complex G	Cu found G	Error G
1	0.02563	0.1966	0.02562	-0.00001
2	0.02563	0.1964	0.02565	+0.00002
3	0.02563	0.1972	0.02569	+0.00006
4	0.01281	0.0983	0.01281	0.00000
5	0.01677	0.1282	0.01672	-0.00005
6	0.01677	0.1287	0.01677	.00000

Hydrolytic conversion of the excess of the reagent, at low pH, to water soluble products, is comparatively much easier way of eliminating it than the above procedure. For this reason, it was not actually pursued further.

Determination of copper at pH between 2.3 to 3.0

This was the pH range which was used by us in all our major estimations and separations and is recommended by us for general use. The proposed procedure is given below:

In practice two slightly different procedures can be employed.

To about 25 ml. of standard Cu(II) solution containing 10 to 25 mg. of the metal, 5 ml. of each of 10% w/v. solution of sodium acetate or sodium potassium tartrate, N-hydrochloric acid and rectified spirit was added. To this mixture, an excess (20 to 25%) of 1% w/v. alcoholic solution of the reagent was added with stirring, followed by 120 to 130 ml. of hot water. The pH was between 2.3 to 3.

Alternatively, the copper solution, which may or may not contain foreign ions, was diluted to 150 ml. and the same amount of sodium acetate or sodium potassium tartrate, N-hydrochloric acid and alcohol, as described earlier, added to it. The reaction mixture was heated on the water bath for sometime and then an excess (20 to 25%) of 1% w/v. solution of the reagent in alcohol added with stirring.

In most of our estimations and separations, we preferred the earlier procedure, where the reagent was added before dilution. In both the cases, however, the copper complex separated out as a light, chocolate-coloured precipitate. It was heated on a boiling water bath for 45 to 60 minutes with occasional stirring. The excess of the reagent present was hydrolysed by this procedure. Unnecessary excess of the reagent, above what has been suggested in the procedure, should be avoided, as in that case longer time will be necessary for its hydrolytic removal. During the course of heating, the complex became very granular and deepened in colour, and the medium also became clear and was free from any colloidal suspension. The complex was filtered hot through a weighed sintered crucible No:2 or 3, washed 1 to 2, times with 0.5% w/v. hydrochloric acid solution and then 5 to 6 times with hot water. The hydrolysed reagent in the filtrate when tested on a spot plate with a drop of an alkali solution develops a blue to bluish violet color due to the presence of p.aminophenol and phenol. The completeness of washing can, therefore, be easily tested by this method. The complex was dried to a constant weight at 120 to 125°C. for 30-45 minutes and weighed. The weight of the complex multiplied by 0.1303 gives the weight of copper. The results are recorded in Table III.

TABLE III

Determination of copper
pH- 2.3 to 3.0

	Cu taken G.	Cu complex G.	Cu found G.	Error G.
1	0.01281	0.0979	0.01276	-.00005
2	0.01677	0.1286	0.01676	-.00001
3	0.01677	0.1289	0.01679	+.00002
4	0.01533	0.1174	.01530	-.00003
5	0.02563	0.1969	0.02565	+.00002
6	0.02563	0.1962	0.02558	-.00005

Determination of copper in presence of foreign ions

Observations recorded earlier in the determinations of palladium in presence of foreign ions are also more or less applicable in the case of copper. For the sake of brevity we have not included these details in this part.

Separation of copper from cobalt and nickel

Cobalt and nickel are also precipitated by 3-hydroxy-1,3-diphenyltriazine at higher pH, but below pH 3.5, there is no precipitation of these elements. Hence, at the pH range (2.3 - 3.0) used for the estimation of copper, there was no interference by these elements.

Copper was determined, in presence of cobalt and nickel, following the procedure described earlier. The results are recorded in Table IV.

TABLE IV.

Determination of copper in presence of cobalt and nickel.

	Cu taken G	Foreign ion G	Cu-complex G	Cu found G	Error G
1	0.01281	0.05Ni(II)	0.0979	0.01276	-.00005
2	0.01533	0.05Ni(II)	0.1178	0.01534	+.00001
3	0.01533	0.05Ni(II)	0.1180	0.01536	+.00002
4	0.01677	0.05Co(II)	0.1286	0.01676	-.00001
5	0.01281	0.05Co(II)	0.0985	0.01283	+.00002
6	0.01281	0.05Co(II)	0.0980	0.01277	-.00004

Separation of copper from zinc, manganese and cadmium

There was no interference by zinc, manganese and cadmium in the determination of copper by 3-hydroxy-1,3-diphenyltriazine, at the pH range 2.3 to 3.0, used by us.

Copper was determined by following the usual procedure described earlier. The results are recorded in table V.

.....Table V.

TABLE V.

Determination of copper in presence of zinc, manganese and cadmium

	Cu taken G	Foreign ion G	Cu complex G	Cu found G	Error G
1	0.01281	0.05Zn(II)	0.0979	0.01276	-.00005
2	0.01281	0.05Zn(II)	0.0984	0.01282	+.00001
3	0.01281	0.05Mn(II)	0.0982	0.01279	-.00002
4	0.01281	0.05Mn(II)	0.0981	0.01280	-.00003
5	0.01281	0.05Cd(II)	0.0985	0.01283	+.00002
6	0.01281	0.05Cd(II)	0.0981	0.01280	-.00003

Determination of copper in presence of nitrate, fluoride and phosphate

Copper can be quantitatively precipitated in presence of large concentrations of nitrate, fluoride and and phosphate ions. The determinations were carried out by the usual procedure and the results are recorded in table VI.

TABLE VI

Determination of copper in presence of nitrate, fluoride and phosphate

	Cu taken G	Foreign ion G	Cu complex G	Cu found G	Error G
1	0.01677	0.10 nitrate	0.1285	0.01675	-.00002
2	0.01677	0.20 nitrate	0.1287	0.01677	.00000
3	0.01677	0.40 nitrate	0.1282	0.01672	-.00005
4	0.01677	0.50 nitrate	0.1281	0.01671	-.00006
5	0.01387	0.20 fluoride	0.1064	0.01386	-.00001
6	0.01387	0.50 fluoride	0.1067	0.01390	+.00003
7	0.01533	0.10 phosphate	0.1177	0.01533	. 00000
8	0.01533	0.30 phosphate	0.1172	0.01528	-.00005

Separation of copper from iron (II) and iron (III)

It has been indicated in part IV that palladium can be quantitatively separated from iron (II) and iron (III) because the iron complex which is simultaneously formed is quantitatively decomposed on prolonged digestion on a water bath, leaving the palladium complex in pure condition. Alternatively, iron could be completely masked by the addition of sodium or potassium fluoride. The same procedure is equally applicable in the case of copper also, which can be separated from iron (II) and iron (III) either by following the technique of digestion or by masking with fluoride. In case of the later procedure, 0.5 g. of sodium fluoride was used before the addition of the reagent. The results are recorded in table VII.

TABLE VII

Determination of copper in presence of iron (II) and Iron (III)

	Cu taken G	Foreign ion G	Cu complex G	Cu found G	Error G
1	0.01677	0.05 Fe(II)	0.1289	0.01679	+.00002
2	0.01677	0.10 Fe(II)	0.1283	0.01673	-.00004
3	0.01677	0.15 Fe(II)	0.1294	0.01684	+.00007
47	0.01677	0.05 Fe(III)	0.1282	0.01672	-.00005
5	0.01677	0.05 Fe(III)	0.1289	0.01679	+.00002
6	0.01677	0.10 Fe(III)	0.1290	0.01680	+.00003

Separation of copper from bismuth (III) and antimony (III)

Determination of copper in presence of bismuth and antimony was done using 10 ml. of 10% sodium potassium tartrate to prevent hydrolysis. Initial washings of the complex were done with a solution containing 1 g. sodium potassium tartrate and 0.5 ml. conc. hydrochloric acid per 100 ml. of water. The results are recorded in table VIII.

TABLE VIII

Determination of copper in presence of bismuth (III) and antimony (III)

	Cu taken G	Foreign ion G	Cu complex G	Cu found G	Error G
1	0.01281	0.05 Bi(III)	0.0979	0.01276	-.00005
2	0.01281	0.05 Bi(III)	0.0984	0.1282	+.00001
3	0.01281	0.05 Bi(III)	0.0985	0.1283	+.00002
4	0.01533	0.05 Sb(III)	0.1182	0.01538	+.00005
5	0.01533	0.05 Sb(III)	0.1178	0.01534	+.00001
6	0.01533	0.05 Sb(III)	0.1180	0.01536	+.00003

Separation of copper from aluminium, beryllium, chromium and magnesium

Determination of copper in presence of aluminium, beryllium, chromium and magnesium was done by the usual procedure. The results are recorded in table IX.

TABLE IX

Determination of copper in presence of aluminium, beryllium, chromium and magnesium.

	Cu taken G	Foreign ion G	Cu complex G	Cu found G	Error G
1	0.01281	0.05 Al(III)	0.0980	0.01277	-.00004
2	0.01281	0.05 Al(III)	0.0985	0.01283	+.00002
3	0.01533	0.05 Be(II)	0.1179	0.01535	+.00002
4	0.01533	0.05 Be(II)	0.1174	0.01530	-.00003
5	0.01281	0.05 Cr(III)	0.0980	0.01277	-.00004
6	0.01281	0.05 Cr(III)	0.0982	0.01279	-.00002
7	0.01677	0.05 Mg(II)	0.1286	0.01676	-.00001
8	0.01677	0.05 Mg(II)	0.1289	0.01679	+.00002

Separation of copper from cerium (IV), zirconium (IV) and tin (IV).

To prevent the hydrolysis of cerium, zirconium and tin (IV) salts, the same procedure, as mentioned in part IV on the separation of palladium from these elements, was followed. Tin(II), however, cannot be prevented from hydrolysis even by using fluoride, hence separation was not possible. The results are recorded in table X.

TABLE X

Determination of copper in presence of cerium (IV), zirconium(IV) and tin (IV).

	Cu taken G	Foreign ion G	Cu complex G	Cu found G	Error G
1	0.01533	0.05 Ce(IV)	0.1174	0.01530	-.00003
2	0.01533	0.05 Ce(IV)	0.1179	0.01535	+.00002
3	0.01533	0.05 Zr(IV)	0.1179	0.01535	+.00002
4	0.01533	0.05 Zr(IV)	0.1182	0.01538	+.00005
5	0.01387	0.05 Sn(IV)	0.1067	0.01390	+.00003
6	0.01387	0.05 Sn(IV)	0.1064	0.01386	-.00001

Separation of copper from thorium (IV), uranyl (II) and tungstate.

Determination of copper in presence of thorium, uranyl and tungstate ions was done by the usual procedure. The results are recorded in Table IX.

TABLE XI

Determination of copper in presence of thorium(IV), uranyl(II) and tungstate.

	Cu taken G	Foreign ions G	Cu complex G	Cu found G	Error G
1	0.01533	0.05Th(IV)	0.1172	0.01528	-.00005
2	0.01533	0.05 Th(IV)	0.1180	0.01536	+.00003
3	0.01533	0.05 Uo_2(II)	0.1180	0.01536	+.00003
4	0.01533	0.05 Uo_2(II)	0.1177	0.01533	.00000
5	0.01387	0.05 tungstate	0.1063	0.01385	-.00002
6	0.01387	0.05 tungstate	0.1068	0.01391	+.00004

Separation of copper from titanium (IV) and molybdate

0.5 g. of sodium or potassium fluoride was used before the addition of the reagent, to mask the precipitation of titanium and molybdate complexes. The remaining procedure was the same as described earlier. The results are recorded in table XII.

