"OXIME DERIVATIVES OF ACETOPHENONES AS CHELATING AND ANALYTICAL REAGENTS"

Thesis submitted for the award of the degree
of
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in
Chemistry

By
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CERTIFICATE

Certified that the thesis entitled " OXIME DERIVATIVES OF ACETOPHENONES AS CHELATING AND ANALYTICAL REAGENTS", which is being submitted by Sri Banarsi Dass Gupta, for the award of the degree of DOCTOR OF PHILOSOPHY in Chemistry, at the University of Roorkee, is a record of his own work under my supervision and guidance. The matter embodied in this thesis, has not been submitted for the award of any other degree of any University.

This is, further, to certify that he has worked for a period of two years to prepare this thesis.

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GENERAL INTRODUCTION

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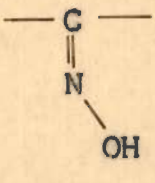
GENERAL INTRODUCTION

The importance of organic compounds as analytical reagents, is well recognised. Of surpassing value as analytical reagents, are the compounds which are capable of forming chelates particularly inner-complex salts or chelate non-electrolytes, with metals. Certain oximes, e.g., orthodioximes, acyloin-oximes, ortho-hydroxy aromatic oximes monoximes of diketones etc. belong to this class of organic reagents.

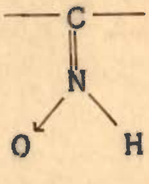
Ortho-dioximes :

The reaction between nickel salts and dimethyl-glyoxime[1], $CH_3-C(=NOH)-C(=NOH)-CH_3$, the often quoted example of ortho-dioximes, takes place through the central group, $-C(=NOH)-C(=NOH)-$, resulting in the formation of brilliant red, insoluble nickel chelate. The replacement of the methyl groups by other aliphatic, aromatic or hetero-cyclic groups, does not prevent the formation of similar nickel compounds. The composition $(C_4H_7O_2N_2)_2Ni$ of the nickel-dimethylglyoxime indicates that one of the hydrogen atoms of each of the two molecules of dimethylglyoxime, $C_4H_8O_2N_2$, has been replaced by the bivalent nickel atom.

Following the demonstration of the existence of two tautomeric forms of the oxime group[2],

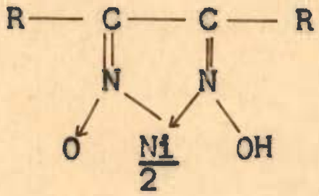


Oxime form

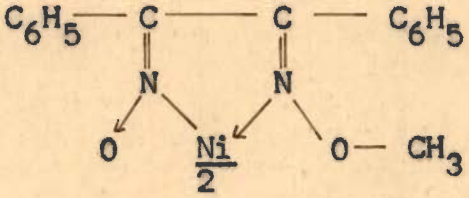


Nitrone form

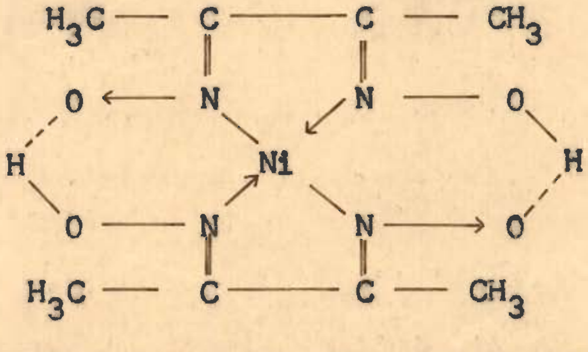
Pfeiffer[3,4] proposed that the nitrone form is involved in the formation of the nickel derivative and a five-membered ring is formed in which the nickel is attached directly to the nitrogen atom.



That the hydroxyl radical of the second oxime group is not involved in the formation of the metal complex, is further demonstrated by the fact that mono-O-ether of benzildioxime forms an exactly similar compound with nickel[4,5]



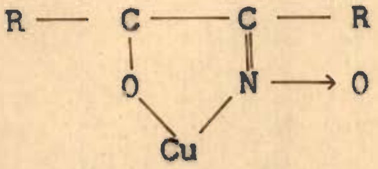
Brady and Meurs[5] have proposed the following formula for nickel dimethylglyoxime,



The postulated hydrogen bonding eliminates the possibility of cis-trans isomerism and also explains the lack of reactivity of the hydroxyl group.

Acyloin oximes :

The mode of reaction of acyloin oximes containing the group >C(OH)- C(= NOH)-, with metals is different. Available evidence seems to indicate that α-acyloin oximes react as dibasic acids towards cupric salts to form compounds of the type,



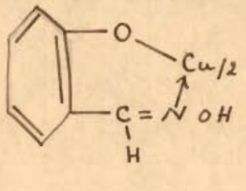
Under special conditions α-benzoinoxime forms compounds with cobalt, nickel and with bivalent platinum and palladium, but in the formation of these compounds, the oxime functions as monobasic acid[6].

Ortho-hydroxy aromatic oximes :

Ortho hydroxyaromaticoximes, however, differ from th ortho-dioximes and acyloinoximes, in their reactions with metals. In these phenolic compounds of unusual analytical importance, the hydroxyl group is so located with respect to the nitrogen atom of the oxime group that six-membered rings instead of five-membered (as in the case of ortho - dioximes and acyloinoximes), are formed with metals. The structures of the metal compounds of hydroxyarometicoximes have, however, not yet been systematically investigated, although quite a few references dealing with their applications in analytical chemistry, are available in the literature. The need of investigating the structure of these metal complexes as well as the desirability of finding new reactions of analytical importance, exist. Before proceeding further with this aspect, a brief survey of the existing literature is desirable.

Most of the salts of hydroxyaldoximes are insoluble in water and consequently adaptable to the detection and determination of numerous cations. Inorder to increase the selectivity and sensitivity of these reactions, many derivatives have been prepared and studied. The most readily available compound of this class is salicylaldoxime.

Ephraim[7], for the first time, used this compound for the detection and gravimetric determination of copper. The following structures for the copper-salicylaldoxime, based on the replacement of the hydrogen atom of either acidic phenolic or the oxime group by the metal and coordination of the metal to the other group resulting in the formation of typical inner-complex were proposed,



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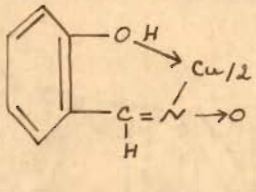
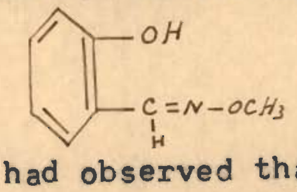
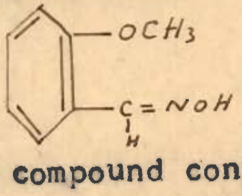


Feigl and Bondi[8] while investigating the reactions of the isomeric methyl ethers of salicylaldoxime





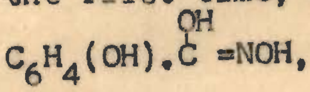
with copper, had observed that the compound containing the free hydroxyl group reacted with copper to form a dark brown salt, while the isomeric phenolic ether did not react and hence reached the conclusion that the phenolic hydrogen was replaced by the metal. Ephraim[9] had studied the reactions of a number of other compounds which contain the same reactive grouping as salicylaldoxime.

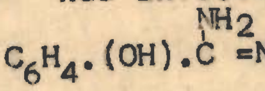
The presence of the group $HO-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}=NOH$ in o-hydroxyaldoximes, is not in itself sufficient to yield a specific copper reaction. For example, pentanol-2-one-4-oxime, $CH_3-CH(OH)-CH_2-C(=NOH)-CH_3$ and chloral acetophenone-oxime, $CCl_3-CH(OH)-CH_2-C(=NOH)-C_6H_5$, containing the same grouping, neither yield insoluble copper salts nor characteristic colour reactions with copper. In fact, the enhanced acidity of the hydroxyl group because of its linkage to the aromatic ring and lack of any steric hinderance between the $=NOH$ and the $-OH$ group, are responsible for the copper specific action of the group $HO-C_6H_4-C(=NOH)-$.

Flagg and Furman[10] had made a detailed study of the reactions of many ions with salicylaldoxime and found that positive reactions were obtained in many cases. The same authors had also studied the effect of introducing a halogen atom or nitro-group into the salicylaldoxime and had found that the resulting derivatives offered no special advantages as analytical reagents, over the parent compound. The colours of certain metal salts of the 5-nitro-oxime, however, were more vivid than those of the corresponding metal compounds with salicylaldoxime.

Salicylaldoxime has also been found to be useful for the quantitative determination of lead[11,12], palladium[13,14], iron[15], nickel[16] and bismuth[17].

Resorcylaldoxime (2,4-dihydroxybenzaldoxime) yields a purple colour with ferric iron in slightly acidic solution and this reaction may be used for the detection and colorimetric determination of ferric iron.

Musante[18], for the first time, introduced salicylhydroxamic acid,  $C_6H_4(OH).\overset{OH}{C}=NOH$, as an analytical reagent and studied its nickel and cobalt salts. Subsequently Bhaduri[19] had studied the qualitative reactions of this compound with various other metallic ions. Bhaduri and Ray[20,21] had also suggested the application of this compound for the colorimetric estimation of uranium, molybdenum, vanadium and ferric iron.

Bandyopadhayay and Ray[22] had investigated the reactions of salicylamidoxime,  $C_6H_4.(OH).\overset{NH_2}{C}=NOH$, with a number of metallic ions. They observed that salicylamidoxime resembled salicylaldoxime, in its general behaviour, with respect to the colour, solubility etc. of its metallic derivatives but the pHs of incipient precipitation of metals with salicylamidoxime are somewhat higher.

Poddar[23] studied the reactions of o-hydroxyacetophenoneoxime, an aryl hydroxyketoxime, with a number of metallic ions such as Ag^+, Hg^{++}, Pb^{++}, Cu^{++}, Cd^{++}, Zn^{++}, Fe^{++}, Fe^{+++}, Ce^{+++}, Ni^{++}, Mn^{++}, Ti^{++++}, Co^{++}, Uo_2^{++}, Vo_3^- and MoO_4^{--}. He also studied the application of this compound as an analytical reagent and employed it successfully for the gravimetric estimation of copper[24], nickel[24], palladium[25], vanadium[26], titanium[27] and for colorimetric estimation of uranium[28], vanadium[29] and ferric iron[30].

Appala and Neelkantam[31] employed successfully resacetophenoneoxime as an analytical reagent for quantitative separation of copper and cadmium. Bhatki[32] employed this reagent for the gravimetric estimation of nickel. Reddy[33] used this reagent for the amperometric determination of copper in the presence of cadmium and nickel.

Singh and Sharma[34] studied the reactions of 2-hydroxy-5-methyl acetophenoneoxime with various metallic ions and also successfully carried out the quantitative estimations of nickel and copper and their separation when present in the same solution, with this reagent.

The Problem :

The above survey of the existing literature supports the view point that much remains to be investigated so far as the structural and analytical aspects of the chemistry of metal-dihydroxy aldoximes, is concerned. The present studies were planned with an aim to study the structure and analytical uses of some soluble and insoluble metal complexes of hydroxy acetophenoneoximes. The soluble complexes were exploited for colorimetric estimation while insoluble complexes were made the basis for the amperometric estimation of these metals.

The investigations may roughly be divided under the following heads :-

(1) Reactions of Mo(VI) with the oximes of o-hydroxyacetophenone and its derivatives namely 2-hydroxy-5-methyl acetophenone and 2,5-dihydroxyacetophenone.

(2) Colorimetric estimation of molybdenum using 2,5-dihydroxyacetophenoneoxime as a colorimetric reagent.

(3) Reactions of copper(II), palladium(II) and nickel(II) with the oximes of hydroxyacetophenones mentioned above.

(4) Amperometric determination of copper, palladium and nickel with 2,5-dihydroxyacetophenoneoxime.

(5) Reactions of uranium and thorium(IV) with 2-hydroxy-5-methyl acetophenone.

The composition and structure of the chelates formed in the above reactions, were determined using spectrophotometric (in the case of soluble complexes), conductometric, amperometric, pH metric methods, chemical analysis and I.R. studies.

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CHAPTER I

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" Metal complexes of o-hydroxyacetophenoneoxime "

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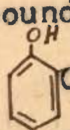
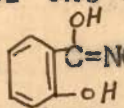
INTRODUCTION

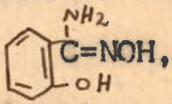
The aryl aldoximes containing an ortho-hydroxyl group, are capable of forming chelate compounds. Best known example of this class is salicylaldoxime 

CH=NOH, which was first employed by Ephraim[1] for the detection and gravimetric determination of copper. Ephraim[2] has also studied the reactions of a number of compounds which contain the same atomic grouping, HO-C-C-C=NOH, as salicylaldoxime and has found that all of them give yellowish copper salts. None of these seems to offer any special advantage over the more readily available salicylaldoxime, but their reactions illustrate the selective or specific action of certain atomic groupings. Subsequently Flagg and Furman[3] studied the reactions of salicylaldoxime and also of its 5-chloro-,3,5-dibromo-and 5-nitro-derivatives, with various metal ions. Since then several papers have appeared on the use of salicylaldoxime for the separation and determination of metals.

Musante[4], for the first time, introduced salicylhydroxamic acid, 

C=NOH, as an analytical reagent and studied its nickel and cobalt salts. Later on Bhaduri[5,6] studied its qualitative reactions with various other metallic ions and suggested this reagent for the colorimetric estimation of uranium, molybdenum, vanadium and ferric iron. He also investigated the composition of the molybdenum complex of salicylhydroxamic acid, employing spectrophotometric method and reported the existence of two complexes, $H_2MoO_2X_2$ or

H_2MoO_3X, depending upon the concentration in the pH range 6.6-7.2.

Bandyopadhayay and Ray[7] investigated the reactions of a number of metallic ions with salicylamidoxime, 

and compared the results of their investigations with those of Flagg and Furman (loc.cit.). They found that salicylamidoxime resembled the salicylaldoxime, in its general behaviour, with respect to the colour, solubility etc. of its metallic derivatives but the pHs of the incipient precipitation of metals with salicylamidoxime were somewhat higher.

Poddar[8] studied the qualitative reactions of orthohydroxyacetophenoneoxime, an aryl o-hydroxy-ketoxime, with a number of metallic ions such as Ag^+, Cu^{++}, Cd^{++}, Zn^{++}, Fe^{++}, Fe^{+++}, Ce^{+++}, Ni^{++}, Co^{++}, Mn^{++}, Ti^{++++}, Uo_2^{++} and MoO_4^{--}. He also studied the application of this compound as an analytical reagent and employed it successfully for the gravimetric estimation of copper and nickel[9], palladium[10], vanadium[11], titanium[12] and for colorimetric estimation of uranium[13], vanadium[14] and ferric iron[15].

From the existing literature surveyed as above, it is quite apparent that although ortho-hydroxyacetophenoneoxime has been employed for the quantitative estimation of few metals, no attempt has, so far, been made to study the nature and composition of the resulting complexes. With this aim in view, the physico-chemical studies on the soluble (in the case of molybdenum) and insoluble complexes (copper, nickel and palladium) were considered worth investigating.

The investigations carried out for the determination of the composition of the said complexes consisted of:

(1) Spectrophotometric studies on the composition of soluble complex of molybdenum (VI),

(2) Conductometric titrations on the composition of the complexes of molybdenum, copper, nickel and palladium.

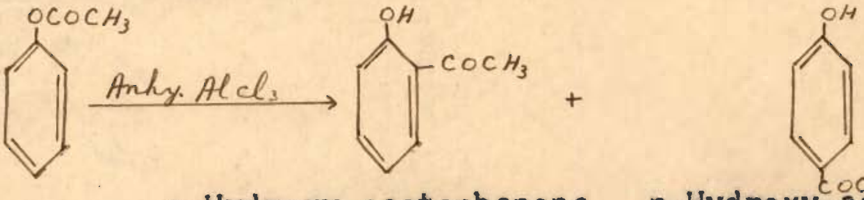
(3) Amperometry of the copper, nickel and palladium complexes.

(4) Chemical analysis and I.R. spectra of the isolated complexes.

EXPERIMENTAL

Preparation of o-hydroxy-acetophenone :-

o-Hydroxy-acetophenone was prepared by Fries reaction[16] on treating phenyl acetate with anhydrous aluminium chloride.



o-Hydroxy-acetophenone   p-Hydroxy-acetophenone

187 gm. of anhydrous aluminium chloride and 200 ml. of carbon disulphide were placed in one litre, three-necked flask fitted with a dropping funnel, a stirrer and a reflux condenser. The suspension was stirred and 170 gm. (158 ml.) of phenyl acetate were added slowly at such a rate that the solvent boiled vigorously. When all the phenyl acetate had been added, the reaction mixture was gently refluxed on a water bath for about two hours until the evolution of hydrogen chloride ceased. The solvent was distilled off the reaction mixture which was then placed in an oil-bath maintained at 140-150°C, for three hours. The contents of the flask got thickened and finally became a brown resinous mass which was cooled, treated with 1:1 hydrochloric acid and allowed to stand overnight. The contents were further treated with benzene to extract both ortho-and para-hydroxy-acetophenones. The benzene layer was separated, dried over anhydrous magnesium sulphate and benzene was then distilled off, leaving behind a mixture of ortho-and para-hydroxy-acetophenones which was subjected to steam distillation. The

ortho-hydroxy-acetophenone, being volatile in steam, distilled off, leaving behind para-isomer in the distillation flask.

Preparation of ortho-hydroxy-acetophenoneoxime :-

It was prepared by refluxing 1 gm. of o-hydroxy-acetophenone with 1 gm. hydroxylamine hydrochloride and 2 gm. sodium acetate, over water bath for 1 hour. On cooling the solution, o-hydroxy-acetophenoneoxime separated out. The compound was recrystallized from alcohol (white crystals, m.p. 114-116°C).

The solution of the oxime was prepared in 50% alcohol.

Copper sulphate :-

Copper sulphate (B.D.H) of A.R. quality was used for the preparation of stock solution of copper. The strength of the solution was determined iodometrically[17].

Palladium chloride :-

1 gm. of palladium chloride (Johnson Matthey, London) was dissolved in 2 ml. of conc. hydrochloric acid and the solution was diluted to 100 ml. with double distilled water. The strength of the solution was determined gravimetrically as palladium-dimethyl glyoxime[18].

Nickel sulphate :-

Nickel sulphate (B.D.H., A.R.) was used to prepare the stock solution of nickel. The strength of the solution was determined gravimetrically as nickel - dimethyl-glyoxime[19].

Ammonium molybdate :-

A stock solution of molybdenum (VI) (approx. 0.02M) was prepared by dissolving ammonium molybdate (E.Merck) in double distilled water. The molybdenum content was determined gravimetrically as lead molybdate[20].

Weaker solutions of desired concentrations were obtained by diluting the stock solutions with double distilled water.

Gelatine solution :-

0.1% gelatine (E.Merck) solution was prepared in hot double distilled water.

Buffer solutions :-

Sodium acetate-acetic acid buffers[21] (Walpole) of pH 4.0 and 4.6 and ammonia-ammonium chloride buffer of pH 9.0 were prepared.

All pH measurements were carried out with a Beckman pH meter (Model H), previously standardized with phthalate buffer of pH 4.0 and borax buffer of pH 9.1.

Isolation and chemical analysis of Molybdenum-o-hydroxy-acetophenoneoxime complex :-

Ammonium molybdate and o-hydroxy-acetophenoneoxime solutions were mixed in 1:2 molar ratio respectively. The pH of the mixture solution was adjusted to 3.5-4.5.

The solution was concentrated under vacuum when yellow crystals of molybdenum complex separated out. The yellow crystals were filtered on a sintered crucible and washed with alcohol to remove the adhering ligand if any. The isolated complex was dried in a vacuum dessicator.

For estimation of molybdenum content, a weighed quantity of dried sample of the complex was heated with aqua-regia to decompose the organic matter. To this solution was added concentrated sulphuric acid and the mixture was evaporated to dryness. The residue was extracted with ammonia and molybdenum was estimated gravimetrically as molybdenum oxinate[22].

The estimation of nitrogen content in the complex was carried out, using Kjeldahl's method[23]. A weighed quantity (0.1 gm.) of the complex was Kjeldahlized and the ammonia evolved was absorbed in 50 ml. of decinormal sulphuric acid. The ammonia evolved was found out from the back titration of unreacted sulphuric acid against decinormal sodium hydroxide. Knowing the volume of ammonia evolved, the percentage of nitrogen was calculated.

Calculated for bis(O-hydroxy-acetophenoneoxime)MoO_2

$(C_8H_8O_2N)_2MoO_2$

N - 6.55, Mo - 22.42

Found : N - 6.8 , Mo - 23.0

Spectrophotometric studies of the Molybdenum(VI)complex :-

Molybdenum(VI) complex was studied spectrophotometrically. Job[24] has developed a method called "the method of continued variation" for determining the composition of complexes.

Job's method of continued variation is applicable to the systems involving the formation of only one complex and is not useful to those in which more than one complexes are formed. Vosburgh and Cooper[25] extended this method particularly to deal with such cases. They have shown that the results are independent of the wave length of light used only when a single complex is formed while in a system with more than one complexes, wave length of light plays an important role and a careful selection of wave lengths for different complexes is required while studying the complex ion formation. These authors have studied the complexes of Ni(II) with o-phenanthroline and ethylenediamine formed in 1:1, 1:2 and 1:3 proportions and copper ammonia complexes (Cu^{++}: NH_3 as 1:2 and 1:4) to prove their view point.

Another method which is common with spectrophotometric measurements is the "slope ratio method[26]". This method is helpful in two ways;it provides confirmation of the results of Job's method of continued variation and also helps in establishing the composition of the complex.

In the reaction

$$mA + nB \rightleftharpoons A_mB_n$$

if the concentration of B is kept constant and in sufficient excess to make dissociation negligible, the equilibrium concentration of the complex A_mB_n will be essentially proportional to the analytical or total concentration of A added in the reaction; so

$$(A_mB_n) = C_{A/m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where the brackets refer to the equilibrium concentration and C to the analytical or total concentration.

From Beer's law

$$E = ed.\ (A_mB_n) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where E is the measured extinction, e, the molecular extinction coefficient and d, the thickness of the cell in cm. Substituting the value of (A_mB_n) from (1) into (2).

$$E = ed.\ C_{A/m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

E is plotted against different analytical (or total) concentrations of A, keeping the concentration of B constant and in excess. The equation (3) is valid over the straight line portion of the curve and this straight line will have a slope given by

$$\text{slope}_1 = ed/m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Similarly if A is the component in constant excess and the concentration of B is varied

$$(A_mB_n) = C\ B/n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

and if E is plotted against C_B, the slope of the straight line portion of the curve will be

$$\text{Slope}_2 = ed/n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

The ratio of n to m in the complex may be determined by taking the ratio of the two slopes.

$$\text{Slope}_1 / \text{slope}_2 = n/m$$

Nature of the complex :-

Vosburgh and Cooper's method (loc.cit.) was applied to determine the number of complexes formed in solution by the interaction of o-hydroxy-acetophenoneoxime (designated hereafter as H.A.O) and ammonium molybdate.

Ammonium molybdate and H.A.O, both of concentration 1×10^{-3}M, were mixed in the following ratios :

	1:1	1:2	1:3	2:1	3:1	
MoO_4^{--}	6.0	4.0	3.0	8.0	9.0	ml.
H.A.O.	6.0	8.0	9.0	4.0	3.0	ml.

All absorption measurements were made with Bausch and Lomb "spectronic 20", after allowing sufficient warming up period for the instrument.

Table - 1

Vosburgh Cooper's method applied to Mo- H.A.O.complex

Concentration of ammonium molybdate = 1×10^{-3}M
Concentration of H.A.O. = 1×10^{-3}M

Wave length (mμ)	optical density Ratio of ammonium molybdate to H.A.O.				
	1:1	1:2	1:3	2:1	3:1
325	0.30	0.53	0.72	0.27	0.20
330	0.32	0.55	0.77	0.29	0.22
335	0.36	0.59	0.82	0.32	0.24
340	0.40	0.63	0.88	0.34	0.26
345	0.43	0.67	0.93	0.37	0.28
350	0.38	0.58	0.83	0.325	0.245
355	0.33	0.52	0.75	0.28	0.21
360	0.29	0.46	0.66	0.245	0.185
365	0.24	0.40	0.585	0.21	0.155
370	0.21	0.35	0.52	0.18	0.13
375	0.18	0.30	0.47	0.16	0.12
380	0.16	0.27	0.41	0.13	0.09
390	0.13	0.21	0.32	0.10	0.07
400	0.10	0.16	0.26	0.08	0.055
	Curve(a)	Curve(b)	Curve(c)	Curve(d)	Curve(e)

Fig. 1

The maximum absorbance of the mixtures occurs at 345 mμ.

Influence of pH on stability of the complex :-

In order to study the influence of pH on the complex formation, a series of solutions containing 4.0 ml. of ammonium molybdate and 8.0 ml. of H.A.O, both of concentration 2×10^{-3}M, were adjusted to different pH values and the total volume was made up to 25 ml. The optical density of these solutions was measured over a range of wave lengths (325-400 mμ).

Table - 2

Wave length (mμ)	O.D. of 1:2 Mo- H.A.O mixture at different pHs						
	2.5	3.0	3.5	4.0	4.5	5.0	5.5
325	0.44	0.47	0.50	0.52	0.53	0.36	0.1
330	0.48	0.50	0.52	0.55	0.55	0.40	0.13
335	0.50	0.52	0.57	0.59	0.59	0.44	0.16
340	0.55	0.56	0.61	0.63	0.63	0.47	0.19
345	0.58	0.61	0.65	0.66	0.66	0.50	0.23
350	0.48	0.50	0.55	0.57	0.56	0.44	0.18
360	0.38	0.40	0.43	0.45	0.44	0.33	0.13
370	0.29	0.31	0.33	0.33	0.35	0.25	0.09
380	0.21	0.23	0.25	0.25	0.25	0.16	0.06
390	0.15	0.17	0.18	0.19	0.20	0.10	0.06
400	0.11	0.13	0.14	0.15	0.15	0.05	0.02
Curves	(a)	(b)	(c)	(d)	(e)	(f)	(g)

Fig. 2 a.

The λmax of the complex occurs at 345 mμ in the pH range (2.5-5.5).

Composition of the complex :-

For determining the composition of the complex by Job's method of continued variation, following sets of mixtures were prepared:

Set I

1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 ml.

of ammonium molybdate were mixed with 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0, 1.0 ml. of H.A.O. respectively; the initial concentration of both the reactants was 5×10^{-3}M. The pH of the mixtures was adjusted to 4.0-4.5 and the final volume was made up to 25 ml. with double distilled water.

Set II

Initial concentration of the reactants being 3.33×10^{-3}M, all other details were the same as in Set I.

Set III

Initial concentrations of the reactants was 2.5×10^{-3}M.

The optical density measurements of the mixtures were made at 345 mμ, 350 and 360 mμ. Curves were plotted of the difference between the optical density of the mixture and that of ammonium molybdate and H.A.O against the ratio $(MoO_4^{--})/(MoO_4^{--}) + (H.A.O)$.

The observations are summarized in the following tables :

Table -3

Wave length 345 mμ

Final concentration of the reactants = 2×10^{-3}M

Vol. of ammonium molybdate (ml.)	Vol.of H.A.O. (ml.)	Optical density			
		Mixture	H.A.O.	Amm.molybdate	Difference
1.0	9.0	0.94	0.03	0.02	0.89
2.0	8.0	1.1	0.02	0.03	1.05
3.0	7.0	1.155	0.015	0.04	1.1
4.0	6.0	1.1	0.01	0.045	1.045
5.0	5.0	0.96	0.005	0.05	0.905
6.0	4.0	0.77	0.00	0.06	0.71
7.0	3.0	0.62	0.00	0.07	0.55
8.0	2.0	0.44	0.00	0.08	0.36
9.0	1.0	0.27	0.00	0.09	0.18

Fig.3, curve 1

Table -4

Wave length 345 mμ

Final concentration of the reactants = 1.333×10^{-3}M

Vol.of Amm.molybdate (ml.)	Vol.of H.A.O. (ml.)	Optical density			
		Mixture	H.A.O.	Amm.molybdate	Difference
1.0	9.0	0.56	-	0.01	0.55
2.0	8.0	0.68	-	0.02	0.66
3.0	7.0	0.74	-	0.025	0.715
4.0	6.0	0.68	-	0.03	0.65
5.0	5.0	0.60	-	0.035	0.565
6.0	4.0	0.49	-	0.04	0.45
7.0	3.0	0.37	-	0.05	0.32
8.0	2.0	0.27	-	0.06	0.21
9.0	1.0	0.15	-	0.06	0.09

Fig.3, curve 2

Wave length 345 mμ

Table - 5

Final concentration of the reactants = 1×10^{-3}M

Vol. of amm.molybdate (ml.)	Vol. of H.A.O. (ml.)	Optical density			
		Mixture	H.A.O.	Amm.molybdate	Difference
1.0	9.0	0.37	-	0.0	0.37
2.0	8.0	0.49	-	0.01	0.48
3.0	7.0	0.51	-	0.01	0.50
4.0	6.0	0.475	-	0.015	0.46
5.0	5.0	0.39	-	0.02	0.37
6.0	4.0	0.33	-	0.03	0.30
7.0	3.0	0.25	-	0.04	0.21
8.0	2.0	0.18	-	0.05	0.13
9.0	1.0	0.09	-	0.05	0.04

Fig. 3, curve 3

Wave length 350 mμ

Table - 6

Final concentration of the reactants = 2×10^{-3}M

Vol. of Amm.molybdate (ml.)	Vol. of H.A.O. (ml.)	Optical density			
		Mixture	H.A.O.	Amm. molybdate	Difference
1.0	9.0	0.855	-	0.005	0.85
2.0	8.0	1.0	-	0.01	0.99
3.0	7.0	1.05	-	0.015	1.035
4.0	6.0	1.0	-	0.02	0.98
5.0	5.0	0.855	-	0.025	0.83
6.0	4.0	0.68	-	0.03	0.65
7.0	3.0	0.53	-	0.04	0.49
8.0	2.0	0.36	-	0.05	0.31
9.0	1.0	0.20	-	0.05	0.15

Fig. 4, curve 1

Table - 7

Wave length 350 mμ

Final Concentration of the reactants = 1.333×10^{-3}M

Vol. of amm.molybdate (ml.)	Vol. of H.A.O. (ml.)	Optical density			
		Mixture	H.A.O.	Amm. molybdate	Difference
1.0	9.0	0.50	-	0.0	0.50
2.0	8.0	0.61	-	0.01	0.60
3.0	7.0	0.63	-	0.01	0.62
4.0	6.0	0.60	-	0.015	0.585
5.0	5.0	0.52	-	0.02	0.50
6.0	4.0	0.41	-	0.025	0.385
7.0	3.0	0.32	-	0.03	0.29
8.0	2.0	0.22	-	0.035	0.185
9.0	1.0	0.11	-	0.04	0.07

Fig. 4, curve 2

Wave length 350 mμ

Table - 8

Final Concentration of the reactants = 1×10^{-3}M

Vol. of Amm.molybdate (ml.)	Vol. of H.A.O. (ml.)	Optical density			
		Mixture	H.A.O.	Amm. molybdate	Difference
1.0	9.0	0.32	-	0.0	0.32
2.0	8.0	0.40	-	0.0	0.40
3.0	7.0	0.44	-	0.01	0.43
4.0	6.0	0.39	-	0.01	0.38
5.0	5.0	0.35	-	0.02	0.33
6.0	4.0	0.29	-	0.02	0.27
7.0	3.0	0.21	-	0.025	0.185
8.0	2.0	0.15	-	0.03	0.12
9.0	1.0	0.085	-	0.03	0.05

Fig. 4, curve 3

Table - 9

Wave length 360 mμ

Final Concentration of the reactants = 2x10^{-3}M

Vol. of amm.molybdate (ml.)	Vol.of H.A.O (ml.)	Optical density			
		Mixture	H.A.O.	Amm. molybdate	Difference
1.0	9.0	0.695	-	0.0	0.695
2.0	8.0	0.82	-	0.0	0.82
3.0	7.0	0.855	-	0.0	0.855
4.0	6.0	0.77	-	0.0	0.77
5.0	5.0	0.68	-	0.01	0.67
6.0	4.0	0.52	-	0.01	0.51
7.0	3.0	0.40	-	0.01	0.39
8.0	2.0	0.27	-	0.02	0.25
9.0	1.0	0.14	-	0.02	0.12

Fig. 5, Curve 1

Table - 10

Wave length 360 mμ

Final Concentration of the reactants

Set II = 1.333x10^{-3}M; Set III = 1x10^{-3}M

Volume of Amm.molybdate (ml.)	Vol. of H.A.O. (ml.)	Optical density	
		Set II mixture	Set III mixture
1.0	9.0	0.40	0.24
2.0	8.0	0.48	0.30
3.0	7.0	0.495	0.34
4.0	6.0	0.45	0.30
5.0	5.0	0.40	0.27
6.0	4.0	0.31	0.22
7.0	3.0	0.24	0.145
8.0	2.0	0.16	0.10
9.0	1.0	0.08	0.055

Fig.5, Curve 2 Fig.5, Curve 3

The optical density of ammonium molybdate and H.A.O. was negligible in Set II and Set III at 360 mμ.

Slope ratio method :

The composition of the complex was further investigated by slope ratio method (loc.cit.). Two series of solutions were prepared. In one series, the concentration of amm. molybdate was varied in the presence of constant excess of H.A.O; in the other series H.A.O was varied while ammonium molybdate was kept constant.

Absorbance was measured at 345 mμ and 350 mμ.

Table - 11

Fixed concentration of H.A.O. = 8×10^{-4}M (in 25 ml.)
Initial concentration of Amm. molybdate added =1×10^{-3}M

pH of the solutions = 4-4.5
Final volume = 25 ml.

Vol. of Amm. molybdate (ml.)	Optical density	
	345 mμ	350 mμ
0.0	0.03	0.02
1.0	0.15	0.13
2.0	0.25	0.22
3.0	0.36	0.30
4.0	0.46	0.40
5.0	0.52	0.45
6.0	0.59	0.49
	Fig. 6, curve 1	Fig. 7, Curve 1

Table - 12

Fixed concentration of Amm. molybdate = 8×10^{-4}M (in 25 ml.)

Initial conccentration of H.A.O. added = 1×10^{-3}M

pH of the solutions = 4-4.5

Final volume = 25 ml.

Vol. of H.A.O. (ml.)	Optical density at	
	345 mμ	350 mμ
0.0	0.02	0.015
1.0	0.06	0.045
2.0	0.12	0.10
3.0	0.17	0.15
4.0	0.23	0.19
5.0	0.28	0.24
6.0	0.34	0.30
7.0	0.39	0.35
8.0	0.44	
	Fig.6,Curve 2	Fig.7, Curve 2

Table - 13

Fixed concentration of H.A.O. = 4×10^{-4} (in 25 ml.)

Initial concentration of Amm.molybdate added = 5×10^{-4}M

pH of the solutions = 4-4.5

Final volume = 25 ml.

Vol.of Amm. molybdate (ml.)	Optical density at	
	345 mμ	350 mμ
0.0	0.0	0.0
1.0	0.035	0.03
2.0	0.085	0.07
3.0	0.10	0.09
4.0	0.14	0.125
5.0	0.16	0.14
6.0	0.17	0.15
7.0	0.22	0.19
8.0	0.24	0.20
	Fig.6, Curve 3	Fig.7,Curve 3

Table - 14

Fixed concentration of Amm. molybdate = $4\times10^{-4}M$ (in 25 ml.)
Initial concentration of H.A.O. added = $5\times10^{-4}M$
pH of the solutions = 4-4.5
Final volume = 25 ml.

Vol. of H.A.O. (ml.)	Optical density at	
	345 mμ	350 mμ
0.0	0.025	0.02
1.0	0.04	0.03
2.0	0.04	0.03
3.0	0.055	0.045
4.0	0.07	0.05
5.0	0.07	0.055
6.0	0.09	0.07
7.0	0.105	0.09
8.0	0.11	0.095
9.0	0.13	0.105
	Fig. 6, Curve 4	Fig.7, Curve 4

Formation constant of the complex :-

A number of useful methods are known for the calculation of formation constant of the complexes. The method, described by Anderson et al[27], based on the comparison of the composition of the solutions having identical intensity of colour, i.e., the same absorbance value, has been found very convenient. The limitation of this method is that both the reactants must be colourless. The method was subsequently modified by Dey and co-workers[28] who were able to apply this method to the system where one of the reactants was coloured. This method has, therefore, a much wider application and may be employed conveniently for the study of a large number of complex ion formation reactions. In this method, the absorbance data obtained for Job's method of continued variation, are utilised and the observed absorbance of the mixture solution (not the difference in absorbance) is plotted against (M)/(M)+(A) where (M) is the concentration of the metal ion and (A) that of the complexing agent. The formation constant of the molybdenum - H.A.O. complex was calculated as follows :

Consider the reaction

$$MoO_4^{--} + 2\ H.A.O. \rightleftharpoons MoO_4\ (H.A.O)_2$$

if x represents the concentration of the complex at equilibrium and a and b, the concentrations initially present of the MoO_4^{--} ions and H.A.O respectively, the formation constant is given by

$$K = \frac{x}{(a-x)\ (b-2x)^2} \qquad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

Taking two values of a and b for the solutions showing the same absorbance, i.e., the same value of x, we have

$$K = \frac{x}{(a_1-x)\ (b_1-2x)^2} = \frac{x}{(a_2-x)\ (b_2-2x)^2} \quad \ldots\ (2)$$

$$\text{or } x = \frac{-\left[(b_2^2-b_1^2)+4(a_2b_2-a_1b_1)\right] \pm \sqrt{\left[(b_2^2-b_1^2)+4(a_2b_2-a_1b_1)\right]^2 - 16\left[(a_1+b_1)-(a_2+b_2)\right](a_1b_1^2-a_2b_2^2)}}{8\left[(a_1+b_1)-(a_2+b_2)\right]} \quad \ldots\ldots(3)$$

Thus from equation (3), the value of x could be calculated and consequently the value of K by substituting the value of x in equation (1).

For determining the value of formation constant, the absorbance measurements made during the Job's method of continued variation (Table 10) at 360 mμ were utilised. An arbitrary value 0.20 for absorbance was chosen on the graph (Fig.8) and the concentrations of the reactants were read from the graph in the descending portions of the curves.

Solution I - Concentration of Molybdate (a_1) = 1×10^{-3}M
Concentration of H.A.O. (b_1) = 0.333×10^{-3}M

Solution II- Concentration of Molybdate (a_2) = 6.3×10^{-4}M
Concentration of H.A.O. (b_2) = 3.7×10^{-4}M

Conductometric studies of Molybdenum (VI) complex :-

The composition of the complex of molybdenum was also established by conductometric titrations. The conductivity measurements were carried out with the help of philips magic eye type (P.R.9500) conductivity bridge, using dip type conductivity cell (K=0.44). The effect of temperature on conductance of the solution was minimized by putting the cell in a large beaker of water. Volume correction was applied by multiplying the conductance value by $\frac{V + v}{V}$ where V is the volume taken in the cell and v, the volume of the titrant added.

The titrations were carried out by taking a fixed amount of the amm. molybdate solution in the cell and adding o-hydroxy-acetophenoneoxime solution from the burette.

The reverse titrations were also carried out by taking o-hydroxy-acetephenoneoxime solution in the cell and adding amm. molybdate solution from the burette.

The observations are tabulated below :

Table - 15

Direct titrations (Amm.molybdate in the cell)

Volume of Amm. molybdate = 30 ml.

Concentration of Amm.molybdate = Set I = 1.333×10^{-3}M

Set II= 2×10^{-3}M

Set III=2.666×10^{-3}M

Concentration of H.A.O. = 2×10^{-2}M

Vol. of H.A.O. (ml.)	I Corrected conductance $\times 10^{-3}$ (mhos)	Vol.of H.A.O (ml.)	II Corrected conductance $\times 10^{-3}$ (mhos)	Vol.of H.A.O (ml.)	III Corrected conductance $\times 10^{-3}$ (mhos)
0.0	2.25	0.0	3.15	0.0	4.0
0.5	2.15	1.0	2.95	1.0	3.75
1.0	2.05	2.0	2.7	2.0	3.5
2.0	1.9	3.0	2.45	3.0	3.25
3.0	1.75	4.0	2.2	4.0	3.0
4.0	1.55	5.0	2.05	5.0	2.85
4.5	1.50	6.0	1.9	6.0	2.6
5.0	1.45	6.5	1.85	7.0	2.45
6.0	1.35	7.0	1.77	8.0	2.25
7.0	1.25	8.0	1.65	9.0	1.98
8.0	1.15	9.0	1.55	10.0	1.85
		10.0	1.45	11.0	1.75
				12.0	1.6
				13.0	1.55
				14.0	1.50
	Curve(a)		Curve(b)		Curve(c)

Fig. 9

Curve (a)

30 ml. of 1.333×10^{-3}M Amm.molybdate ≡3.9 ml.of 2×10^{-2}M H.A.O

≡58.5 ml.of 1.333×10^{-3}M H.A.O

Curve (b)

30 ml. of 2×10^{-3}M Amm.molybdate $\equiv$ 5.9 ml.of 2×10^{-2}M H.A.O.
$\equiv$ 59 ml. of 2×10^{-3}M H.A.O.

Curve (c)

30 ml. of 2.666×10^{-3}M Amm.molybdate $\equiv$ 8.2 ml.of 2×10^{-2}M H.A.O.
$\equiv$ 61.5 ml.of 2.666×10^{-3}M H.A.O.

Table - 16

Reverse titrations (H.A.O. in the cell)

Volume of o-hydroxy-acetophenoneoxime solution = 30 ml.

Concentration of o-hydroxy-acetophenoneoxime solutions = 5.333×10^{-3}M (Set I)
= 4×10^{-3}M (Set II)
= 2.666×10^{-3}M (Set III)

Concentration of Amm. molybdate = 2×10^{-2}M

	I		II		III
Vol.of Amm. molybdate (ml.)	Corrected conductance $\times10^{-3}$(mhos)	Vol. of Amm. molybdate (ml.)	Corrected conductance $\times10^{-3}$(mhos)	Vol.of Amm. molybdate (ml.)	Corrected conductance $\times10^{-3}$(mhos)
0.0	0.06	0.0	0.07	0.0	0.08
1.0	0.615	0.5	0.36	0.5	0.435
2.0	1.15	1.0	0.695	1.0	0.8
2.5	1.4	1.5	1.0	1.5	1.15
3.0	1.6	2.0	1.3	2.0	1.5
3.5	1.8	2.5	1.55	2.5	1.8
4.0	2.0	3.0	1.8	3.0	2.05
4.5	2.2	3.5	2.05	3.5	2.4
5.0	2.4	4.0	2.25	4.0	2.65
5.5	2.55	4.5	2.5	4.5	3.0
6.0	2.75	5.0	2.7	5.0	3.25
6.5	2.85	6.0	3.1		
7.0	3.0	7.0	3.5		
	Curve(a)		Curve(b)		Curve(c)

Fig. 10

Curve(a)

30 ml. of 5.333×10^{-3}M H.A.O. $\equiv$ 3.9 ml.of 2×10^{-2}M $\equiv$ 14.63 ml.of 5.333×10^{-3}M Amm.molybdate

COMPOSITION AND STRUCTURE OF COPPER(II), PALLADIUM(II) AND NICKEL (II) COMPLEXES

Isolation and chemical analysis of the complexes :-

Copper - o-hydroxy-acetophenoneoxime complex:

Copper sulphate solution was neutralized with 2N - sodium hydroxide until a slight turbidity appeared. To this turbid solution was added dilute acetic acid sufficient to obtain a clear solution. The solution was diluted and 1% alcoholic solution of o-hydroxy-acetophenoneoxime was added to it in slight excess with constant stirring. The precipitate was digested over water bath for 1 hour, filtered on a sintered glass crucible, washed with hot water and finally with dilute alcohol to ensure complete removal of excess of the reagent. The precipitate was dried at 100-110°C.

A weighed quantity of dried sample of copper complex was decomposed by heating with aqua-regia. To this solution was added concentrated sulphuric acid and the mixture was evaporated to dryness. The residue was extracted with water and copper was estimated gravimetrically as cuprous - thiocyanate[29]. The nitrogen content of the complex was estimated by Kjeldahl's method as described earlier.

Calculated for :

bis (o-hydroxy-acetophenoneoxime) Cu(II), $(C_8H_8O_2N)_2$ Cu

Cu-17.35; N-7.71

Found Cu - 17.7 N - 7.2

Palladium - o - hydroxy-acetophenoneoxime complex :-

Palladium chloride solution was treated with slight excess (a little more than 2 moles) of alcoholic solution of the oxime with constant stirring when palladium complex separated out as yellow precipitate. The precipitate was digested over water bath for half an hour, filtered, washed with hot water and finally with alcohol and dried at 100-110°C.

A weighed quantity of dry palladium complex was decomposed with aqua-regia. The resulting solution was mixed with concentrated sulphuric acid and evaporated to dryness. The residue was extracted with dilute hydrochloric acid and the palladium present in the solution was estimated gravimetrically as palladium dimethyl-glyoxime.

The nitrogen content of the complex was determined by Kjeldahl's method.

Calculated for:

bis (o-hydroxy-acetophenoneoxime) Pd(II), $(C_8H_8O_2N)_2$ Pd

Pd - 26.18, N - 6.88

Found Pd - 25.8, N - 7.2

Ni - O - hydroxy-acetophenoneoxime complex :-

To a solution of nickel sulphate was added a slight excess (a little more than two moles) of an alcoholic solution of the oxime. To this mixture solution was then added dilute ammonia when the nickel complex got precipitated. The precipitate was digested over water bath for an hour, filtered, washed thoroughly with hot water and finally with alcohol. The precipitate was dried at 100-110°C.

A weighed quantity of dry nickel complex was digested with aqua-regia. The resulting solution was mixed with concentrated sulphuric acid and evaporated to dryness. The residue was extracted with water and the nickel content was estimated gravimetrically as nickel dimethyl-glyoxime.

The nitrogen content of the complex was estimated by Kjeldahl's method as described earlier.

Calculated for :

bis (o-hydroxy-acetophenoneoxime) Ni(II), $(C_8H_8O_2N)_2Ni$

Ni - 16.36, N - 7.8

Found: Ni - 16.0, N - 7.5

Since insoluble complexes were formed with these metals, the spectrophotometric method could not be employed. Only conductometric and amperometric methods could be used to determine their compositions.

Conductometric titrations :-

The details of the titrations were the same as in the case of molybdenum complex.

The observations are summarized in the following tables :-

Conductometric titrations between copper sulphate and o-hydroxy-acetophenoneoxime.

Table - 17

Direct titrations (copper sulphate in the cell)

Volume of copper sulphate = 25 ml.

Concentration of copper sulphate = 8×10^{-4}M (Set I)

= 1×10^{-3}M (Set II)

= 1.2×10^{-3}M (Set III)

Concentration of o-hydroxy-acetophenoneoxime = 1×10^{-1}M

	I		II		III
Vol.of H.A.O. (ml.)	Corrected conductance $\times10^{-4}$(mhos)	Vol.of H.A.O. (ml.)	Corrected conductance $\times10^{-4}$(mhos)	Vol. of H.A.O. (ml.)	Corrected conductance $\times10^{-4}$(mhos)
0.0	3.8	0.0	4.7	0.0	5.6
0.1	5.8	0.1	6.7	0.1	7.5
0.2	7.7	0.2	8.8	0.2	9.5
0.3	9.5	0.3	11.0	0.3	11.5
0.4	11.2	0.4	12.5	0.4	13.4
0.5	12.2	0.5	13.9	0.5	15.2
0.6	12.5	0.6	14.6	0.6	16.3
0.7	12.9	0.7	15.1	0.7	17.5
0.8	13.2	0.8	15.5	0.8	18.2
		0.9	15.8	0.9	18.5
		1.0	16.2	1.0	18.8
				1.1	19.1
	Curve(a)		Curve(b)		Curve(c)

Fig. 11

Curve(a)

25 ml. of 8×10^{-4}M copper sulphate $\equiv$ 0.41 ml.of 1×10^{-1}M H.A.O.

$\equiv$ 51.25 ml.of 8×10^{-4}M H.A.O.

Curve(b)

25 ml. of 1×10^{-3}M copper sulphate $\equiv$ 0.49 ml.of 1×10^{-1}M H.A.O.

$\equiv$ 49 ml. of 1×10^{-3}M H.A.O.

Curve (c)

25 ml. of 1.2×10^{-3}M copper sulphate $\equiv$ 0.6 ml.of 1×10^{-1}M H.A.O.

$\equiv$ 50 ml. of 1.2×10^{-3}M H.A.O.

Table - 18

Reverse titrations (H.A.O. in the cell)

Volume of o-hydroxy-acetophenoneoxime = 25 ml.

Concentration of o-hydroxy-acetophenoneoxime = 1.6×10^{-3}M(Set I)
= 2.4×10^{-3}M(Set II)

Concentration of copper sulphate = 1×10^{-2}M

	I		II
Vol.of $CuSo_4$ (ml.)	Corrected conductance $\times 10^{-4}$(mhos)	Vol. of $CuSo_4$ (ml.)	Corrected conductance $\times 10^{-4}$ (mhos)
0.0	0.4	0.0	0.4
0.5	2.5	0.5	1.7
1.0	4.8	1.0	3.15
1.5	6.8	1.5	4.5
2.0	8.1	2.0	5.65
2.5	8.9	2.5	6.65
3.0	9.6	3.0	7.6
3.5	10.1	3.5	8.15
4.0	10.6	4.0	8.65
		4.5	9.05
		5.0	9.35
		6.0	9.75
		7.0	10.5

Curve(a) Curve(b)

Fig. 12

Curve (a)

25 ml. of 1.6×10^{-3}M H.A.O. ≡ 1.9 ml. of 1×10^{-2}M $CuSo_4$
≡ 11.9 ml. of 1.6×10^{-3}M $CuSo_4$

Curve (b)

25 ml. of 2.4×10^{-3}M H.A.O. ≡ 3.0 ml. of 1×10^{-2}M $CuSo_4$
≡ 12.5 ml. of 2.4×10^{-3}M $CuSo_4$

Conductometric titrations between palladium chloride and o-hydroxy-acetophenoneoxime

Table - 19

Direct titrations ($PdCl_2$ in the cell)

Volume of $PdCl_2$ = 25 ml.
Concentration of $PdCl_2$ solutions = 4×10^{-4}M (Set I)
= 6×10^{-4}M (Set II)
Concentration of o-hydroxy-acetophenoneoxime = 1×10^{-2}M

Vol.of H.A.O. (ml.)	I Corrected conductance$\times 10^{-2}$ (mhos)	Vol.of H.A.O. (ml.)	II Corrected conductance$\times 10^{-2}$ (mhos)
0.0	3.10	0.0	4.5
0.5	2.8	0.5	4.2
0.8	2.6	1.0	3.87
1.0	2.5	1.5	3.5
1.2	2.35	2.0	3.25
1.5	2.25	2.5	2.95
2.0	2.0	3.0	2.65
2.2	1.9	3.5	2.5
2.5	1.8	4.0	2.4
3.0	1.65	4.5	2.35
3.5	1.6	5.0	2.30
4.0	1.45		
4.5	1.30		
	Curve(a)		Curve(b)

Fig. 13

<u>Curve (a)</u>

25 ml. of 4×10^{-4}M $PdCl_2$ ≡ 2.0 ml. of 1×10^{-2}M H.A.O.
≡ 50 ml. of 4×10^{-4}M H.A.O.

<u>Curve (b)</u>

25 ml. of 6×10^{-4}M $PdCl_2$ ≡ 3.05 ml.of 1×10^{-2}M H.A.O.
≡ 51 ml. of 6×10^{-4}M H.A.O.

Table - 20

Reverse titrations (H.A.O. in the cell)

Volume of o-hydroxy-acetophenoneoxime = 25 ml.
Concentration of o-hydroxy-acetophenoneoxime = 4×10^{-4}M(Set I)
= 8×10^{-4}M(Set II)

Concentration of $PdCl_2$ = 2.5×10^{-3}M

	I		II
Vol.of $PdCl_2$ (ml.)	Corrected conductancex10^{-2} (mhos)	Vol.of $PdCl_2$ (ml.)	Corrected conductancex10^{-2} (mhos)
0.0	0.0	0.0	0.0
0.5	0.4	0.5	0.36
0.8	0.615	1.0	0.7
1.0	0.75	1.5	1.05
1.2	0.90	2.0	1.42
1.5	1.15	2.5	1.75
1.8	1.4	3.0	2.05
2.0	1.52	3.5	2.35
2.3	1.70	4.0	2.63
2.5	1.85	4.5	2.87
3.0	2.2	5.0	3.15
3.5	2.5	5.5	3.4
4.0	2.8	6.0	3.65
		7.0	4.15
	Curve(a)		Curve(b)

Curve (a)

25 ml. of 4×10^{-4}M H.A.O. $\equiv$ 2.0 ml. of 2.5×10^{-3}M $PdCl_2$
$\equiv$ 12.5 ml.of 4×10^{-4}M $PdCl_2$

Curve (b)

25 ml. of 8×10^{-4}M H.A.O. $\equiv$ 3.85 ml. of 2.5×10^{-3}M $PdCl_2$
$\equiv$ 12.03 ml. of 8×10^{-4}M $PdCl_2$

Conductometric titrations between nickel sulphate and o-hydroxy-acetophenoneoxime :

A standard solution of o-hydroxy-acetophenoneoxime was prepared in equimolar solution of ammonia.

Table - 21

Volume of o-hydroxy-acetophenoneoxime = 25 ml.
Concentration of o-hydroxy-acetophenoneoxime
$=4\times10^{-3}$M (Set I)
$=6.4\times10^{-3}$M (Set II)
Concentration of NiSo$_4$ solution $=2\times10^{-2}$M

Vol.of NiSo$_4$ (ml.)	Corrected conductance$\times10^{-4}$ (mhos)	Vol.of NiSo$_4$ (ml.)	Corrected conductance $\times10^{-4}$ (mhos)
0.0	1.4	0.0	3.8
0.5	2.2	0.5	4.9
1.0	3.1	1.0	6.0
1.5	3.95	1.5	7.2
1.8	4.36	2.0	8.3
2.0	4.65	2.5	9.4
2.2	4.9	3.0	10.5
2.5	5.3	3.5	11.4
2.8	5.7	4.0	12.5
3.0	5.95	4.5	13.5
3.5	6.55	5.0	14.4
4.0	7.1	5.5	15.0
4.5	7.65	6.0	15.9
5.0	8.2	6.5	16.5
		7.0	17.0
	Curve(a)		Curve(b)

Fig.15

Curve(a)

25 ml.of 4×10^{-3}M H.A.O. $\equiv$ 2.55 ml.of 2×10^{-2}M NiSo$_4$
$\equiv$ 12.75 ml.of 4×10^{-3}M NiSo$_4$

Curve(b)

25 ml.of 6.4×10^{-3}M H.A.O. $\equiv$ 3.85 ml.of 2×10^{-2}M NiSo$_4$
$\equiv$ 12.03 ml.of 6.4×10^{-3}M NiSo$_4$

Amperometric titrations :-

Amperometric titrations between o-hydroxy - acetophenoneoxime and copper sulphate, palladium chloride and nickel sulphate were carried out, employing a Toshniwal manual polarograph type CLo-2 (India) with Pye scalamp galvanometer in the external circuit. The polarographic cell was kept immersed in a water thermostat maintained at 30 ± 0.1°C. Fischer capillary with the dropping time 3.4 seconds was used for dropping mercury electrode. Volume correction was applied by multiplying the current values with $\frac{V + v}{V}$ where V was the volume in the cell and v, the volume of the titrant added.

Amperometric titrations between o-hydroxy-acetophenoneoxime and copper sulphate :-

In order to carry out amperometric titrations, the constant potential to be applied during the course of titrations was first of all determined. 20.0 ml. of 1×10^{-3}M copper sulphate solution containing 0.2N sodium acetate - acetic acid buffer (pH 4.63) and 0.01% gelatine solution, were taken in a polarographic cell. The solution was deaerated by passing through hydrogen gas (purified after passing through alkaline pyrogallol and chromous chloride). The current was noted at different potentials. Polarogram was drawn Fig.(16) and the potential to be applied was determined as -0.15 volts.

Amperometric titrations between o-hydroxy-acetophenoneoxime and copper sulphate were carried out using sodium acetate-acetic acid buffer solution (pH 4.63) as supporting electrolyte and 0.01% gelatine solution as maximum suppressor.

The observations are given in the following tables :-

Table - 22

Direct titrations

20 ml. of 1.5×10^{-3}M copper sulphate titrated against 1×10^{-2}M o-hydroxy-acetophenoneoxime.

Vol. of H.A.O. (ml.)	Current (2×10^{-7} amp.)
0.0	4.1
1.0	3.4
2.0	2.65
3.0	2.1
4.0	1.5
5.0	0.95
6.0	0.5
7.0	0.25
8.0	0.25
9.0	0.25
10.0	0.25

Fig. 17, Curve a

20 ml. of 1.5×10^{-3}M $CuSo_4$ ≡ 5.9 ml.of 1×10^{-2}M H.A.O.

≡ 39.3 ml. of 1.5×10^{-3}M H.A.O.

Table -23

20 ml. of 2x10^{-3}M copper sulphate against 1x10^{-2}M H.A.O.

Vol.of H.A.O. (ml.)	Current (2x10^{-7} amp.)	Vol.of H.A.O. (ml.)	Current (2x10^{-7}amp.)
0.0	5.1	7.0	0.8
1.0	4.45	8.0	0.4
2.0	3.7	9.0	0.25
3.0	3.2	10.0	0.25
4.0	2.6	11.0	0.25
5.0	1.95	12.0	0.25
6.0	1.4		

Fig. 17, Curve b

20 ml.of 2x10^{-3}M $CuSo_4$ ≡ 7.9 ml.of 1x10^{-2}M H.A.O.
≡39.5 ml.of 2x10^{-3}M H.A.O.

Table - 24

20 ml. of 2.5x10^{-3}M copper sulphate against 1x10^{-2}M H.A.O.

Vol.of H.A.O. (ml.)	Current (2x10^{-7}amp.)	Vol.of H.A.O (ml.)	Current (2x10^{-7}amp.)
0.0	6.3	9.0	1.0
1.0	5.6	10.0	0.5
2.0	5.0	11.0	0.35
3.0	4.4	12.0	0.25
4.0	3.75	13.0	0.25
5.0	3.1	14.0	0.25
6.0	2.6		
7.0	2.0		
8.0	1.5		

Fig. 17, Curve c

20 ml. of 2.5x10^{-3}M $CuSo_4$ ≡ 10.0 ml. of 1x10^{-2}M H.A.O.
≡ 40.0 ml. of 2.5x10^{-3}M H.A.O.

Table - 25

Reverse titrations

20 ml. of $4x10^{-3}M$ o-hydroxy-acetophenoneoxime against $1x10^{-2}M$ $CuSo_4$

Vol. of $CuSo_4$ (ml.)	Current ($2x10^{-7}$amp.)
0.0	0.15
1.0	0.15
2.0	0.15
3.0	0.15
3.5	0.2
4.0	0.3
4.5	0.8
5.0	1.2
6.0	2.1
7.0	2.85

Fig. 18, curve a

20 ml. of $4x10^{-3}M$ o-hydroxy-acetophenoneoxime
$\equiv$ 3.8 ml.of $1x10^{-2}M$ $CuSo_4$
$\equiv$ 9.5 ml.of $4x10^{-3}M$ $CuSo_4$

Table - 26

20 ml. of $3x10^{-3}M$ o-hydroxy-acetophenoneoxime against $1x10^{-2}M$ $CuSo_4$

Vol. of $CuSo_4$ (ml.)	Current ($2x10^{-7}$amp.)
0.0	0.15
1.0	0.15
2.0	0.15
2.5	0.15
3.0	0.25
3.5	0.7
4.0	1.15
5.0	2.0

Fig. 18, curve b

20 ml.of $3x10^{-3}M$ o-hydroxy-acetophenoneoxime $\equiv$2.9 ml.of $1x10^{-2}M$ $CuSo_4$
$\equiv$9.7 ml.of $3x10^{-3}M$ $CuSo_4$

Table - 27

20 ml. of $2\times10^{-3}M$ o-hydroxy-acetophenoneoxime against $1\times10^{-2}M$ $CuSo_4$

Vol.of $CuSo_4$ (ml.)	Current $(2\times10^{-7}$ amp.)	Vol.of $CuSo_4$ (ml.)	Current $(2\times10^{-7}$ amp.)
0.0	0.15	3.0	1.2
1.0	0.15	3.5	1.7
2.0	0.25	4.0	2.1
2.5	0.7	5.0	3.1

Fig.18, curve c

20 ml. of $2\times10^{-3}M$ o-hydroxy-acetophenoneoxime
$\equiv$ 2.0 ml. of $1\times10^{-2}M$ $CuSo_4$
$\equiv$10.0 ml. of $2\times10^{-3}M$ $CuSo_4$

Amperometric titrations between o-hydroxy-acetophenoneoxime and palladium chloride :

In order to find out the potential to be applied during the course of titrations, 20 ml. of $5\times10^{-4}M$ palladium chloride solution in 0.2N sodium acetate-acetic acid buffer solution (pH 4.0) and 0.01% gelatine solution were taken in a polarographic cell. The solution was deaerated with the purified nitrogen gas and current was noted at different potentials. From the current-voltage curve Fig.(19), the optimum potential tobe applied for carrying out the amperometric titrations was determined to be -0.4 volts vs S.C.E.

Amperometric titrations between o-hydroxy-acetophenoneoxime and palladium chloride were carried out in the presence of 0.2N sodium acetate-acetic acid buffer solution (pH 4.0) as supporting electrolyte and 0.01% gelatine solution as maximum suppressor.

The observations are given in the following tables:

Table - 28

Direct titrations

20 ml. of $5x10^{-4}M$ $PdCl_2$ against $2x10^{-2}M$ H.A.O.

Vol. of H.A.O. (ml.)	Current (2x10^{-7} amp.)
0.0	4.35
0.4	2.95
0.6	2.45
0.8	2.1
1.0	1.9
1.2	1.7
1.4	1.5
1.6	1.4
2.0	1.3
2.4	1.3

Fig. 20, curve a

20 ml. of $5x10^{-4}M$ $PdCl_2$ ≡ 0.96 ml. of $2x10^{-2}M$ H.A.O.

≡ 38.4 ml. of $5x10^{-4}M$ H.A.O.

Table - 29

20 ml. of 1×10^{-3}M $PdCl_2$ against 2×10^{-2}M H.A.O.

Vol.of H.A.O (ml.)	Current (2×10^{-7} amp.)	Vol.of H.A.O (ml.)	Current (2×10^{-7} amp.)
0.0	7.4	2.0	1.8
0.2	6.7	2.2	1.5
0.4	6.2	2.4	1.4
0.8	5.0	2.6	1.3
1.0	4.3	2.8	1.3
1.2	3.8		
1.4	3.2		
1.6	2.6		
1.8	2.1		

Fig. 20, curve b

20 ml. of 1×10^{-3}M $PdCl_2$ ≡ 2.02 ml.of 2×10^{-2}M H.A.O.
≡ 40.4 ml.of 1×10^{-3}M H.A.O.

Table - 30

Reverse titrations

20 ml. of 1×10^{-3}M H.A.O. against 5×10^{-3}M $PdCl_2$

Vol.of $PdCl_2$ (ml.)	Current (2×10^{-7} amp.)	Vol.of $PdCl_2$ (ml.)	Current (2×10^{-7} amp.)
0.0	0.8	3.0	1.6
1.0	0.8	4.0	2.6
2.0	0.8	5.0	3.5
2.4	1.2	6.0	4.4
2.8	1.5		

Fig.21, curve a

20 ml. of 1×10^{-3}M H.A.O ≡ 2.2 ml.of 5×10^{-3}M $PdCl_2$
≡11.0 ml.of 1×10^{-3}M $PdCl_2$

Table - 31

20 ml. of $2x10^{-3}M$ H.A.O. against $5x10^{-3}M$ $PdCl_2$

Vol. of $PdCl_2$ (ml)	Current ($2x10^{-7}$ amp.)	Vol. of $PdCl_2$ (ml)	Current ($2x10^{-7}$ amp.)
0.0	0.8	4.5	1.2
1.0	0.8	5.0	1.8
2.0	0.8	6.0	2.5
3.0	0.8	7.0	3.3
4.0	0.8		

Fig.21, Curve b

20 ml. of $2x10^{-3}M$ H.A.O. ≡ 4.0 ml. of $5x10^{-3}$ $PdCl_2$
≡ 10.0 ml. of $2x10^{-3}M$ $PdCl_2$

Amperometric titrations between o-hydroxy-acetophenoneoxime and nickel sulphate :

The potential to be applied during the course of amperometric titrations of o-hydroxy-acetophenoneoxime and nickel sulphate was determined by taking a polarogram of 20 ml. of $1x10^{-3}M$ $NiSo_4$ solution in ammonia-ammonium chloride buffer solution (pH 9.0) and 0.01% gelatine solution.

From the polarographic wave (Fig.22) for the reduction of nickel, the potential at which nickel yields the maximum diffusion current is found to be -1.2 volts vs S.C.E.

Amperometric titrations between o-hydroxy-acetophenoneoxime and nickel sulphate were carried out, using ammonia-ammonium chloride buffer solution (pH 9.0) as supporting electrolyte and 0.01% gelatine solution as maximum suppressor.

The observations are tabulated below:

Table - 32

Direct titrations

20 ml. of 1.5×10^{-3}M $NiSo_4$ solution against 1×10^{-2}M H.A.O.

Vol. of H.A.O. (ml.)	Current (2×10^{-7} amp.)
0.0	3.6
1.0	3.1
2.0	2.5
3.0	2.0
4.0	1.5
5.0	1.0
6.0	0.55
7.0	0.4
8.0	0.4
9.0	0.4

Fig. 23, Curve a

20 ml. of 1.5×10^{-3}M $NiSo_4$ $\equiv$ 5.9 ml. of 1×10^{-2}M H.A.O.

$\equiv$ 39.3 ml.of 1.5×10^{-3}M H.A.O.

Table - 33

20 ml. of 2×10^{-3}M NiSo$_4$ solution against 1×10^{-2}M H.A.O.

Vol.of H.A.O. (ml.)	Current (2×10^{-7} amp.)	Vol.of H.A.O. (ml.)	Current (2×10^{-7} amp.)
0.0	4.6	7.0	1.3
1.0	4.1	8.0	0.9
2.0	3.5	9.0	0.7
3.0	3.0	10.0	0.6
4.0	2.6	11.0	0.6
5.0	2.1	12.0	0.6
6.0	1.6		

Fig. 23, Curve b

20 ml. of 2×10^{-3}M NiSo$_4$ ≡ 8.1 ml. of 1×10^{-2}M H.A.O.
≡ 40.5 ml. of 2×10^{-3}M H.A.O.

Table - 34

Reverse Titrations

20 ml.of 2×10^{-3}M o-hydroxy-acetophenoneoxime against 1×10^{-2}M NiSo$_4$

Vol. of NiSo$_4$ (ml.)	Current (2×10^{-7} amp.)
0.0	0.25
1.0	0.25
1.5	0.35
2.0	0.45
2.5	0.7
3.0	1.15
3.5	1.45
4.0	1.8
5.0	2.55
5.5	2.9

Fig. 24, Curve a

20 ml. of 2×10^{-3}M H.A.O. ≡ 1.95 ml.of 1×10^{-2}M NiSo$_4$
≡ 9.75 ml.of 2×10^{-3}M NiSo$_4$

Table -35

20 ml. of 4×10^{-3}M H.A.O. solution against 1×10^{-2}M $NiSo_4$

Vol. of $NiSo_4$ (ml.)	Current $(2\times10^{-7}$amp.)
0.0	0.25
1.0	0.25
2.0	0.25
3.0	0.25
3.5	0.25
4.0	0.4
4.5	0.6
5.0	1.0
5.5	1.45
6.0	1.8

Fig. 24, curve b

20 ml. of 4×10^{-3}M H.A.O. = 4.1 ml. of 1×10^{-2}M $NiSo_4$
=10.25 ml. of 4×10^{-3}M $NiSo_4$

Infra-red spectroscopy :

The I.R. spectra of o-hydroxy-acetophenoneoxime and its complexes with molybdenum, copper, nickel and palladium, were recorded in solid state by KBr disc technique, using Perkin-Elmer 337, grating infrared spectrophotometer.

DISCUSSION

Ortho-hydroxy-acetophenoneoxime forms complexes with molybdenum(VI) (soluble, yellow coloured), copper(II) (insoluble, dirty white), palladium(II) (insoluble, yellowish) and nickel (insoluble, green). The composition of these complexes has been investigated by chemical analysis of the isolated products as well as by physical methods.

Composition of molybdenum(VI) complex :

Molybdenum(VI) instantaneously forms a soluble, bright-yellow complex in acidic medium.

The results of chemical analysis of the isolated yellow complex of molybdenum correspond to its formula as $(C_8H_8O_2N)_2MoO_2$.

Spectrophotometric studies :

The spectrophotometric methods employed to study the nature, composition and stability of the complex, furnish the following information :-

(i) Vosburgh and Cooper's method employed to determine the number of complexes formed in solution, shows the existence of only one complex since equimolar solutions containing different proportions of ammonium molybdate and o-hydroxy-acetophenoneoxime, exhibit only one absorption maxima at 345 mu (Fig.1).

(ii) The influence of pH on the complex was studied by measuring the absorbance of several solutions containing ammonium molybdate and o-hydroxy-acetophenoneoxime, of equimolar concentrations in the ratio of 1:2 respectively and adjusted to different pH values (2.5-5.5). The absorbance curves of these solutions show λmax at 345 mµ, (Fig.2a) thus, indicating that the complex is stable in the pH range 2.5-5.5. The complex shows the maximum absorption in the pH range 3.5-4.5 (Fig.2b).

(iii) Job's method of continued variation was followed to find out the composition of the complex. Curves (Figs.3-5) were obtained by plotting $\bar{D}$, the difference between the observed optical density of the mixture solution and that of the metal and the ligand, against the mole fraction of the metal at the wave lengths 345, 350 and 360 mµ at three concentrations. In all these cases the maximum of $\bar{D}$ occurs at the ratio of 1:2 for molybdenum and o-hydroxy-acetophenone-oxime respectively.

(iv) The results of Job's method were further supported by slope ratio method. The ratio of the slopes of the straight line portions of the two curves (Figs.6,7), obtained by plotting the optical density against the concentration of the variable component, comes out to be equal to 2, again providing evidence for the metal: ligand ratio as 1:2.

(v) The formation constant of the complex was determined by the method recommended by Anderson and co-workers. Taking the values of a_1, b_1, a_2, b_2 from the fig. 8 (table 10), the value of K was found to be 9.3×10^8. The free energy of formation $\triangle F$ was worked out to be -12.39 Kcals. at 30°C.

Conductometric studies :

Both direct (ammonium molybdate in the cell) and reverse (o-hydroxy-acetophenoneoxime in the cell) titrations were performed at different concentrations. Sharp inflexion points (Figs. 9,10) were obtained at the stoichiometric ratio corresponding to 1:2 complex of molybdenum with the ligand respectively. Results of the conductometric titrations are summarized below :

S.No.	Fig.& curve No.	Vol.of Amm.molybdate (ml.)	Vol.of H.A.O. (ml.)	Mole ratio Mo/H.A.O.
1	9,a	30.0(1.333×10^{-3}M)	58.5(1.333×10^{-3}M)	1:1.95
2	9,b	30.0(2×10^{-3}M)	59.0(2×10^{-3}M)	1:1.97
3	9,c	30.0(2.666×10^{-3}M)	61.5(2.666×10^{-3}M)	1:2.05
4	10,a	14.63(5.333×10^{-3}M)	30.0(5.333×10^{-3}M)	1:2.05
5	10,b	15.0(4×10^{-3}M)	30.0(4×10^{-3}M)	1:2
6	10,c	15.0(2.666×10^{-3}M)	30.0(2.666×10^{-3}M)	1:2

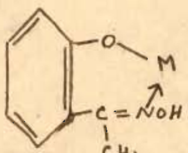
Structure of the Mo(VI) complex :

In o-hydroxy-acetophenoneoxime there are two possibilities of coordination :

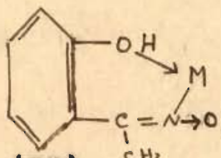
(a) That the hydrogen atom of the acidic phenolic (-oH) group is replaced by the metal which in turn is coordinated to the nitrogen atom of the oxime group to form the inner-complex salt.

(b) The hydrogen atom of the oxime (-C=NOH) group is replaced by metal and coordination takes place through phenolic oxygen.

Hence the two possible structures for the metal complexes of o-hydroxy-acetophenoneoxime may be written as;

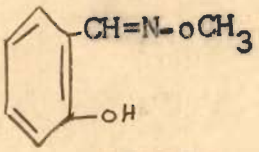


(I)

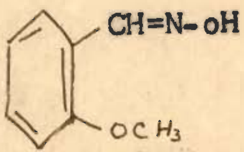


(II)

Structure(I) is assigned to the metal complexes in view of the investigations carried out by Feigl and Bondi[30] on the reactions of isomeric methyl ethers of salicylaldoxime,



(III)



(IV)

They observed that the compound(III) containing the free hydroxyl group reacted with copper to form dark brown salt while the isomeric phenolic ether(IV) did not react.

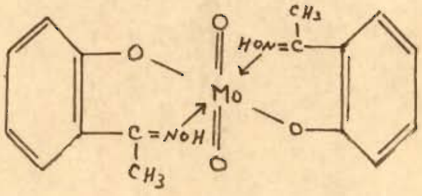
The structure(I) for the molybdenum complex of o-hydroxy-acetophenoneoxime was further confirmed by the study of its infrared spectrum.

The ligand (Fig.25) shows a strong absorption band at 3350 cm^{-1} which is due to the stretching vibrations of phenolic (-oH) group. The complete absence of this band in the spectrum (Fig.26) of the complex suggests that the phenolic hydrogen is replaced by the metal. The stretching frequency due to =C-o of the phenolic group is also shifted from 1265 to 1250 cm^{-1} in the complex.

Another feature worth noting in the spectrum of the complex is the marked shifting in the stretching frequency of C=N- of oxime group from 1620 cm^{-1} (in the ligand) to 1550 cm^{-1}, thus proving that coordination of metal takes place through nitrogen of the oxime group.

Although in weakly acid solutions paramolybdate ions are present, yet a number of compounds react under these conditions with molybdenum(VI) in the form of the cation[31] MoO_2^{2+}. Thus, 8-hydroxy quinoline at pH 2.24 precipitates $MoO_2(C_9H_6ON)_2$. This seems to indicate that at pH 2.24 small amounts of MoO_2^{2+} cations are present, besides the paramolybdate anions $Mo_7O_{24}^{6-}$ (which are not precipitated by 8-hydroxyquinoline). As $MoO_2(C_9H_6ON)_2$ precipitates out, more paramolybdate ions are converted into MoO_2^{2+}.

On the basis of the above evidence available, the following structure is assigned to the molybdenum complex,



Composition of the insoluble complexes of Cu(II), Pd(II) and Ni(II) :

Copper forms a dirty white precipitate in the pH range 2.1-8.0; palladium, a yellowish precipitate in the pH range 1.0-4.5; and nickel, a green precipitate in the pH range 5.0-9.0, with o-hydroxy-acetophenoneoxime.

The results of chemical analysis of these isolated complexes give their composition corresponding to the formula $(C_8H_8O_2N)_2M$ (where M=Cu,Pd,Ni).

The composition of these complexes was further studied by applying conductometric and amperometric methods.