TABLE XII

Determination of copper in presence of titanium (IV) and molybdate.

	Cu taken G	Foreign ion G	Cu complex G	Cu found G	Error G
1	0.01387	0.05 Ti(IV)	0.1062	0.01383	-.00004
2	0.01387	0.05 Ti(IV)	0.1066	0.01389	+.00002
3	0.01387	0.05 Ti(IV)	0.1063	0.01384	-.00002
4	0.01387	0.05 molybdate	0.1068	0.01391	+.00004
5	0.01387	0.05 molybdate	0.1067	0.01390	+.00003
6	0.01387	0.05 molybdate	0.1064	0.01386	-.00001

Separation of copper from arsenic (III) and mercury (II)

Copper was determined in presence of arsenic (III) and mercury (II) by following the usual procedure. The results are recorded in table XIII.

TABLE XIII

Determination of copper in presence of arsenic (III) and mercury (II).

	Cu taken G	Foreign ion G	Cu complex G	Cu found G	Error G
1	0.01533	0.05 As(III)	0.1178	0.01534	+.00001
2	0.01533	0.05 As(III)	0.1174	0.01530	-.00003
3	0.01533	0.05 Hg(II)	0.1180	0.01536	+.00003
4	0.01281	0.05 Hg.(II)	0.0984	0.01282	+.00001

Separation of copper from lead

Standard copper acetate solution was used for the determination of copper in presence of lead. pH was adjusted by using N-nitric acid or 10% acetic acid instead hydrochloric acid. The results are recorded in table XIV.

TABLE XIV.

Determination of copper in presence of lead (II).

	Cu taken G	Foreign ion G	Cu complex G	Cu found G	Error G
1	0.01533	0.05 Pb(II)	0.1169	0.01525	-.00008
2	0.01533	0.05 Pb(II)	0.1178	0.01534	+.00001
3	0.01533	0.05 Pb(II)	0.1174	0.01530	-.00003

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PART VI

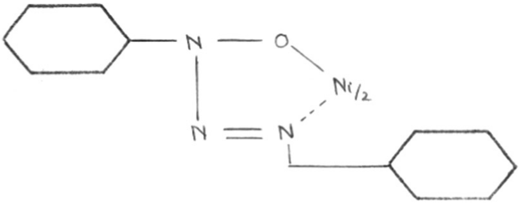
3-HYDROXY-1,3-DIPHENYLTRIAZINE AS A REAGENT
FOR
GRAVIMETRIC ESTIMATION OF
NICKEL.

***

3-Hydroxy-1,3-diphenyltriazine as a reagent for nickel.

SUMMARY

At some what higher pH (4.4 to 7.0) 3-hydroxy-1,3-diphenyltriazine forms a directly weighable complex with nickel, having the following structure:



The nickel complex is stable towards heat and is very granular in nature. With the help of this reagent nickel can be quantitatively estimated as such or in presence of zinc (II), manganese (II), cadmium (II), magnesium (II), arsenic (III), beryllium (II), phosphate, fluoride and alkali and alkaline earth metals.

The reagent does not possess the extremely high specificity of dimethylglyoxime but it also possesses many useful qualities, details of which will be available in the text.

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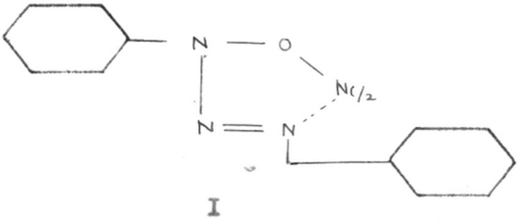
3-Hydroxy-1,3-diphenyltriazine as a reagent for nickel (II)

In two earlier parts (IV and V), we have described the use of 3-hydroxy-1,3-diphenyltriazine as a reagent for palladium and copper. At some what higher pH, the reagent also forms precipitates with few other elements (ref: part III) of which that formed by nickel deserves special mention.

Nickel is quantitatively precipitated between pH 4.4 to 7.0. It is a bright yellow inner complex which is stable towards heat and does not decompose below its melting point 209°C. It is very granular in nature, is of definite composition and is suitable for direct weighing. Elemental analysis of the complex indicated the molecular formula $(C_{12}H_{10}N_{3}O)_{2}$ Ni. It can be represented by the structural formula given below:



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With this reagent nickel can be estimated, through direct weighing, as such or in presence of zinc (II), manganese (II), cadmium (II), magnesium (II), arsenic (III), beryllium, phosphate, fluoride and alkali and alkaline earth metals. As the precipitation of nickel complex is carried out at higher pH, the hydrolytic removal of the excess of the reagent is not possible. Any excess of the same present in the reaction mixture, has to be eliminated by washing with 20% hot alcohol, in which the nickel complex is insoluble.

α-dioximes are the specific nickel reagents about which we have discussed in details in part I and part IV. Though many dioximes have been examined by various workers, only dimethylglyoxime is still the universally accepted nickel reagent. The present reagent does not possess the extremely high specificity of dimethylglyoxime and necessarily has only limited possibilities. However, it also possesses certain qualities for which we felt interested to examine it as a nickel reagent.

1. The nickel complex has an intense bright yellow colour and in this respect it compares with dimethylglyoxime, which, however is pink. In sensitivity as a spot test reagent, it is as good as dimethylglyoxime.

2. Unlike the dimethylglyoxime nickel complex which is flocculent in nature, the nickel complex of 3-hydroxy-1,3-diphenyltriazine is extrmely granular and can be filtered very easily.

3. The nickel complex is more stable towards heat and acid than the Dmg-nickel complex.

4. The precipitation of nickel with Dmg is usually done in the alkaline pH (about 8), with the present reagent precipitation can be done in slightly acidic pH (5.0).

From our experience with various azo derivatives of phenylhydroxylamine, we have an impression that by some suitable modification in the structural features of these compounds, it may be ultimately possible to develop a nickel reagent which will precipitate nickel in highly acidic medium. This, however, is not, now possible with any of the existing nickel reagents.

EXPERIMENTAL.

Determination of nickel (II)

Standard nickel (II) solution was prepared by dissolving nickel chloride analytical reagent and the amount of nickel was determined by using dimethylglyoxime. Other solutions and apparatus were the same as described earlier.

Effect of pH on the precipitation of nickel (II)

Nickel (II) is completely precipitated between pH 4.4 to 7.0 by using a slight excess of the reagent. It does not form any complex below pH 3.5. The completeness of precipitation was checked gravimetrically and by spot test using dimethylglyoxime.

Properties of nickel complex

The bright yellow nickel complex is very stable towards heat. It is very granular and not at all voluminous like dimethylglyoxime complex. It is very soluble in chloroform, benzene and carbon tetrachloride, fairly soluble in ether and acetone and only slightly soluble in alcohol. It can be crystallised from acetone in the form of silky, bright-yellow needles, melting at 209°C. It corresponds to the formula $(C_{12}H_{10}N_3O)_2$ Ni.
Analysis showed N, 17.76%; $(C_{12}H_{10}N_3O)_2$ Ni requires: N, 17.39%.
The alcoholic solution showed the following spectral characteristics.
λ max. 248, 320, 410 mμ; log $E = 4.4545, 4.3910, 4.1988$ respectively.
The complete absorption curve of 3.25 p.p.m. alcoholic solution of nickel complex is given in figure No: 6.

Procedure for nickel (II)

A solution of nickel (II) containing 10 to 25 mg. of the metal was diluted to 125 ml. and 5 ml. of alcohol added to it. Requisite amount of 10% w/v. solution of sodium acetate (2 to 3 ml.)

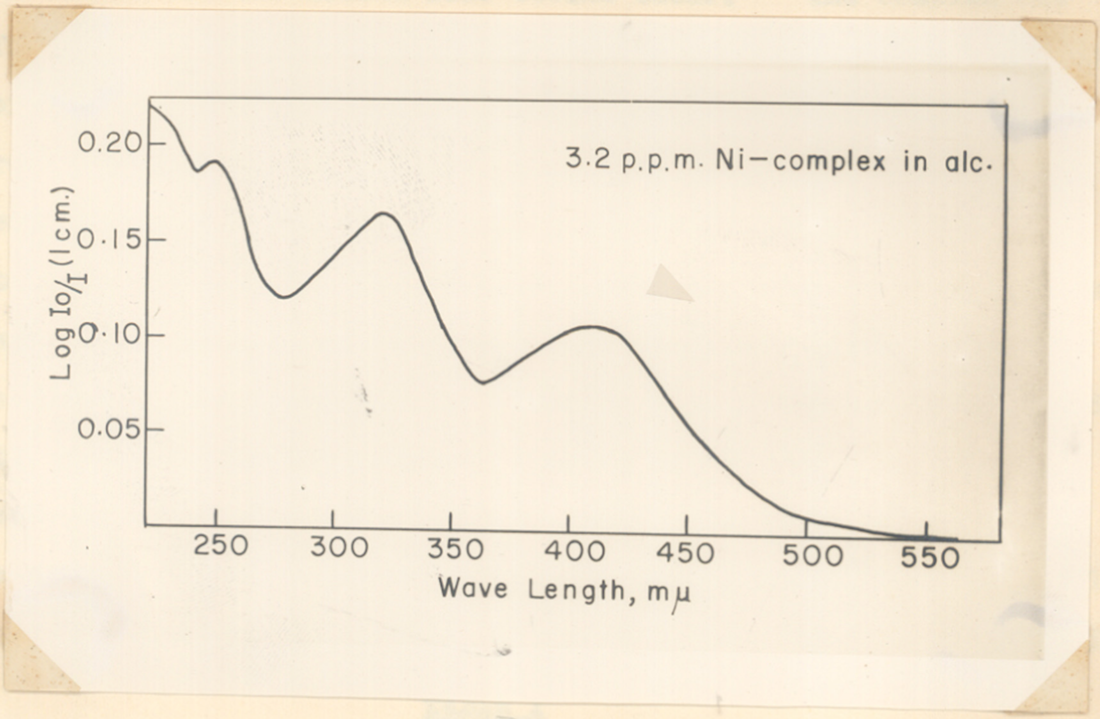

Figure No. 6. Absorption curve for 3.2 p.p.m. alcoholic solution of nickel complex.

was added to bring the pH between 5 to 5.5. To this solution, which may also contain foreign ions, an excess (about 20%) of 1% w/v. reagent solution in alcohol was added with stirring. The bright yellow nickel complex was immediately thrown out. The mixture was heated on a boiling water bath for about 30 minutes with occasional stirring, when the complex became granular and deepened in colour and the medium also became clear. The complex was filtered hot through a weighed sintered crucible No:2 or 3. Most of the excess of the reagent, which is fairly soluble in hot reaction medium, was eliminated at this stage. It was washed repeatedly with 20% hot alcohol till the filterate failed to give any test for the reagent. (The reagent, even when it is present in traces, develops a yellow color on a spot plate with a drop of alkali solution). Usually 6 to 8 washings were found to be sufficient for complete removal of the reagent. The complex was then dried at 120 to 125°C. for 30 to 45 minutes to a constant weight. The weight of the complex multiplied by 0.1215 gives the weight of nickel. The results are recorded in table I.

TABLE I

Determination of nickel.

	Ni taken G	Ni complex G	Ni found G	Error G
1	0.01011	0.0831	0.01009	-.00002
2	0.01011	0.0833	0.01012	+.00001
3	0.01011	0.0836	0.01015	+.00004
4	0.01215	0.0999	0.01214	-.00001
5	0.01215	0.1004	0.01219	+.00005
6	0.01215	0.1000	0.01215	.00000

Separation of nickel from Zn(II), Mn(II), Cd(II), Mg(II), As(III) Be(II), phosphate and fluoride

The same procedure as described earlier for nickel was followed and the results are recorded in table II.