The conductometric titrations of the ligand against nickel sulphate as titrant give sharp breaks at the stoichiometric ratio corresponding to 1:2 complex of nickel with the ligand. The reverse titrations ($NiSo_4$ in the cell) could not be carried out as the conductance variations on the addition of the titrant were too small to be observed.

Conductometric titrations of copper and palladium, also correspond to the combining ratio of 1:2 for the metal and the ligand respectively.

The results are summarized in the following tables :

Conductometric titrations between copper sulphate and H.A.O

S.No.	Fig.& curve	Vol.of copper sulphate (ml.)	Vol.of H.A.O. (ml.)	Mole ratio Cu/H.A.O
1	11,a	25.0(8×10^{-4}M)	51.25(8×10^{-4}M)	1:2.05
2	11,b	25.0(1×10^{-3}M)	49.0(1×10^{-3}M)	1:1.96
3	11,c	25.0(1.2×10^{-3}M)	50.0(1.2×10^{-3}M)	1:2
4	12,a	11.9(1.6×10^{-3}M)	25.0(1.6×10^{-3}M)	1:2.10
5	12,b	12.5(2.4×10^{-3}M)	25.0(2.4×10^{-3}M)	1:2

Conductrometric titrations between palladium chloride and H.A.O.

S.No.	Fig.& curve	Vol. of $PdCl_2$ (ml.)	Vol.of H.A.O. (ml.)	Mole ratio Pd/H.A.O
1	13,a	25.0(4×10^{-4}M)	50.0(4×10^{-4}M)	1:2
2	13,b	25.0(6×10^{-4}M)	51.0(6×10^{-4}M)	1:2.04
3	14,a	12.5(4×10^{-4}M)	25.0(4×10^{-4}M)	1:2
4	14,b	12.03(8×10^{-4}M)	25.0(8×10^{-4}M)	1:2.08

Conductometric titrations between nickel sulphate and H.A.O

S.No.	Fig.& curve	Vol.of $NiSo_4$ (ml.)	Vol.of H.A.O (ml.)	Mole ratio Ni/H.A.O
1	15,a	12.75(4×10^{-3}M)	25.0(4×10^{-3}M)	1:1.96
2	15,b	12.03(6.4×10^{-3}M)	25.0(6.4×10^{-3}M)	1:2.08

Both direct (metal in the cell) and reverse (H.A.O in the cell) amperometric titrations further reveal a combining ratio of 1:2 for the metal and the ligand respectively.

The results of the amperometric titrations are summarized below :

Amperometric titrations between copper sulphate and H.A.O

S.No.	Fig.& curve	Vol. of $CuSo_4$ (ml.)	Vol.of H.A.O. (ml.)	Mole ratio Cu/H.A.O
1	17,a	$20.0(1.5\times10^{-3}M)$	$39.3(1.5\times10^{-3}M)$	1:1.965
2	17,b	$20.0(2\times10^{-3}M)$	$39.5(2\times10^{-3}M)$	1:1.975
3	17,c	$20.0(2.5\times10^{-3}M)$	$40.0(2.5\times10^{-3}M)$	1:2
4	18,a	$9.5(4\times10^{-3}M)$	$20.0(4\times10^{-3}M)$	1:2.1
5	18,b	$9.7(3\times10^{-3}M)$	$20.0(3\times10^{-3}M)$	1:2.06
6	18,c	$10.0(2\times10^{-3}M)$	$20.0(2\times10^{-3}M)$	1:2

Amperometric titrations between palladium chloride and H.A.O.

S.No.	Fig.& curve	Vol.of $PdCl_2$ (ml.)	Vol.of H.A.O (ml.)	Mole ratio Pd/H.A.O
1	20,a	$20.0(5\times10^{-4}M)$	$38.4(5\times10^{-4}M)$	1:1.92
2	20,b	$20.0(1\times10^{-3}M)$	$40.4(1\times10^{-3}M)$	1:2.02
3	21,a	$11.0(1\times10^{-3}M)$	$20.0(1\times10^{-3}M)$	1:1.82
4	21,b	$10.0(2\times10^{-3}M)$	$20.0(2\times10^{-3}M)$	1:2

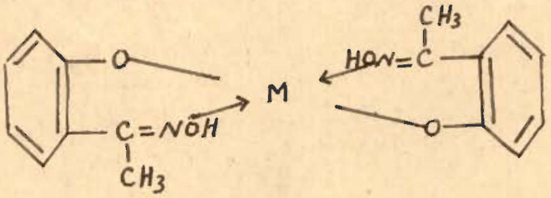
Amperometric titrations between nickel sulphate and H.A.O

S.No.	Fig.& curve	Vol.of $NiSo_4$ (ml.)	Vol.of H.A.O. (ml.)	Mole ratio Ni/H.A.O
1	23,a	$20.0(1.5\times10^{-3}M)$	$39.3(1.5\times10^{-3}M)$	1:1.965
2	23,b	$20.0(2\times10^{-3}M)$	$40.5(2\times10^{-3}M)$	1:2.025
3	24,a	$9.75(2\times10^{-3}M)$	$20.0(2\times10^{-3}M)$	1:2.05
4	24,b	$10.25(4\times10^{-3}M)$	$20.0(4\times10^{-3}M)$	1:1.95

Structure of the complexes of Cu(II), Pd(II) and Ni(II):

The I.R.spectra of the complexes of copper (Fig.27), palladium (Fig.28) and nickel (Fig.29) show no band corresponding to phenolic (-oH) group (3350 cm^{-1} in the ligand), thus pointing to replacement of the phenolic hydrogen by the metal ion. The frequency of C=N- is exhibited at 1560 cm^{-1} in copper complex, at 1540 cm^{-1} in palladium complex and at 1550 cm^{-1} in nickel complex. In the ligand (Fig.25) the band at 1620 cm^{-1} may be attributed to C=N- group. The shift in the C=N- frequencies in the complexes from 1620 cm^{-1} leads to the inference that the coordination of the metal takes place through nitrogen of C=N-.

On the basis of the information furnished by both chemical and physical studies, the following structure may be assigned to these metal complexes :



M = Cu(II), Pd(II), Ni(II)

VOSBURGH COOPER'S METHOD

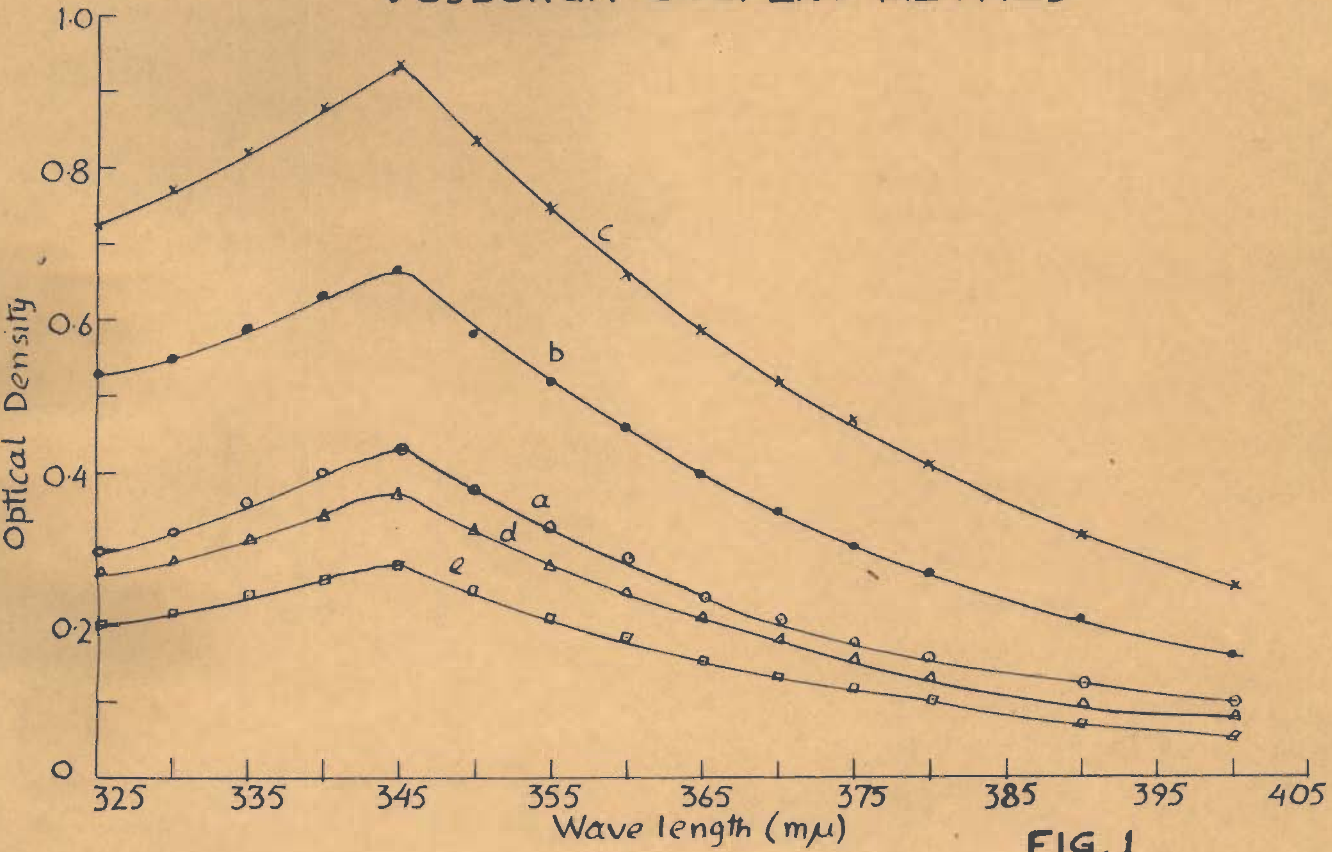


FIG. 1

INFLUENCE OF pH ON STABILITY OF COMPLEX

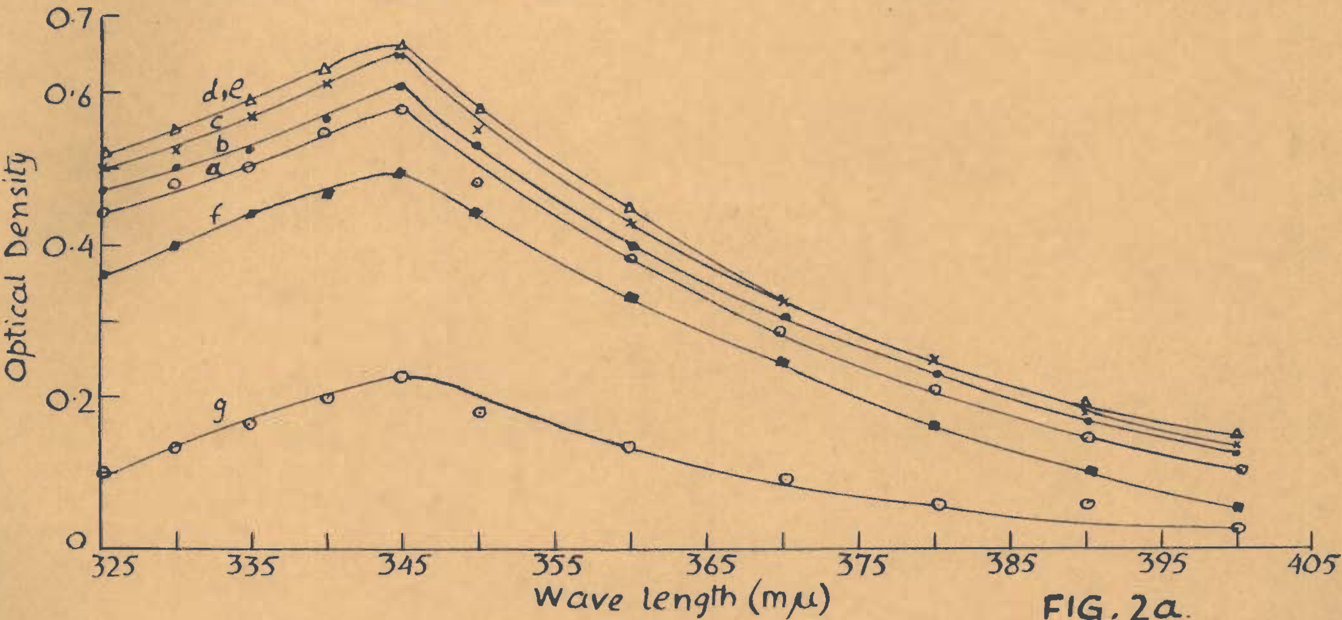


FIG. 2a.

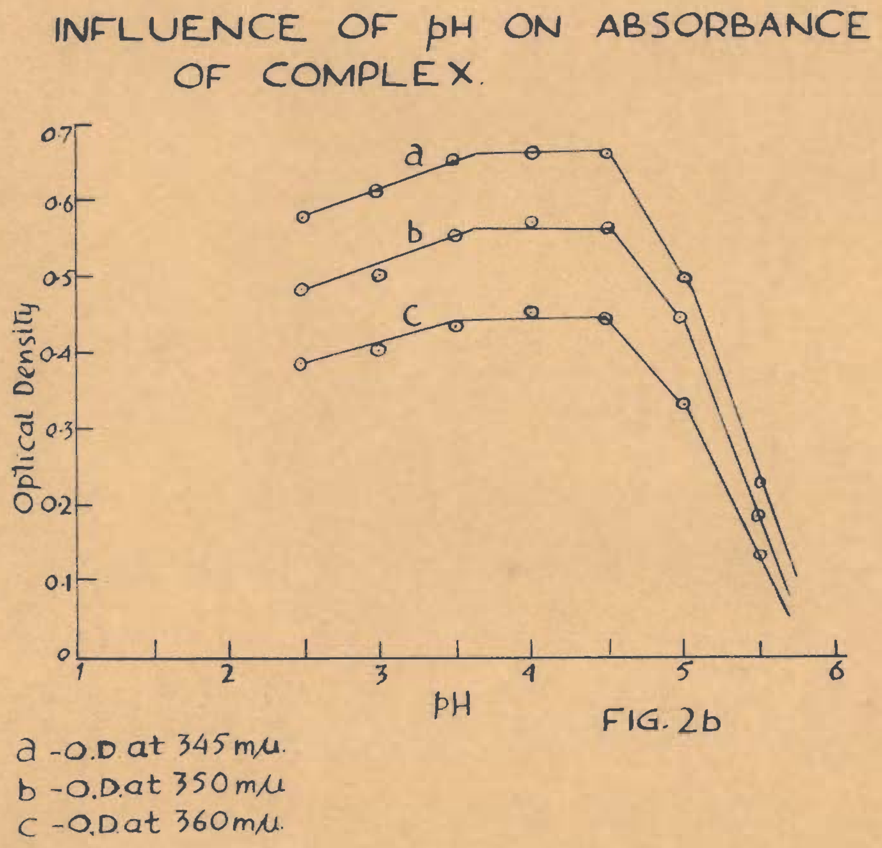

INFLUENCE OF pH ON ABSORBANCE OF COMPLEX.
Optical Density
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
1
2
3
4
5
6
pH
a
b
c
a -O.D at 345 mμ.
b -O.D.at 350 mμ
c -O.D.at 360 mμ.

FIG. 2b

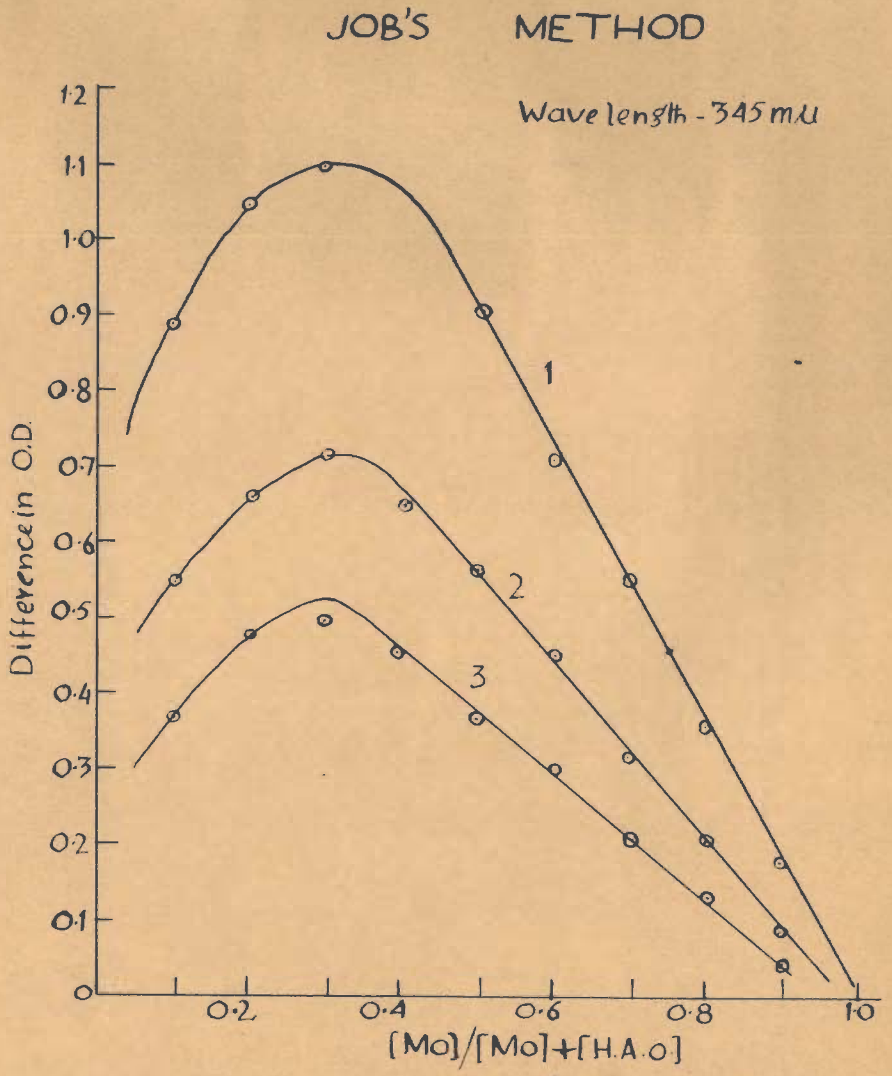

JOB'S METHOD
Wave length - 345 mμ
Difference in O.D.
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
0.2
0.4
0.6
0.8
1.0
[Mo]/[Mo]+[H.A.O]
1
2
3

FIG. 3

JOB'S METHOD

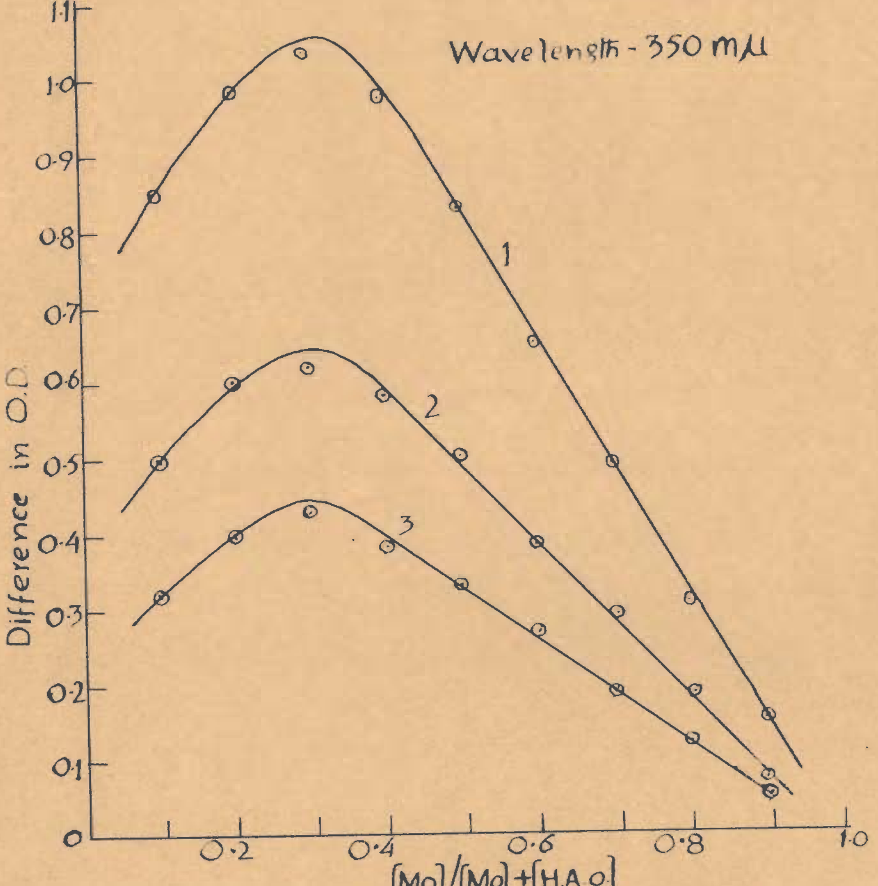


FIG. 4

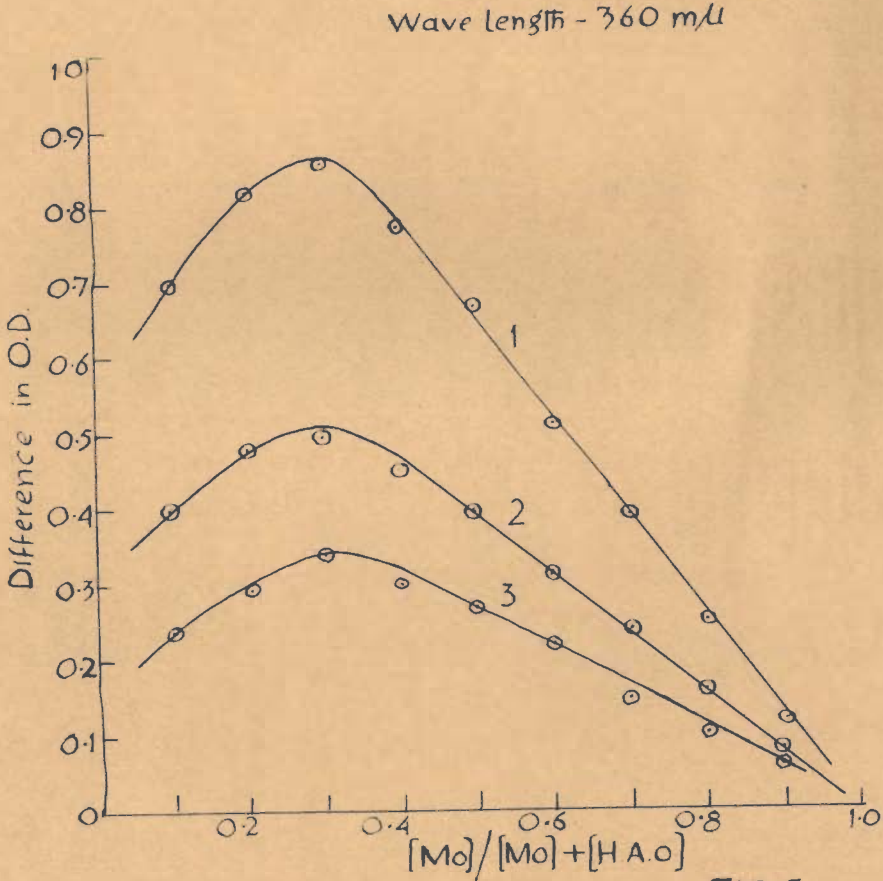


FIG. 5

SLOPE RATIO METHOD

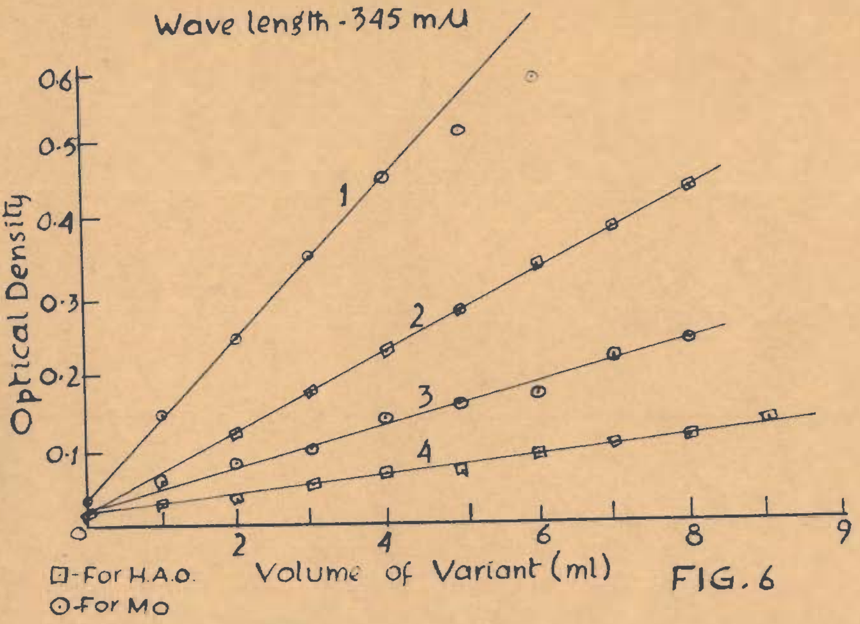


FIG. 6

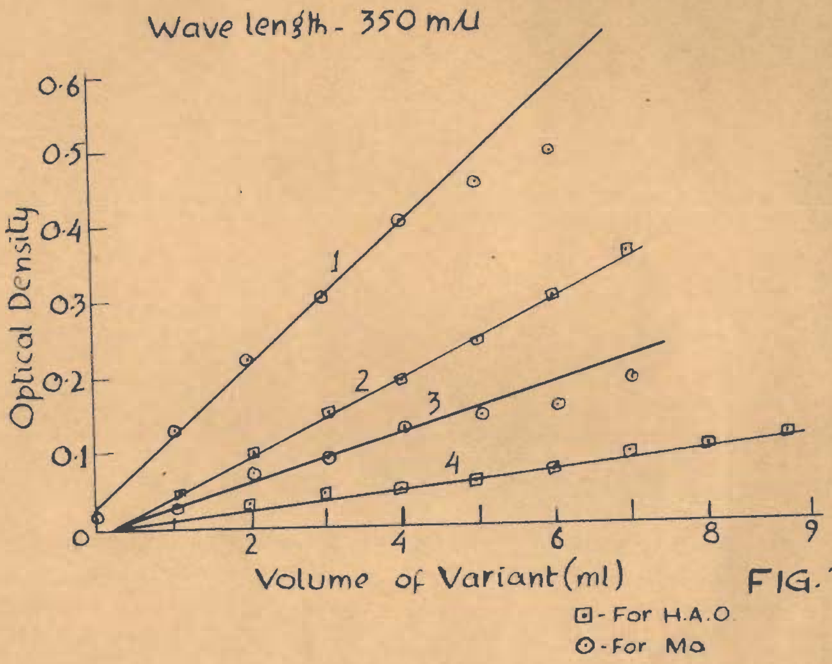


FIG. 7

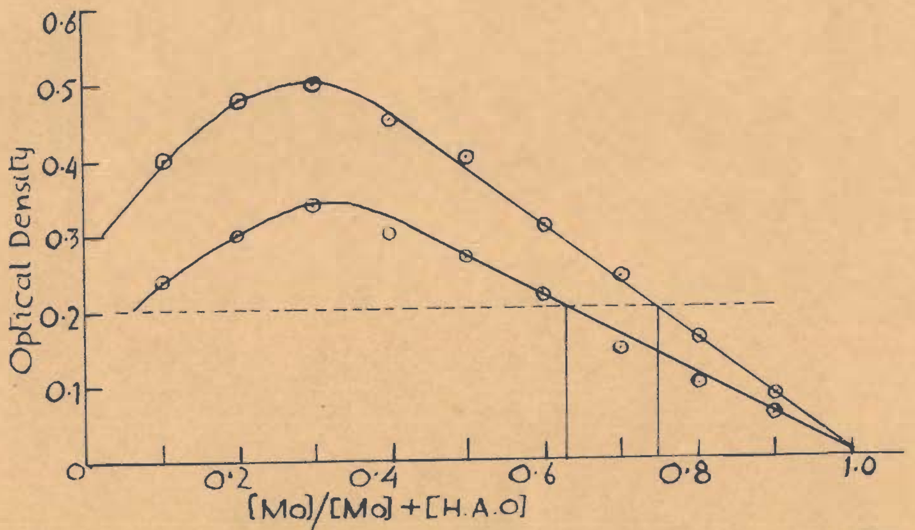


FIG. 8

FORMATION CONSTANT OF THE COMPLEX.

CONDUCTOMETRIC TITRATIONS

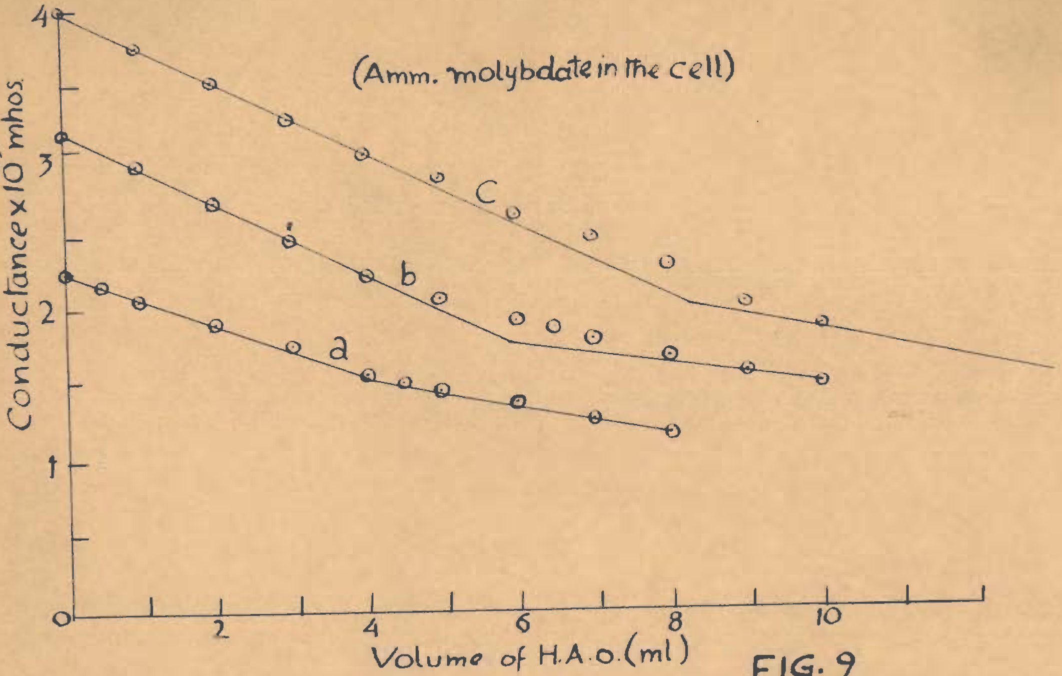


FIG. 9

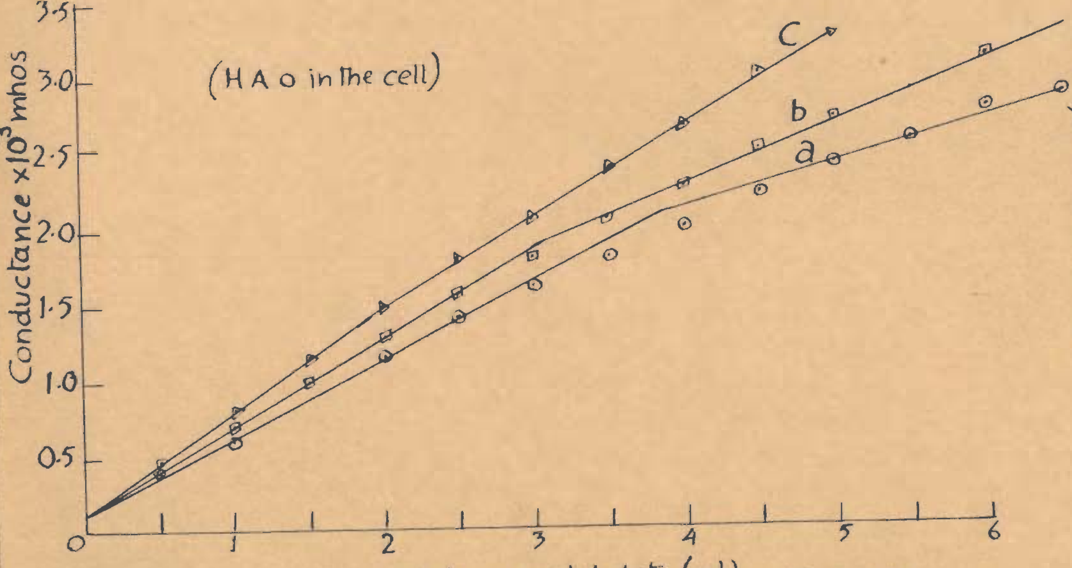


FIG. 10

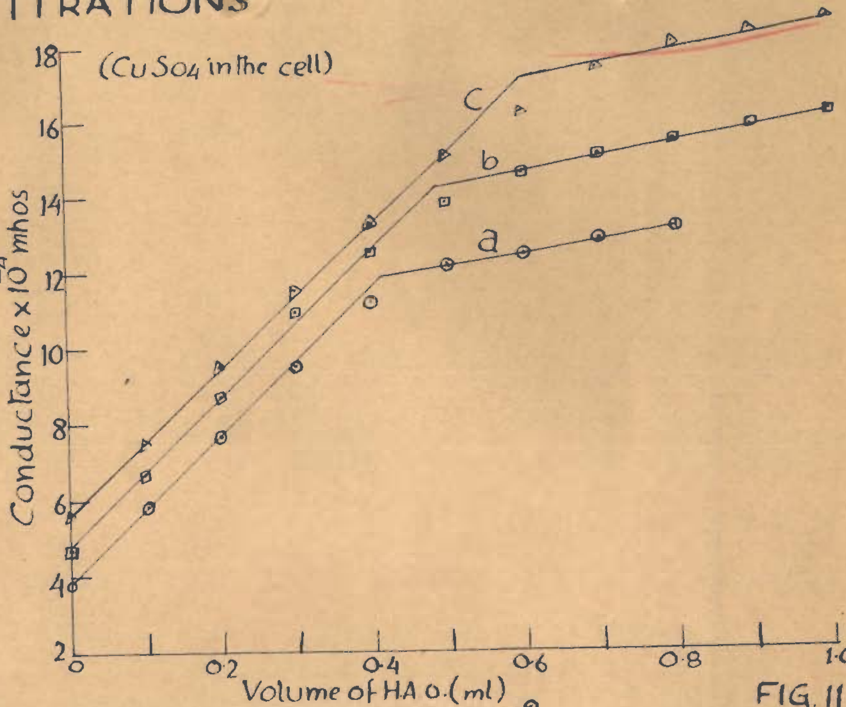


FIG. 11

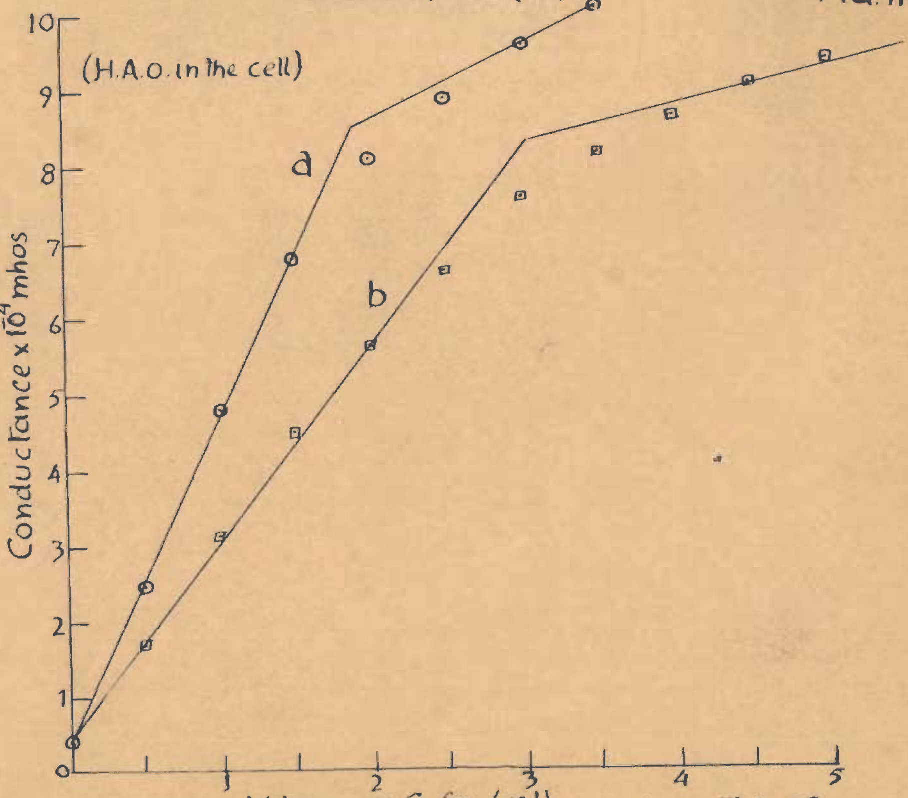


FIG. 12

CONDUCTOMETRIC TITRATIONS.

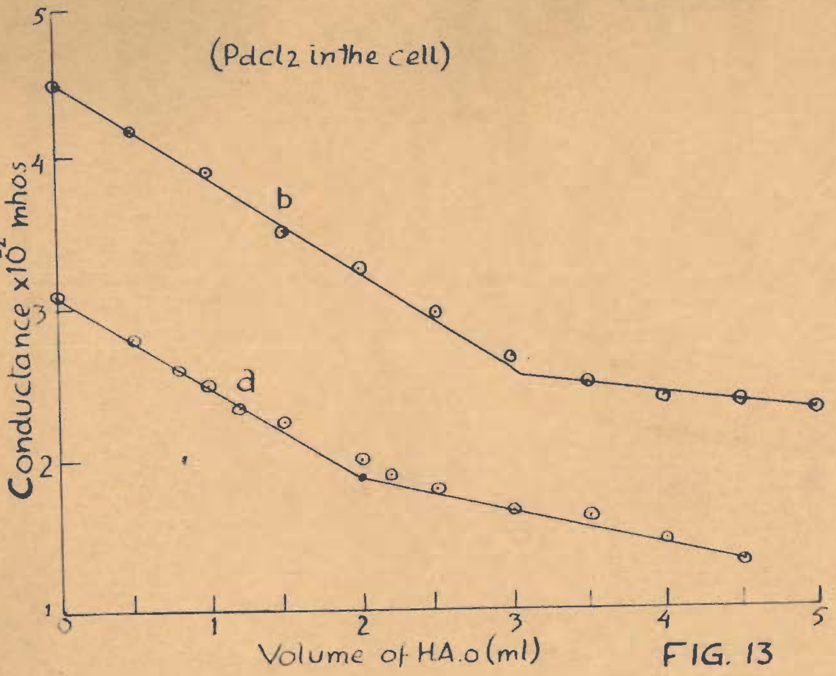


FIG. 13

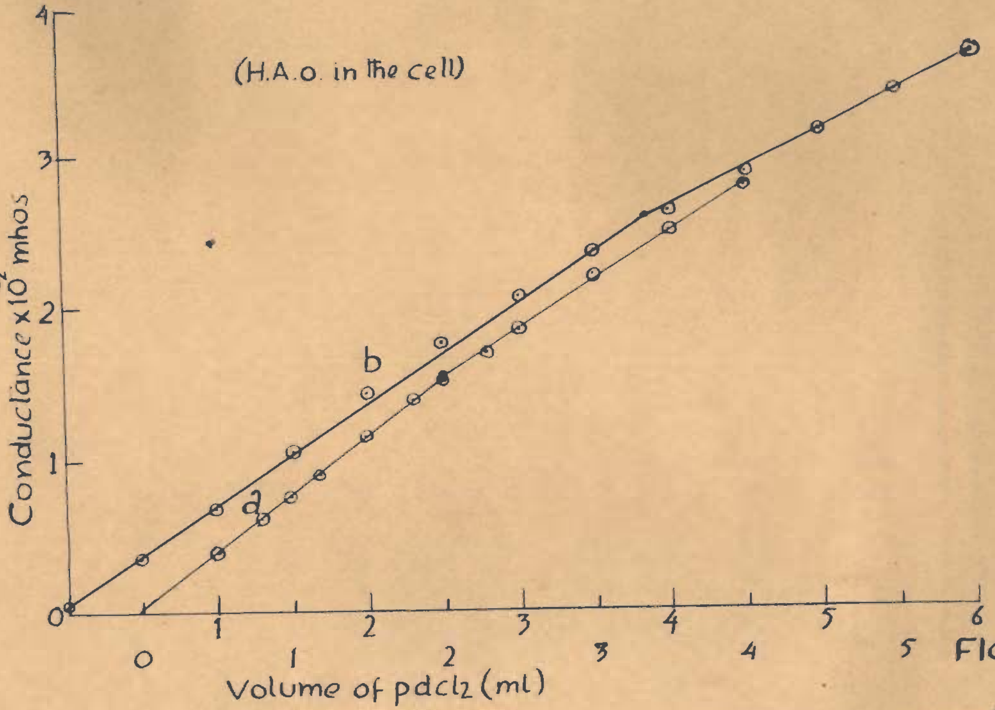


FIG.14

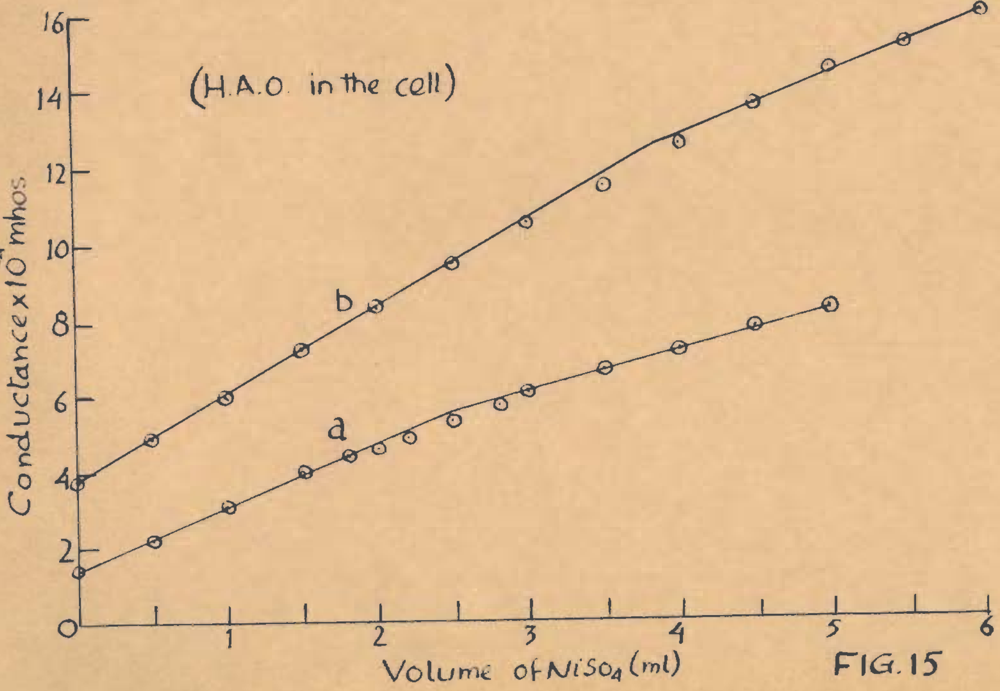
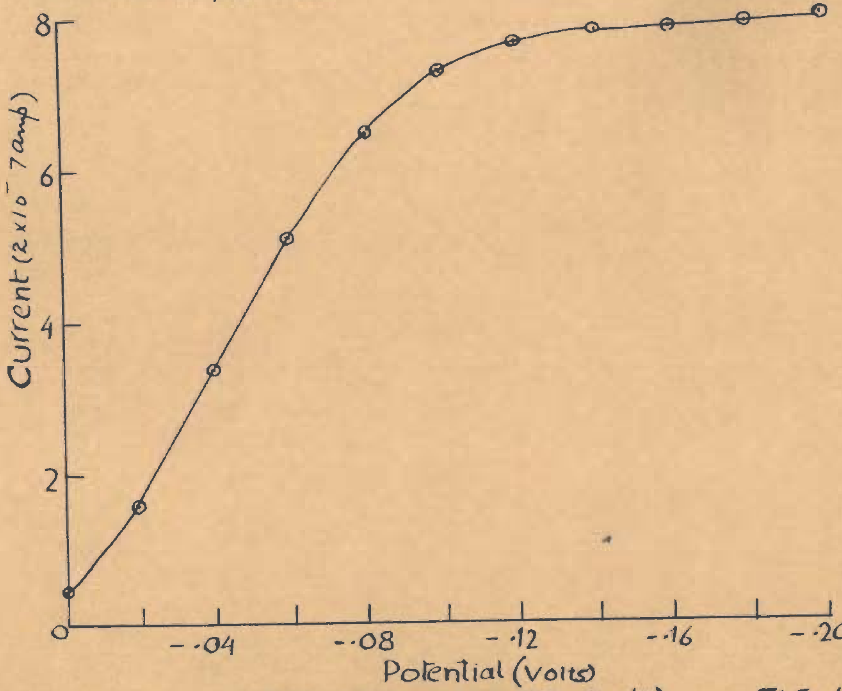


FIG.15



POLAROGRAM OF Cu(II)

FIG. 16

AMPEROMETRIC TITRATIONS

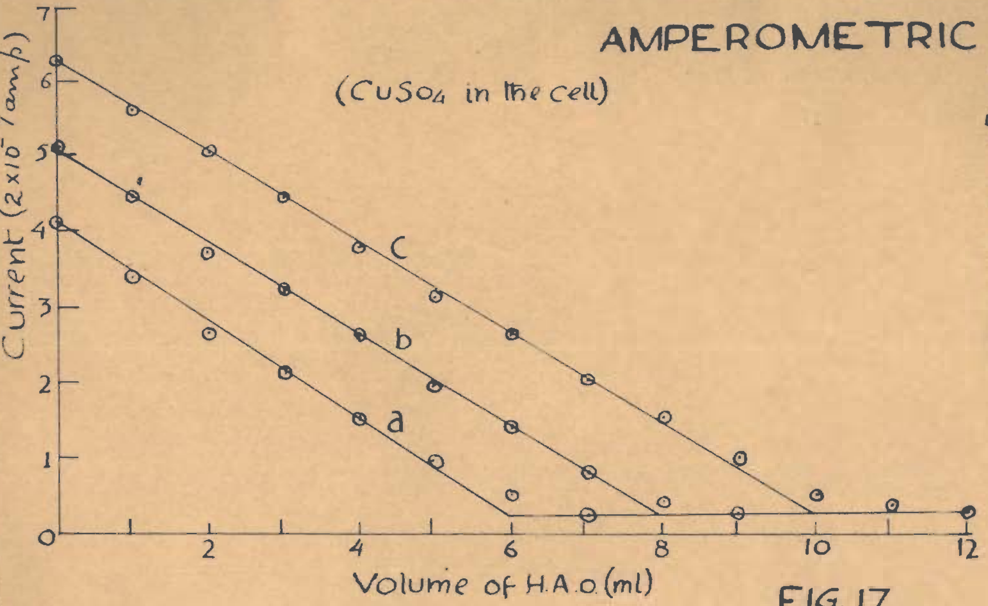


FIG. 17

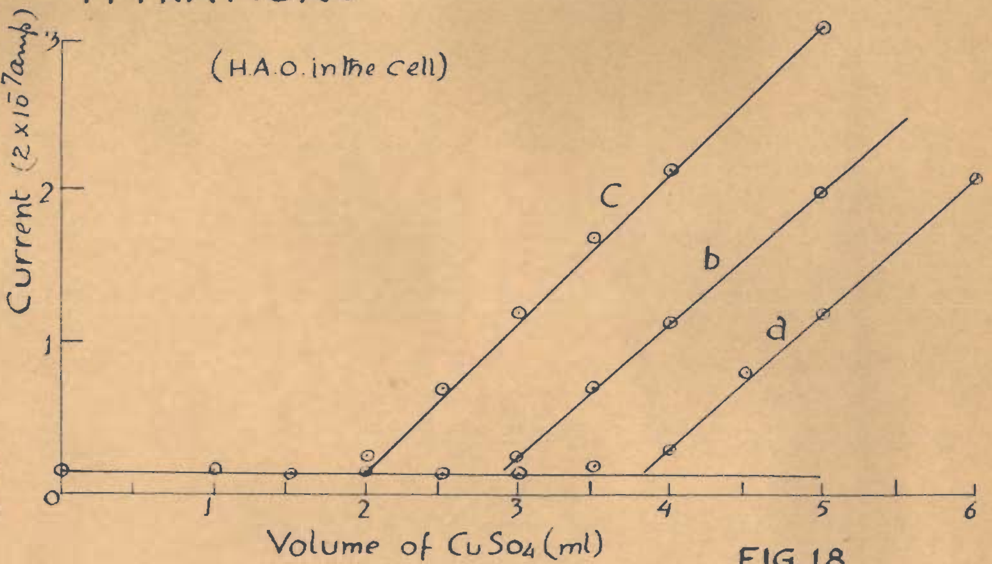
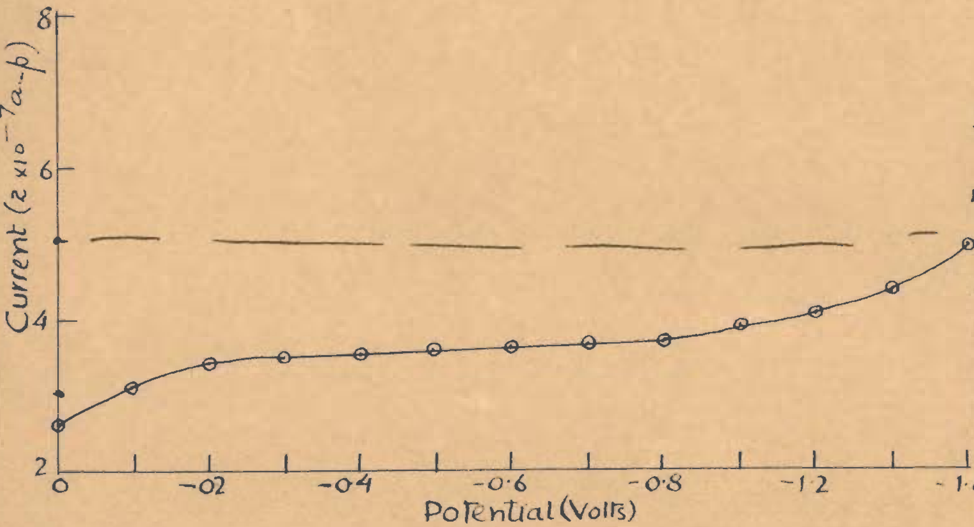


FIG. 18



POLAROGRAM OF Pd.

FIG. 19

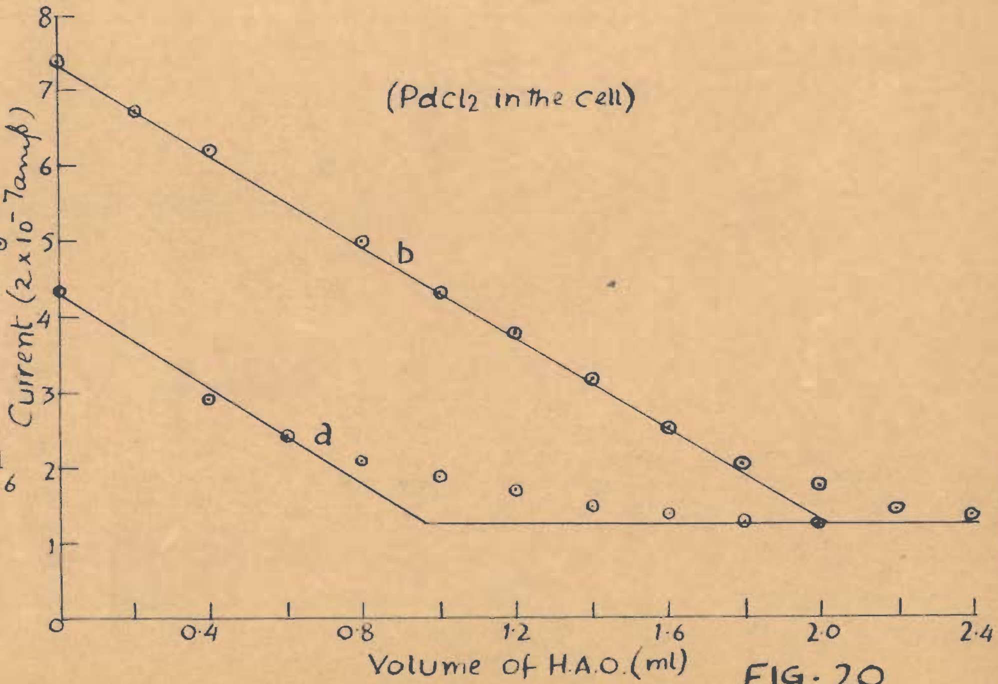


FIG. 20

AMPEROMETRIC TITRATIONS

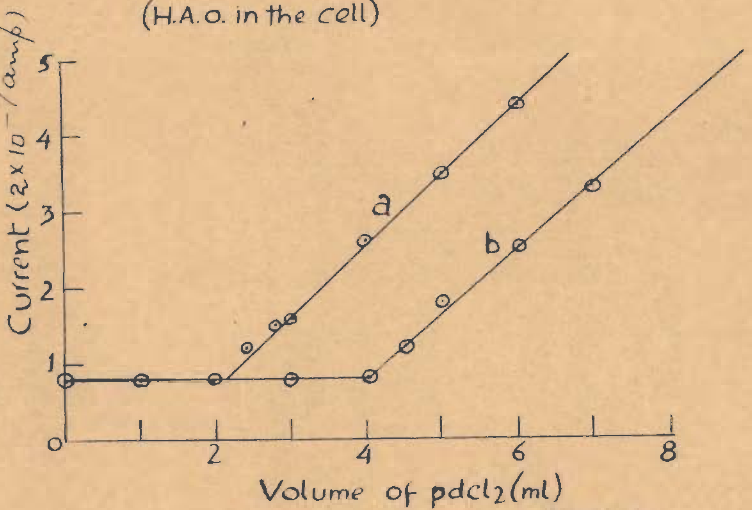
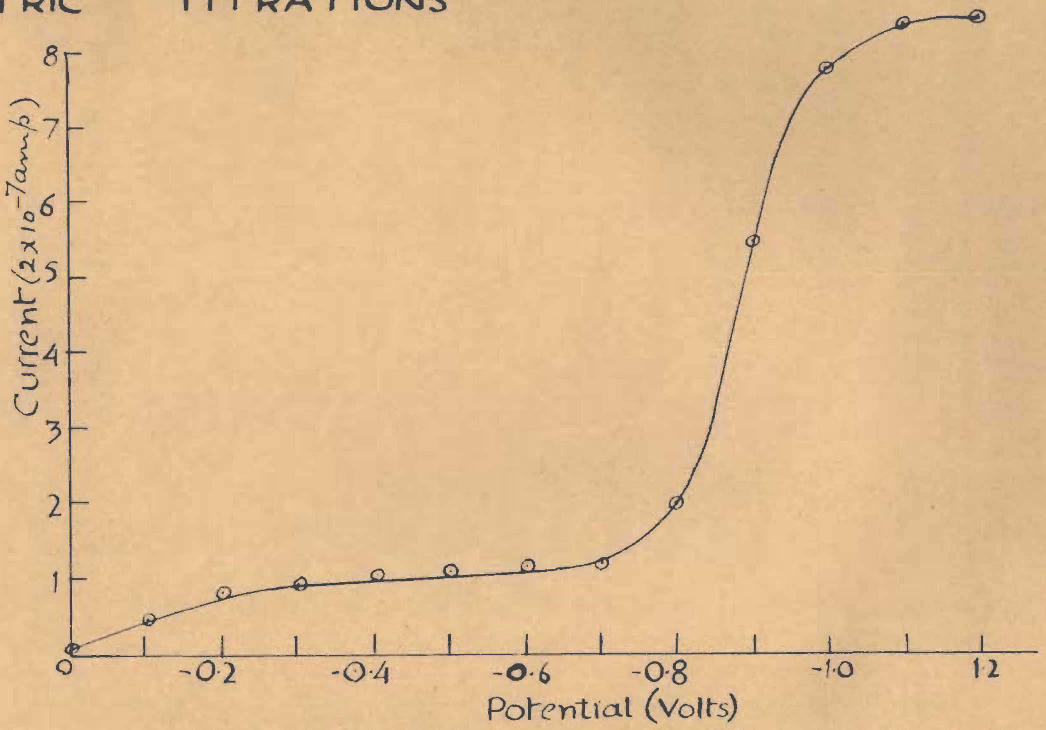


FIG. 21



POLAROGRAM OF Ni(II)

FIG. 22

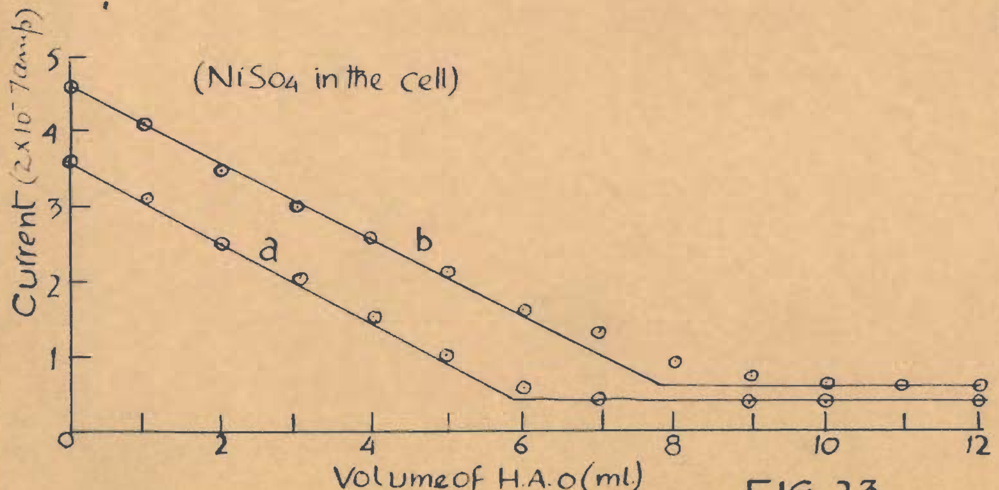


FIG. 23

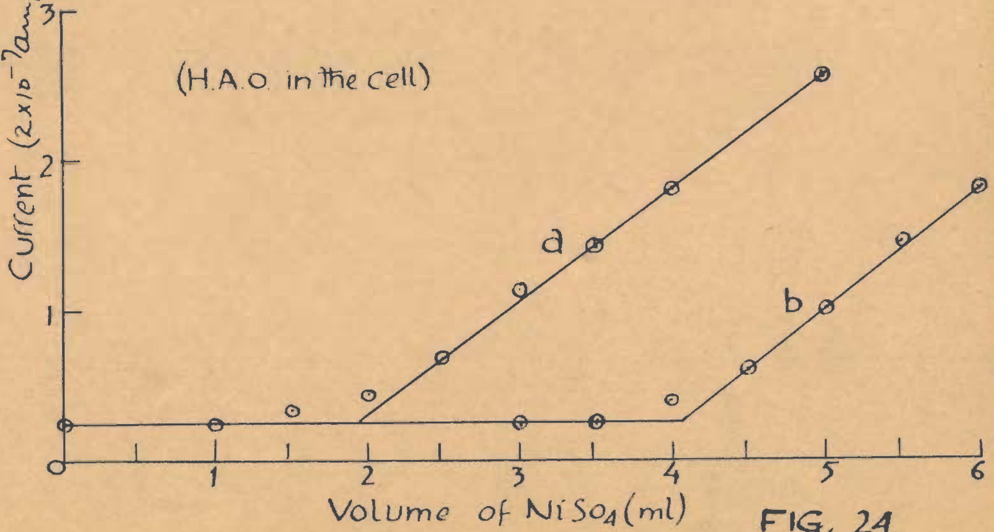
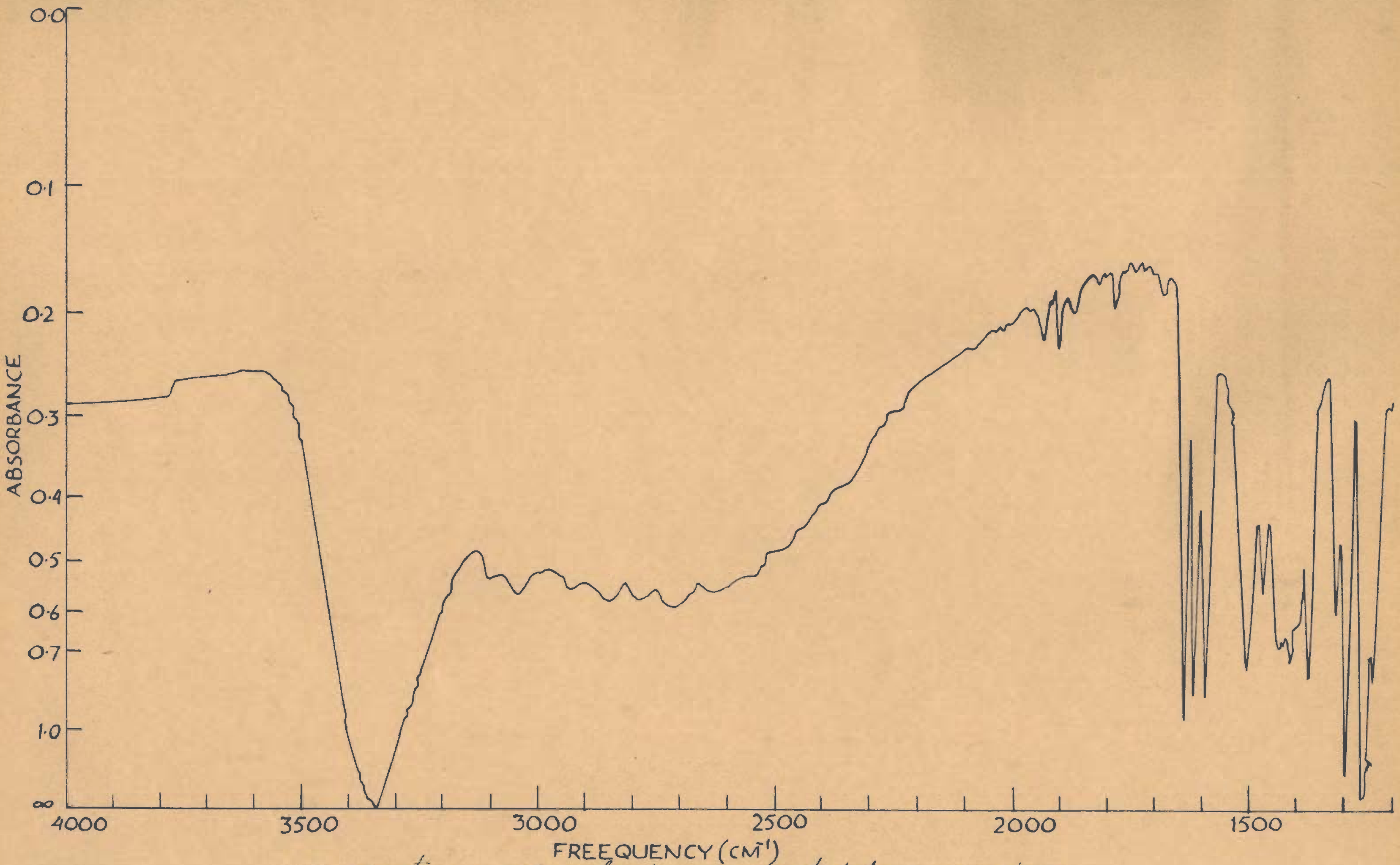
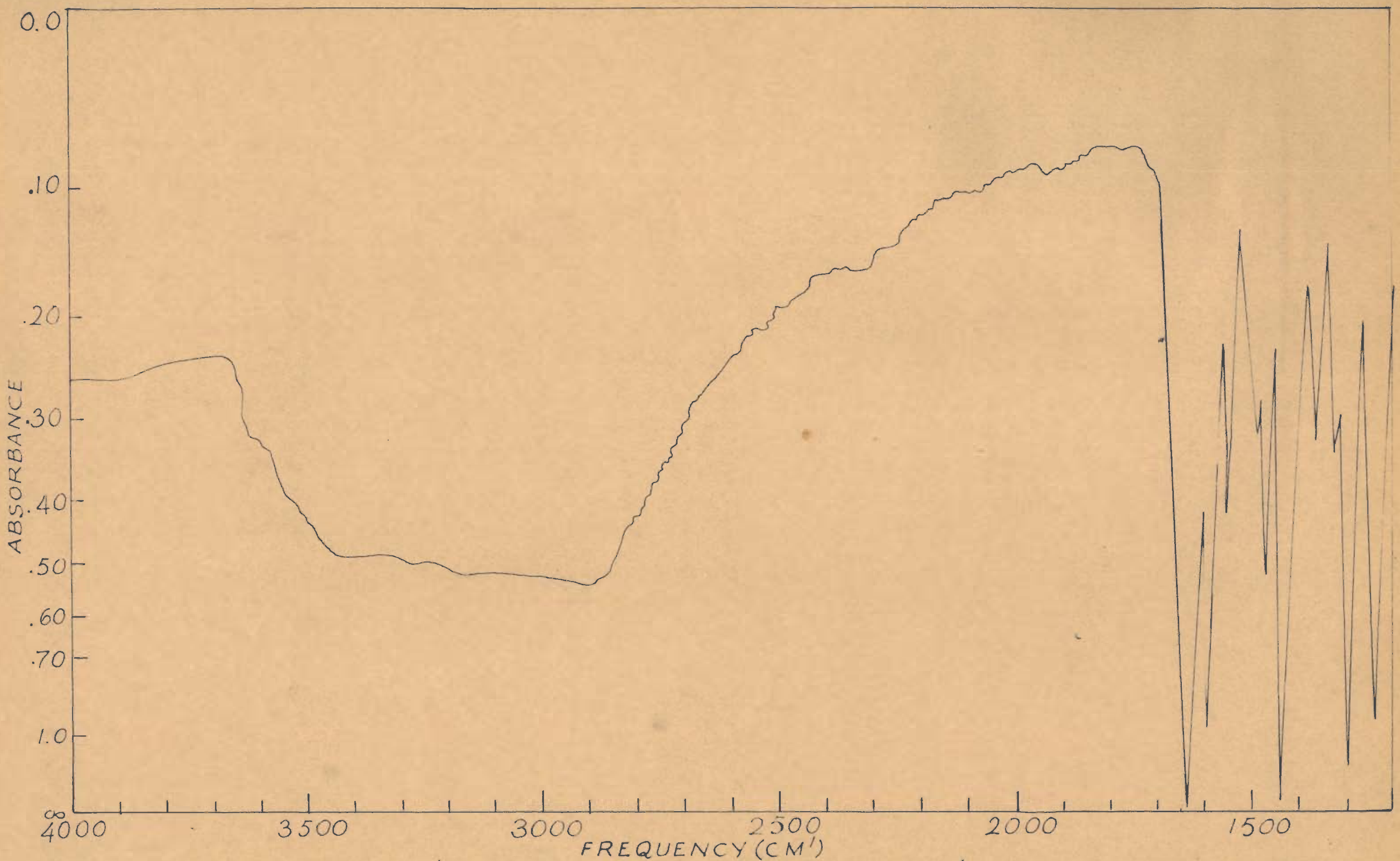


FIG. 24

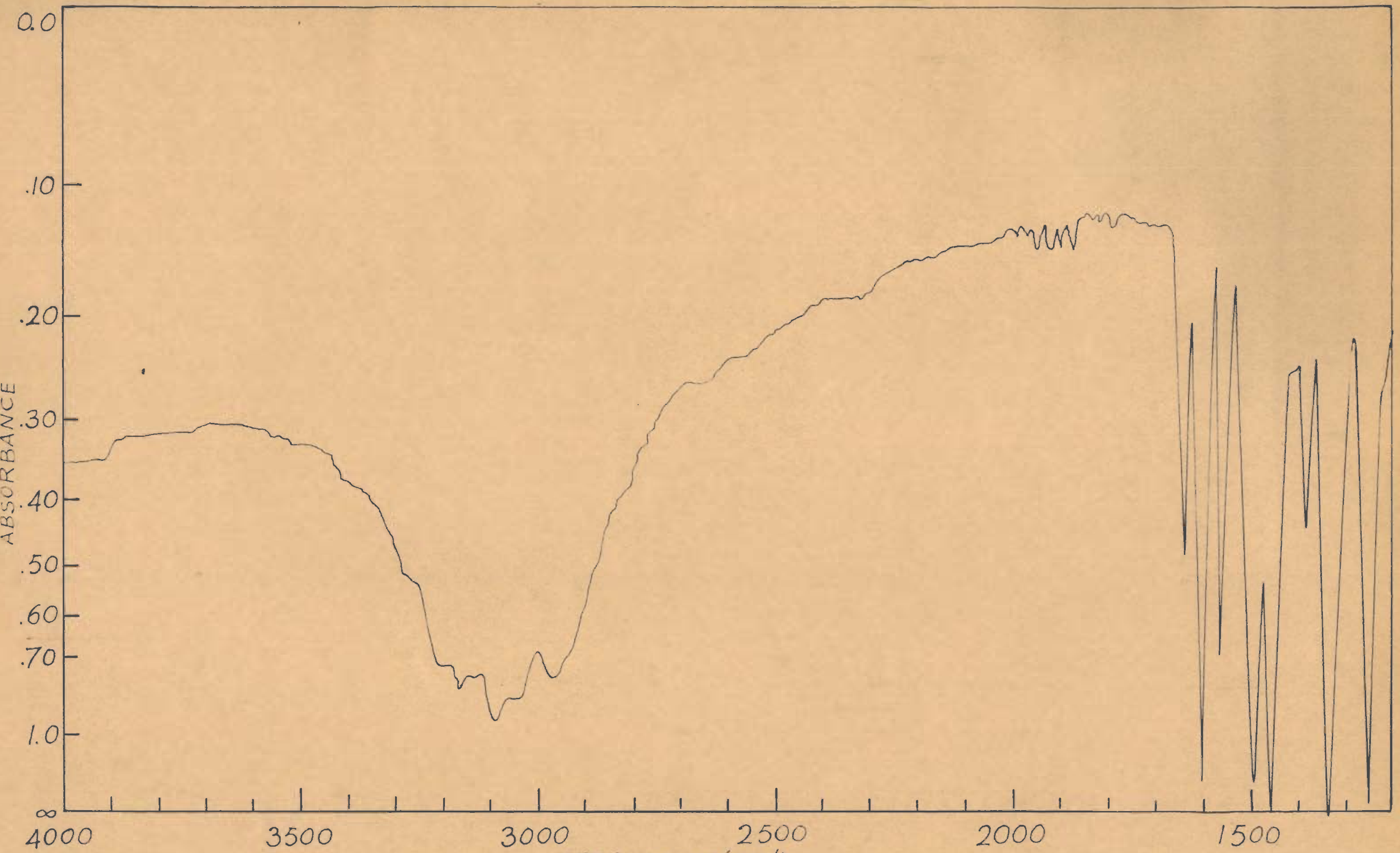


I.R. spectrum of o-hydroxy-acetophenone oxime

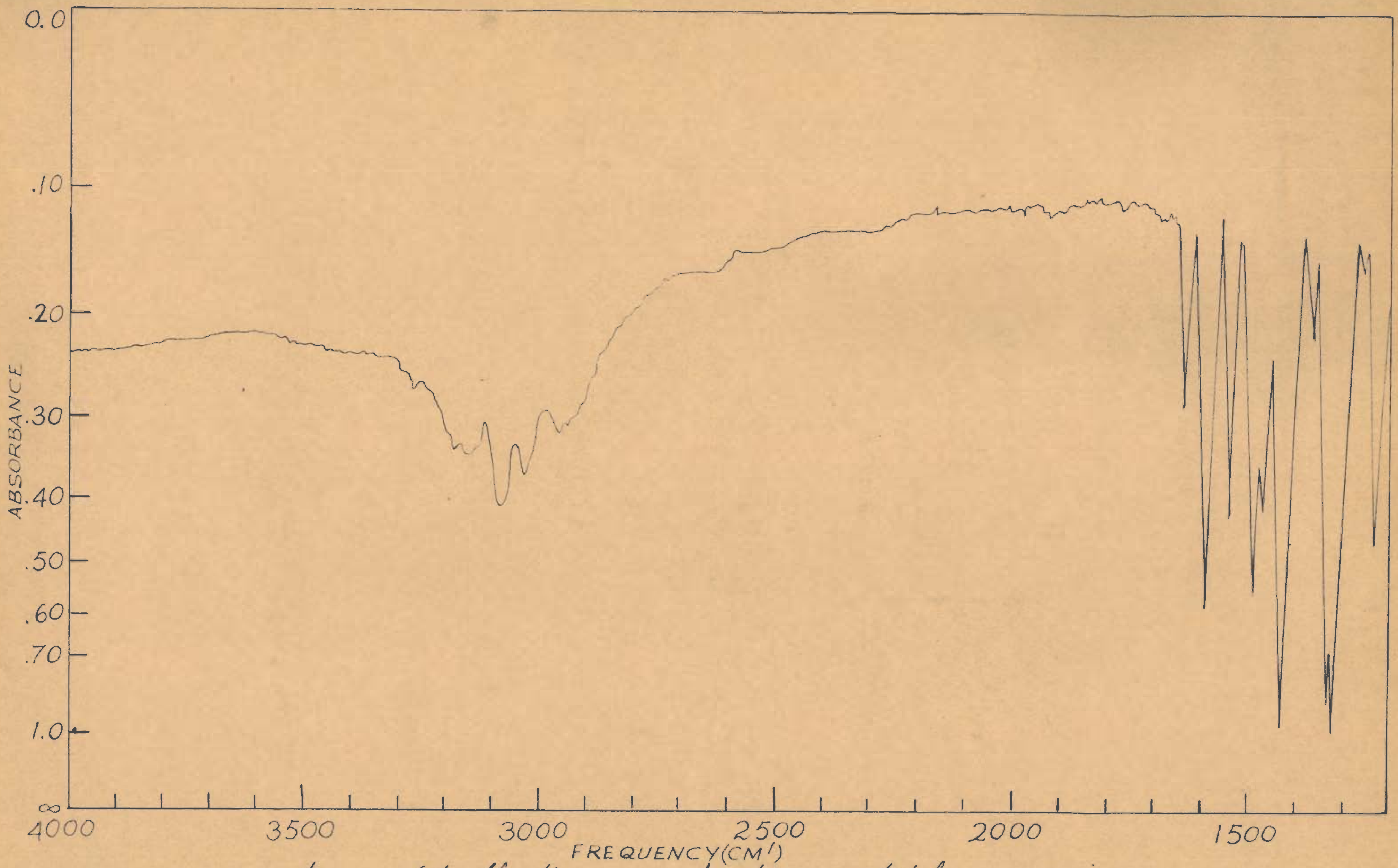
FIG. 25



I.R. spectrum of molybdenum-o-hydroxy acetophenone oxime
FIG. 26

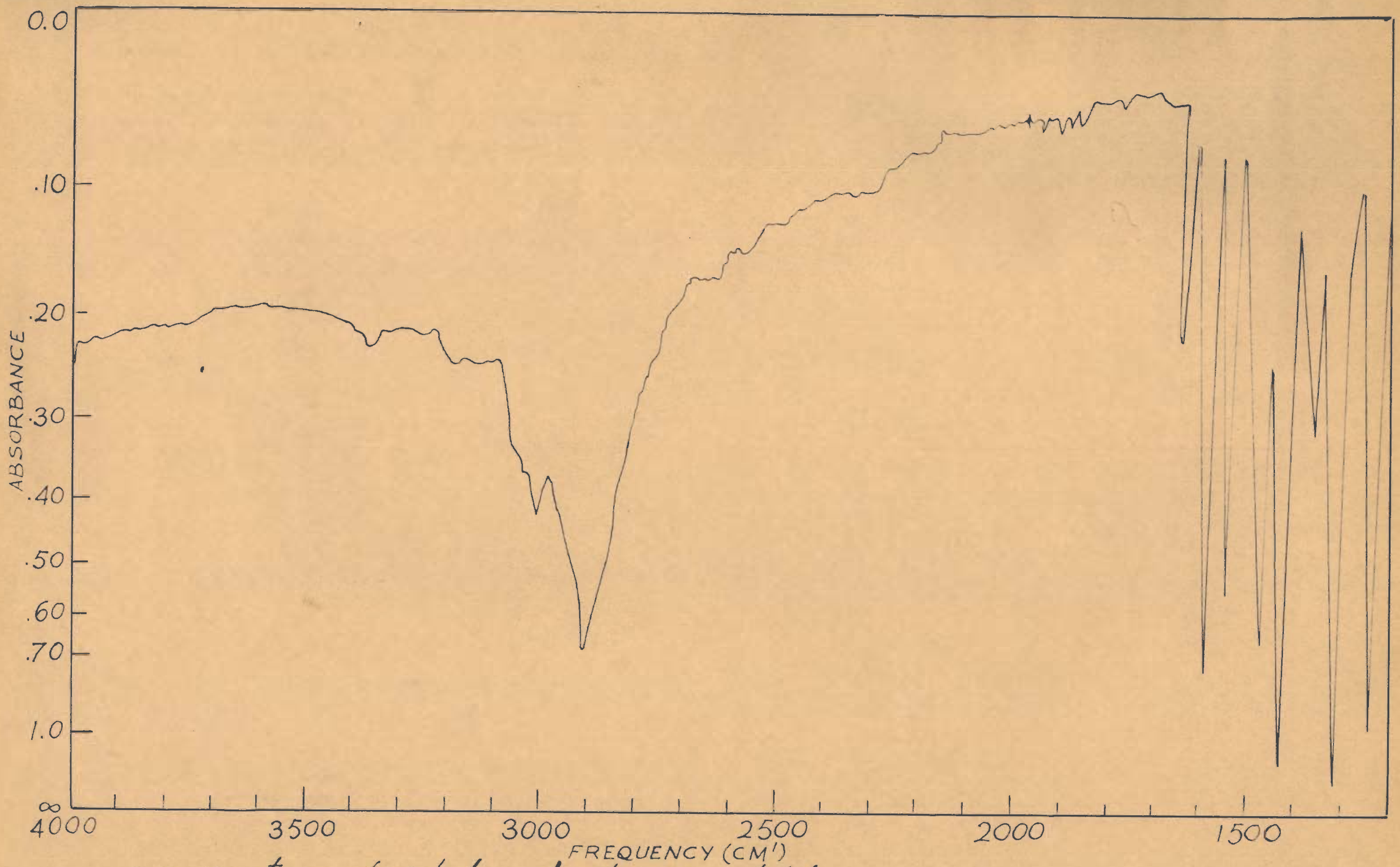


I.R. spectrum of copper-o-hydroxy acetophenone oxime
FIG. 27



I.R. spectrum of palladium - o- hydroxy acetophenone oxime.