TABLE II

Determination of nickel in presence of Zn(II), Mn(II), Cd(II), Mg(II) As(III), Be(II), phosphate and fluoride.

	Ni taken G	Foreign ion G	Ni complex G	Ni found G	Error G
1	0.01011	0.05 Zn(II)	0.0833	0.01012	+.00001
2	0.01011	0.05 Zn(II)	0.0836	0.01015	+.00004
3	0.01011	0.05 Mn(II)	0.0828	0.01006	-.00005
4	0.01011	0.05 Mn(II)	0.0834	0.01013	+.00002
5	0.01011	0.05 Cd(II)	0.0832	0.01010	-.00001
6	0.01011	0.05 Cd(II)	0.0836	0.01015	+.00004
7	0.01011	0.05 Mg(II)	0.0834	0.01013	+.00002
8	0.01011	0.05 Mg(II)	0.0832	0.01010	-.00001
9	0.01011	0.05 As(III)	0.0832	0.01010	-.00001
10	0.01011	0.05 As(III)	0.0828	0.01006	-.00005
11	0.01011	0.05 Be(II)	0.0832	0.01010	-.00001
12	0.01011	0.05 Be(II)	0.0835	0.01014	+.00003
13	0.01011	0.05 PO_4	0.0836	0.01015	+.00004
14	0.01011	0.05 PO_4	0.0830	0.01008	-.00003
15	0.01011	0.05 F'	0.0834	0.01013	+.00002
16	0.01011	0.05 F'	0.0829	0.01007	-.00004

Nickel is not completely precipitated in presence of sodium potassium tartrate. For this reason, it could not be separated from antimony (III), bismuth (III), chromium (III) and aluminium(III).

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PART VII

3-HYDROXY-1-p.CHLOROPHENYL-3-PHENYLTRIAZINE AS A REAGENT FOR GRAVIMETRIC ESTIMATION OF TITANIUM.

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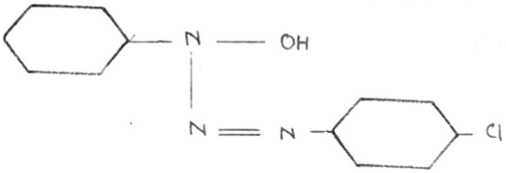
3-Hydroxy-1-p.chlorophenyl-3-phenyltriazine as a reagent for titanium (IV).

SUMMARY.



3-hydroxy-1-p.chlorophenyl-3-phenyltriazine, quantitatively precipitates titanium (IV) as a bright orange complex, which is stable towards heat and can be used for the estimation of titanium (IV) and its separation from zinc (II), manganese (II), cadmium (II), cobalt (II), nickel (II), mercury (II), arsenic (III), uranyl (II), uranium (IV), thorium (IV), magnesium (II), beryllium(II), chromium (III) alkali and alkaline earth metals and specially from large amounts of aluminium. The separation from platinum metals - platinum (IV), rhodium (IV), ruthenium (III) and iridium (III), though, also possible, was not actually carried out to avoid unnecessary loss of valuable chemicals.

It compares very well with the other titanium reagents described in the literature and is superior to N-benzoylphenylhydroxylamine and N-nitrosophenylhydroxylamine (cupferron), and also superior to p-hydroxyphenylarsonic acid as regards the easy processing of the titanium complex is concerned.

The titanium complex is not of definite composition and has to be ignited to TiO_2 before weighing, which is also true with other titanium reagents.

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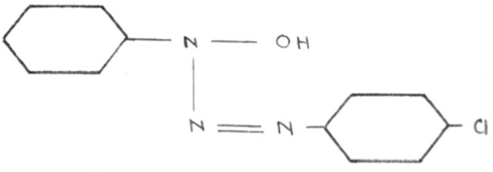
3-Hydroxy-1-p.chlorophenyl-3-phenyltriazine as a reagent for titanium (IV).

In the general introduction and also at other places, we have mentioned that in acidic medium cupferron[1] precipitates titanium quantitatively. This reaction has been used for the estimation of titanium and also for its separation from other elements. The Ti-complex is, however, unstable and decomposes above room temperature. Consequently, cupferron as a titanium reagent has only limited possibility. Shome[2] examined N-benzoylphenylhydroxylamine for the same purpose. His reagent is in no way an improvement over cupferron, as the Ti-complex formed by it is also unstable at higher temperatures.

During our investigation, we found that the parent diazo-compound - 3-hydroxy-1,3-diphenyltriazine-forms a titanium complex at low pH, which, unlike the titanium complexes of cupferron and N-benzoylphenylhydroxylamine, was stable upto 55°C. From this observation we were led to believe that a negative substituent in the ring of the "phenylazo moiety", should give a reagent, whose titanium complex will be more stable and comparatively more convenient for using for quantitative purposes. This has been found to be true, as 3-hydroxy-1-parachlorophenyl-3-phenyltriazine



I

precipitates titanium quantitatively as a bright orange complex, which is stable at 100°C in the aqueous acidic reaction medium so that the excess of alcohol used during estimation may be removed by heating directly on a water bath. The ortho-chloro analogue, which was also examined simultaneously was found to be unsuitable, as the complexes formed by it were not granular and were comparatively less stable. This, possibly, was due to the stecric hinderance provided by the chlorine atom, which is analogous to that observed in the case of the derivatives[3] of 8-hydroxyquinoline, containing a substituent in the 2-position.

Estimation and separation of titanium(IV)

In this part, the use of 3-hydroxy-1-p.chlorophenyl-3-phenyltriazine for quantitative estimation of titanium (IV), and its separation from zinc (II), manganese (II), cadmium (II), cobalt (II), nickel (II), mercury (II), arsenic (III), uranyl(II), uranium (IV), thorium (IV), magnesium (II), beryllium (II), chromium (III), alkali and alkaline earth metals and large amounts of aluminium has been described.

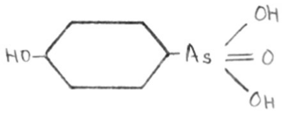
Titanium could not be determined in presence of zirconium (IV), zirconyl (II), thallium (II), cerium (IV), copper (II), palladium (II), iron (II), iron (III), molybdate and vanadate due to co-precipitation. Phosphate and tungstate precipitated the corresponding titanium salts and hence interfered in the determination; fluoride completely masked titanium. The titanium estimation in presence of tartrate gave slightly lower results, and hence its separation from antimony (III) and bismuth (III) could not be carried out.

The titanium complex, however, is not of definite composition and has to be ignited to TiO_2 before weighing. This is also true with other titanium reagents.

Comparison with other titanium reagents

3-hydroxy-1-p.chlorophenyl-3-phenyltriazine compares well with the other important titanium reagents like (i) p-hydroxyphenylarsonic acid[4], (ii) 8-hydroxyquinoline[5], and its substituted derivatives[6], (iii) N-benzoylphenylhydroxylamine[2] and (iv) cupferron[1]. It's all round superiority over (iii) and (iv) has already been indicated earlier (p. 116).

8-hydroxyquinoline forms a titanium complex of the formula $TiO\ (C_9H_6ON)_2\ 2H_2O$, which appears to be directly weighable. However, 8-hydroxyquinoline seriously lacks in specificity, and with it titanium can only be separated from alkali and alkaline earth metals. While carrying out an important separation like that of titanium from aluminium, about 70 to 80 times the weight of malonic acid is to be added for suppressing the precipitation of aluminium, even then, according to Clasen and Visser[8], the results are undependable. No direct separation from cadmium, copper, zinc, magnesium etc. is possible.

p-Hydroxyphenylarsonic acid 

quantitatively precipitates titanium at low pH, which is stable towards heat. The Ti precipitate is, however, a true salt of arsonic acid and not an inner complex, and has to be ignited to TiO_2 before weighing. With this compound titanium can be separated from iron, aluminium, zinc, cobalt, nickel, beryllium, chromium, manganese, thallium, magnesium, molybdate, phosphate, alkali and alkaline earth metals. The following elements interfere - zirconium, cerium and tin. However, the reagent suffers from one very serious defect. The titanium precipitate is very fine in nature and is difficult to filter. Filtration has to be done under suction using special filter paper. Richter[7] has suggested the use of ammonium thiocyanate as a filtration aid. This fineness of the precipitate necessitates the cooling of the precipitate before filtration.

The present reagent, 3-hydroxy-1-p.chlorophenyl-3-phenyltriazine is comparable to p-hydroxyphenylarsonic acid in some respects and superior to it in others:

1. The titanium complex is stable towards heat and can be heated in dilute acidic medium on a boiling water bath for an indefinite period.

2. The titanium complex is very granular and unlike the titanium salt of the arsonic acid, can be filtered very easily in the hot state even through filter paper No:40. The washings can also be done with hot water, making the process comparatively much easier.

3. In specificity, however, it is slightly inferior to p-hydroxyphenylarsonic acid.

Like the parent compound - 3.hydroxy-1,3-diphenyltriazine, the present reagent also forms precipitates with a large number of elements under similar pH conditions. The complexes in this case are comparatively more stable, but the reagent did not offer any special advantage in the estimations of copper (II), palladium (II) and nickel (II) as the excess of the reagent could not be removed easily either through hydrolysis or by washing with alcohol.

EXPERIMENTAL.

Standard titanium (IV) solution: 1 g. of titanium dioxide was fused with 10 g. of potassiumpyrosulfate for about 10 minutes. It was cooled and extracted with 200 ml. of 6% v/v. sulfuric acid and diluted to one litre. The amount of titanium present in it was estimated as titanium dioxide in the conventional way.

Buffering solutions: Normal hydrochloric acid and 10% w/v. sodium acetate solutions were used for the adjustment of pH. Sodium potassium tartrate gives slightly lower results due to masking and hence cannot be used for this purpose.

Reagent solutions: 1% w/v. solution of the reagent in hot methyl alcohol was used.

Other solutions and apparatus: Reagent grade soluble salts of various elements as described in the earlier parts were used. Ashless filter paper No:40 was used for collecting the precipitates, and platinum crucible for ignition.

Properties of titanium (IV) complex: It is a bright orange substance, very soluble in chloroform, benzene and acetone and fairly soluble in methyl and ethyl alcohol. It is very stable towards heat in aqueous-acidic medium but decomposed at 105° to 110°C, when heated in a dry state. The complex was crystallised from alcohol in the form of light orange yellow crystals, melting point 146°C. Analysis showed that it was not of definite composition. The crystalline material also on prolonged heating at 105 to 110° showed signs of decomposition.

Effect of pH: Titanium (IV) is quantitatively precipitated by the reagent between pH 1.6 to 2.8. Prolonged heating (over 1 hour) of the complex at lower pH slightly decomposed it. At higher pH, the complex is not very granular and shows signs of hydrolysis. The optimum pH was found to be between 2.2 to 2.5 and most of the determinations were carried out at pH 2.3. The complex formed under these conditions is very granular, stable towards heat and can be safely heated in the reaction medium for two hours. Completeness of precipitation during the initial stage was tested gravimetrically as well as by spot test using hydrogen peroxide, catechol and chromotropic acid according to Feigl[9].