FIG. 28



I. R. spectrum of nickel-o-hydroxy acetophenone oxime
FIG. 29

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CHAPTER II

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" Metal complexes of 2-hydroxy-5-methyl acetophenoneoxime "

***

INTRODUCTION

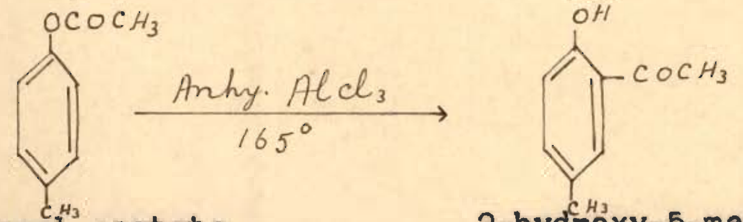
During the course of study of the metal complexes of o-hydroxy-acetophenoneoxime, it was considered worthwhile to investigate the reactions of its methyl derivative which has not yet been studied in detail. From the existing literature it appears that complexes of copper, nickel and cobalt have only been studied from analytical point of view. Singh and Sharma[1] have suggested the utility of 2-hydroxy-5-methyl acetophenoneoxime as a gravimetric reagent for copper and nickel and their separation when present in the same solution but they did not study the physico-chemical aspect of the problem.

The investigations described in this Chapter deal with the physico-chemical studies on the composition and structure of the complexes formed by the interaction between 2-hydroxy-5-methyl acetophenoneoxime and copper, nickel, palladium and molybdenum. The physical methods applied are spectrophotometry, conductometry and amperometry. The results achieved by the physical methods have been supplemented by the chemical analysis and infrared spectroscopy of the isolated complexes.

EXPERIMENTAL

Preparation of 2-hydroxy-5-methyl-acetophenone :

It was obtained by the Fries migration[2] of p-cresyl acetate in presence of anhydrous aluminium chloride.



p-cresyl acetate   2-hydroxy-5-methyl acetophenone

200 gm. of anhydrous aluminium chloride and 200 ml. of carbon disulphide were placed in a three-necked flask. To this suspension was added slowly p-cresyl acetate (190 mg.) with constant stirring. When all the p-cresyl acetate had been added, the solution was refluxed over water-bath for 2 hours till the evolution of hydrogen chloride ceased. The solvent was distilled off the reaction mixture which was then placed in an oil-bath at 160-165°, for three hours. The contents were then cooled, treated with hydrochloric acid and allowed to stand over-night. The solid product was filtered, dissolved in sodium hydroxide and shaken with ether in a separating funnel. The aquous layer was acidified with hydrochloric acid when 2-hydroxy-5-methyl acetophenone separated out as yellowish solid. It was recrystallized from alcohol when fine needle like yellowish crystals (m.p.50°) were obtained.

Preparation of 2-hydroxy-5-methyl acetophenoneoxime :

It was prepared by refluxing 1 gm. of 2-hydroxy-5-methyl acetophenone with 1 gm. hydroxylamine-hydrochloride and 2 gm. of sodium acetate for 1 hour. On cooling the solution, white crystals of the oxime separated out. It was recrystallized from alcohol.

The solution of the oxime was prepared in 50% alcohol.

Standard stock solutions of ammonium molybdate, copper sulphate, palladium chloride, nickel sulphate and buffers were prepared and standardized in the manner as described earlier in Chapter I.

MOLYBDENUM(VI)-2-HYDROXY-5-METHYL ACETOPHENONEOXIME COMPLEX

Isolation and chemical analysis of the complex :

To a solution of ammonium molybdate was added aquous-alcoholic solution of the oxime (a little more than 2 moles). The pH of the solution was adjusted to 3.5-4.0. The solution was concentrated under vacuum when yellow coloured molybdenum complex crystallized out. The yellow crystals were filtered, washed with alcohol and dried in vacuum dessicator.

A known weight of the complex was digested with aqua-regia and the molybdenum content was estimated as molybdenum oxinate.

The nitrogen content of the complex was estimated by Kjeldahl's method.

Calculated for $(C_9H_{10}O_2N)_2MoO_2$

Mo - 21.04, N - 6.14

Found Mo - 21.7 , N - 6.0

Spectrophotometric studies on the nature, composition and stability of the complex :

Vosburgh and Cooper's method (loc.cit.) was employed to find out the number of complexes formed in solution by the interaction between ammonium molybdate and 2-hydroxy-5-methyl acetophenoneoxime (designated as H.M.A.O) and to choose the wave length suitable for carrying out further studies. Several equimolar solutions were prepared by mixing ammonium molybdate and H.M.A.O in various proportions, viz., 1:1, 1:2, 1:3, 2:1 and 3:1, keeping the total concentration of the reactants at $1x10^{-3}M$. The absorbance of these solutions was measured at different wave lengths (325-450 mµ), employing Bausch and Lomb 'Spectronic 20'.

The effect of pH on the stability of the complex was studied by measuring the absorbance at difference wave lengths, of equimolar solutions containing ammonium molybdate and H.M.A.O. in 1:2 ratio and adjusted to various pH values (2.0-6.0).

Table - 1

Vosburgh Cooper's method applied to Mo-H.M.A.O. complex

Concentration of ammonium molybdate = 1×10^{-3}M
Concentration of H.M.A.O = 1×10^{-3}M

Wave length (mμ)	Optical density				
	Ratio of Amm.molybdate to H.M.A.O				
	1:1	1:2	1:3	2:1	3:1
325	0.36	0.46	0.59	0.32	0.22
330	0.42	0.54	0.70	0.36	0.27
335	0.45	0.60	0.79	0.40	0.31
340	0.48	0.63	0.84	0.41	0.34
345	0.50	0.66	0.88	0.44	0.36
350	0.45	0.59	0.83	0.39	0.28
355	0.40	0.52	0.76	0.35	0.25
360	0.36	0.46	0.70	0.32	0.21
365	0.31	0.41	0.64	0.27	0.18
370	0.27	0.37	0.56	0.23	0.16
375	0.23	0.33	0.50	0.20	0.13
380	0.195	0.29	0.44	0.17	0.115
385	0.18	0.26	0.40	0.15	0.095
390	0.17	0.23	0.36	0.13	0.082
400	0.15	0.18	0.29	0.12	0.065
410	0.13	0.15	0.23	0.11	0.05
425	0.10	0.105	0.165	0.09	0.03
450	0.05	0.07	0.12	0.05	0.01
Curves	(1)	(2)	(3)	(4)	(5)

Fig. 1

All the solutions have maximum absorbance at 345 mμ

Table - 2

Effect of pH on the stability of molybdenum complex

Concentration of Ammonium molybdate = 4×10^{-4}M

Concentration of H.M.A.O = 8×10^{-4}M

Wave length (mμ)	Optical density of solutions at pH						
	2.0	3.0	3.5	4.0	4.5	5.0	6.0
325	0.47	0.48	0.50	0.50	0.47	0.30	0.02
330	0.52	0.55	0.57	0.61	0.575	0.34	0.02
335	0.57	0.60	0.63	0.62	0.59	0.38	0.03
340	0.59	0.63	0.66	0.66	0.63	0.41	0.04
345	0.60	0.64	0.68	0.68	0.65	0.44	0.05
350	0.57	0.60	0.64	0.64	0.60	0.40	0.03
355	0.51	0.54	0.60	0.61	0.57	0.38	0.02
360	0.45	0.48	0.56	0.56	0.52	0.34	0.02
365	0.40	0.43	0.50	0.50	0.46	0.30	0.01
370	0.35	0.38	0.45	0.45	0.41	0.27	0.0
380	0.285	0.31	0.40	0.41	0.37	0.23	
390	0.21	0.24	0.32	0.33	0.29	0.18	
400	0.165	0.19	0.25	0.26	0.23	0.15	
425	0.09	0.10	0.11	0.11	0.11	0.07	
450	0.05	0.06	0.08	0.08	0.08	0.04	
Curves	(1)	(2)	(3)	(4)	(5)	(6)	(7)

Fig. 2

λmax of the complex lies at 345 mμ in the pH range 2.0-6.0.

Job's method of continued variation was followed for determining the composition of the complex. Equimolar solutions of ammonium molybdate and H.M.A.O. of concentrations, 3.333×10^{-3}M, 2.5×10^{-3}M, and 2×10^{-3}M, were mixed in the same manner as described in Chapter I, the pH of each solution being kept at 3.5-4.0 and the final volume at 25 ml. The absorbance of the solutions was measured at 345,350 and 360 mμ. The difference between the optical density of the mixture and that of Ammonium molybdate and H.M.A.O. was plotted against the ratio $(MoO_4^{--})/(MoO_4^{--})+(H.M.A.O)$.

The absorbance values recorded at 345 and 360 mu are given in the following tables while those at 350 mμ are depicted in Fig.4 :

Table - 3

Job's method of continued variation applied to Mo-H.M.A.O complex

Wave length 345 mμ Final concentration of the reactants = 1.333×10^{-3}M

Vol.of Amm. molybdate (ml.)	Vol.of H.M.A.O (ml.)	Optical density			
		Mixture	H.M.A.O.	Amm.molybdate	Difference
1.0	9.0	0.89	0.09	0.01	0.79
2.0	8.0	1.04	0.08	0.02	0.94
3.0	7.0	1.07	0.07	0.02	0.98
4.0	6.0	1.02	0.07	0.03	0.92
5.0	5.0	0.915	0.065	0.035	0.815
6.0	4.0	0.745	0.06	0.04	0.645
7.0	3.0	0.57	0.045	0.05	0.475
8.0	2.0	0.405	0.04	0.06	0.305
9.0	1.0	0.24	0.02	0.06	0.16

Fig.3, Curve 1

Table - 4

Wave length 345 mμ

Final concentration of the reactants = 1×10^{-3}M

Vol.of Amm. molybdate (ml.)	Vol.of H.M.A.O (ml.)	Optical density Mixture	H.M.A.O	Amm.molybdate	Difference
1.0	9.0	0.62	0.06	0.0	0.56
2.0	8.0	0.73	0.06	0.01	0.66
3.0	7.0	0.80	0.05	0.01	0.74
4.0	6.0	0.75	0.05	0.015	0.685
5.0	5.0	0.635	0.045	0.02	0.57
6.0	4.0	0.52	0.04	0.03	0.45
7.0	3.0	0.42	0.035	0.04	0.345
8.0	2.0	0.31	0.03	0.05	0.23
9.0	1.0	0.17	0.015	0.05	0.105

Fig.3, curve 2

Table - 5

Wave length 345 mμ

Final concentration of the reactants = 8×10^{-4}M

Vol.of Amm. molybdate (ml.)	Vol.of H.M.A.O (ml.)	Optical density of Mixture	H.M.A.O	Amm.molybdate	Difference
1.0	9.0	0.41	0.05	0.0	0.36
2.0	8.0	0.54	0.05	0.01	0.48
3.0	7.0	0.56	0.04	0.01	0.51
4.0	6.0	0.52	0.035	0.02	0.465
5.0	5.0	0.45	0.03	0.02	0.40
6.0	4.0	0.37	0.025	0.03	0.315
7.0	3.0	0.285	0.02	0.03	0.235
8.0	2.0	0.20	0.02	0.04	0.14
9.0	1.0	0.11	0.01	0.04	0.06

Fig.3, Curve 3

Table - 6

Wave length 360 mμ

Final concentration of the reactants = $1.333 x 10^{-3} M$

Vol.of Amm. molybdate (ml.)	Vol. of H.M.A.O. (ml.)	Optical density of		
		Mixture	H.M.A.O.	Difference
1.0	9.0	0.66	0.03	0.63
2.0	8.0	0.75	0.03	0.72
3.0	7.0	0.825	0.025	0.80
4.0	6.0	0.74	0.02	0.72
5.0	5.0	0.64	0.02	0.62
6.0	4.0	0.52	0.01	0.51
7.0	3.0	0.40	0.01	0.39
8.0	2.0	0.27	-	0.27
9.0	1.0	0.14	-	0.14

Fig.5, Curve 1

Table - 7

Wave length 360 mμ

Final concentration of the reactants = $1 x 10^{-3} M$

Vol. of Amm. molybdate (ml.)	Vol.of H.M.A.O (ml.)	Optical density of		
		Mixture	H.M.A.O.	Difference
1.0	9.0	0.44	0.02	0.42
2.0	8.0	0.56	0.02	0.54
3.0	7.0	0.59	0.01	0.58
4.0	6.0	0.54	0.01	0.53
5.0	5.0	0.46	0.01	0.45
6.0	4.0	0.37	-	0.37
7.0	3.0	0.29	-	0.29
8.0	2.0	0.20	-	0.20
9.0	1.0	0.10	-	0.10

Fig.5, Curve 2

Table - 8

Wave length 360 mµ

Final concentration of the reactants = 8×10^{-4}M

Vol.of Amm. molybdate (ml.)	Vol.of H.M.A.O (ml.)	Optical density of Mixture	Optical density of H.M.A.O.	Optical density of Difference
1.0	9.0	0.29	0.02	0.27
2.0	8.0	0.37	0.02	0.35
3.0	7.0	0.41	0.01	0.40
4.0	6.0	0.37	0.01	0.36
5.0	5.0	0.32	-	0.32
6.0	4.0	0.255	-	0.255
7.0	3.0	0.18	-	0.18
8.0	2.0	0.125	-	0.125
9.0	1.0	0.06	-	0.06

Fig.5, Curve 3

Ammonium molybdate solutions have no absorption at 360 mµ

Further confirmation of its composition was achieved by performing slope ratio method (loc.cit.). The mixing of the solutions of the reactants was done in the same manner as described in Chapter I.

The observations are tabulated below :

Table - 9

Slope-ratio method applied to Mo-H.M.A.O. complex

Fixed concentration of H.M.A.O = 6.666x10^{-4}M (in 25 ml.)
Initial concentration of Amm.molybdate added=3.333x10^{-3}M
pH of the solutions = 3.5-4.0
Final volume = 25 ml.

Vol.of Amm.molybdate added (ml.)	O.D.of solutions at 345 mμ
0.0	0.03
0.5	0.19
1.0	0.33
1.5	0.48
2.0	0.55
2.5	0.58

Fig.6, Curve 1

Table - 10

Fixed concentration of Amm.molybdate =6.666x10^{-4}(in 25 ml)
Initial concentration of H.M.A.O. added = 3.333x10^{-3}M
pH of the solutions = 3.5-4.0
Final volume = 25 ml.

Vol.of H.M.A.O.added (ml.)	O.D.of solutions at 345 mμ
0.0	0.03
0.5	0.10
1.0	0.17
1.5	0.23
2.0	0.30
2.5	0.40
3.0	0.45

Fig.6,Curve 2

Table - 11

Fixed concentration of H.M.A.O = 5×10^{-4}M (in 25 ml.)

Initial concentration of Amm.molybdate added = 2.5×10^{-3}M

pH of solutions = 3.5-4.0

Final volume = 25 ml.

Vol.of Amm.molybdate added (ml.)	O.D. of solutions at 345 mµ
0.0	0.03
0.5	0.14
1.0	0.25
1.5	0.32
2.0	0.36
2.5	0.38

Fig.6, Curve 3

Table - 12

Fixed concentration of Amm.molybdate = 5×10^{-4}M (in 25 ml.)

Initial concentration of H.M.A.O.added= 2.5×10^{-3}M

pH of the solutions = 3.5-4.0

Final volume = 25 ml.

Vol.of H.M.A.O.added (ml.)	O.D.of solutions at 345 mµ
0.0	0.02
0.5	0.075
1.0	0.11
1.5	0.16
2.0	0.21
2.5	0.24
3.0	0.31
3.5	0.35

Fig.6, Curve 4

Stability constant of the complex :

The method recommended by Dey and co-workers (loc.cit.) was employed for determining the stability constant of the complex. For calculating the value of K, the absorbance measurements made during Job's method of continued variation (tables 7,8) at 360 mμ, were utilised. For an arbitrary absorbance value of 0.19 on the graph (Fig.7) in the descending portions of the curves, the values of a_1, b_1, a_2, b_2 were found to be:

$a_1 = 8\times10^{-4}M$

$b_1 = 2\times10^{-4}M$

$a_2 = 5.6\times10^{-4}M$

$b_2 = 2.4\times10^{-4}M$

Conductometric studies :

The composition of the Mo(VI) complex was further confirmed by performing conductometric titrations. The apparatus and the procedure for performing these titrations were the same as described in Chapter I.

The observations are summarized below :

Table - 13

Direct titrations (Amm.molybdate in the cell)

Volume of Ammonium molybdate = 30 ml.

Fixed concentration of Amm.molybdate = Set I: 1.333×10^{-3}M
Set II: 2×10^{-3}M
Set III: 2.666×10^{-3}M

Initial concentration of H.M.A.O added = 2×10^{-2}M

Vol.of H.M.A.O (ml.)	Set I Corrected conductance $\times 10^{-3}$mhos	Vol. of H.M.A.O (ml.)	Set II Corrected conductance $\times 10^{-3}$mhos	Vol.of H.M.A.O (ml.)	Set III Corrected conductance $\times 10^{-3}$mhos
0.0	2.6	0.0	3.9	0.0	4.7
0.5	2.56	0.5	3.8	1.0	4.5
1.0	2.43	1.0	3.7	2.0	4.25
1.5	2.35	1.5	3.64	3.0	3.95
2.0	2.32	2.0	3.5	3.5	3.90
2.5	2.30	2.5	3.33	4.0	3.77
3.0	2.17	3.0	3.2	5.0	3.64
3.5	2.04	3.5	3.1	5.5	3.57
4.0	1.96	4.0	3.03	6.0	3.45
4.5	1.92	4.5	2.9	6.5	3.33
5.0	1.90	5.0	2.86	7.0	3.10
5.5	1.85	5.5	2.74	7.5	3.0
6.0	1.80	6.0	2.63	8.0	2.94
		6.5	2.56	9.0	2.85
		7.0	2.50	10.0	2.75
		7.5	2.47	11.0	2.65
		8.0	2.44	12.0	2.55
		9.0	2.32		
		10.0	2.22		
Fig.8, curves (a)			(b)		(c)

Curve a
30 ml.of 1.333×10^{-3}M Amm.molybdate ≡ 4.0 ml.of 2×10^{-2}M H.M.A.O.
≡60.0 ml.of 1.333×10^{-3}M H.M.A.O

Curve b
30 ml.of 2×10^{-3}M Amm.molybdate ≡ 6.1 ml.of 2×10^{-2}M H.M.A.O
≡61.0 ml.of 2×10^{-3}M H.M.A.O

Curve c
30 ml. of 2.666×10^{-3}M Amm.molybdate ≡ 7.5 ml.of 2×10^{-2}M H.M.A.O.
≡56.3 ml.of 2.666×10^{-3}M H.M.A.O

Table - 14

Reverse titrations (H.M.A.O.in the cell)

Volume of H.M.A.O = 30 ml.

Fixed concentration of H.M.A.O. = Set I 4×10^{-3}M

Set II 5.33×10^{-3}M

Initial concentration of Amm.molybdate added= 2×10^{-2}M

Vol.of Amm. molybdate (ml.)	Set I Corrected conductance ($\times10^{-3}$ mhos)	Vol.of Amm. molybdate (ml.)	Set II Corrected conductance ($\times10^{-3}$ mhos)
0.0	0.013	0.0	0.01
0.5	0.63	0.5	0.55
1.0	1.13	1.0	1.0
1.5	1.7	1.5	1.5
2.0	2.2	2.0	1.9
2.5	2.7	2.5	2.25
3.0	3.1	3.0	2.8
3.5	3.33	3.5	3.12
4.0	4.0	4.0	3.33
4.5	4.2	4.5	3.45
5.0	4.5	5.0	4.0
5.5	5.0	5.5	4.25
6.0	5.1	6.0	4.4
6.5	5.4	6.5	4.6
Fig.9, curve		(a)	(b)

Curve (a)

30 ml. 4×10^{-3}M H.M.A.O. ≡ 3.15 ml.of 2×10^{-2}M Amm.molybdate
≡ 15.75 ml.of 4×10^{-3}M Amm.molybdate

Curve (b)

30 ml. of 5.33×10^{-3}M H.M.A.O ≡ 3.75 ml.2×10^{-2}M Amm. molybdate
≡ 14.0 ml.of 5.33×10^{-3}M Amm.molybdate

COMPLEXES OF Cu(II), Pd(II) AND Ni(II) WITH 2-HYDROXY-5-METHYL ACETOPHENONEOXIME

Isolation and chemical analysis of the complexes :-

Copper-2-hydroxy-5-methyl acetophenoneoxime:

To a solution of copper sulphate was added, with constant stirring, an alcoholic solution of the oxime(>2 moles The pH of the solution was adjusted to about 2.5 and the precipitate was digested over water bath for an hour. The precipitate was filtered, washed with hot water, followed by dilute alcohol and dried at 100-110°C.

A weighed quantity of dry complex was decomposed by boiling it with aqua-regia and its copper content was estimated as cuprous thiocyanate.

The nitrogen content of the complex was also determined by Kjeldahl's method.

Calculated for $(C_9H_{10}O_2N)_2Cu$

Cu - 16.22, N - 7.15

Found Cu - 16.52, N - 7.0

Palladium-2-hydroxy-5-methyl-acetophenoneoxime :

Palladium chloride solution was treated with an alcoholic solution of the oxime (>2 moles), with constant stirring, when a yellow precipitate of palladium complex was obtained. The precipitate was digested over water bath for an hour, filtered, washed with water and finally with dilute alcohol and dried at 100-110°C.

A known weight of the dry complex was decomposed with aqua-regia and the palladium content was estimated as palladium dimethyl-glyoxime.

The nitrogen content of the complex was also determined by Kjeldahl's process.

Calculated for $(C_9H_{10}O_2N)_2Pd$

Pd - 24.5, N - 6.44

Found Pd - 25.1, N - 6.6

Nickel-2-hydroxy-5-methyl-acetophenoneoxime :

To a solution of nickel sulphate was added, with constant stirring, an alcoholic solution of the oxime (a little more than 2 moles). The pH of the solution was adjusted to about 6.0 and the green precipitate of the nickel complex was digested over water bath for an hour. The precipitate was filtered, washed with hot water and then with dilute alcohol. It was dried at 100-110°C.

A weighed quantity of the dry sample of the complex was decomposed with aqua-regia and the nickel content was determined gravimetrically as nickel dimethyl-glyoxime.

The nitrogen content of the complex was also determined by Kjeldahl's process.

Calculated for $(C_9H_{10}O_2N)_2Ni$

Ni - 15.17, N - 7.24

Found Ni - 14.9 , N - 7.40

Since these complexes were insoluble in nature, therefore conductometric and amperometric methods could only be employed to determine their compositions.

Conductometric titrations :-

The apparatus and the procedure adopted for these titrations was the same as described earlier.

The observations are given in the following tables :

Conductometric titrations between copper sulphate and 2-hydroxy-5-methyl-acetophenoneoxime (H.M.A.O)

Table - 15

Direct titrations (Copper sulphate in the cell)

Volume of copper sulphate = 25 ml.

Fixed concentration of copper sulphate solutions
= Set I: 8×10^{-4}M
= Set II: 1.2×10^{-3}M
= Set III: 1.6×10^{-3}M

Initial concentration of H.M.A.O. added = 1×10^{-1}M

Vol.of H.M.A.O. (ml.)	Set I Conductance $\times 10^{-4}$mhos	Vol.of H.M.A.O (ml.)	Set II Conductance $\times 10^{-4}$mhos	Vol.of H.M.A.O (ml.)	Set III Conductance $\times 10^{-4}$mhos
0.0	4.0	0.0	5.2	0.0	6.68
0.1	5.3	0.1	6.8	0.1	8.1
0.2	6.7	0.2	8.6	0.2	10.0
0.3	8.8	0.3	10.4	0.3	11.5
0.4	10.5	0.4	12.2	0.4	13.2
0.5	11.1	0.5	13.8	0.5	14.9
0.6	11.5	0.6	15.3	0.6	16.5
0.7	12.2	0.7	16.5	0.7	18.2
0.8	12.7	0.8	17.2	0.8	19.1
0.9	13.3	0.9	18.1	0.9	20.6
1.0	13.8	1.0	19.0	1.0	21.5
		1.1	19.8	1.1	22.1
				1.2	23.0
	Curve(a)		Curve(b)		Curve(c)

Fig.10

Curve(a)
25 ml.of 8×10^{-4}M $CuSo_4$ ≡ 0.4 ml.of 1×10^{-1}M H.M.A.O
≡ 50 ml.of 8×10^{-4}M H.M.A.O.

Curve(b)
25 ml. of 1.2×10^{-3}M $CuSo_4$ ≡ 0.62 ml.of 1×10^{-1}M H.M.A.O
≡51.70 ml.of 1.2×10^{-3}M H.M.A.O

Curve(c)
25 ml.of 1.6×10^{-3}M $CuSo_4$ ≡ 0.79 ml.of 1×10^{-1}M H.M.A.O
≡49.4 ml.of 1.6×10^{-3}M H.M.A.O

Table - 16

Reverse titrations (H.M.A.O. in the cell)

Volume of H.M.A.O. = 25 ml.

Fixed Concentration of H.M.A.O = Set I: $2.4x10^{-3}M$

Set II: $1.6x10^{-3}M$

Initial Concentration of $CuSo_4$ added = $1x10^{-2}M$

Vol.of $CuSo_4$ (ml)	Set I Corrected conductance $x10^{-4}$mhos	Vol.of $CuSo_4$ (ml)	Set II Corrected conductance $x10^{-4}$mhos
0.0	0.04	0.0	0.05
0.5	1.96	0.5	1.9
1.0	3.74	1.0	3.7
1.5	5.4	1.5	5.2
2.0	6.96	2.0	6.2
2.5	8.5	2.5	6.6
3.0	9.5	3.0	6.85
3.5	10.5	3.5	7.2
4.0	11.4	4.0	7.5
4.5	12.0		
5.0	12.6		
6.0	13.6		
	Curve (a)		Curve(b)

Fig.11

Curve(a)

25 ml. of $2.4x10^{-3}M$ H.M.A.O $\equiv$ 2.85 ml.of $1x10^{-2}M$ $CuSo_4$

$\equiv$ 12 ml.of $2.4x10^{-3}M$ $CuSo_4$

Curve(b)

25 ml. of $1.6x10^{-3}M$ H.M.A.O $\equiv$ 1.8 ml.of $1x10^{-2}M$ $CuSo_4$

$\equiv$ 11.3 ml.of $1.6x10^{-2}M$ $CuSo_4$

Conductometric titrations between palladium chloride and 2-hydroxy-5-methyl-acetophenoneoxime (H.M.A.O)

Table -17

Direct titrations ($PdCl_2$ in the cell)

Volume of $PdCl_2$ = 25 ml.
Fixed concentration of $PdCl_2$ solutions = $4x10^{-4}M$ (Set I)
= $6x10^{-4}M$ (Set II)
Initial concentration of H.M.A.O. added = $1x10^{-2}M$

Vol.of H.M.A.O. (ml.)	Set I Corrected conductance $x10^{-2}$ mhos	Vol.of H.M.A.O (ml.)	Set II Corrected conductance $x10^{-2}$ mhos
0.0	3.0	0.0	4.4
0.5	2.75	0.5	4.1
1.0	2.40	1.0	3.8
1.5	2.15	1.5	3.5
2.0	1.90	2.0	3.25
2.5	1.75	2.5	2.95
3.0	1.60	3.0	2.70
3.5	1.5	4.0	2.5
4.0	1.35	4.5	2.45
4.5	1.22	5.0	2.40
		5.5	2.30
			2.20

Curve(a) Curve (b)

Fig.12

Curve (a)

25 ml. of $4x10^{-4}M$ $PdCl_2$ ≡ 2.0 ml. of $1x10^{-2}M$ H.M.A.O.
≡ 50.0 ml. of $4x10^{-4}M$ H.M.A.O.

Curve (b)

25 ml. of $6x10^{-4}M$ $PdCl_2$ ≡ 3.1 ml. of $1x10^{-2}M$ H.M.A.O.
≡ 51.7 ml.of $6x10^{-4}M$ H.M.A.O.

Table - 18

Reverse titrations (H.M.A.O. in the cell)

Volume of H.M.A.O. = 25 ml.

Fixed concentration of H.M.A.O. = 1×10^{-3}M (Set I);

= 4×10^{-4}M (Set II)

Initial concentration of $PdCl_2$ added = 2.5×10^{-3}M

Vol.of $PdCl_2$ (ml.)	Set I Corrected conductance $\times10^{-2}$ mhos	Vol.of $PdCl_2$ (ml.)	Set II Corrected conductance $\times10^{-2}$ mhos
0.0	0.002	0.0	0.00
0.5	0.355	0.5	0.405
1.0	0.68	1.0	0.70
1.5	1.05	1.5	1.0
2.0	1.37	2.0	1.4
2.5	1.65	2.5	1.8
3.0	1.98	3.0	2.1
3.5	2.25	3.5	2.45
4.0	2.55	4.0	2.75
4.5	2.8	4.5	3.05
5.0	3.05		
6.0	3.3		
7.0	3.55		
8.0	3.75		
9.0	3.92		

Curve(a) Curve(b)

Fig.13

Curve (a)

25 ml. of 1×10^{-3}M H.M.A.O. ≡ 5.0 ml.of 2.5×10^{-3}M $PdCl_2$

≡ 12.5 ml.of 1×10^{-3}M $PdCl_2$

Curve (b)

25 ml. of 4×10^{-4}M H.M.A.O. ≡ 2.25 ml. of 2.5×10^{-3}M $PdCl_2$

≡ 14.0 ml. of 4×10^{-4}M $PdCl_2$

Conductometric titrations between nickel sulphate and 2-hydroxy,5-methyl acetophenoneoxime (H.M.A.O)

A standard solution of 2-hydroxy,5-methyl acetophenoneoxime was prepared in equimolar solution of ammonia

Table - 19

Volume of H.M.A.O. = 25 ml.

Fixed concentration of H.M.A.O = 6.4×10^{-3}M (Set I)
= 4×10^{-3}M (Set II)

Initial concentration of $NiSo_4$ added = 2×10^{-2}M

Volume of $NiSo_4$ (ml.)	Set I Corrected conductance $\times10^{-4}$ mhos	Vol.of $NiSo_4$ (ml.)	Set II Corrected conductance $\times10^{-4}$ mhos
0.0	2.0	0.0	1.4
0.5	2.95	0.5	2.3
1.0	3.85	1.0	3.0
1.5	5.0	1.5	4.0
2.0	6.0	2.0	4.7
2.5	6.8	2.5	5.2
3.0	7.5	3.0	6.0
3.5	8.05	3.5	6.6
4.0	8.65	4.0	7.0
4.5	9.3	4.5	7.6
5.0	10.0	5.0	8.1
5.5	10.5	6.0	9.3
6.0	11.0		
6.5	11.5		
7.0	11.75		
	Curve(a)		Curve(b)

Fig.14

Curve(a)
25 ml.of 6.4×10^{-3}M H.M.A.O ≡ 3.9 ml.of 2×10^{-2}M $NiSo_4$
≡12.2 ml.of 6.4×10^{-3}M $NiSo_4$

Curve(b)
25 ml.of 4×10^{-3}M H.M.A.O. ≡2.45 ml.of 2×10^{-2}M $NiSo_4$
≡12.2 ml.of 4×10^{-3}M $NiSo_4$

Nickel sulphate solution could not be successfully titrated against H.M.A.O. as titrant as the variations in the conductance on adding the titrant were too small to be observed.

Amperometric titrations :-

The apparatus and the procedure used for these titrations was the same as described in Chapter I. Both direct (metal in the cell) and reverse (H.M.A.O. in the cell) titrations were performed.

Amperometric titrations between copper sulphate and 2-hydroxy-5-methyl acetophenoneoxime (H.M.A.O)

Amperometric titrations between copper sulphate and H.M.A.O. were carried out, using sodium acetate-acetic acid buffer solution (pH 4.63) as supporting electrolyte and 0.01% solution of gelatine as maximum suppressor, at -0.15 volts (the reduction potential of copper as described earlier in Chapter I).

The observations are given in the following tables :

Table -20

Direct titrations

20 ml.of 2×10^{-3}M $CuSo_4$ titrated against 2×10^{-2}M H.M.A.O.

Vol.of H.M.A.O. (ml.)	Current (2×10^{-7}amp.)	Vol.of H.M.A.O. (ml.)	Current (2×10^{-7} amp.)
0.0	6.3	4.0	1.65
0.5	5.7	4.5	1.15
1.0	5.1	5.0	0.75
1.5	4.5	5.5	0.35
2.0	3.9	6.0	0.25
2.5	3.2	6.5	0.25
3.0	2.7	7.0	0.25
3.5	2.0		

Fig.15, curve (a)

25 ml. of 2×10^{-3}M $CuSo_4$ ≡ 5 ml. of 2×10^{-2}M H.M.A.O.
≡50 ml. of 2×10^{-3}M H.M.A.O.

Table - 21

25 ml.of $1.6\times10^{-3}M$ $CuSo_4$ titrated against $2\times10^{-2}M$ H.M.A.O.

Vol.of H.M.A.O. (ml.)	Current (2×10^{-7}amp.)	Vol.of H.M.A.O. (ml.)	Current (2×10^{-7} amp.)
0.0	5.15	3.5	1.1
0.5	4.4	4.0	0.6
1.0	3.85	4.5	0.25
1.5	3.2	5.0	0.25
2.0	2.65	5.5	0.25
2.5	2.10	6.0	0.25
3.0	1.55		

Fig.15, curve (b)

25 ml. of $1.6\times10^{-3}M$ $CuSo_4$ ≡ 3.9 ml.of $2\times10^{-2}M$ of H.M.A.O.
≡ 48.75 ml.of $1.6\times10^{-3}M$ of H.M.A.O.

Table - 22

25 ml. of $1.2\times10^{-3}M$ $CuSo_4$ titrated against $2\times10^{-2}M$ H.M.A.O.

Vol.of H.M.A.O. (ml.)	Current (2×10^{-7}amp.)	Vol.of H.M.A.O (ml.)	Current (2×10^{-7}amp.)
0.0	3.9	2.5	1.1
0.5	3.3	3.0	0.6
1.0	2.7	3.5	0.25
1.5	2.15	4.0	0.25
2.0	1.6	5.0	0.25

Fig.15, curve (c)

25 ml.of $1.2\times10^{-3}M$ $CuSo_4$ ≡ 3.0 ml.of $2\times10^{-2}M$ of H.M.A.O.
≡ 50 ml. of $1.2\times10^{-3}M$ of H.M.A.O.

Table - 23

Reverse titrations

25 ml.of 3.2×10^{-3}M H.M.A.O. titrated against 1×10^{-2}M $CuSo_4$

Vol.of $CuSo_4$ (ml.)	Current (2×10^{-7} amp.)
0.0	0.25
1.0	0.25
2.0	0.25
3.0	0.25
3.5	0.40
4.0	0.85
4.5	1.75
5.0	2.7
5.5	3.55
6.0	4.5

Fig.16, curve (a)

25 ml. of 3.2×10^{-3}M H.M.A.O. ≡ 3.65 ml.of 1×10^{-2}M $CuSo_4$
≡ 11.4 ml. of 3.2×10^{-3}M $CuSo_4$

Table - 24

25 ml. of 2.4×10^{-3}M H.M.A.O. titrated against 1×10^{-2}M $CuSo_4$

Vol.of $CuSo_4$ (ml.)	Current (2×10^{-7} amp.)
0.0	0.25
1.0	0.25
2.0	0.25
2.5	0.6
3.0	1.1
3.5	2.05
4.0	3.05
4.5	4.0
5.0	5.25

Fig.16, curve (b)

25 ml.of 2.4×10^{-3}M H.M.A.O. ≡ 2.8 ml.of 1×10^{-2}M $CuSo_4$
≡ 11.7 ml.of 2.4×10^{-3}M $CuSo_4$

Table - 25

25 ml. of 1.6×10^{-3}M H.M.A.O titrated against 1×10^{-2}M $CuSo_4$

Vol. of $CuSo_4$ (ml.)	Current (2x10^{-7} amp.)
0.0	0.25
1.0	0.25
1.5	0.25
2.0	0.5
2.5	1.55
3.0	2.5
3.5	3.6

Fig.16, curve (c)

25 ml. of 1.6×10^{-3}M H.M.A.O. $\equiv$ 2.0 ml.of 1×10^{-2}M $CuSo_4$
$\equiv$12.5 ml.of 1.6×10^{-3}M $CuSo_4$

Amperometric titrations between palladium chloride and 2-hydroxy-5-methyl acetophenoneoxime :

Amperometric titrations between palladium chloride and 2-hydroxy-5-methyl acetophenoneoxime were carried out, using sodium acetate-acetic acid buffer solution (pH 4.0) as supporting electrolyte and 0.01% gelatine solution as maximum suppressor, at a potential of -0.4 volts vs S.C.E (Chapter I).

The observations are tabulated below :

Table - 26

Direct titrations ($PdCl_2$ in the cell)

25 ml. of $4x10^{-4}M$ $PdCl_2$ titrated against $2x10^{-2}M$ H.M.A.O.

Vol.of H.M.A.O. (ml.)	Current (2x10^{-7}amp.)	Vol.of H.M.A.O (ml.)	Current (2x10^{-7}amp.)
0.0	4.5	1.2	1.7
0.2	3.9	1.4	1.4
0.4	3.2	1.6	1.3
0.6	2.5	2.0	1.2
0.8	2.2	2.4	1.2
1.0	1.9	2.6	1.2
		3.0	1.2

Fig.17, curve (a)

25 ml. of $4x10^{-4}M$ $PdCl_2$ ≡ 1.0 ml. of $2x10^{-2}M$ of H.M.A.O.
≡50.0 ml. of $4x10^{-4}M$ of H.M.A.O.

Table - 27

25 ml. of $6.4x10^{-4}M$ $PdCl_2$ titrated against $2x10^{-2}M$ H.M.A.O.

Vol.of H.M.A.O. (ml.)	Current (2x10^{-7}amp.)	Vol.of H.M.A.O (ml.)	Current (2x10^{-7}amp
0.0	6.8	1.6	2.5
0.2	6.1	1.8	2.5
0.4	5.6	2.0	2.4
0.6	5.0	2.2	2.3
0.8	4.5	2.4	2.2
1.0	3.6	2.6	2.2
1.2	3.2	3.0	2.2

Fig.17, curve (b)

25 ml. of $6.4x10^{-4}M$ $PdCl_2$ ≡ 1.6 ml.of $2x10^{-2}M$ of H.M.A.O
≡50.0 ml. of $6.4x10^{-4}M$ of H.M.A.O

Table - 28

Reverse titrations (H.M.A.O. in the cell)

25 ml. of 8×10^{-4}M H.M.A.O titrated against 5×10^{-3}M $PdCl_2$

Vol. of $PdCl_2$ (ml.)	Current (2×10^{-7} amp.)
0.0	0.6
1.0	0.6
1.5	0.6
2.0	0.8
2.5	1.1
3.0	1.5
3.5	2.0
4.0	2.5
5.0	3.6

Fig.18, curve (a)

25 ml. of 8×10^{-4}M H.M.A.O $\equiv$ 2.25 ml. of 5×10^{-3}M $PdCl_2$
$\equiv$ 14.1 ml. of 8×10^{-4}M $PdCl_2$

Table - 29

25 ml. of 1.6×10^{-3}M H.M.A.O titrated against 5×10^{-3}M $PdCl_2$

Vol.of $PdCl_2$ (ml.)	Current (2×10^{-7} amp.)
0.0	0.6
1.0	0.6
2.0	0.6
3.0	0.6
4.0	0.8
4.5	1.0
5.0	1.6
5.5	2.0
6.0	2.5
7.0	3.4

Fig.18, curve (b)

25 ml. of 1.6×10^{-3}M H.M.A.O. = 4.1 ml.of 5×10^{-3}M $PdCl_2$
=12.8 ml.of 1.6×10^{-3}M $PdCl_2$

Amperometric titrations between nickel sulphate and 2-hydroxy-5-methyl-acetophenoneoxime :

Amperometric titrations of nickel sulphate against 2-hydroxy-5-methyl-acetophenoneoxime and reverse (H.M.A.O against $NiSo_4$) were performed at a potential of -1.2 volts vs S.C.E. (Chapter I), using ammonia-ammonium chloride buffer solution (9.0 pH) as supporting electrolyte and 0.01% gelatine solution as maximum suppressor. The observations are recorded in the following tables :

Table - 30

Direct titrations ($NiSo_4$ in the cell)

25 ml. of 1.6×10^{-3}M $NiSo_4$ titrated against 2×10^{-2}M H.M.A.O.

Vol.of H.M.A.O (ml.)	Current (2×10^{-7} amp.)	Vol.of H.M.A.O (ml.)	Current (2×10^{-7}amp.
0.0	5.3	3.0	1.75
0.5	4.7	3.5	1.3
1.0	4.15	4.0	0.8
1.5	3.6	4.5	0.7
2.0	2.9	5.0	0.6
2.5	2.3	5.5	0.6

Fig.19, curve (a)

25 ml. of 1.6×10^{-3}M $NiSo_4$ ≡ 3.95 ml.of 2×10^{-2}M H.M.A.O.
≡ 49.4 ml. of 1.6×10^{-3}M H.M.A.O.

Table - 31

25 ml.of 1.2×10^{-3}M $NiSo_4$ titrated against 2×10^{-2}M H.M.A.O

Vol.of H.M.A.O (ml.)	Current (2×10^{-7} amp.)	Vol.of H.M.A.O (ml.)	Current (2×10^{-7} amp.)
0.0	4.25	3.0	0.85
0.5	3.6	3.5	0.60
1.0	3.0	4.0	0.60
1.5	2.35	4.5	0.60
2.0	1.75	5.0	0.60
2.5	1.25		

Fig.19, curve (b)

25 ml. of 1.2×10^{-3}M $NiSo_4$ ≡ 2.9 ml.of 2×10^{-2}M H.M.A.O.
≡48.3 ml.of 1.2×10^{-3}M H.M.A.O.

Table - 32

Reverse titrations (H.M.A.O. in the cell)

25 ml. of 3.2×10^{-3}M H.M.A.O. titrated against 1×10^{-2}M $NiSo_4$

Vol.of $NiSo_4$ (ml.)	Current (2×10^{-7} amp.)	Vol.of $NiSo_4$ (ml.)	Current (2×10^{-7} amp.)
0.0	0.35	5.0	1.5
1.0	0.35	5.5	2.1
2.0	0.35	6.0	2.55
3.0	0.35		
3.5	0.35		
4.0	0.6		
4.5	1.1		

Fig.20, curve (a)

25 ml. of 3.2×10^{-3}M H.M.A.O ≡ 3.8 ml.of 1×10^{-2}M $NiSo_4$
≡ 11.9 ml.of 3.2×10^{-3}M $NiSo_4$

Table - 33

25 ml.of $2x10^{-3}M$ H.M.A.O. titrated against $1x10^{-2}M$ $NiSo_4$

Volume of $NiSo_4$ (ml.)	Current ($2x10^{-7}$ amp.)
0.0	0.35
1.0	0.35
2.0	0.35
2.5	0.60
3.0	1.1
3.5	1.7
4.0	2.2
4.5	2.8

Fig.20, curve (b)

25 ml. of $2x10^{-3}M$ H.M.A.O. $\equiv$ 2.4 ml.of $1x10^{-2}M$ $NiSo_4$
$\equiv$ 12.0 ml.of $2x10^{-3}M$ $NiSo_4$

DISCUSSION

2-Hydroxy-5-methyl acetophenoneoxime (designated as H.M.A.O) forms complexes with molybdenum(VI), copper(II), nickel(II) and palladium(II). The nature, composition and structure of these complexes have been investigated by both chemical and physical methods.

Nature and composition of Mo(VI)-H.M.A.O.complex :

Molybdenum(VI) reacts instantaneously with 2-hydroxy-5-methyl acetophenoneoxime to form a bright yellow, soluble complex in the acidic medium.

Application of Vosburgh and Cooper's method demonstrated the existence of only one complex in the yellow solution. The λmax. of the complex was found to lie at 345 mu (Fig.1).

In order to study the effect of pH on the stability of the complex, a series of equimolar solutions containing ammonium molybdate and H.M.A.O. in 1:2 ratio, were prepared at different pH values. The absorbance of these solutions was measured over a range of wave lengths (325-450 mμ). The absorbance curves (Fig.2) show λmax. at 345 mμ, showing thereby the stability of the complex in the pH range of 2.0-5.0.

Job's method of continued variation was applied to ascertain the composition of the complex. From the absorption curves (Figs.3-5), it could be found that the combining ratio of Mo and H.M.A.O. comes out to be 1:2

respectively.

Further support to the results of Job's method was extended by slope ratio method. The ratio of slopes of the straight line portions on the curves (Fig.6) also revealed the existence of 1:2 complex.

The formation constant of the complex was determined by the method recommended by Dey and co-workers (loc.cit.). The value of K was calculated to be 4.87×10^{8} and that of free energy of formation $\triangle F$ to be -12·0Kcals.

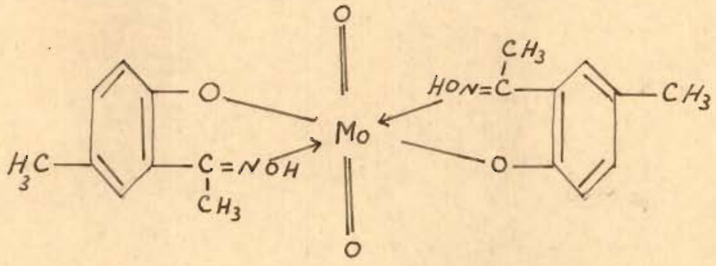
The conductometric titrations between ammonium molybdate and H.M.A.O. also confirm the formation of 1:2 complex for molybdenum and H.M.A.O. respectively.

The results of the titrations are summarized below:

S.No.	Fig.& curve	Volume of Amm. molybdate (ml.)	Volume of H.M.A.O. (ml.)	Mole ratio Mo/H.M.A.O
1.	8,a	$30.0(1.333\times10^{-3}M)$	$60.0(1.333\times10^{-3}M)$	1:2
2.	8,b	$30.0(2\times10^{-3}M)$	$61.0(2\times10^{-3}M)$	1:2.03
3.	8,c	$30.0(2.666\times10^{-3}M)$	$56.3(2.666\times10^{-3}M)$	1:1.9
4.	9,a	$15.75(4\times10^{-3}M)$	$30.0(4\times10^{-3}M)$	1:1.9
5.	9,b	$14.0(5.33\times10^{-3}M)$	$30.0(5.33\times10^{-3}M)$	1:2.14

The results of chemical analysis of the isolated yellow complex correspond to its formula $(C_9H_{10}O_2N)_2MoO_2$.

On the basis of the above evidence, the following structure may be written for the complex,



Composition and structure of Cu(II)-H.M.A.O. complex :

2-Hydroxy-5-methyl acetophenoneoxime forms insoluble, dirty white complex with copper ions in the pH range 1.5-8.0.

The conductometric titrations between copper sulphate and H.M.A.O. reveal the formation of 1:2 (Cu:H.M.A.O.) complex. The results of the titrations are tabulated below:

S.No.	Fig. & curve	Volume of $CuSo_4$ (ml.)	Volume of H.M.A.O. (ml.)	Mole ratio Cu/H.M.A.O
1.	10,a	25.0($8x10^{-4}M$)	50.0($8x10^{-4}M$)	1:2
2.	10,b	25.0($1.2x10^{-3}M$)	51.7($1.2x10^{-3}M$)	1:2.07
3.	10,c	25.0($1.6x10^{-3}M$)	49.4($1.6x10^{-3}M$)	1:1.98
4.	11,a	12.0($2.4x10^{-3}M$)	25.0($2.4x10^{-3}M$)	1:2.08
5.	11,b	11.3($1.6x10^{-3}M$)	25.0($1.6x10^{-3}M$)	1:2.21

The composition ofthe complex was further confirmed by carrying out both direct (copper sulphate in the cell) and reverse (H.M.A.O.in the cell) amperometric titrations at a potential of -0.15 volts vs S.C.E., using dropping mercury electrode.

A combining ratio of 1:2 for Cu and H.M.A.O. was realized from the inflexion points on the volume - current curves.

The results of these titrations are summarized below:

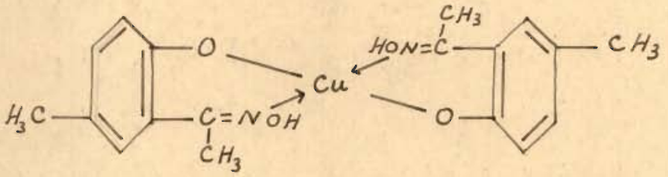
S.No.	Fig.& curve No.	Volume of $CuSo_4$ (ml.)	Volume of H.M.A.O (ml.)	Mole ratio Cu/H.M.A.O
1.	15,a	$25.0(2\times10^{-3}M)$	$50.0(2\times10^{-3}M)$	1:2
2.	15,b	$25.0(1.6\times10^{-3}M)$	$48.75(1.6\times10^{-3}M)$	1:1.95
3.	15,c	$25.0(1.2\times10^{-3}M)$	$50.0(1.2\times10^{-3}M)$	1:2
4.	16,a	$11.4(3.2\times10^{-3}M)$	$25.0(3.2\times10^{-3}M)$	1:2.2
5.	16,b	$11.7(2.4\times10^{-3}M)$	$25.0(2.4\times10^{-3}M)$	1:2.13
6.	16,c	$12.5(1.6\times10^{-3}M)$	$25.0(1.6\times10^{-3}M)$	1:2

The results of the chemical analysis of the complex were also in agreement with those achieved by physical methods and corresponded to the composition of the complex as $(C_9H_{10}O_2N)_2Cu$.

From the composition of the complex it is evident that H.M.A.O., $C_9H_{11}O_2N$, during the reaction with copper ion, behaves as a monobasic acid in which the hydrogen atom of either the phenolic or the oxime group may be replaced by an equivalent of the metal.

The infrared spectrum (Fig.22) of the complex confirms that it is the phenolic hydrogen which is replaced by the metal since the spectrum shows no band of phenolic (oH) group at 3340 cm^{-1} of the ligand (Fig.21). That the other group involved in chelation is the nitrogen of the C=N-, is shown by the lowering in the stretching frequency of C=N- from 1590 cm^{-1} (in the ligand) to 1540 cm^{-1} in the complex. The bands at 2910 and 3030 cm^{-1} in both ligand and the complex are due to =N-OH group.

Hence the structure of the copper complex may be written as :



Composition and structure of Pd-H.M.A.O. complex :

2-Hydroxy-5-methyl acetophenoneoxime reacts with palladium to give yellow, insoluble complex in the pH range 1.0-5.0.

The conductometric titrations carried out to ascertain composition ofthe said complex, reveal that the complex contains one mole of palladium and two moles of H.M.A.O. The results of the titrations are given below:

S.No.	Fig.& curve	Volume of $PdCl_2$ (ml.)	Volume of H.M.A.O (ml.)	Mole ratio Pd/H.M.A.O
1.	12,a	25.0($4x10^{-4}M$)	50.0($4x10^{-4}M$)	1:2
2.	12,b	25.0($6x10^{-4}M$)	51.7($6x10^{-4}M$)	1:2.07
3.	13,a	12.5($1x10^{-3}M$)	25.0($1x10^{-3}M$)	1:2
4.	13,b	14.0($4x10^{-4}M$)	25.0($4x10^{-4}M$)	1:1.8

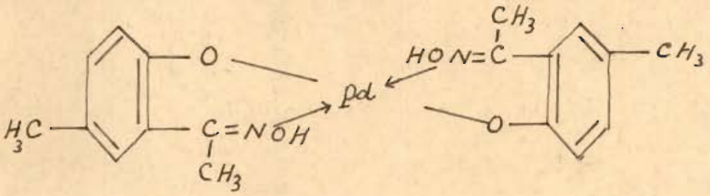
The amperometric titrations of palladium chloride against H.M.A.O. and reverse (H.M.A.O. against $PdCl_2$) also exhibited the same combining ratio of 1:2 (Pd:H.M.A.O.) from the inflexion points in the volume-current curves.

The results are given in the following table :

S.No.	Fig.& curve	Volume of $PdCl_2$ (ml.)	Volume of H.M.A.O. (ml.)	Mole ratio Pd/H.M.A.O.
1.	17,a	25.0(4×10^{-4}M)	50.0(4×10^{-4}M)	1:2
2.	17,b	25.0(6.4×10^{-4}M)	50.0(6.4×10^{-4}M)	1:2
3.	18,a	14.1(8×10^{-4}M)	25.0(8×10^{-4}M)	1:1.77
4.	18,b	12.8(1.6×10^{-3}M)	25.0(1.6×10^{-3}M)	1:1.95

The chemical analysis of the complex also gave the composition of the complex as $(C_9H_{10}O_2N)_2Pd$.

The I.R.spectrum (Fig.21) of the ligand shows the absorption bands of phenolic (-oH) at 3340 cm^{-1}, =NOH at 2915, 3030 cm^{-1}, C=N- at 1590 cm^{-1} and =C-O (of phenolic) at 1260 cm^{-1}. The spectrum (Fig.23) of the complex shows =N-OH at 2915, 3020 cm^{-1}, C=N- at 1535 cm^{-1} and =C-O at 1232 cm^{-1}. On comparing these spectra, it is found that the complex shows no band corresponding to phenolic group and that marked shifting takes place in the frequency of C=N- from 1590 to 1535 cm^{-1} in the complex. The bands due to =N-OH appear more or less at the same positions in both the spectra. The frequency due to =C-O is also shifted from 1260 to 1232 cm^{-1}. Thus the absence of phenolic group and the shifting in the C=N- frequency in the complex lead to the conclusion that phenolic hydrogen and nitrogen of oxime group are involved in chelation of palladium with H.M.A.O. Hence the structure of the chelate may be written as :



Composition and structure of Ni-H.M.A.O. complex :

2-Hydroxy-5-methyl acetophenoneoxime gives a light green, insoluble complex in the pH range 4.5-9.0.

The conductometric and amperometric titrations carried out between nickel sulphate and H.M.A.O. showed the formation of 1:2 complex between nickel and H.M.A.O. respectively.

The results of the titrations are summarized below:

Results of conductometric titrations

S.No.	Fig.& curve	Volume of $NiSo_4$ (ml.)	Volume of H.M.A.O (ml.)	Mole ratio Ni/H.M.A.O
1.	14,a	12.2(6.4x10^{-3}M)	25.0(6.4x10^{-3}M)	1:2.05
2.	14,b	12.25(4x10^{-3}M)	25.0(4x10^{-3}M)	1:2.04

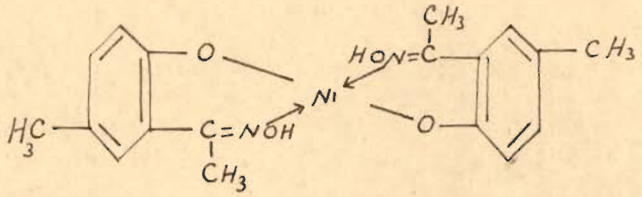
Results of amperometric titrations

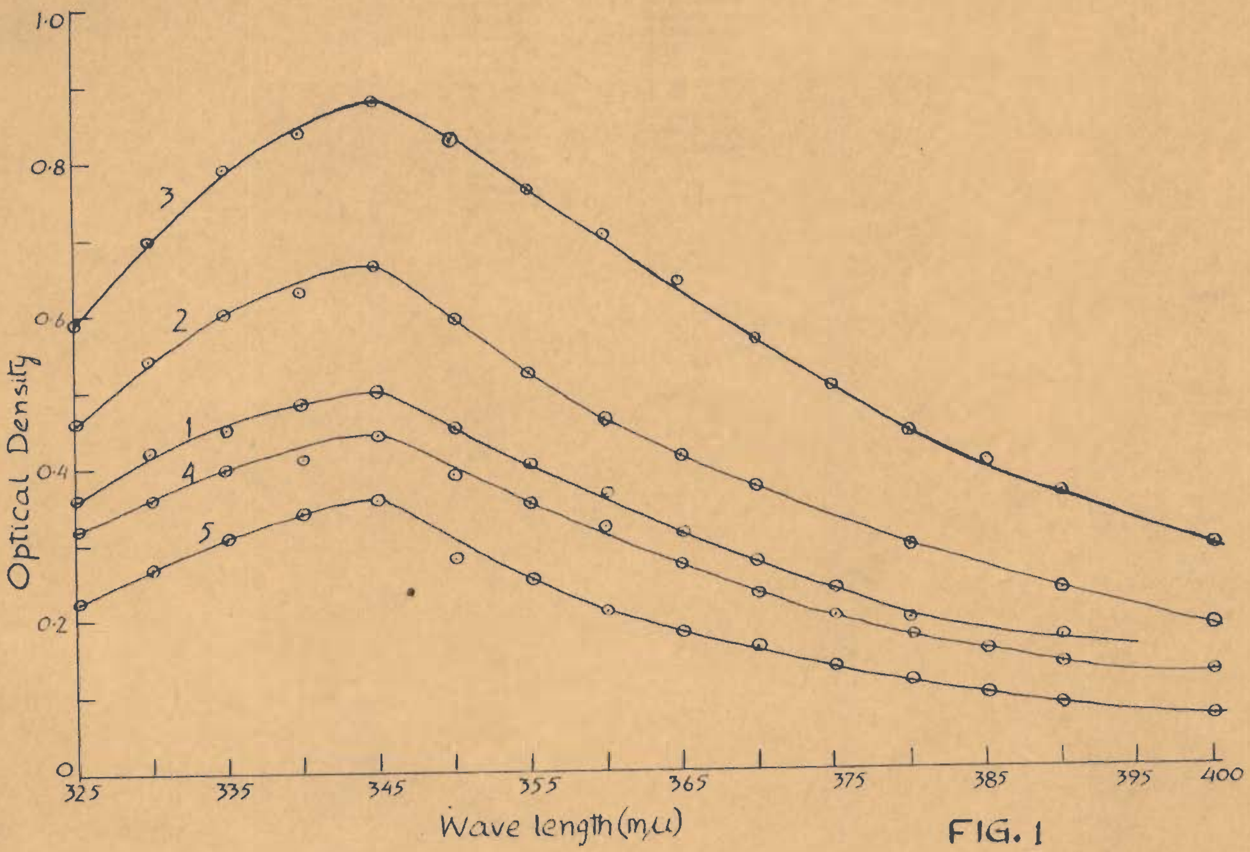
S.No.	Fig.& curve	Volume of $NiSo_4$ (ml.)	Volume of H.M.A.O (ml.)	Mole ratio Ni/H.M.A.O
1.	19,a	25.0(1.6x10^{-3}M)	49.4(1.6x10^{-3}M)	1:1.98
2.	19,b	25.0(1.2x10^{-3}M)	48.3(1.2x10^{-3}M)	1:1.93
3.	20,a	11.9(3.2x10^{-3}M)	25.0(3.2x10^{-3}M)	1:2.1
4.	20,b	12.0(2x10^{-3}M)	25.0(2x10^{-3}M)	1:2.08

The results of chemical analysis of the nickel complex also corresponded to its composition as $(C_9H_{10}O_2N)_2Ni$.

The I.R.spectroscopic studies of the complex were undertaken to locate the groups involved in the formation of the nickel chelate. The most characteristic feature of the spectrum (Fig.24) of the complex is the complete disappearance of phenolic band (at 3340 cm^{-1} in the ligand) and the shift in the C=N- frequency from 1590 (in the ligand) to 1545 cm^{-1}. These observations point to replacement of phenolic hydrogen by nickel which is coordinated through nitrogen of C=N- (oxime group) to form a chelate.

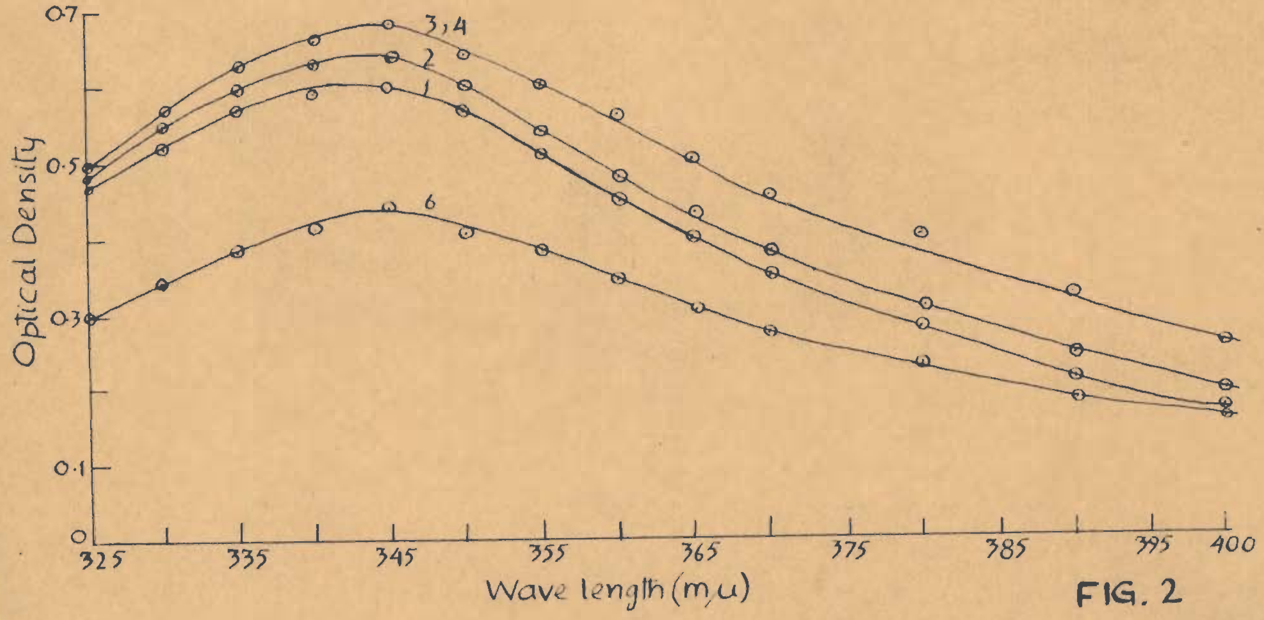
On the basis of the above evidence, the structure of the complex may be written as :