Procedure for titanium (IV): A number of titanium determinations were carried out according to the following procedure. 10 ml. of titanium (IV) solution containing 1.0040 g. titanium dioxide per lit. was taken in a 400 ml. beaker and 4 ml. of N-hydrochloric acid and 5 ml. of 10% w/v. sodium acetate solution added to it to bring its pH to about 2.3. A solution containing foreign ion may also be added at this stage. Requisite amount of a 1% w/v. solution of the reagent in hot methanol was added with stirring (0.5 g. of the reagent for every 10 mg. of titanium). The bright orange titanium complex was immediately thrown out. 200 ml. of hot water was added and the reaction mixture was kept on boiling water bath, without any cover, for about 1½ to 2 hours with occasional stirring. This heating is necessary for complete removal of methanol, as the titanium complex is slightly soluble when the alcoholic concentration is more than 5%. The complex was then filtered hot, using ashless filter paper No:40, washed with hot water to make it free from chloride and sulphate ions and dried at 105°C. for 10 to 15 minutes. It was ignited to a constant weight in a platinum crucible, taking usual precautions necessary for igniting organic complexes. Use of hydrochloric acid and sodium acetate for stabilizing the pH was very necessary. When pH is adjusted without these reagents by dilution only, the titanium complex formed is not very granular and has a tendency to pass through the filter paper. The results of titanium determination are recorded in table I.

TABLE I

Determination of titanium (IV).

	TiO_2 taken G	TiO_2 found G	Error G
1	0.01004	0.01005	+.00001
2	0.01004	0.01010	+.00006
3	0.01004	0.01007	+.00003
4	0.01004	0.01006	+.00002
5	0.01004	0.01002	-.00002

Separation of titanium (IV) and aluminium

Titanium was determined in presence of large amounts of aluminium by following the usual procedure. The results are recorded in table II.

TABLE II

Determination of titanium (IV) in presence of aluminium.

	TiO_2 taken G	Al added G	TiO_2 found G	Error G
1	0.01004	0.20	0.01003	-.00001
2	0.01004	0.20	0.01008	+.00004
3	0.01004	0.30	0.01001	-.00003
4	0.01004	0.30	0.01009	+.00005
5	0.01004	0.50	0.01006	+.00002
6	0.01004	0.50	0.01009	+.00005

Separation of titanium (IV) from beryllium, magnesium and chromium

The usual procedure for titanium was followed and the results are recorded in table III.

TABLE III

Determination of titanium (IV) in presence of Be(II), Mg(II) and Cr(III)

	TiO_2 taken G	Foreign ion G	TiO_2 found G	Error G
1	0.01004	0.05 Be(II)	0.01005	+.00001
2	0.01004	0.05 Be(II)	0.01008	+.00004
3	0.01004	0.05 Mg(II)	0.01002	-.00002
4	0.01004	0.05 Mg(II)	0.01009	-.00005
5	0.01004	0.05 Cr(III)	0.01004	.00000
6	0.01004	0.05 Cr(III)	0.01007	+.00003

Separation of titanium (IV) from cobalt, nickel, zinc and manganese

No interference was caused by cobalt, nickel, zinc and manganese, in the usual procedure for the determination of titanium. The results are recorded in table IV.

TABLE IV.

Determination of titanium (IV) in presence of Co(II), Ni(II), Zn(II) and Mn(II).

	TiO_2 taken G	Foreign ion G	TiO_2 found G	Error G
1	0.01004	0.05 Co(II)	0.01001	-.00003
2	0.01004	0.05 Co(II)	0.01006	+.00002
3	0.01004	0.05 Ni(II)	0.01009	+.00005
4	0.01004	0.05 Ni(II)	0.01002	-.00002
5	0.01004	0.05 Zn(II)	0.01007	+.00003
6	0.01004	.05 Zn(II)	0.01004	.00000
7	0.01004	0.05 Mn(II)	0.01008	+.00004
8	0.01004	0.05 Mn(II)	0.01003	-.00001

Separation of titanium (IV) from thorium(IV), uranium(IV) and uranyl(II

Usual procedure was followed and the results are recorded in table V.

TABLE V.

Determination of titanium (IV), in presence of Th(IV), U(IV) and UO_2(II).

	TiO_2 taken G	Foreign ion G	TiO_2 found G	Error G
1	0.01004	0.05 Th(IV)	0.01004	.00000
2	0.01004	0.05 Th(IV)	0.01007	+ .00003
3	0.01004	0.05 U(IV)	0.01005	+ .00001
4	0.01004	0.05 U(IV)	0.01008	+ .00004
5	0.01004	0.05 UO_2(II)	0.01009	+ .00005
6	0.01004	0.05 UO_2(II)	0.01002	- .00002

Separation of titanium (IV) from arsenic(III), mercury(II) and cadmium (II)

The usual procedure for the determination of titanium was followed and the results are recorded in table VI.

TABLE VI.

Determination of titanium(IV) in presence of As(III), Hg(II) and Cd(II).

	TiO_2 taken G	Foreign ion G	TiO_2 found G	Error G
1	0.01004	0.05 As(III)	0.01006	+ .00002
2	0.01004	0.05 As(III)	0.01001	- .00003
3	0.01004	0.05 Hg(II)	0.01003	- .00001
4	0.01004	0.05 Hg(II)	0.01006	+ .00002
5	0.01004	0.05 Cd(II)	0.01009	+ .00005
6	0.01004	0.05 Cd(II)	0.01004	.00000

Separation of titanium from alkali and alkali earth metals was also possible, but the data have not been included here for the sake of brevity. Platinum (IV), rhodium(IV), ruthenium (III) and iridium (III) can also be separated, but the actual experiments were not carried out to avoid unnecessary loss of valuable chemicals.

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PART VIII

3-HYDROXY-1-p.SULPHONATOPHENYL-3-PHENYLTRIAZINE AS A REAGENT FOR COLORIMETRIC ESTIMATION OF PALLADIUM.

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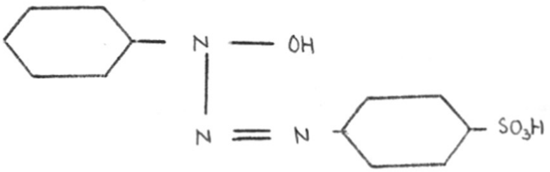
3-Hydroxy-1-p.sulphonatophenyl-3-phenyltriazine as a colorimetric reagent for palladium

SUMMARY

3-Hydroxy-1-p.sulphonatophenyl-3-phenyltriazine



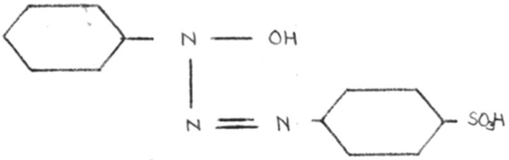
has proved to be an excellent reagent for the colorimetric estimation of palladium, either as such or in presence of Ni(II), Cu(II), Fe(III), Co(II), Ag and specially the members of the platinum group -Pt(IV), Rh(IV), Ir(III) and Ru(III).

Apart from its other highly desirable qualities, like the solubility of the reagent and the complex in water, almost instantaneous development of colour and its stability over a period of 24 hours and a wide range of temperature, wide range of permissible pH (1.7 to 4.4) and its easy adjustment using mineral acid alone etc., the reagent has much greater tolerance for the members of the platinum group and is undoubtedly superior to other palladium reagents used so far for this purpose.

***

3-Hydroxy-1-p.sulphonatophenyl-3-phenyltriazine as a colorimetric reagent for palladium.

In part IV, we have described the use of the parent compound - 3-hydroxy-1,3-diphenyltriazine-as a gravimetric reagent for palladium. From the extremely high selectivity of this reagent towards palladium and also its fairly high sensitivity, we were led to believe that the sulphonic acid derivative of such a compound, either as such, or in the form of its sodium salt, both of which will be soluble in water, should prove extremely useful as a colorimetric reagent for palladium. This has been found to be true as 3-hydroxy-1-p.sulphonatophenyl-3-phenyltriazine (I).



I

has proved to be an excellent reagent for the colorimetric estimation of palladium either as such, or in presence of other elements specially the members of the platinum group. In many respects, it is superior to all the other known palladium reagents, now described in the literature for the colorimetric estimation of palladium. Details about the comparative superiority of this reagent over all the other known palladium reagents have been given in the latter part of this paper (ref.p. 140).

Before going into the experimental details, we would like to discuss briefly the important properties which an ideal colorimetric reagent should possess.

1. The reagent should be stable towards heat, light and air.

2. It should be soluble in water, or water miscible solvents.

3. The complex formed by it, should also be soluble in water, failing which, in a mixture of water and water miscible solvents.

4. The development of colour should take place within a reasonable time. The colour should be stable and should not fade out with time.

5. It should not be affected by too much of procedural limitations like (a) variation of pH , (b) variation of temperature, (c) presence of neutral salts and (d) quantity of reagent etc.

6. The colour development should follow the Lambert-Beers' Law.

7. The reagent and the complex formed by it should have widely separated absorption peaks so that the interference by the reagent may be nil or negligible.

8. Above all the colour reaction should be highly specific so that the element concerned can be estimated in presence of diverse ions without interference.

The present reagent - 3-hydroxy-1-p.sulphonatophenyl-3-phenyltriazine possesses most of these desirable properties enumerated above.

1. The reagent is stable towards heat, light and air, and can be preserved indefinitely at room temperature.

2. It is soluble in water, and the aqueous solution remains practically unaltered upto 48 hours.

3. The Pd-complex formed by it is also soluble in water.

3. The Pd-complex formed by it is also soluble in water.

4. The colour development with palladium is almost instantaneous. Full development takes place in less than five minutes and the intensity remains unaltered, even after 24 hours.

5. Colour development is not so sensitive to pH variation. It remains steady between pH 1.7 to 4.5. pH can be adjusted with mineral acid alone. The colour intensity is also unaffected by variation in temperature, from 25°C. to 85°C. Full development of colour takes place without any undue excess of reagent.

6. The colour development follows the Lambert-Beers Law.

7. The reagent and the complex formed by it have reasonably well separated absorption peaks so that the excess of the reagent present does not create interference in the photometric estimation.

8. Above all, the colour development is very highly selective. There is no interference by most of the foreign ions, including other members of the platinum group.

EXPERIMENTAL.

Standard palladium solution: Approximately 0.5 g. of palladium chloride was dissolved in a little water containing 3 ml. conc. hydrochloric acid, and then the volume was made to 500 ml. The palladium content was determined, using dimethylglyoxime and also 3-hydroxy-1,3-diphenyltriazine, (developed by us) which was found to be 0.6216 g. Pd/lit. 159.9 ml. of this solution when made to a litre, contained 100 pd.per ml. This stock solution was further diluted 10 times for estimation purposes so that 1 ml. of the diluted solution contained 10 γ Pd.

Reagent solution: The reagent, as will be evident from its preparative description and elemental analysis described in part II, is the sodium salt of sulphonic acid, and this is the form in which it was actually obtained during the preparation. 0.1% w/v. solution of the reagent in distilled water was used.

Solutions of diverse ions: The reagent grade soluble salts, usually chloride, nitrate, or sulphate were employed for the preparation of the solutions of inorganic ions. The solutions were diluted in such a way that these contained 1 mg. of the metallic element per ml.

Instruments: Single pan 'Mettlers' - macro and semi-micro balances were used for weighing. Beckman pH meter model H-2 was used for pH measurements. Absorbancy measurements were made with a Beckman quartz spectrophotometer, model DU, using 1.00 cm. quartz cells for UV region and corex cells for visible region. Visual colour comparisons were made in 50 ml. Nessler's tubes of the standard type. Spot tests were carried out on a white porcelain spot plate.

Absorbtion curves for the Palladium complex and the reagent

20 ml. of palladium solution containing 10 p.p.m. of Pd. was pipetted into a 100 ml. measuring flask. 0.1 ml. of N-hydrochloric acid was added to it so that the pH after dilution etc. was about 3.0. 5 ml. of 0.1% w/v. aqueous reagent solution was added to the solution. After a little shaking the volume was made to 100 ml. The resulting solution contained 2 p.p.m. of palladium.