VOSBURGH COOPER'S METHOD

FIG. 1



INFLUENCE OF pH ON STABILITY OF COMPLEX

FIG. 2

JOB'S METHOD

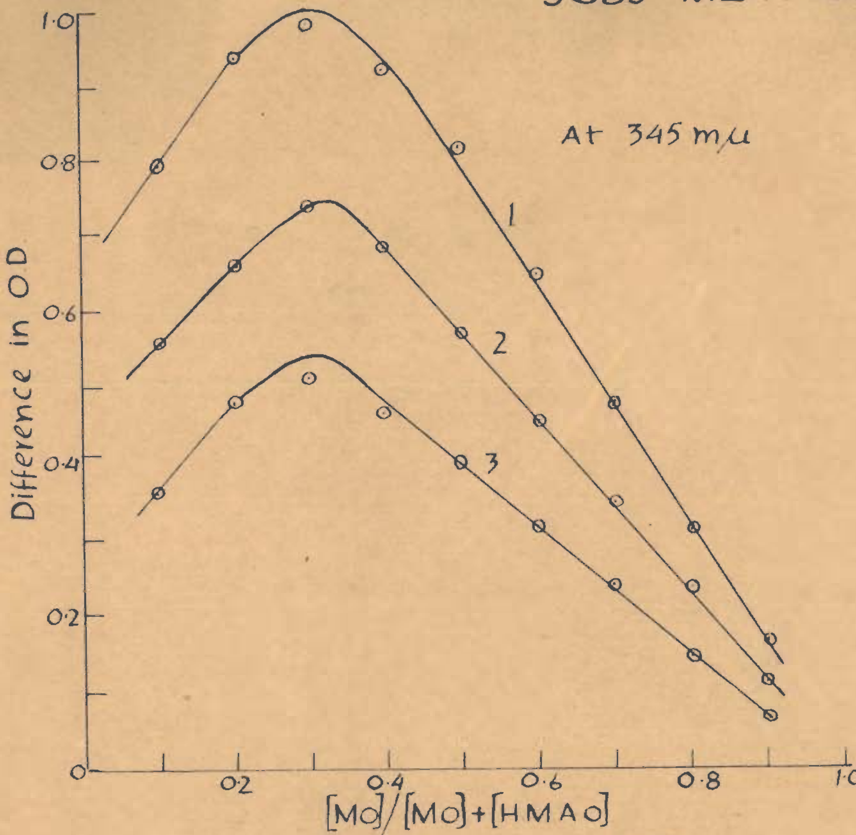


FIG. 3

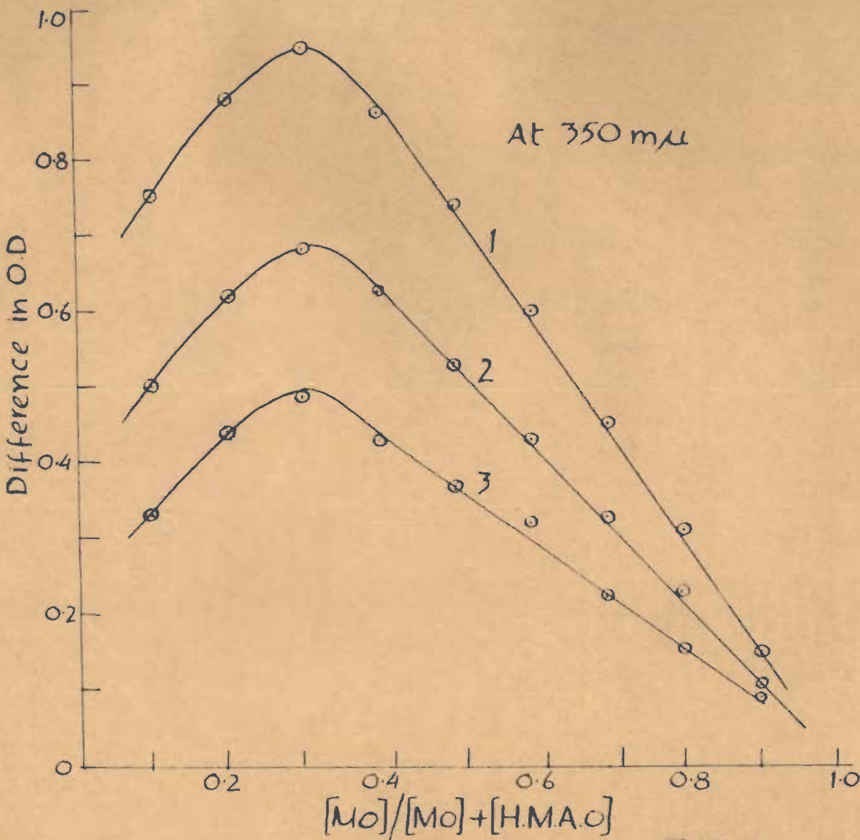


FIG. 4

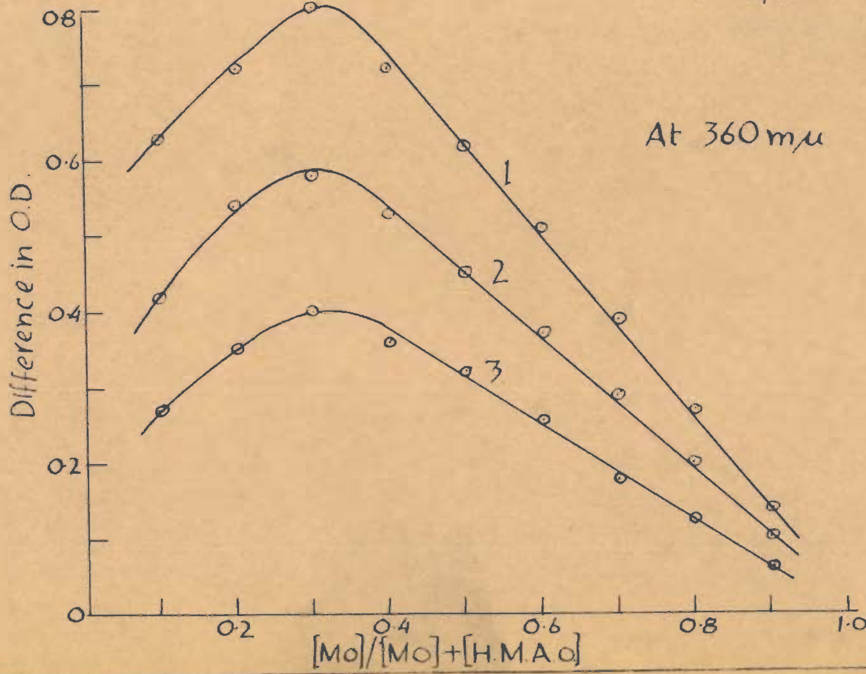


FIG. 5

FORMATION CONSTANT OF COMPLEX

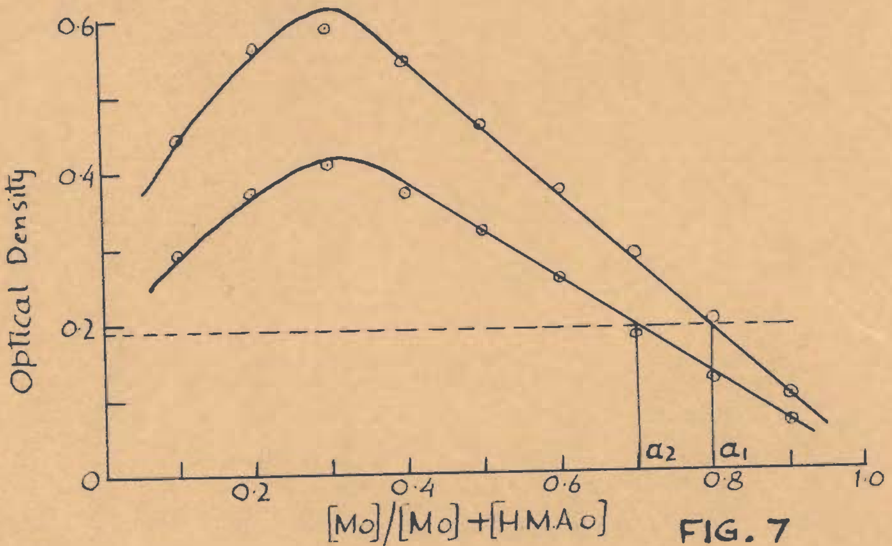


FIG. 7

SLOPE RATIO METHOD

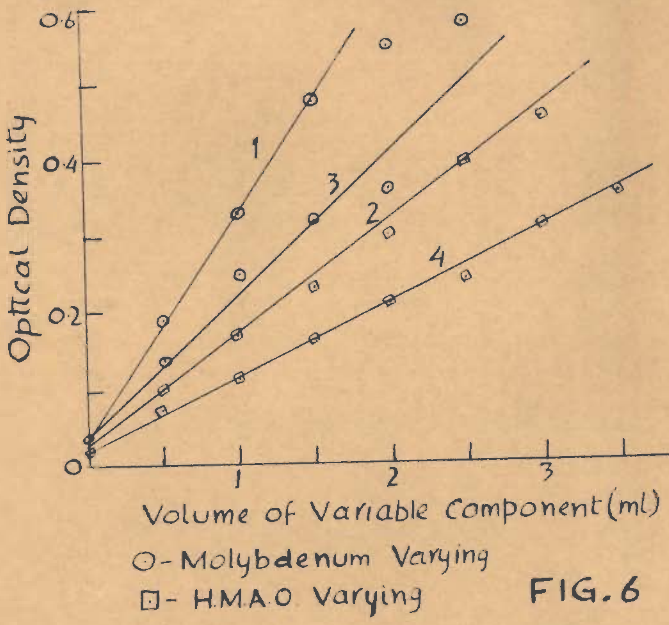


FIG. 6

CONDUCTOMETRIC TITRATIONS

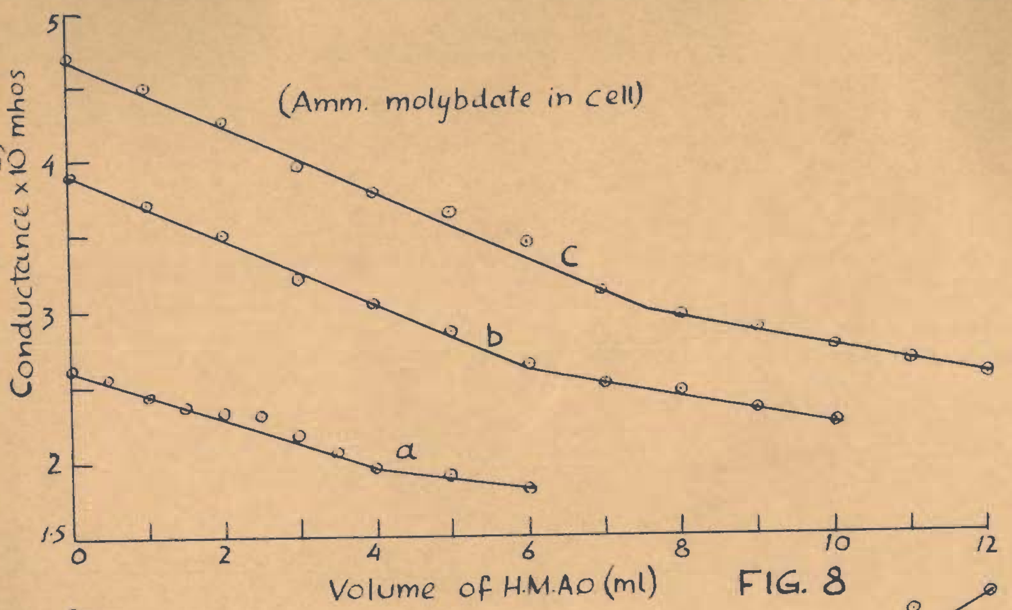


FIG. 8

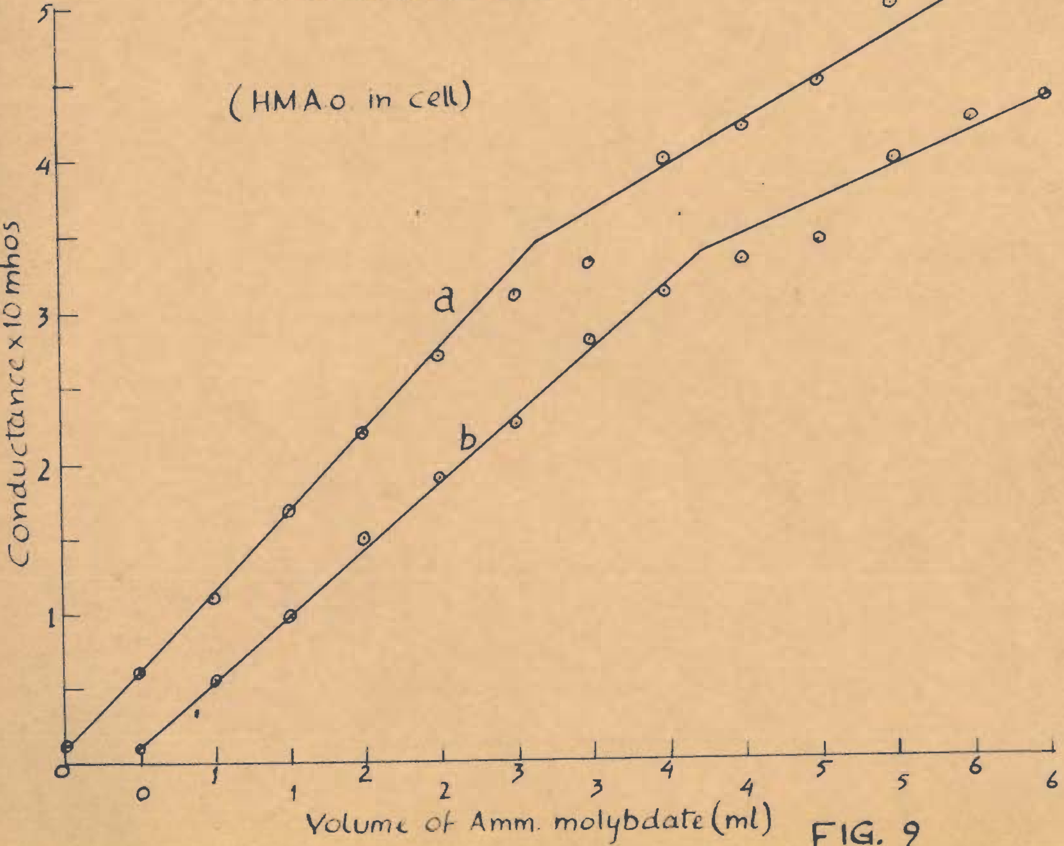


FIG. 9

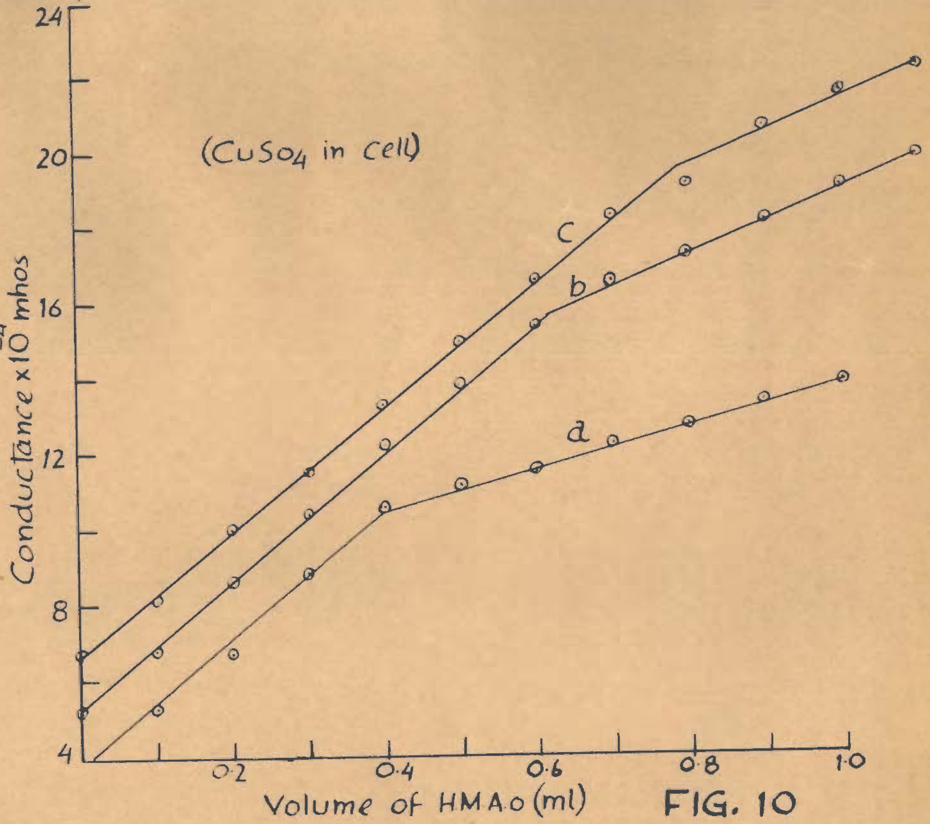


FIG. 10

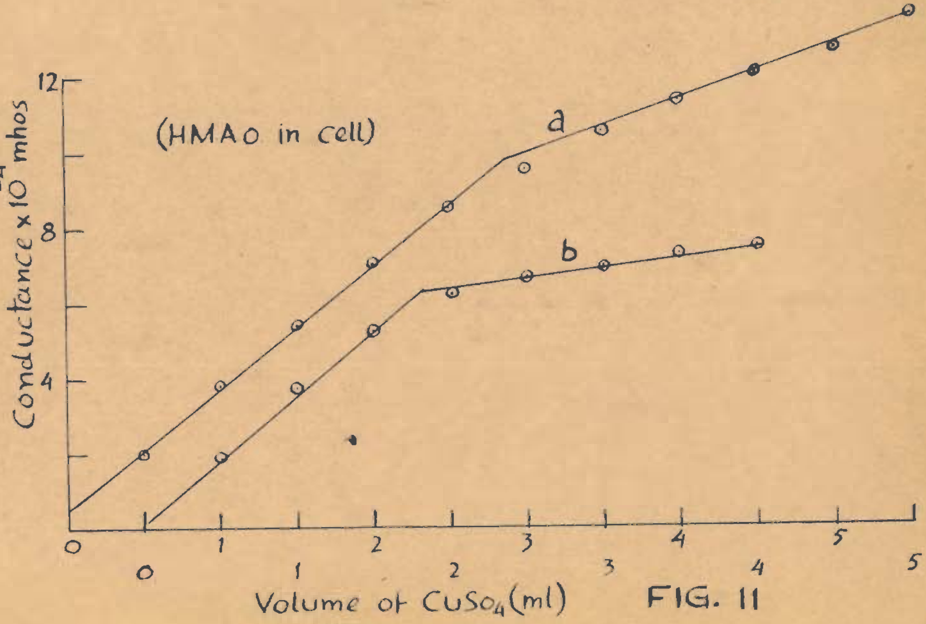


FIG. 11

CONDUCTOMETRIC TITRATIONS

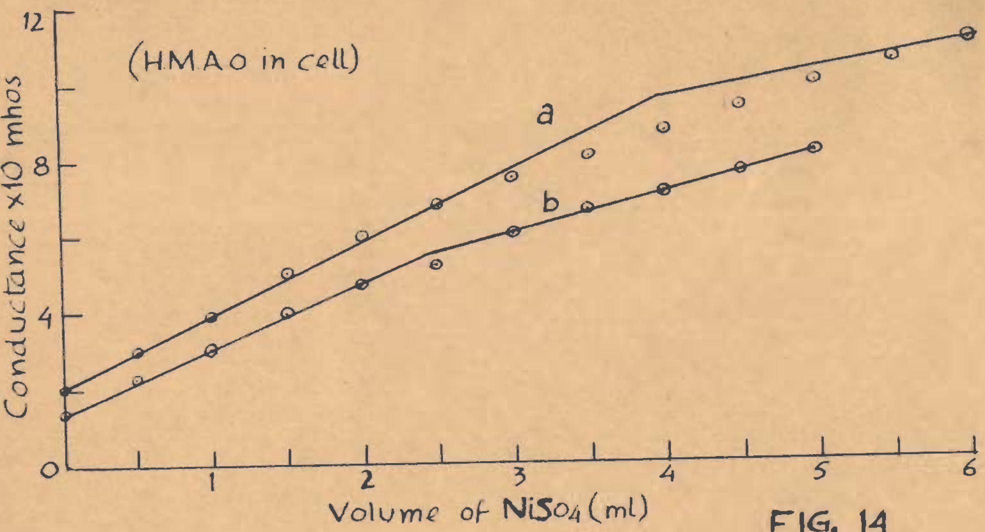


FIG. 14

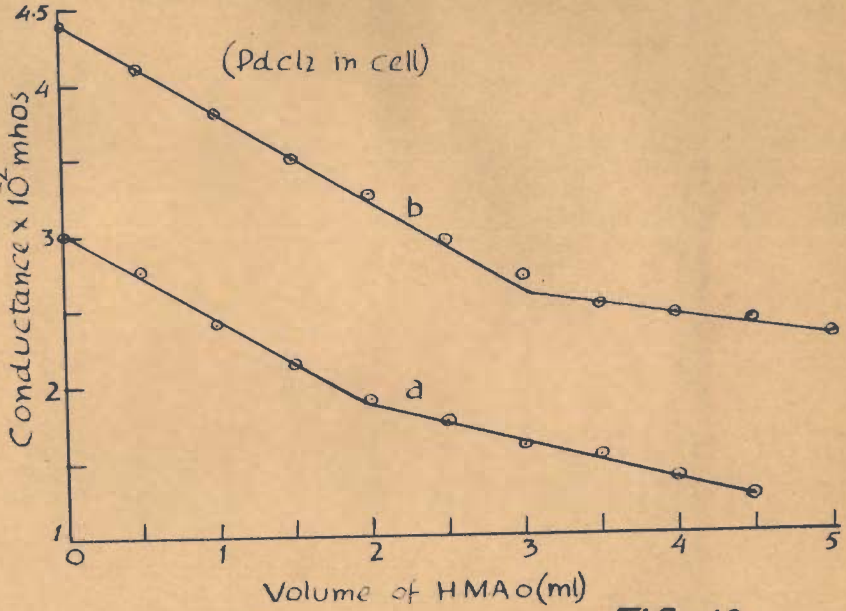


FIG. 12

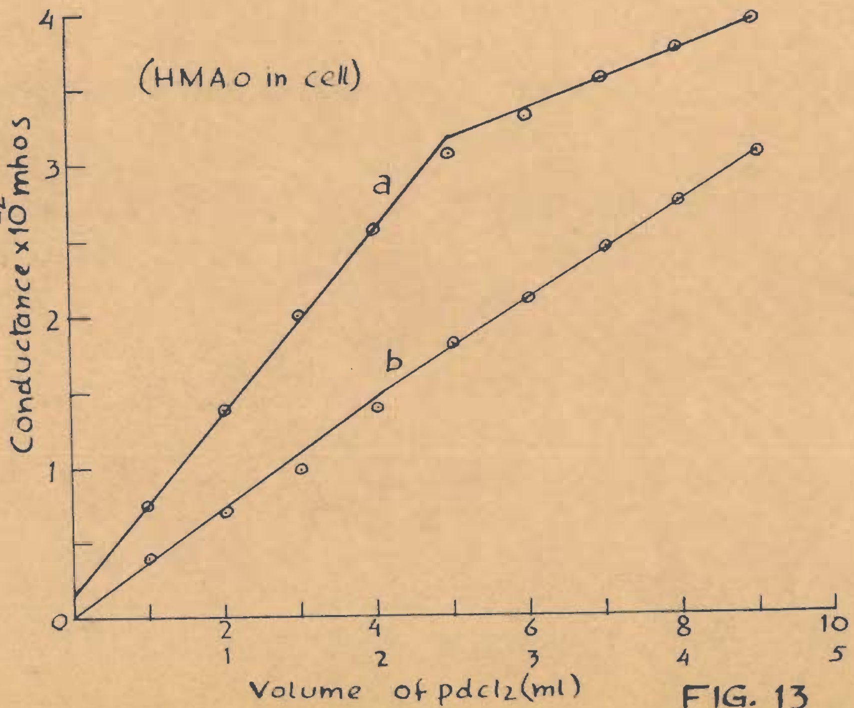


FIG. 13

AMPEROMETRIC TITRATIONS

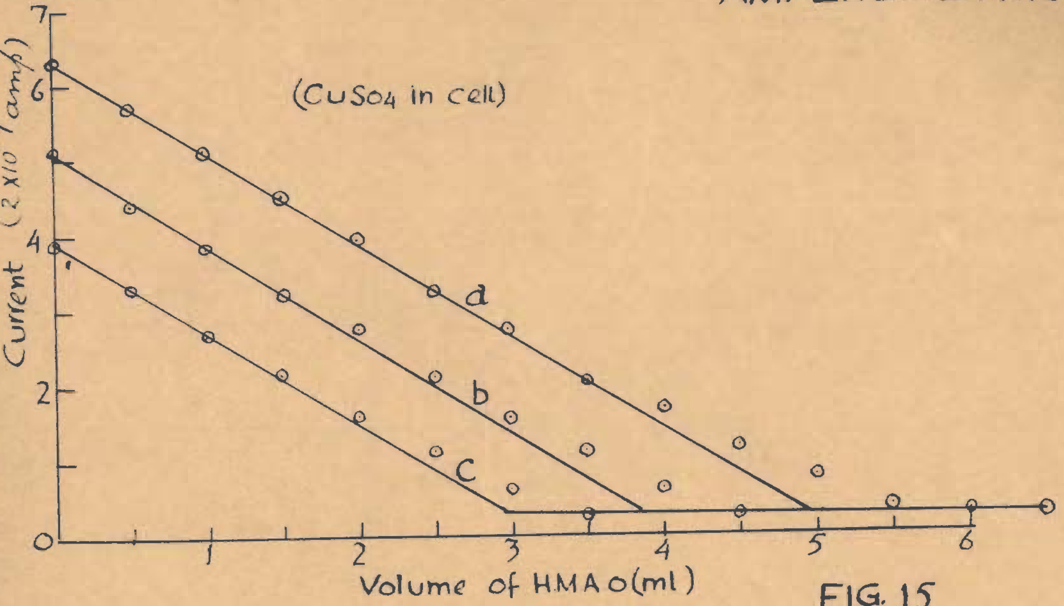


FIG. 15

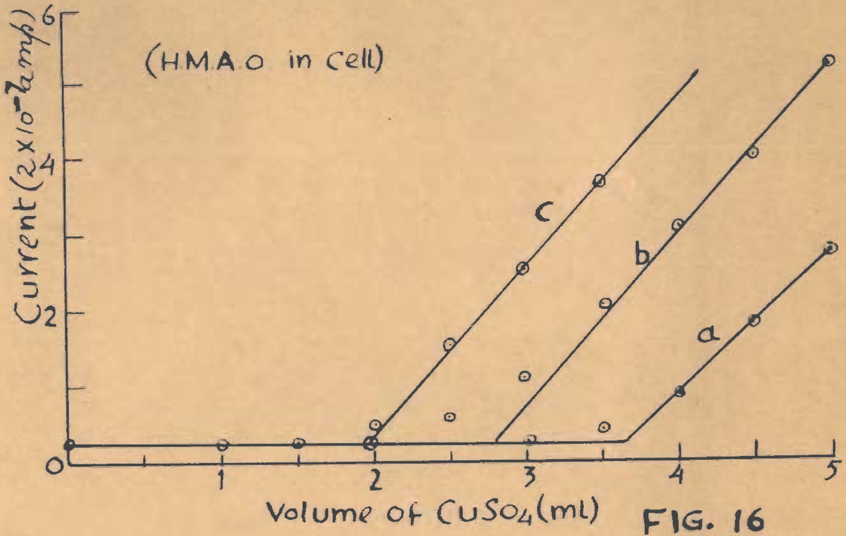


FIG. 16

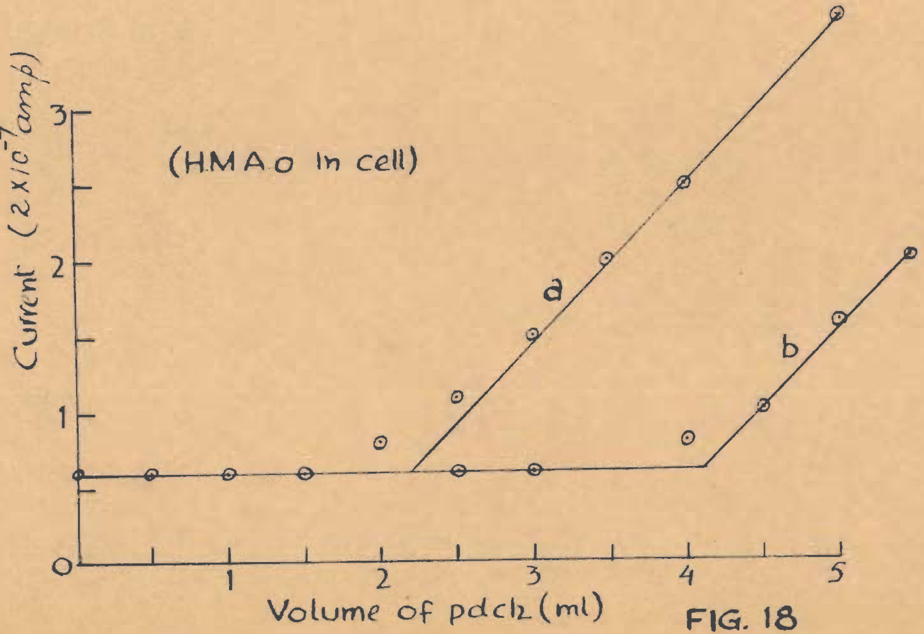


FIG. 18

AMPEROMETRIC TITRATIONS

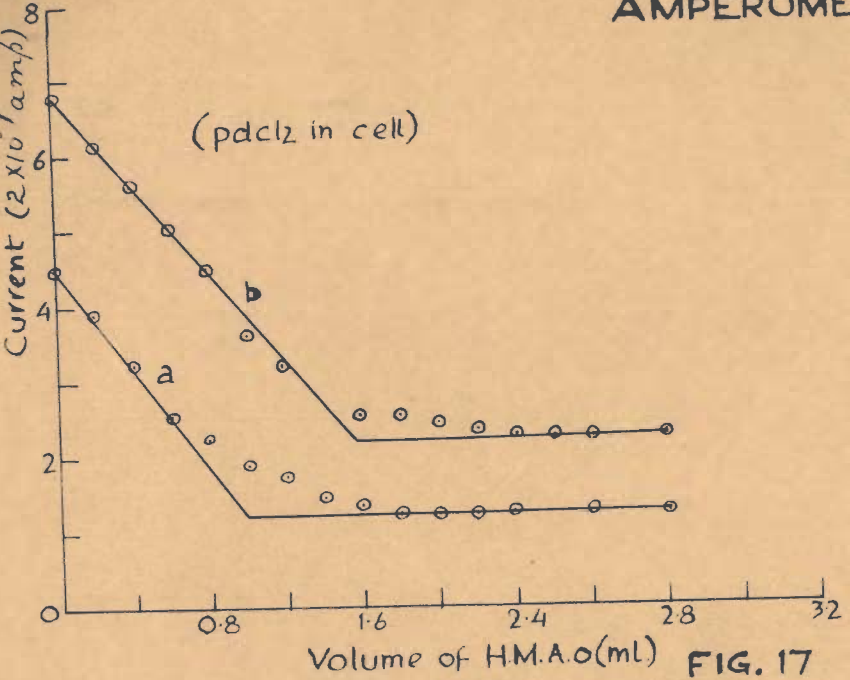


FIG. 17

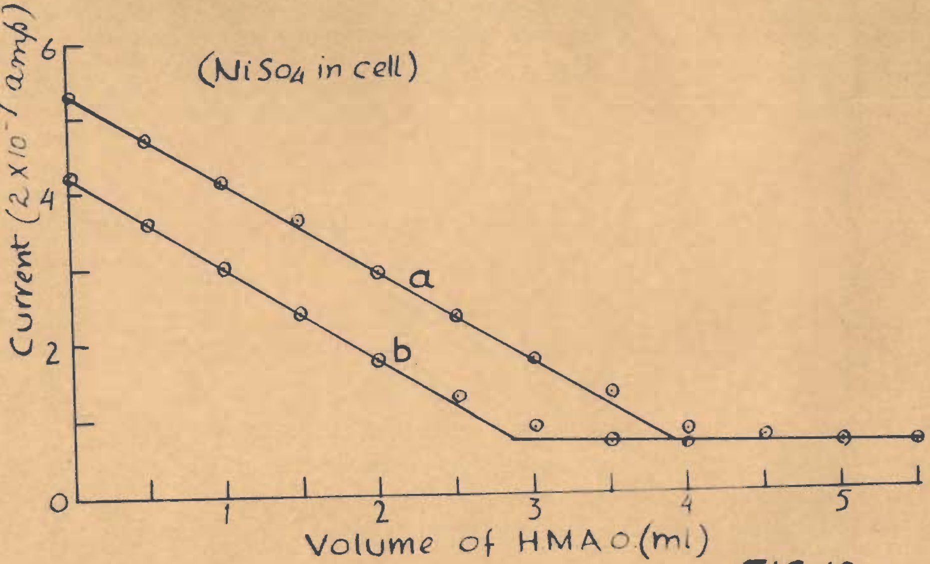


FIG. 19

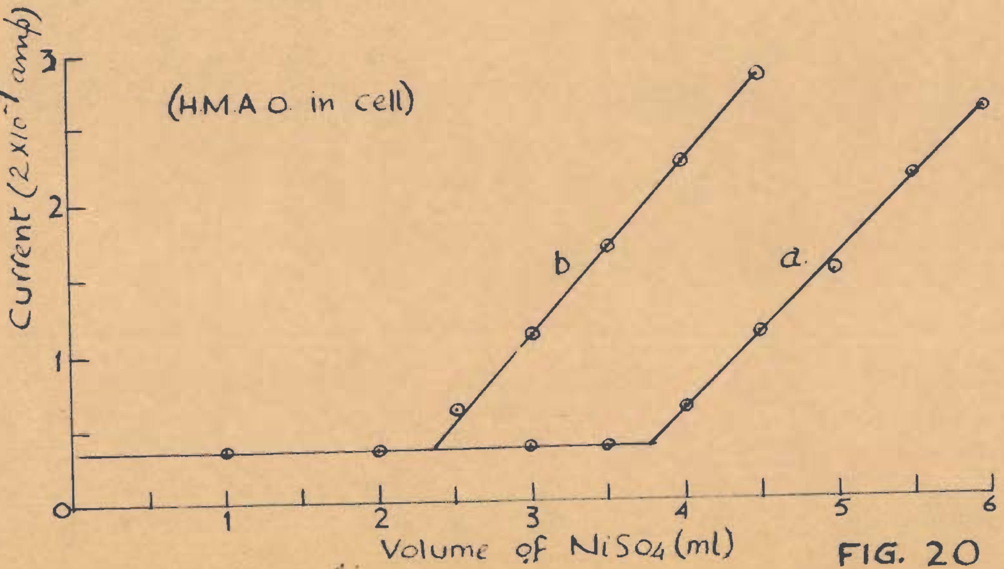
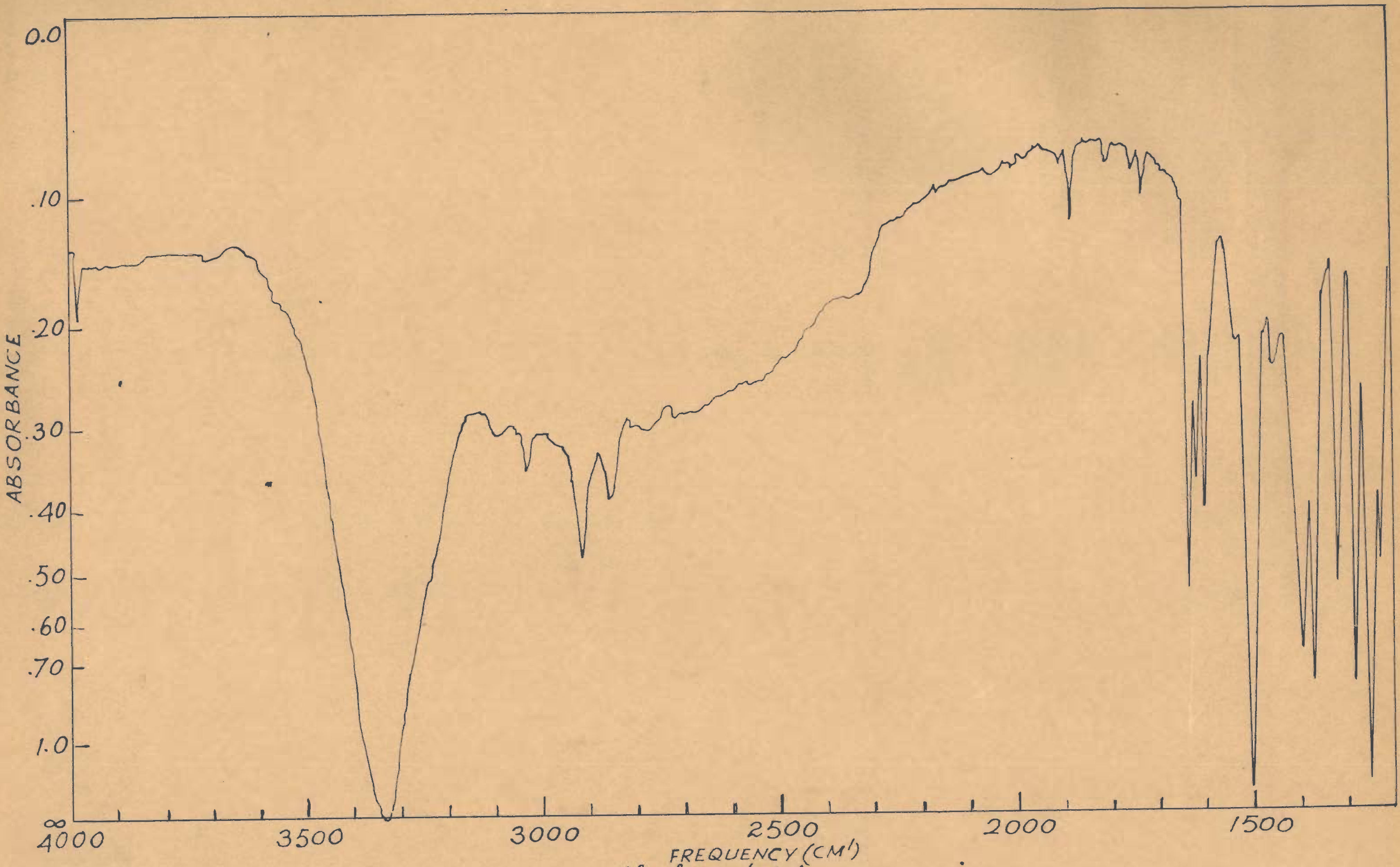
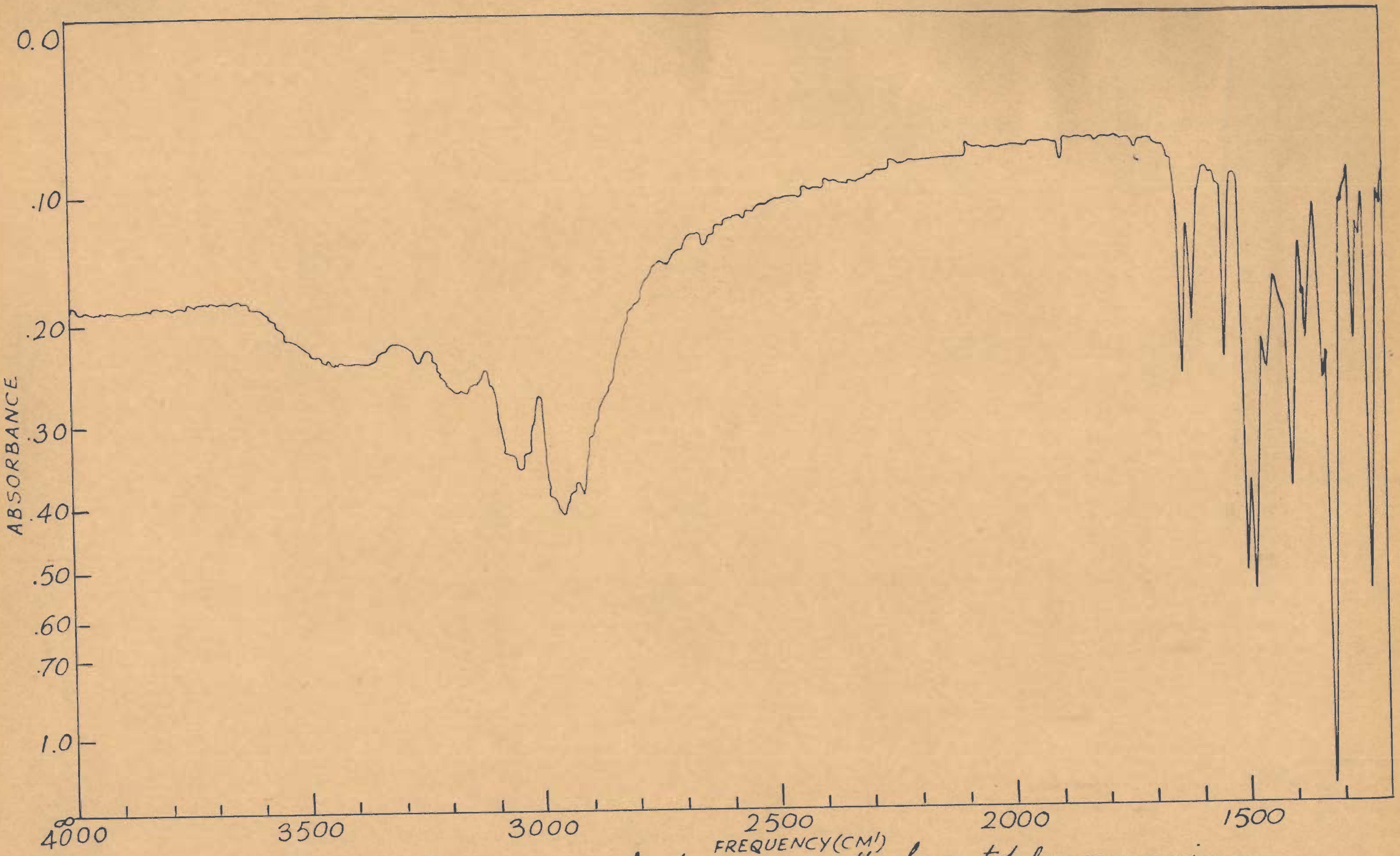


FIG. 20



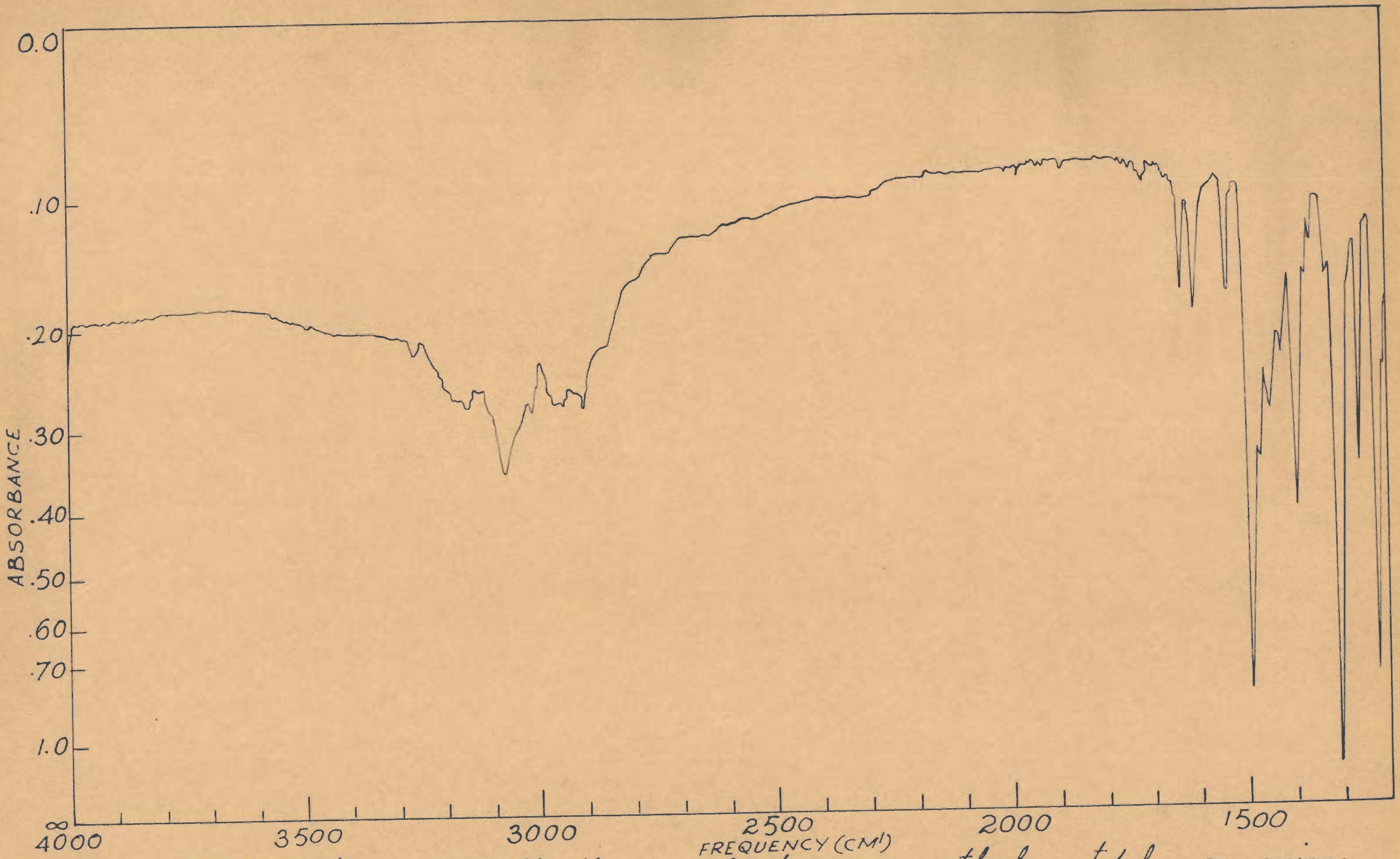
I.R. spectrum of 2-hydroxy-5-methyl acetophenone oxime

FIG. 21

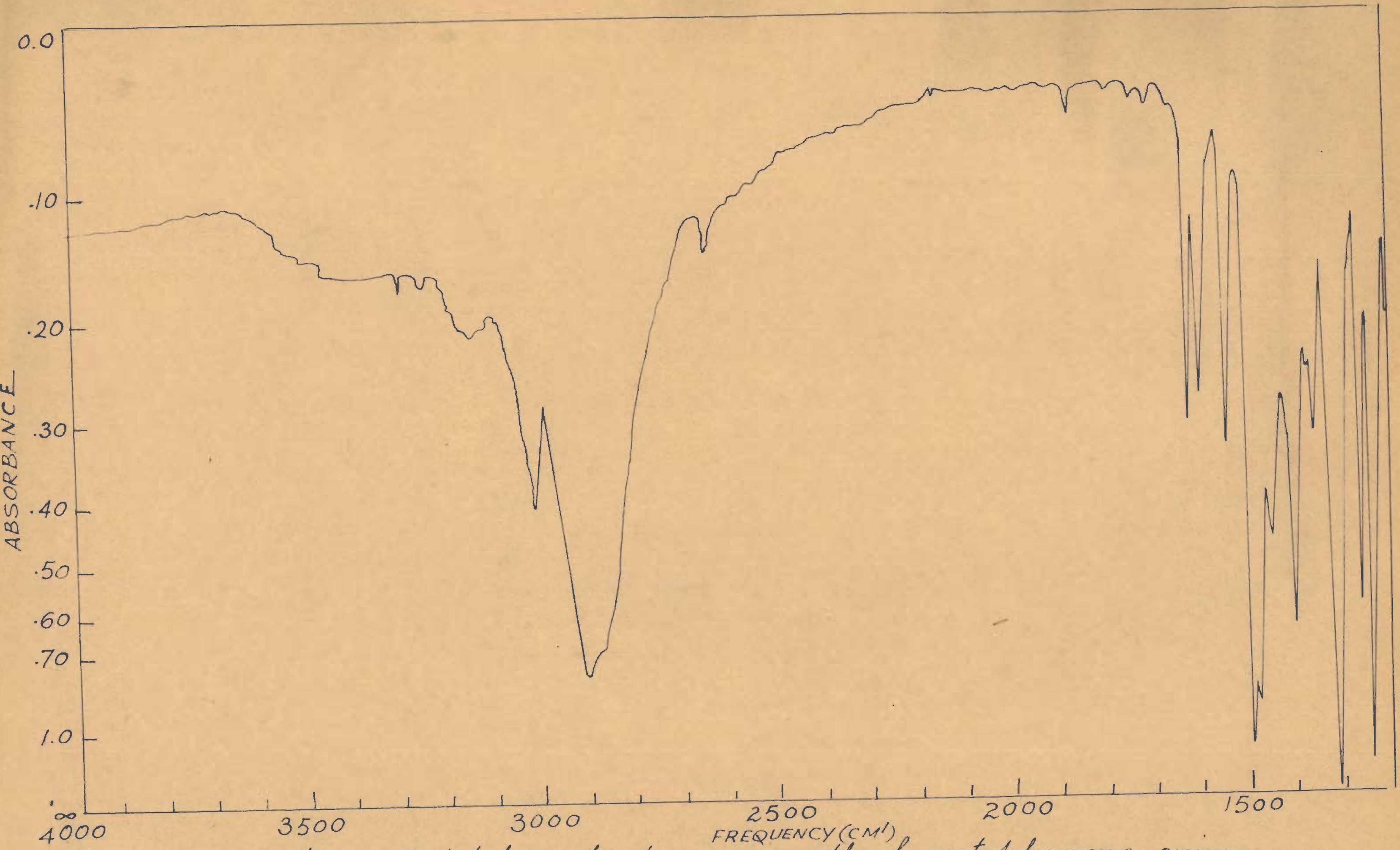


I.R. SPECTRUM of copper-2-hydroxy-5-methyl acetophenone oxime

FIG-22



I.R. spectrum of palladium -2- hydroxy -5- methyl acetophenone oxime
FIG-23



I.R. spectrum of nickel-2-hydroxy-5-methyl acetophenone oxime.
FIG. 24

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1. Singh, H. and Sharma, K.C., Indian J. Appl. Chem. 28, (2), 43 (1965).