A blank solution was prepared by pipetting out 5 ml. of the reagent solution into a 100 ml. flask and making the volume to the mark. It was found that there was no difference in the blank solution prepared as given above and that prepared by adding 0.1 ml. of hydrochloric acid for bringing the pH to about 3.0. Hence the addition of the acid in the blank solution was not considered to be imperative.

Figure No: 7 gives the absorbancy curves of (i) palladium complex using a "reagent-blank solution" and (ii) reagent solution using water as blank. The absorbancy of the reagent solution falls sharply after 390 mμ and is almost negligible at 430 mμ. The absorption peak of palladium complex, in this region, is at 413 mμ, which is also true for the palladium complex of the parent reagent (ref: p. 59). However, as there is no substantial fall in absorbancy upto 420 mμ, where the interference by the reagent is also decreased, we preferred 420 mμ to be the suitable wavelength for the palladium estimations. 430 mμ can also be used with advantage, as, at this wavelength, the interference by the reagent is almost negligible and so water can be used as a blank.

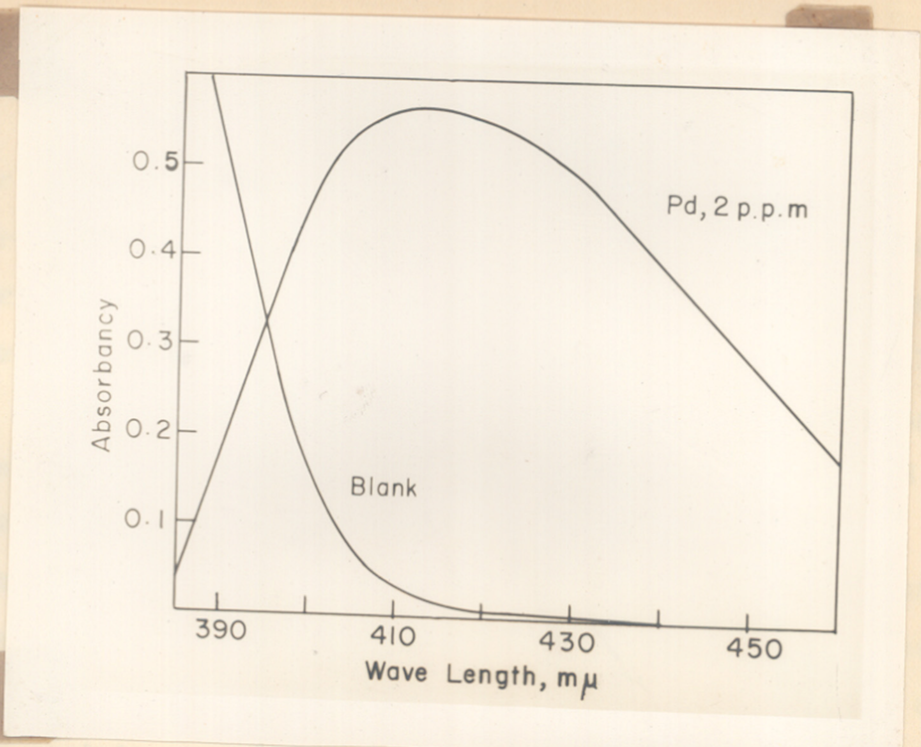


Figure No. 7. Absorption curves for the palladium complex and the reagent.

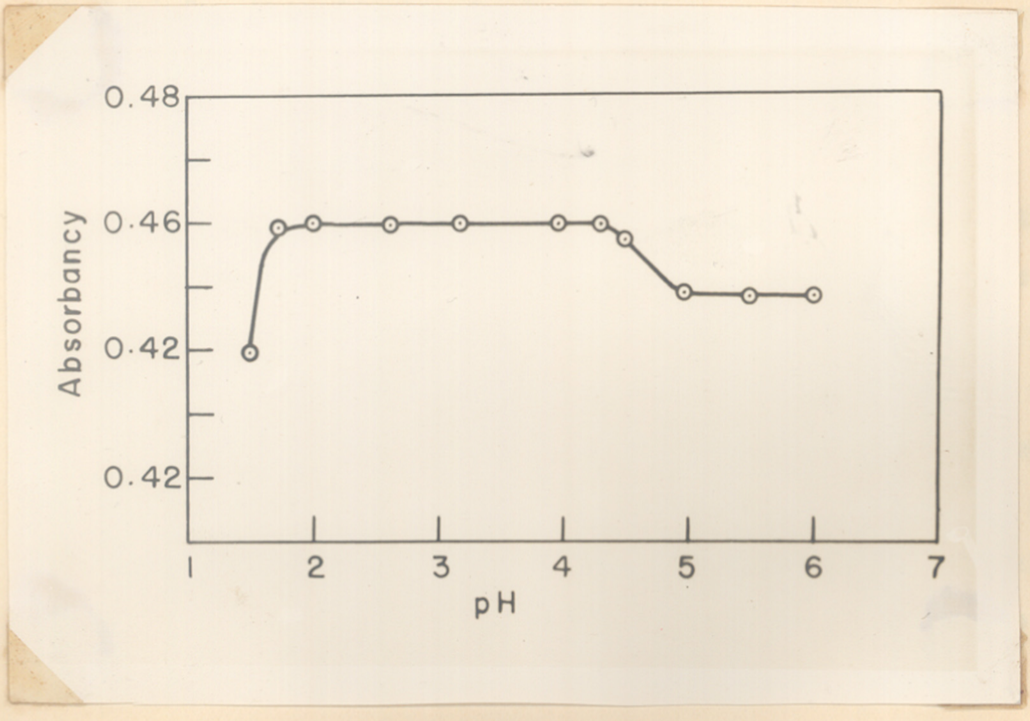


Figure No. 8 . Effect of pH on absorbancy.

Effect of pH

Solutions used for the study of the effect of pH on colour reaction were prepared as directed above, excepting that different amounts of N-hydrochloric acid, N-sulphuric acid or N-nitric acid and 10% w/v. sodium acetate or sodium potassium tartrate was added so that the final pH values ranged from 1.2 to 6.5. On using N-HCl or N-H_2SO_4, for adjusting pH, the range of constant maximum absorbance was between 2.5 to 4.4. At pH lower than 2.5, there was slight turbidity, resulting in lower absorbance. However, on using N-HNO_3, the pH range increased and was between 1.7 to 4.4 (Figure No. 8). It was also observed that pH can be better adjusted by using acid alone without using sodium acetate or sodium potassium tartrate, as these buffering agents are also prone to give turbidity when used in higher concentrations. Hence in the estimations, only N-nitric acid was used for the adjustment of pH, which was kept between 2.5 to 3.0 to increase the specificity of the reagent.

Reagent concentration and Mole Ratio

A series of solutions was prepared in which the mole ratio of palladium to reagent was from 1:1 to 1:15. pH was adjusted to about 2.5 by using about 0.2 ml. of N-HNO_3. Absorbance was measured for each solution after about 5 minutes at 430 mμ using water as blank. Figure No: 9 gives absorbancy against moles of reagent per mole of palladium. The fact, that there is no sharp peak indicates that the complex is appreciably dissociated in solution. Full colour development is ensured at 1:8 ratio of palladium to reagent, which is very reasonable.

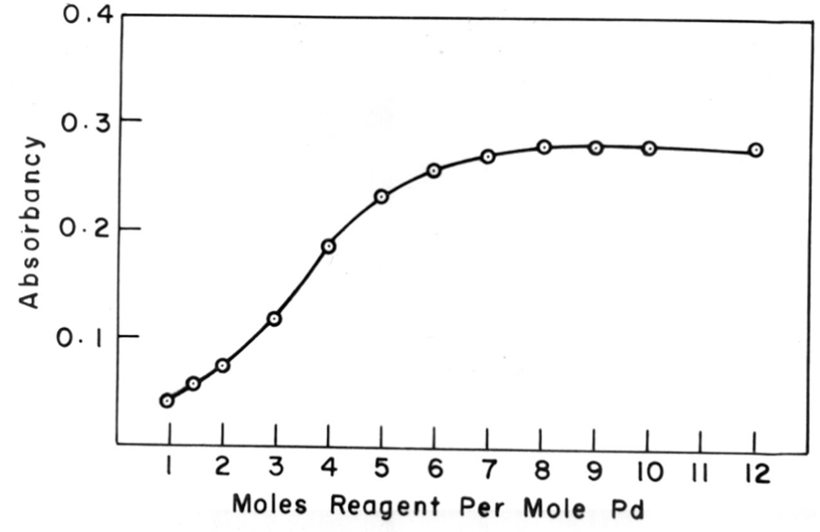


Figure No. 9. Reagent concentration and mole ratio.

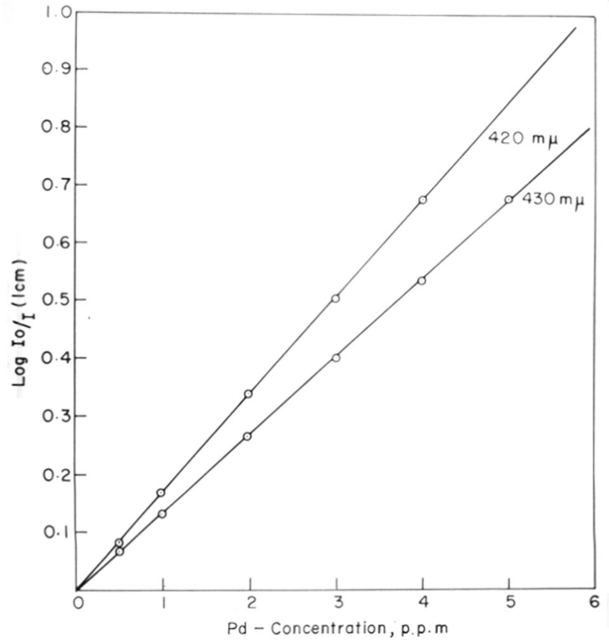


Figure No 10. Lambert- Beers law.

Rate of reaction and stability of complex

The colour formation of palladium complex with the reagent was found to be almost instantaneous and the colour was also very stable. There was no difference in the absorbancy taken after 5 minutes and that taken after 24 hours.

Lambert-Beers Law

Aliquot portions of standard palladium solution were pipetted into 100 ml. flasks so that the palladium concentration finally corresponded to 0.2 p.p.m. to 6 p.p.m. 0.2 ml. of N-nitric acid and 10 ml. of the reagent solution were then added. The volume was made upto the mark and the absorbancy was measured after about 5 minutes both at 420 mu using reagent as blank and at 430 mu using water as blank. Figure No. 10 shows that Lambert-Beer's Law is obeyed in both the cases. At 420 mμ the concentration range is from 0.2 to 5 p.p.m. and at 430 mμ it is from 0.4 to 6 p.p.m. of palladium. Larger amounts of palladium can be estimated at higher wave lengths i.e.435 to 450 mu.

Effect of temperature on the reaction

Two, 10 ml. samples of standard palladium solution containing 10 p.p.m. of Pd were taken in two beakers. To one, 0.2 ml. of N-HNO_3 and to the other 0.1 N-HCl was added followed by 5 ml. of the reagent solution in each case. 50 ml. of water was then added to each of these beakers and the contents kept for heating on a water bath. Initial temperature was 25°C. The beakers with the contents were heated upto 85°C. and maintained at that temperature for about 10 minutes. After cooling, the contents were separately transferred into 100 ml. flasks and volume made upto the mark. Blank reagent solution was also treated simultaneously in a similar way. Absorbancy was measured at 420 mu. There was no difference in the absorbancy at 25°C. and 85°C, and the use of hydrochloric acid or nitric acid for the adjustment of pH, made no difference.

It can, therefore, be concluded that there is no change in the colour intensity over a temperature range of 25 to 85^{o}C.

Sensitivity of the reaction

50 ml. of solutions containing 0.5 ml. of the reagent solution, 0.1 N-HCl and 0.02 to 0.10 p.p.m. of palladium solution were prepared in Nessler's cyclinders. The 0.05 p.p.m. palladium solution was easily distinguishable from a blank. Thus the sensitivity of the colour reaction could be taken to be 1 part of palladium in 20,000,000 parts of solution.

Spot plate sensitivity was determined by taking 0.05 ml. of standard palladium solution to a depression of a white porcelain spot plate. 0.05 ml. of N/10 HCl and 0.05 ml. of 0.05% reagent solution was added to it. 0.05γ of palladium in 0.15 ml. of solution could be distinctly detected.

Effect of adding neutral salts (sodium chloride was used)

10 ml. of standard palladium solution containing 10 p.p.m. was pipetted into a 100 ml. flask and N-HCl or N-HNO_3 were added for pH adjustment. Different quantities of 5% sodium chloride solution, followed by 5 ml. of reagent solution was added. The permissible concentration was found to be 0.025 mole of NaCl/lit. There was no appreciable difference by using hydrochloric or nitric acid.

Tolerance of diverse ions

10 ml. of standard palladium solution containing 10 p.p.m

of Pd. was pipetted into 100 ml. flask and the diverse ion solution was added. The pH was adjusted by adding 0.2 ml. of N-HNO_3. 5 ml. of the reagent solution was then added and the volume made to 100 ml. The final solution contained 1 p.p.m. of Pd. The absorbancy was measured after about 5-10 minutes at 420 mμ using reagent as blank, and also some times at 430 mμ using water as blank.

An ion was considered to interfere if the resulting solution differed by 0.005 in absorbancy from that containing only palladium without any diverse ion. Table I. summarises the tolerance of the diverse ions as p.p.m. of respective ion.

TABLE I

Tolerance of diverse ions

	Ion	Added as	Limiting conc., p.p.m.
1	Ni(II)	chloride	10
2	Cu(II)	sulphate	3
3	Fe(II)	sulphate	2
4	Fe(III)	sulphate	20
5	Co(II)	sulphate	2
6	Rh(IV)	sulphate	10
7	Ir(III)	chloride	30
8	Pt(IV)	chloride	40
9	Ru(III)	chloride	1
10	*Ag(I)	Nitrate	75

Iron(III) also reacts with the reagent at low pH, which shows a peak at about 400 mu and interferes with the palladium estimation. This interference, however, was completely eliminated by masking it with 1ml. of 5% sodium fluoride.

The colour of iridium chloride was bleached by the addition of the reagent, but this did not create any interference.

*For testing the tolerance of silver, a solution of palladium nitrate was used, preparation of which has been described earlier (p.68 .).

Gold (III) is reduced by the reagent to the metallic state and hence causes interference. Lead salts also created some interference in the estimation of palladium, which is, however, difficult to explain.

In examining the tolerance of various diverse ions, we have used only those ions which normally occur with palladium or are usually present in the important alloys of palladium. Considering the specificity of the reagent at low pH, it is certain that palladium could be estimated in presence of many other elements without any interference, but the actual experiments were not carried out as it was not likely to serve any useful purpose.

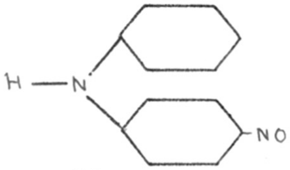
Comparison with other reagents

For the comparative evaluation of the qualitites of 3-hydroxy-1-p.sulphonatophenyl-3-phenyltriazine as a colorimetric reagent for palladium, it is necessary to have a brief survey of the other compounds used for the same purpose. For this assessment we should be guided by the 8 "desirable properties" for a colorimetric reagent, which we have enumerated earlier. The other palladium reagents are:

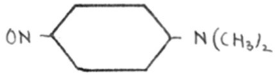
1. 2-mercapto-4,5-dimethylthiazole[1]
2. 1-nitroso-2-naphthol[2] and 2-nitroso-1-naphthol
3. β-furfuraldoxime and p-bromoaniline[3]
4. bromide ion[4]
5. stannous chloride[5]
6. thiourea[6]
7. p.nitrosodiphenylamine[7]
8. p.nitrosodialkylaniline[8]

Majority of these reagents do not possess many of the desirable properties discussed earlier. In certain cases, the pH adjustment is very rigid and the range allowed is almost unworkable; in others, the coloured complex has to be extracted with solvent before taking absorbancy; very often, the coloured complexes are stable only over a short period and very susceptible to temperature variation. Above all, in most of the cases, neither the reagents nor the complexes formed by them are soluble in water. For these reasons we are only discussing about the p.nitrosodiphenylamine and dialkyl substituted p.nitrosoaniline, which are now currently favoured for the colorimetric estimation of palladium.

Yoe and Overholser[7] developed p.nitrosodiphenylamine (II) as a sensitive reagent for colorimetric estimation of palladium.



II



III

IV.

The coloured compound is a coordination complex of the composition $Pd(C_6H_5NHC_6H_4NO)_2Cl_2$ yielding a red solution in water containing small amount of alcohol. However, this colour reaction suffers from several limitations: (i) the reagent can be used only with a sodium acetate and hydrochloric acid buffer, (ii) pH control is also very rigid and very little variation from optimum pH of 2.0 is permissible, (iii) colour development takes 30 minutes and is stable for 1 to 2 hours only, (iv) temperature variation is not permissible and is to be kept within 5°C. and (v) neutral salts have marked deleterious effect and interference is created by oxidising agents.

Yeo and Overholser[8] have also examined p.nitrosodimethylaniline (III) and p.nitrosodimethylaniline (IV) as possible reagents. These two compounds possess advantage over the former because of faster reaction rate, greater stability of the colour (4 hours), small temperature variation effect and also there is less interference by the excess of the reagent, as the absorption peaks for the reagents and the complexes are comparatively wide apart. However, in practice p.nitrosodiphenylaniline is likely to have greater possibility because of its greater tolerance for diverse ions.

A comparative table indicating the basic properties of the various reagents along with those of the present one is given below:

TABLE II

Comparative properties of 3-hydroxy-1-p.sulphonatophenyl-3-phenyltriazine, p-nitrosodiphenylamine, p.nitrosodiethyl and dimethylaniline.

	Properties	p.nitroso-diphenylamine	p.nitroso diethyl or methylaniline	3-hydroxy-1-p.sulphonatophenyl-3-phenyltriazine
1	Solubility	Insoluble in water, moderately soluble in alcohol	slightly sol. in water, insoluble in alcohol	soluble in water
2	Time of maximum colour intensity	30 minutes	5 minutes	5 minutes
3	Stability of colour	1 to 2 hours	4 hours	24 hours or more
4	pH	2.0 to 2.1	4.0 to 5.0	1.7 to 4.4
5	Use of buffer	absolutely essential	absolutely essential	not necessary
6	Temp.effect	must keep within 5°C	slight difference at 20°C variation	no difference even upto 60°C variation.
7	Concentration of sodium chloride permissible	0.03 M	0.05 M	0.025 M
8	Tolerance of diverse ions in p.p.m.			
	Ni(II)	20	15	10
	Cu(II)	50	3	3
	Fe(II)	data not given		2
	Fe(III)	30	2	20
	Co(II)	10	10	2
	Rh(IV)	1	1	10
	Ir(III)	1	1	30
	Pt(IV)	20	20	40
	Ru(III)	data not given		1
	Ag(I)	200	200	75
	Au(III)	1	0.5	0

Superiority of the present reagent

From the properties recorded in the above table and also from those mentioned at other places in the text, it will be apparent that the present reagent - 3-hydroxy-1-p.sulphonatophenyl-3-phenyltriazine is very much superior to other reagents known so far. Its superiority may be attributed mainly to the following outstanding properties: (i) the solubility of the reagent and the complex in water, (ii) the instantaneous development of the colour and its stability over a period of 24 hours and a wide temperature variation range i.e. from 25 to 85°C. (iii) wide pH range allowed and its possible adjustment with mineral acid alone without using any buffer and (iv) above all, the greater over all tolerance for the other members of the platinum group, a property which is specially noteworthy.

The exceptional stability of the palladium complex of 3-hydroxy-1-p.sulphonatophenyl-3-phenyltriazine is mainly due to the fact that it is an inner complex and not a coordination complex, as is the case with the other reagents discussed above.

Difficulties of partial salting out of the complex in presence of an excess of neutral salts could possibly be encountered by introducing a second sulphonic group in the reagent. Such a compound, as well as the complexes formed by it, will be much more soluble in water and may prove to be more useful as a colorimetric reagent.

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PART IX

3-HYDROXY-1-p.SULPHONATOPHENYL-3-PHENYLTRIAZINE
AS A REAGENT FOR COLORIMETRIC
ESTIMATION OF MOLYBDENUM.

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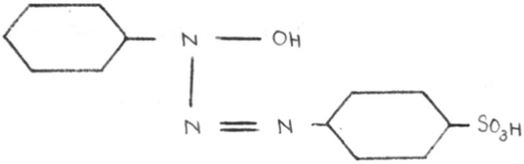
3-Hydroxy-1-p.sulphonatophenyl-3-phenyltriazine as a colorimetric reagent for molybdenum.

SUMMARY

3-Hydroxy-1-p.sulphonatophenyl-3-phenyltriazine



has also proved to be a useful reagent for the colorimetric estimation of molybdenum, as such, or in presence of Co(II), Ni(II), Zn(II), Mn(II), U(IV), Ca(II) and specially tungsten.

It is superior to most of the other molybdenum reagents and compares well, and in certain respects is also superior to potassium thiocynate - stannous chloride and mercapto-acetic acid, the latter reagent has, only recently, been developed by Yoe and Will.

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3-Hydroxy-1-p.sulphonato-3-phenyltriazine as a colorimetric reagent for molybdenum

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In part VIII of this series, the use of 3-hydroxy-1-p.sulphonato-3-phenyltriazine as a colorimetric reagent for palladium has been described. The reagent also develops a deep orange yellow colour with molybdate ions at low pH,(2.8 to 3.7) which is suitable for the colorimetric estimations of molybdenum.

With this reagent molybdenum can be estimated as such or in the presence of nickel (II), cobalt (II), manganese (II), zinc (II), copper (II), uranium (IV), calcium (II) and specially tungstate. Considering the very high selectivity of this reagent, it is quite possible that molybdenum could also be estimated in presence of many other diverse ions, but for the sake of brevity we have chosen only the more important ones, with which molybdenum may occur as such in nature or as component of important industrial alloys and other allied preparations.

The most important advantage with this reagent is that the reagent and the complex formed by it are water-soluble. As regards the other necessary qualities, the reagent is quite reasonable and is superior to most of the molybdenum reagents now described in the literature. A comparative study of the various reagents will be available in the latter part of this paper. Now we are going to describe the experimental details about the estimation of molybdenum.

EXPERIMENTAL.

Standard molybdenum solution: Approximately 3 g. of sodium molybdate was dissolved in 1000ml. of water. Molybdenum content, as determined by using 8-hydroxyquinoline, was found to be 2.3620 g. Mo/lit. 42.3 ml. of this solution diluted to a lit. contained 100 γ Mo per ml. This solution was used for estimation purposes.

Reagent solution: 0.5% w/v. solution of the reagent in distilled water was used.

Solutions of diverse ions and instruments: Solutions of diverse ions were prepared as described earlier in part VIII on palladium. Instruments were also the same.

Absorbtion curves for molybdenum complex and the reagent

10 ml. of standard sodium moblybdate solution containing 100 p.p.m. Mo was pipetted into 100 ml. flask. 0.2 ml. of N-hydrochloric acid was added to it so that the pH after dilution etc., was about 3.2. 15 ml. of the reagent solution was then added and the volume made to 100 ml. It was kept for 30 minutes before taking absorbancy. A blank reagent solution was also prepared in a similar way.

Figure No. 11 gives the absorbancy curves of (i) molybdenum complex using a reagent blank solution and (ii) reagent solution using water as blank. The absorbancy of the reagent solution falls sharply after 390 mµ and is very little at 430 mµ. The absorption peak of molybdenum complex is at 416 mµ. To minimise the interference by the reagent, we preferred 420 mµ to be the suitable wave length for molybdenum estimations.

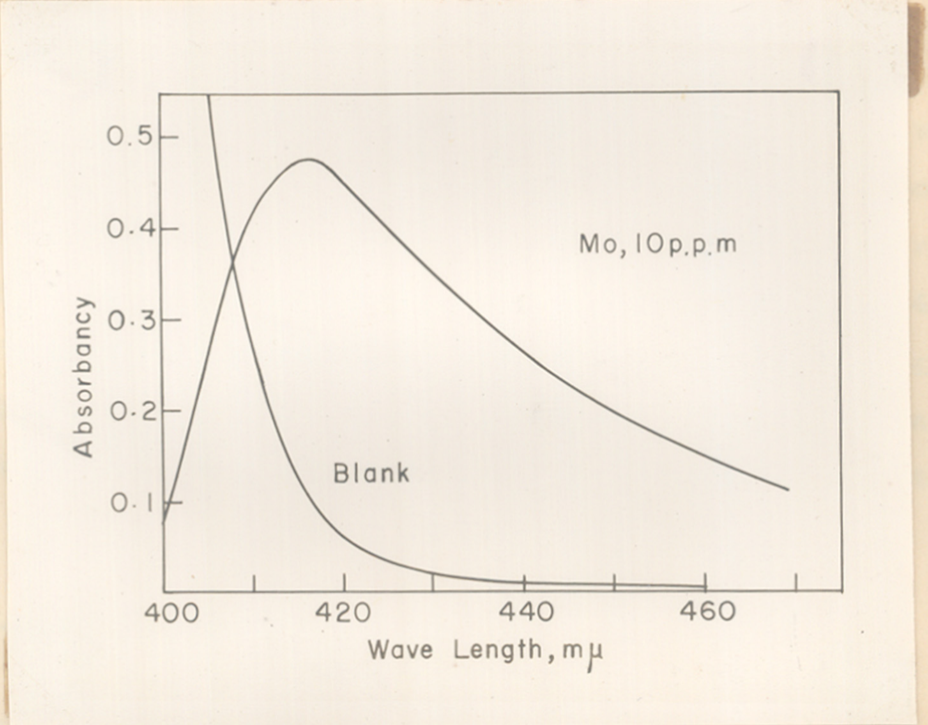

Figure No. 11. Absorption curves for the molybdenum complex and the reagent.

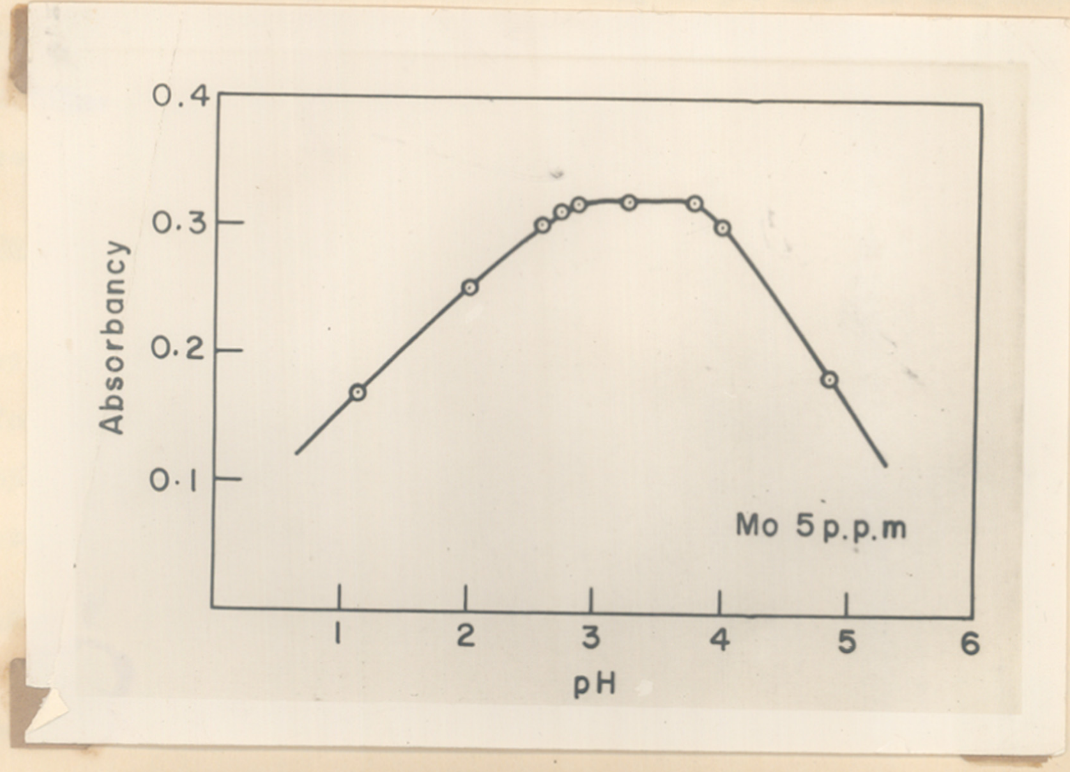

Figure No. 12. Effect of pH on absorbancy.

Effect of pH

A number of 5 ml. of standard sodium molybdate solution containing 100 p.p.m. were pipetted into 100 ml. flasks and varying amounts of N-hydrochloric acid, N-nitric acid and 10% w/v. sodium acetate solutions added to them so that the final pH values ranged from 1.2 to 6.0. Absorbancy was taken after 30 minutes at 420 mμ using a "reagent-blank" solution. The curve for absorbancy against pH is given in figure No. 12 . The range of constant maximum absorbance was between pH 2.8 to 3.7. In molybdenum estimation a pH of 3.2 to 3.5 was used.

Reagent concentration and mole ratio

A series of experiments was conducted in which the mole ratio of molybdenum to reagent was from 1:2 to 1:25. Absorbance was measured after 30 minutes at 430 mμ. Figure No: 13 gives absorbancy against moles of reagent per mole of molybdenum. There is a very gradual rise in absorbancy and the full colour is developed at 1:20 ratio of molybdenum to reagent indicating that the complex is in highly dissociated form in solution.

Rate of reaction and stability of complex

The full colour development of molybdenum complex with the reagent took about 22 minutes. It was stable afterwards for 3 hours. Absorbancy taken after 24 hours was increased by 5%. Figure No: 14 gives the curve for absorbancy against time at 430 mμ.

Lambert-Beers Law

A series of experiments was conducted in which aliquot portions of standard molybdenum solution were taken into 100 ml.flask. 0.2 ml. of N-hydrochloric acid and 10 ml. of 1% reagent solution were

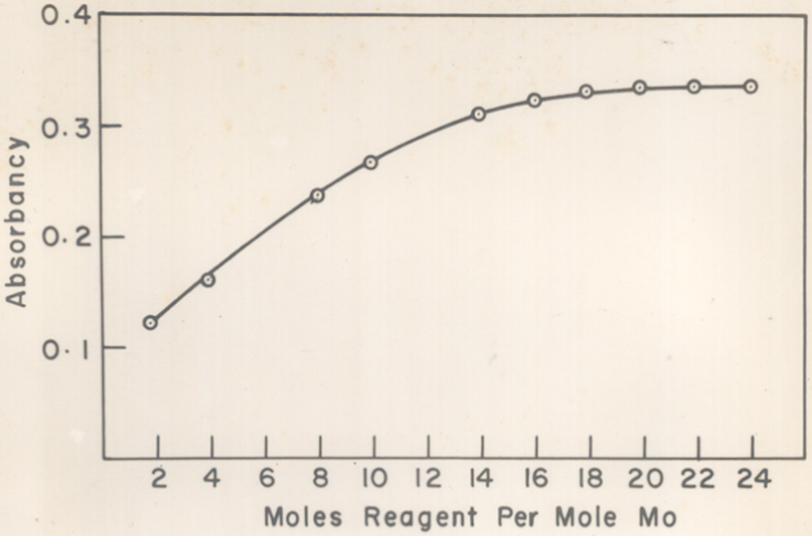

Figure No.13. Reagent concentration and mole ratio.

Figure No.14. Rate of reaction and stability of complex.

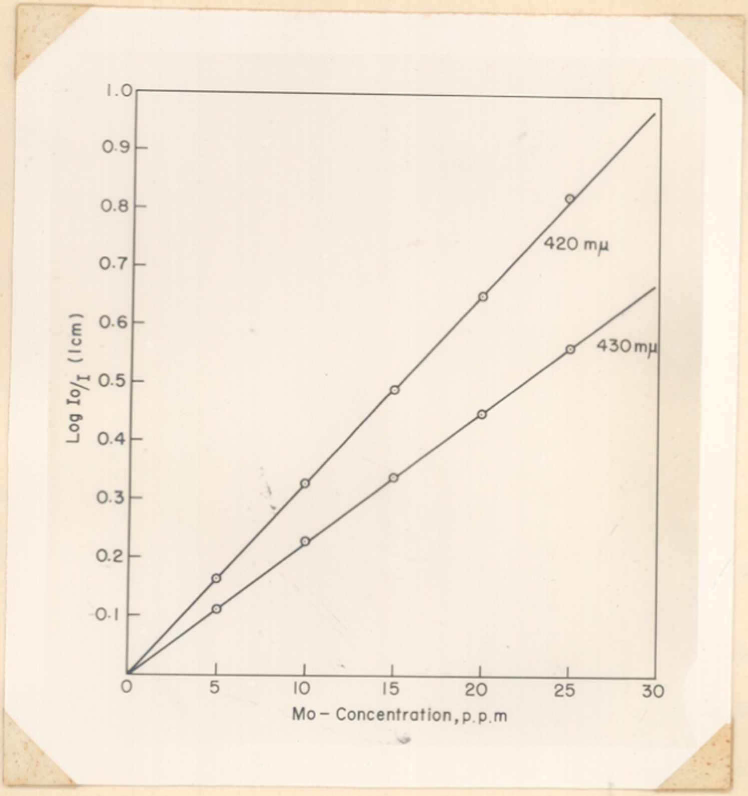

Figure No. 15. Lambert-Beers Law.

then added. The volume was made upto the mark and the absorbancy was measured after 30 minutes both at 420 mμ and 430 mμ using reagent as blank. Figure No: 15 gives that Lambert-Beer's Law is obeyed in both the cases. At 420 mμ the concentration range is from 1 to 25 p.p.m. of molybdenum.

Effect of temperature on the reaction

The colour intensity of molybdenum complex decreased with the increase in temperature. Hence, maintaining the temperature within about 10°C. was considered to be desirable.

Sensitivity of the reaction

Sensitivity test of the colour reaction was done in 50 ml. Nessler's cylinders. After mixing up the molybdenum solution, N-HCl and the reagent, it was kept for 20 minutes for the full development of the colour. In this way, 1 part of molybdenum in 5,000,000 parts of solution could be easily distinguished.

0.05 ml. of standard molybdenum, solution, 0.05 ml. N/10 HCl and 0.05 ml. of 0.5% reagent solution were taken on a spot plate, and the development of colour was noted after 30 seconds. 1γ of molybdenum could be easily detected in this way.

Tolerance of diverse ions

5 ml. of standard molybdenum solution containing 100 p.p.m. of Mo was pipetted into 100 ml. flask and the diverse ion solution was added. The pH was adjusted to about 3.2 to 3.5 by adding 0.2 ml. of N-hydrochloric acid. 10 ml. of the reagent solution was then added and the volume made to 100 ml. The final solution contained 5 p.p.m. of molybdenum. The absorbancy was measured after 25-30 minutes at 420 mμ using reagent as blank. Table I summarises the tolerance of the diverse ions.

TABLE I

Tolerance of diverse ions.

	Ion	Added as	Ratio of limiting conc,p.p.m
1	Ni(II)	chloride	40
2	W(VI)	sod.tungstate	20
3	Co(II)	sulphate	40
4	Mn(II)	chloride	10
5	Zn(II)	acetate	30
6	Cu(II)	sulphate	0.5
7	U(IV)	acetate	50
8	Ca(II)	acetate	200

Comparison with other reagents

A large number of colorimetric reagents have been recommended for the determination of molybdenum. The following are being mentioned as more important examples:

1. hydrogen peroxide[1]
2. potassium xanthate[2]
3. phenylhydrazine[3]
4. tannic acid[4]
5. potassium thiocyanate and stannous chloride[5]
6. dithiol[6]
7. disodium-1,2-dihydroxybenzene-3,5-disulphonate[7] 'tiron'.

It is rather difficult to discuss about all of them in details. In certain cases, the colours developed has to be extracted with organic solvents; in others, pH has to be adjusted rather rigidly, and estimation of molybdenum in presence of diverse ions, specially tungsten is difficult. In case of 'tiron' mole ratio of reagent is as high as 1:600 and the tolerance of diverse ions is also not very encouraging.

Of the above reagents only potassium thiocyanate-stannous chloride method appears to be currently favoured as an accepted analytical procedure. This method also suffers from many serious limitations. The colour developed in acidic medium fades rather quickly and hence has to be extracted with organic solvents before taking absorbancy.

Recently Yoe and Will[8] have recommended mereapto-acetic acid ($SH-CH_2COOH$) as a reagent for the colorimetric estimation of molybdenum. According to them, the reagent is useful for the determination of molybdenum in steels. In this respect, it is superior to the present reagent, though the estimation of molybdenum in presence of iron requires considerable manipulation; mole ratio of the reagent as high as 1:1000 is required and potassium chlorate has to be used for counteracting the reducing property of the reagent. The mole ratio of the reagent, even in absence of diverse ions is very high (1:500). Morevoer, tolerance for tungsten is very low. Yoe has estimated molybdenum in presence of many diverse ions, some of these are, however, not important from analytical point of view, and could certainly also be carried out with present reagent, with better advantage, as at low pH it reacts with only a very few ions. A comparison of the properties of the two reagents including their tolerance for common diverse ions, which have been examined in both the cases, is given in table II.

TABLE II

Comparative properties of 3-hydroxy-1-p.sulphonatophenyl-3-phenyltriazine and mercaptoacetic acid.

	Properties	mercaptoacetic acid	3-hydroxy-1-p.sulphonato-phenyl-3-phenyltriazine
1	Solubility	soluble in water	soluble in water
2	Time of max.colour intensity	5 minutes	22 minutes
3	pH	3.0 to 5.0	2.8 to 3.7
4	Stability of colour	30 minutes	3 hours
5	Temp.effect	no difference upto 20° variation	no difference upto 10°C variation
6	Moles of reagent	1:500	1:20
7	Tolerance of diverse ions in p.p.m.		
	Co(II)	4	40
	Ni(II)	20	40
	Fe(III)	2 (normal procedure) 100 (modified "")	0
	Zn(II)	2000	30
	Mn(II)	300	10
	Cu(II)	1	0.5
	UO_2(II)	2	no data
	U(IV)	no data	50
	Cr(III)	0	0
	Ca(II)	2000	200 (or more)
	W(VI)	1	20

With our reagent, Co(II), Ni(II), Zn(II), Mn(II), U(IV) and specially tungsten do not create any interference, unless present in very large quantities. With none of the important reagents discussed above, molybdenum can be estimated in presence of tungsten without difficulty. The mole ratio of the present reagent (1:20) is also very favourable with respect to that Yoe's reagent, which in the latter case is as high as 1:500.

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PART X

3-Hydroxy-1,3-diphenyltriazine as a reagent for microgravimetric estimation of palladium and copper.

SUMMARY.

Preliminary investigation has indicated that 3-hydroxy-1,3-diphenyltriazine is likely to prove to be a dependable reagent for the microgravimetric estimation of palladium and copper.

3-Hydroxy-1,3-diphenyltriazine as a reagent for microgravimetric estimation of palladium and copper.

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Considering the very favourable factors of the complexes formed by 3-hydroxy-1,3-diphenyltriazine with palladium and copper (0.2009 for palladium and 0.1303 for copper), its possible use for the micro-gravimetric estimation of these elements has been preliminarily investigated. The reagent appears to be suitable for such estimations.

Standard procedure employing micro-beaker, filterstick etc., as described in standard books was adopted for these estimations. The procedure, which was same for both palladium and copper was not fundamentally different from the usual macro method described earlier. The only difference was that micro-apparatus of adequate size was used. Micro and semi-micro balances were used for weighing.

Micro-gravimetric procedure for palladium and copper.

25 ml. jena glass beaker with a micro filter-stick and a small glass rod was cleaned, dried in an oven for 1 hour at 120°C, cooled in a dessicator and weighed. The filter stick was removed for the time being, till the precipitation and digestion of the complex was complete.

5 ml. of standard palladium or copper solution containing 0.6 to 2.0 mg. of the metal was pipetted into the beaker and 0.2 ml. of N-hydrochloric acid and 0.2 ml. of 10% w/v. sodium acetate solution was added to it. The mixture was warmed a little on a water bath and then 1 ml. of 1 % w/v. reagent solution was added to it with stirring followed by 10 ml. of hot water and the reaction mixture was kept for digestion on a boiling water bath for about 1 hour, with occasional stirring. After this digestion of the complex, the filter stick was introduced and the liquid sucked off while hot.

Contents of the beaker and the filter stick were washed four times with hot water. The beaker along with the stick and the glass rod was dried to a constant weight in an oven at 120°C. for 1 hour. The results are recorded in tables I and II.

TABLE I

Microgravimetric determination of palladium

Pd.taken mg.	Pd.complex mg	Pd.found mg.	Error mg
0.954	4.72	0.948	- 0.006
0.954	4.76	0.955	+ 0.001
1.908	9.52	0.912	+ 0.004
1.908	9.53	1.914	+ 0.006

TABLE II

Microgravimetric determination of copper

Cu.taken mg.	Cu.complex mg.	Cu.found mg.	Error mg.
0.684	5.20	0.677	- 0.007
0.684	5.29	0.689	+ 0.005
1.025	7.88	1.026	+ 0.001
1.025	7.90	1.029	+ 0.004

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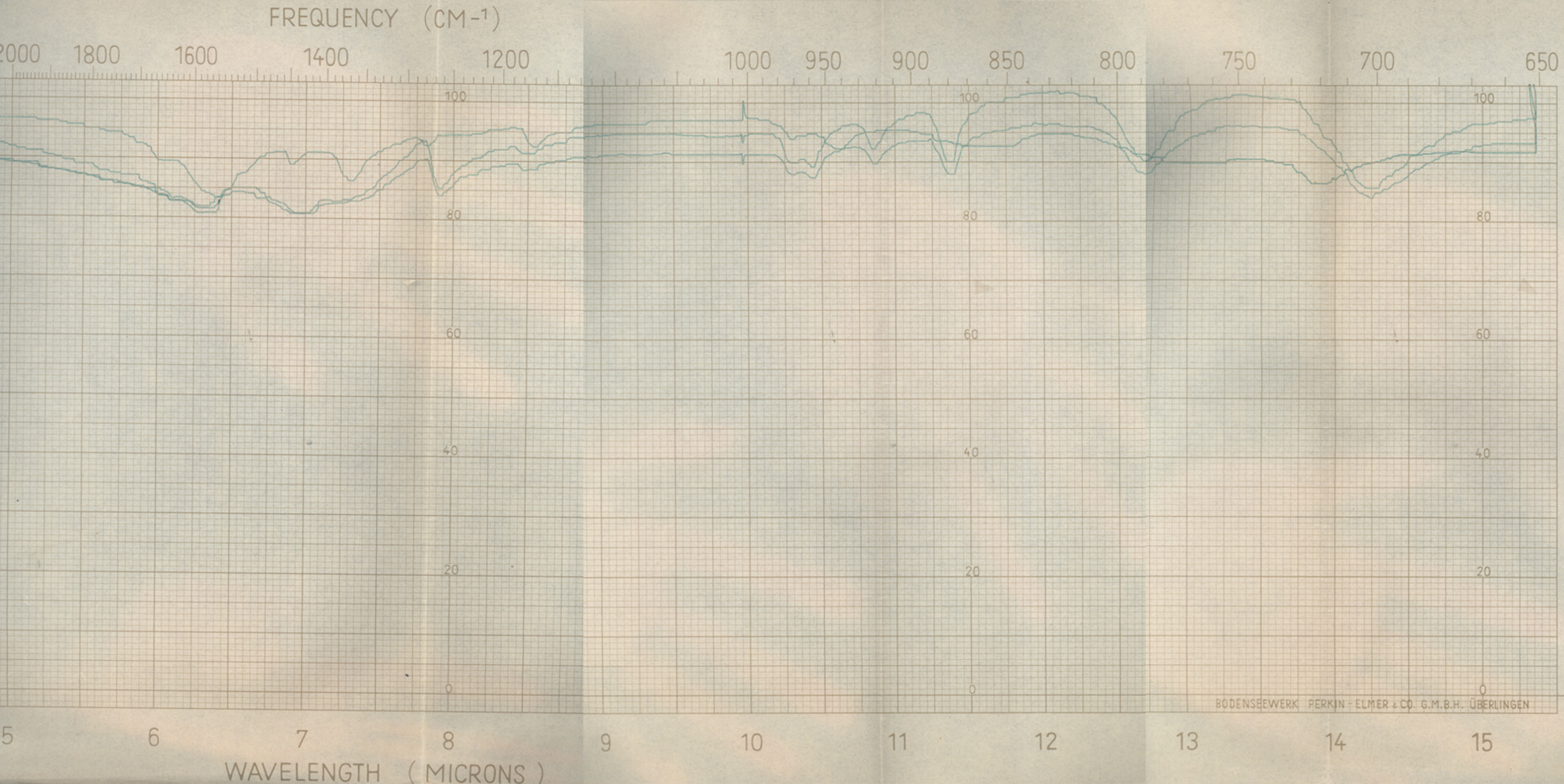

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SPECTRUM NO:
SAMPLE
ORIGIN
PURITY
PHASE
THICKNESS
1.
2.
3.
DATE
OPERATOR
REMARKS

PRISM
RESOLUTION
RESPONSE
GAIN
SPEED
SUPPRESSION
SCALE

Nº:021-6319