2. Vogel, Arthur I., A Text Book of practical organic chemistry, 3rd Ed. pp.676, Longmans Green and Co.,London.

CHAPTER III

****

" Metal complexes of 2,5-dihydroxyacetophenoneoxime "

***

INTRODUCTION

Resacetophenoneoxime (2,4-dihydroxy acetophenoneoxime) has been employed for the estimation of copper in the presence of nickel and cadmium by a number of workers[1-3]. The use of this reagent for the amperometric determination of copper has also been reported by Reddy[4]. The corresponding 2-5 dihydroxy-acetophenoneoxime has attracted no attention so far either from the view point of its analytical utility or as a chelating agent. It was, therefore, considered worthwhile to study these two aspects by investigating its reactions with some metal salts. The present chapter gives the results of the structural studies while the data of analytical investigations are incorporated in the following chapter.

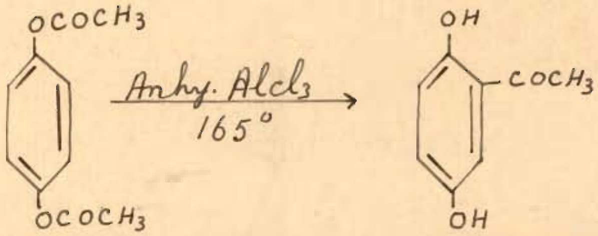
Preliminary experiments show that copper, nickel and palladium form insoluble complexes with this compound while molybdenum gives a soluble complex. The former reaction was studied by conductometric, amperometric and pH-metric methods while the composition of the molybdenum complex was investigated by spectrophotometric and conductometric methods.

The results of these investigations were further confirmed by isolating these complexes and subjecting them to chemical analysis and infrared spectroscopy.

EXPERIMENTAL

Preparation of 2,5-dihydroxy-acetophenone :

The compound was prepared[5] by heating hydroquinone diacetate in presence of 3.3 moles of anhydrous aluminium chloride.



Finely powdered mixture of 8.0 gm. of dry hydroquinone diacetate and 17.4 gm. of anhydrous aluminium chloride was placed in a 100 ml. round-bottomed flask with an air condenser which was protected by a calcium chloride tube and connected to a gas-absorption trap. The flask was slowly heated in an oil bath at 110-120°. When the evolution of hydrogen chloride started, the temperature of the oil bath was slowly raised to 160-165° and maintained for an hour. The flask was cooled and the contents were treated with crushed ice and concentrated hydrochloric acid to decompose the aluminium chloride complex. The solid was filtered, washed with water, dried and crystallized from ethyl alcohol. Green-yellow crystals of 2,5-dihydroxy acetophenone (m.p.203°C) were obtained.

Preparation of 2,5-dihydroxy-acetophenoneoxime :

It was prepared by refluxing 2,5-dihydroxy-acetophenone with equimolar quantities of hydroxylamine hydrochloride (B.D.H.) and sodium acetate over water bath for an hour. The solution was concentrated and cooled when 2,5-dihydroxy-acetophenoneoxime separated out as brownish crystals (m.p. 150°C).

The solution of the oxime was prepared in 40% alcohol.

Reagents :

The solutions of ammonium molybdate, copper sulphate, palladium chloride, nickel sulphate and buffers were prepared as described in Chapter I.

0.1% gelatine solution was prepared in hot double distilled water.

Apparatus :

The details of the various apparatus used for these studies, are the same as described in Chapter I.

Mo(VI)-2-5-DIHYDROXY ACETOPHENONEOXIME COMPLEX

Chemical analysis of the complex :

The complex of molybdenum was isolated and its metal and nitrogen contents were estimated in the same manner as described in Chapter I.

Calculated for :

bis (2,5-dihydroxy-acetophenoneoxime)MoO_2, $(C_8H_8O_3N)_2MoO_2$

Mo - 20.86, N - 6.088

Found Mo - 21.25, N - 6.0

Spectrophotometric studies on the nature, composition and stability of the complex :

Nature of the complex :-

Vosburgh and Cooper's method (loc.cit.) was followed to determine the nature and the number of complexes formed in solution by the interaction of ammonium molybdate and 2,5-dihydroxy-acetophenoneoxime (designated as D.H.A.O). Equimolar solutions were prepared by mixing ammonium molybdate and D.H.A.O. of concentration 1×10^{-3}M in the ratio of 1:1, 1:2, 1:3, 2:1 and 3:1 respectively. The absorbance of these solutions was measured at different wave lengths(325-450 mµ) using reagent as blank.

Effect of pH on stability of the complex :

A series of solutions containing 1.0 ml. of ammonium molybdate and 2.0 ml. of D.H.A.O., both of concentration 5×10^{-3}M, were adjusted to various pH values (2.0-4.5) by adding buffers and the final volume was made up to 25 ml. The absorbance of these solutions was measured at different wave lengths.

Table - 1

Vosburgh and Cooper's method applied to Mo(VI)-D.H.A.O.

Concentration of Amm.molybdate = 1×10^{-3}M
Concentration of D.H.A.O. = 1×10^{-3}M

Wave length (mμ)	Optical density				
	Ratio of Amm.molybdate: D.H.A.O.				
	1:1	1:2	1:3	2:1	3:1
325	0.06	0.17	0.25	0.0	0.0
330	0.04	0.15	0.20	0.0	0.0
335	0.07	0.145	0.18	0.05	0.0
340	0.13	0.22	0.30	0.10	0.03
345	0.20	0.265	0.455	0.17	0.10
350	0.32	0.39	0.65	0.24	0.15
355	0.37	0.47	0.75	0.30	0.21
360	0.40	0.54	0.815	0.32	0.24
365	0.41	0.56	0.82	0.34	0.27
370	0.42	0.57	0.84	0.35	0.28
375	0.37	0.52	0.80	0.31	0.25
380	0.325	0.47	0.75	0.275	0.225
390	0.25	0.38	0.605	0.22	0.175
400	0.19	0.31	0.51	0.18	0.15
410	0.15	0.26	0.41	0.13	0.11
420	0.12	0.21	0.34	0.11	0.085
430	0.10	0.18	0.28	0.085	0.07
450	0.07	0.12	0.17	0.05	0.04
	Curve(a)	Curve(b)	Curve(c)	Curve(d)	Curve(e)

Fig.1

All these solutions exhibited λmax. at 370 mμ.

Table - 2

Concentration of Amm. molybdate = 2×10^{-4}M

Concentration of D.H.A.O. = 4×10^{-4}M

Wave length (mμ)	O.D.values of 1:2 amm.molybdate and D.H.A.O. mixture at different pH values					
	2.0	2.5	3.0	3.5	4.0	4.5
325	0.17	0.16	0.15	0.15	0.15	0.14
335	0.09	0.09	0.09	0.085	0.085	0.075
340	0.10	0.10	0.095	0.09	0.09	0.08
345	0.11	0.11	0.011	0.11	0.11	0.10
350	0.15	0.155	0.16	0.16	0.16	0.14
360	0.32	0.335	0.345	0.34	0.34	0.28
365	0.38	0.405	0.41	0.41	0.40	0.325
370	0.39	0.42	0.425	0.425	0.42	0.34
375	0.38	0.41	0.41	0.41	0.41	0.33
380	0.35	0.37	0.365	0.36	0.36	0.30
390	0.25	0.26	0.26	0.26	0.26	0.22
400	0.195	0.20	0.20	0.205	0.20	0.15
410	0.12	0.13	0.13	0.125	0.13	0.11
425	0.09	0.095	0.09	0.095	0.09	0.07
450	0.05	0.05	0.05	0.05	0.05	0.03
Curves	(1)	(2)	(3)	(4)	(5)	(6)

Fig. 2

The λmax.of the complex was found to be at 370 mμ in the pH range of 2.0-4.5.

Composition of the complex :

Job's method of continued variation (loc.cit.) was followed to determine the composition of the complex. Equimolar solutions of ammonium molybdate and D.H.A.O. were prepared in the usual manner and pH adjusted between 3.5 and 4.0.

The optical density of the solutions was measured at 370, 380 and 390 mμ. Ammonium molybdate solutions did not give any absorbance at these wave lengths. The difference between the optical density of the mixtures and that of D.H.A.O. solutions was plotted against the mole fraction of ammonium molybdate. The absorbance data recorded at 370 mu are summarized in the following tables while the data at 380 and 390 mμ are depicted in the Figs. 4 and 5:

Table - 3

Wave length 370 mμ

Concentration of the reactants = 1.333×10^{-3}M

Vol.of Amm.molybdate (ml.)	Volume of D.H.A.O. (ml.)	Optical density		
		Mixture	D.H.A.O.	Difference
1.0	9.0	0.82	0.07	0.75
2.0	8.0	0.98	0.06	0.92
3.0	7.0	1.05	0.05	1.00
4.0	6.0	1.0	0.04	0.96
5.0	5.0	0.82	0.04	0.78
6.0	4.0	0.66	0.03	0.63
7.0	3.0	0.50	0.02	0.48
8.0	2.0	0.33	0.01	0.32
9.0	1.0	0.16	0.0	0.16

Fig.3, Curve 1

Table - 4

Wave length 370 mµ

Concentration of the reactants = $1\times10^{-3}M$

Vol.of Amm. molybdate (ml.)	Vol.of D.H.A.O. (ml.)	Optical density		
		Mixture	D.H.A.O.	Difference
1.0	9.0	0.54	0.05	0.49
2.0	8.0	0.67	0.045	0.625
3.0	7.0	0.75	0.03	0.72
4.0	6.0	0.69	0.03	0.66
5.0	5.0	0.57	0.025	0.545
6.0	4.0	0.445	0.02	0.425
7.0	3.0	0.34	0.01	0.33
8.0	2.0	0.22	0.01	0.21
9.0	1.0	0.10	0.0	0.10

Fig,3, curve 2

Table - 5

Wave length 370 mµ

Concentration of reactants = $8\times10^{-4}M$

Vol.of Amm. molybdate (ml.)	Vol.of D.H.A.O. (ml.)	Optical density		
		Mixture	D.H.A.O.	Difference
1.0	9.0	0.38	0.04	0.34
2.0	8.0	0.48	0.035	0.445
3.0	7.0	0.53	0.03	0.50
4.0	6.0	0.51	0.025	0.485
5.0	5.0	0.41	0.02	0.39
6.0	4.0	0.35	0.02	0.33
7.0	3.0	0.27	0.01	0.26
8.0	2.0	0.17	0.0	0.17
9.0	1.0	0.095	0.0	0.095

Fig.3, curve 3

The results of Job's method were further subjected to confirmation by slope ratio method. Two series of solutions were prepared in the same manner as described earlier. The optical density of these solutions is recorded in the following tables :

Table - 6

Set I

Fixed concentration of D.H.A.O. = 8×10^{-4}M (in 25 ml.)
Initial concentration of Amm.molybdate added = 1×10^{-3}M
Total volume = 25 ml.
pH of the solutions = 3.5-4.0

Vol.of Amm.molybdate (ml.)	O.D.at 370 mμ
0.0	0.052
1.0	0.16
2.0	0.27
3.0	0.38
4.0	0.48
5.0	0.52
6.0	0.56
7.0	0.58
8.0	0.62

Fig.6, curve (1)

Table - 7

Set II

Fixed concentration of Amm.molybdate = 8×10^{-4}M(in 25 ml)
Initial concentration of D.H.A.O.added = 1×10^{-3}M
Total volume = 25 ml.
pH of the solutions = 3.5-4.0

Vol.of D.H.A.O. (ml.)	O.D. at 370 mµ
0.0	0.01
1.0	0.055
2.0	0.11
3.0	0.16
4.0	0.215
5.0	0.27
6.0	0.32
7.0	0.37
8.0	0.42

Fig.6, curve (2)

Table - 8

Set III

Fixed concentration of D.H.A.O. = 4×10^{-4}M (in 25 ml.)
Initial concentration of Amm.molybdate added = 5×10^{-4}M
pH of the solutions = 3.5-4.0
Total volume = 25 ml.

Vol.of Amm.molybdate (ml.)	O.D. at 370 mµ
0.0	0.02
1.0	0.04
2.0	0.065
3.0	0.09
4.0	0.11
5.0	0.135
6.0	0.16
7.0	0.18
8.0	0.20

Fig.6, curve (3)

Table - 9

Set IV

Fixed concentration of Amm.molybdate = 4×10^{-4}M (in 25 ml.)
Initial concentration of D.H.A.O.added = 5×10^{-4}M
pH of the solutions = 3.5-4.0
Total volume = 25 ml.

Vol.of D.H.A.O. (ml.)	O.D. at 370 mμ
0.0	0.0
1.0	0.01
2.0	0.015
3.0	0.025
4.0	0.04
5.0	0.048
6.0	0.055
7.0	0.068
8.0	0.078
9.0	0.088
10.0	0.20

Fig.6,curve (4)

Formation constant of the complex :

The formation constant of the complex was determined by the method recommended by Dey and co-workers. For calculating the value of K, the absorbance data recorded during Job's method of continued variation (Tables 4,5) were made use of.

For an arbitrary absorbance value of 0.3 on the descending portions of the curves (Fig.7), the initial concentration of the reactants were as follows:

Solution I $a_1 = 7.3\times10^{-4}M$

$b_1 = 2.7\times10^{-4}M$

Solution II $a_2 = 5.28\times10^{-4}M$

$b_2 = 2.72\times10^{-4}M$

Conductometric titrations :

The composition of the complex was further studied by carrying out conductometric titrations between the reactants. The practical details of these titrations were the same as described earlier.

The observations are given in the following tables :

Table - 10

Direct titrations (Amm.molybdate in the cell)

Fixed concentration of Amm.molybdate = Set I: 0.666×10^{-3}M(in 30 ml)
Set II: 1.333×10^{-3}M(in 30 ml)
Set III: 2×10^{-3}M (in 30 ml)

Initial concentration of D.H.A.O.added = 2×10^{-2}M

Vol.of D.H.A.O. (ml.)	I Corrected conductance $\times 10^{-3}$(mhos)	Vol.of D.H.A.O (ml.)	II Corrected conductance $\times 10^{-3}$(mhos)	Vol.of D.H.A.O (ml.)	III Corrected conductance $\times 10^{-3}$(mhos)
0.0	1.38	0.0	2.45	0.0	3.5
0.5	1.31	1.0	2.32	1.0	3.28
1.0	1.26	1.5	2.2	2.0	3.08
1.5	1.22	2.0	2.15	2.5	3.0
2.0	1.17	2.5	2.1	3.0	2.94
2.5	1.13	3.0	2.0	3.5	2.8
3.0	1.09	3.5	1.96	4.0	2.75
3.5	1.03	4.0	1.9	4.5	2.70
4.0	1.0	4.5	1.85	5.0	2.60
4.5	0.99	5.0	1.8	5.5	2.56
5.0	0.95	5.5	1.7	6.0	2.50
		6.0	1.65	6.5	2.40
		7.0	1.57	7.0	2.39
		8.0	1.5	8.0	2.24
				9.0	2.16
				10.0	2.07
Curves	(a)	(Fig.8)	(b)		(c)

Curve(a)
30 ml. of 0.666×10^{-3}M Amm.molybdate = 2.0 ml.of 2×10^{-2}M D.H.A.O.
=60.0 ml.of 0.666×10^{-3}M D.H.A.O

Curve(b)
30 ml. of 1.333×10^{-3}M Amm.molybdate = 4.1 ml.of 2×10^{-2}M D.H.A.O.
=61.5 ml.of 1.333×10^{-3}M D.H.A.O

Curve(c)
30 ml. of 2×10^{-3}M Amm.molybdate = 6.0 ml.of 2×10^{-2}M D.H.A.O.
= 60 ml.of 2×10^{-3}M D.H.A.O.

Table - 11

Reverse titrations (D.H.A.O.in the cell)

Fixed concentration of D.H.A.O. = 2.666×10^{-3}M (in 30 ml.)-Set I
= 5.333×10^{-3}M (in 30 ml.)-Set II

Initial concentration of Amm.molybdate added = 2×10^{-2}M

I Vol.of Amm. molybdate (ml.)	I Corrected conductance $\times 10^{-3}$(mhos)	II Vol.of Amm. molybdate (ml.)	II Corrected conductance $\times 10^{-3}$(mhos)
0.0	0.0	0.0	0.0
0.5	0.62	0.5	0.5
1.0	1.2	1.0	0.95
1.5	1.64	1.5	1.4
2.0	2.2	2.0	1.82
2.5	2.65	2.5	2.25
3.0	2.92	3.0	2.53
3.5	3.40	3.5	3.0
4.0	3.65	4.0	3.33
4.5	4.1	4.5	3.65
5.0	4.5	5.0	3.92
		5.5	4.3
		6.0	4.35
		6.5	4.66
		7.0	4.9
Curve(a)		Curve(b)	

Fig.9

Curve(a)

30 ml. of 2.666×10^{-3}M D.H.A.O. = 2.0 ml.of 2×10^{-2}M Amm.molybdate
=15.0 ml.of 2.666×10^{-3}M Amm. molybdate

Curve(b)

30 ml. of 5.33×10^{-3}M D.H.A.O. =4.05 ml.of 2×10^{-2}M Amm.molybdate
=15.2 ml.of 5.333×10^{-3}M Amm. molybdate

COPPER(II), PALLADIUM(II) AND NICKEL(II) COMPLEXES OF 2,5-DIHYDROXY-ACETOPHENONEOXIME

2-5-Dihydroxy-acetophenoneoxime gives insoluble complexes with copper(II), palladium(II) and nickel(II). The composition of these complexes was determined by chemical analysis, conductometric and pH metric titrations.

Chemical analysis of the complexes :

The complexes were isolated and analysed for the metal and nitrogen contents in the same manner as described earlier. The results of the analysis are given below :

1. Calculated for :

   bis (2,5-dihydroxy-acetophenoneoxime)Cu(II), $(C_8H_8O_3N)_2Cu$

   Cu - 16.06, N - 7.07

   Found Cu - 15.8 , N - 7.20

2. Calculated for :

   bis (2,5-dihydroxy-acetophenoneoxime)Pd(II), $(C_8H_8O_3N)_2Pd$

   Pd - 24.27, N - 6.38

   Found Pd - 24.65, N - 6.52

3. Calculated for :

   bis (2,5-dihydroxy-acetophenoneoxime)Ni(II), $(C_8H_8O_3N)_2Ni$

   Ni - 15.02, N - 7.16

   Found Ni - 15.30, N - 7.0

Conductometric titrations :

Both direct (metal solution in the cell) and reverse (D.H.A.O. in the cell) titrations were carried out. The results are given in the following tables :

Conductometric titrations between copper sulphate and 2,5-dihydroxy-acetophenoneoxime :

Table - 12

Direct titrations (copper sulphate in the cell)

Fixed concentration of copper sulphate: $5x10^{-4}$M(in 20 ml.) - Set I
$1x10^{-3}$M(in 20 ml.) - Set II
$1.25x10^{-3}$M(in 20ml.) - Set III

Initial concentration of D.H.A.O. = $2x10^{-2}$M

Vol.of D.H.A.O (ml.)	I Corrected conductance x10-4(mhos)	Vol.of D.H.A.O. (ml.)	II Corrected conductance x10-4(mhos)	Vol.of D.H.A.O (ml.)	III Corrected conductance x10-4(mhos)
0.0	1.9	0.0	3.4	0.0	4.1
0.5	2.8	0.5	4.1	0.5	5.1
1.0	3.3	1.0	4.7	1.0	5.95
1.5	3.7	1.5	5.4	1.5	6.8
2.0	3.9	2.0	5.9	2.0	7.7
2.5	4.1	2.5	6.3	2.5	8.6
		3.0	6.7	3.0	9.0
		3.5	6.9	3.5	9.2
		4.0	7.2	4.0	9.5
				4.5	9.7
				5.0	10.0
Curve(a)		Curve(b)		Curve(c)	

Fig. 10

Curve(a)
20 ml.of $5x10^{-4}$M $CuSo_4$ = 1.1 ml.of $2x10^{-2}$M D.H.A.O.
= 44.0 ml.of $5x10^{-4}$M D.H.A.O.

Curve(b)
20 ml.of $1x10^{-3}$M $CuSo_4$ = 2.05 ml.of $2x10^{-2}$M D.H.A.O.
= 41.0 ml.of $1x10^{-3}$M D.H.A.O.

Curve(c)
20 ml. of $1.25x10^{-3}$M $CuSo_4$ = 2.6 ml.of $2x10^{-2}$M D.H.A.O.
=41.6 ml.of $1.25x10^{-3}$M D.H.A.O.

Table - 13

Reverse titrations (D.H.A.O.in the cell)

Fixed concentration of D.H.A.O - Set I : 2.5×10^{-3}M(in 20 ml.)
Set II : 2×10^{-3}M (in 20 ml.)

Initial concentration of copper sulphate added = 1×10^{-2}M

I		II	
Vol.of $CuSo_4$ (ml.)	Corrected conductance $\times10^{-4}$(mhos)	Vol.of $CuSo_4$ (ml.)	Corrected conductance $\times10^{-4}$(mhos)
0.0	1.3	0.0	1.3
0.5	2.6	0.5	2.6
1.0	4.0	1.0	3.7
1.5	5.2	1.5	4.6
2.0	6.6	2.0	5.8
2.5	7.7	2.5	6.8
3.0	8.2	3.0	7.4
3.5	8.5	3.5	7.8
4.0	9.0	4.0	8.6
	Curve(a)		Curve(b)

Fig.11

Curve (a)

20 ml.of 2.5×10^{-3}M D.H.A.O. = 2.4 ml.of 1×10^{-2}M $CuSo_4$
= 9.6 ml.of 2.5×10^{-3}M $CuSo_4$

Curve (b)

20 ml. of 2×10^{-3}M D.H.A.O. = 2.2 ml.of 1×10^{-2}M $CuSo_4$
= 11.0 ml. of 2×10^{-3}M $CuSo_4$

Conductometric titrations between palladium chloride and 2,5-dihydroxy-acetophenoneoxime :

Table - 14

Direct titrations($PdCl_2$ in the cell)

Fixed doncentration of $PdCl_2$ - Set I : 7.5×10^{-4}M (in 20 ml.)
- Set II : 1.5×10^{-3}M (in 20 ml.)

Initial concentration of D.H.A.O. added = 1×10^{-2}M

	I		II
Vol.of D.H.A.O. (ml.)	Corrected conductance $\times10^{-3}$(mhos)	Vol.of D.H.A.O. (ml.)	Corrected conductance $\times10^{-3}$(mhos)
0.0	10.5	0.0	12.5
0.5	10.0	1.0	11.4
1.0	9.1	2.0	10.5
1.5	8.4	3.0	9.5
2.0	7.7	4.0	8.5
3.0	6.5	5.0	7.3
4.0	5.6	6.0	6.6
5.0	4.9	7.0	6.2
6.0	4.2	8.0	5.7
7.0	3.7	9.0	5.1
		10.0	4.8
		11.0	4.35
		Curve(a)	Curve(b)

Fig. 12

Curve (a)

20 ml.of 7.5×10^{-4}M $PdCl_2$ = 3.2 ml.of 1×10^{-2}M D.H.A.O.
= 42.7 ml.of 7.5×10^{-4}M D.H.A.O.

Curve (b)

20 ml.of 1.5×10^{-3}M $PdCl_2$ = 6.0 ml.of 1×10^{-2}M D.H.A.O.
= 40 ml.of 1.5×10^{-3}M D.H.A.O.

Table - 15

Reverse titrations (D.H.A.O. in the cell)

Fixed concentration of D.H.A.O. - Set I: 4×10^{-4}M (in 20 ml.)
Set II: 6×10^{-4}M (in 20 ml.)

Initial concentration of $PdCl_2$ added = 5×10^{-3}M

I		II	
Vol.of $PdCl_2$ (ml.)	Corrected conductance $\times 10^{-3}$(mhos)	Vol.of $PdCl_2$ (ml.)	Corrected conductance $\times 10^{-3}$(mhos)
0.0	-	0.0	-
0.2	0.16	0.4	0.8
0.4	0.8	0.8	1.7
0.6	1.5	1.0	2.1
0.8	2.45	1.2	2.7
1.0	3.1	1.4	2.9
1.2	3.7	1.6	3.1
1.4	4.2	2.0	3.8
1.6	5.1	2.4	4.3
2.0	6.0	2.8	4.9
Curve(a)		Curve(b)	

Fig. 13

Curve (a)

20 ml. of 4×10^{-4}M D.H.A.O. = 0.9 ml.of 5×10^{-3}M $PdCl_2$
= 11.25 ml. of 4×10^{-4}M $PdCl_2$

Curve (b)

20 ml. of 6×10^{-4}M D.H.A.O. = 1.2 ml. of 5×10^{-3}M $PdCl_2$
= 10.0 ml. of 6×10^{-4}M $PdCl_2$

Conductometric titrations between nickel sulphate and 2,5-dihydroxy-acetophenoneoxime

The solution of 2,5-dihydroxy-acetophenoneoxime was prepared in an equivalent amount of ammonium hydroxide.

Table - 16

Fixed concentration of D.H.A.O. Set I: $5\times10^{-3}M$ (in 20 ml.)
Set II: $8\times10^{-3}M$ (in 20 ml.)

Initial concentration of nickel sulphate = $2\times10^{-2}M$

Vol.of $NiSo_4$ (ml.)	I Corrected conductance $\times10^{-4}$ (mhos)	Vol.of $NiSo_4$ (ml.)	II Corrected conductance $\times10^{-4}$ (mhos)
0.0	2.8	0.0	3.95
0.5	4.05	0.5	4.95
1.0	5.25	1.0	6.0
1.5	6.2	1.5	7.0
2.0	7.4	2.0	8.15
2.2	8.0	2.5	9.2
2.5	8.4	3.0	10.3
3.0	9.0	3.5	11.2
3.5	10.0	4.0	12.1
4.0	10.5	4.5	12.7
4.5	11.4	5.0	13.7
5.0	12.2	5.5	14.4
		6.0	15.4
		6.5	16.0
		7.0	16.6
	Curve(a)		Curve(b)

Fig.14

<u>Curve(a)</u>
20 ml.of $5\times10^{-3}M$ D.H.A.O. = 2.5 ml.of $2\times10^{-2}M$ $NiSo_4$
= 10.0 ml.of $5\times10^{-3}M$ $NiSo_4$

<u>Curve(b)</u>
20 ml.of $8\times10^{-3}M$ D.H.A.O. = 4.15 ml.of $2\times10^{-2}M$ $NiSo_4$
= 10.375 ml.of $8\times10^{-3}M$ $NiSo_4$

The titration of nickel sulphate using D.H.A.O. as titrant, could not be carried out successfully as the conductance variations on the addition of the titrant were too small to be observed.

pH metric titrations :

The pH-metric titrations were carried out separately with the solutions of the metal, the ligand and the mixtures of the two, using standard KOH as titrant. The observations obtained during the titrations are summarized in the following tables :

pH-metric titrations between copper(II) and 2,5-dihydroxyacetophenoneoxime :

Table - 17

Solution I : 10 ml.of 1×10^{-2}M $CuSo_4$+40 ml.of 40% alcohol.
" II : 10 ml.of 1×10^{-2}M $CuSo_4$+10 ml.of 1×10^{-2}M D.H.A.O. +30 ml.of 40% alcohol.
" III : 10 ml.of 1×10^{-2}M $CuSo_4$+20 ml.of 1×10^{-2}M D.H.A.O. +20 ml.of 40% alcohol.
" IV : 10 ml.of 1×10^{-2}M $CuSo_4$+30 ml.of 1×10^{-2}M D.H.A.O. +10 ml.of 40% alcohol.
" V : 20 ml.of D.H.A.O. + 30 ml. of 40% alcohol.

Vol.of 0.1M KOH added (ml.)	pH of solutions				
	I	II	III	IV	V
0.0	5.5	3.0	2.85	2.85	5.35
0.1	-	-	-	-	8.2
0.2	5.8	3.2	2.95	2.95	8.7
0.3	-	-	-	-	8.95
0.4	5.85	3.4	3.02	3.0	9.1
0.6	5.9	3.6	3.12	3.1	-
0.8	5.95	4.1	3.2	3.18	9.5
0.9	-	5.0	-	-	-
1.0	6.0	5.8	3.38	3.22	9.65
1.1	-	5.95	-	-	-
1.2	6.1	6.0	3.5	3.3	-
1.4	6.2	6.18	3.7	3.45	-
1.5	-	6.25	-	-	10.0
1.6	6.6	6.35	3.95	3.6	-
1.7	7.4	6.48	4.2	-	-
1.8	9.7	6.65	4.5	3.85	-
1.9	10.1	7.65	5.0	4.1	-
2.0	10.2	9.6	6.45	4.98	10.4
2.1	-	10.1	9.6	8.0	-
2.2	10.35	10.3	10.1	8.7	-
2.4	10.45	10.3	10.2	9.3	-
2.5	-	-	-	-	10.8
2.6	10.6	10.6	10.5	9.6	-
2.8	10.7	-	-	9.8	-
3.0	10.8	-	-	10.1	11.1
Curves	(a)	(b)	(c)	(d)	(e)

Fig. 15

pH metric titrations between palladium(II) and 2,5-dihydroxy acetophenoneoxime :

Table -18

Solution I : 5 ml.of 1×10^{-2}M $PdCl_2$ in 0.05N HCl+20 ml. 40% alcohol.
" II : 5 ml.of 1×10^{-2}M $PdCl_2$ in 0.05N HCl+5 ml. of 1×10^{-2}M D.H.A.O.+ 15 ml. 40% alcohol.
" III : 5 ml.of 1×10^{-2}M $PdCl_2$ in 0.05N HCl+10 ml. of 1×10^{-2}M D.H.A.O.+ 10 ml.40% alcohol.
" IV : 5 ml.of 1×10^{-2}M $PdCl_2$ in 0.05N HCl+15 ml.of 1×10^{-2}M D.H.A.O. + 5 ml.40% alcohol.

Vol.of 0.1M KOH added (ml.)	pH of solutions			
	I	II	III	IV
0.0	2.1	2.0	1.98	1.98
0.5	2.22	2.08	2.0	2.0
1.0	2.35	2.18	2.1	2.1
1.5	2.52	2.32	2.22	2.2
2.0	2.8	2.45	2.3	2.3
2.3	3.1	-	-	-
2.5	3.9	2.78	2.5	2.48
2.8	4.0	3.1	2.7	2.7
3.0	4.1	3.62	2.88	2.9
3.2	4.2	3.8	3.1	3.1
3.3	4.4	4.1	3.4	3.4
3.4	4.6	-	3.6	3.5
3.5	10.25	5.9	4.78	4.5
3.8	11.0	10.3	10.1	9.68
4.0	11.2	10.55	10.3	10.1
4.5	11.45	10.95	10.7	10.5
5.0	11.6	11.2	11.1	10.9
Curves	(a)	(b)	(c)	(d)

Fig.16

pH-metric titrations between nickel(II) and 2,5-dihydroxyacetophenoneoxime :

Table - 19

Solution I : 5 ml.of $2x10^{-2}M$ $NiSo_4$+15 ml.of 40% alcohol.
" II : 5 ml.of $2x10^{-2}M$ $NiSo_4$+ 5 ml.of $2x10^{-2}M$ D.H.A.O. +10 ml.of 40% alcohol.
" III : 5 ml.of $2x10^{-2}M$ $NiSo_4$+10 ml.of $2x10^{-2}M$ D.H.A.O. + 5 ml.of 40% alcohol.
" IV : 5 ml.of $2x10^{-2}M$ $NiSo_4$+15 ml.of $2x10^{-2}M$ D.H.A.O.

Vol.of 0.1M KOH added (ml.)	pH of solutions			
	I	II	III	IV
0.0	6.72	5.95	5.7	5.6
0.1	7.88	6.3	-	-
0.2	8.0	6.48	5.9	5.7
0.4	8.1	6.52	5.95	5.78
0.6	8.15	6.6	6.0	5.8
0.7	-	6.7	-	-
0.8	8.25	6.9	6.0	5.8
0.9	-	7.1	-	-
1.0	8.35	7.8	6.0	5.8
1.1	-	7.95	-	-
1.2	8.4	8.02	6.05	5.8
1.4	8.5	8.1	6.1	5.8
1.6	8.68	8.2	6.3	5.9
1.7	8.92	-	6.35	-
1.8	9.52	8.35	6.5	6.1
1.9	10.12	8.5	6.75	6.2
1.95	-	-	7.0	6.35
2.0	10.42	8.8	8.45	7.0
2.05	-	-	9.1	8.3
2.1	10.6	9.2	9.2	8.6
2.2	10.72	9.4	9.3	8.8
2.4	10.9	9.7	9.55	9.0
2.6	11.0	9.9	9.68	9.2
2.8	11.1	10.05	9.8	9.5
3.0	-	10.1	9.9	-
Curves	(a)	(b)	(c)	(d)

Fig.17

DISCUSSION

Composition and stability of Mo(VI) complex :

Molybdenum(VI) reacts instantaneously with D.H.A.O. in acidic medium, giving a soluble orange-yellow complex.

Spectrophotometric studies reveal the formation of only one complex having maximum absorption at 370 mµ (Fig.1).

The complex is stable in the pH range 2.0-4.5 as found from the absorption spectra of the solutions at various pH values (Fig.2).

Job's method of continued variation (Figs.3-5) and slope ratio method (Fig.6) give evidence for the formation of 1:2 (molybdenum: D.H.A.O) complex.

The formation constant was determined by the modified Anderson's method. The formation constant was calculated from the absorbance data taken for Job's method (Tables 4,5). Since molybdate ions do not absorb at 370 mµ (λmax. of the complex), hence the absorbance of the solution may be due to D.H.A.O and the coloured complex. In the descending portion of the curves (Fig.7) where the molybdate ions are in excess, it may be safely assumed that D.H.A.O. is fully complexed with molybdenum and does not contribute to the colour of the solution, hence the absorbance of the solution is due to the coloured complex alone. Taking into account these assumptions, the value of K was calculated and found to be 1.39×10^{10} and that of free energy $-\Delta F = 14.02$ Kcals. at 30°C.

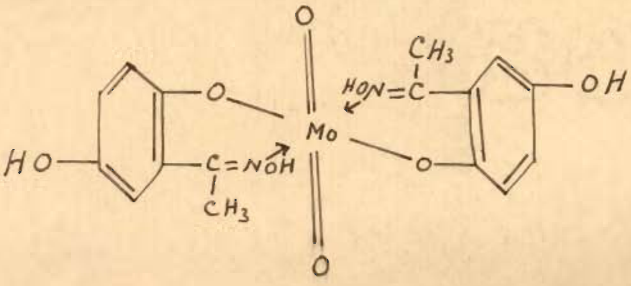
Conductometric titrations were also carried out to determine the composition of the molybdenum complex. Both direct and reverse titrations give the combining ratio of 1:2 for metal and ligand respectively. The results of these titrations are summarized below :

S.No.	Fig.& curve	Vol.of Amm. Molybdate (ml.)	Vol.of D.H.A.O. (ml.)	Mole ratio Mo/D.H.A.O.
1.	8,a	$30(0.666 \times 10^{-3}M)$	$60.0(0.666 \times 10^{-3}M)$	1:2
2.	8,b	$30(1.333 \times 10^{-3}M)$	$61.5(1.333 \times 10^{-3}M)$	1:2.05
3.	8,c	$30(2 \times 10^{-3}M)$	$60.0(2 \times 10^{-3}M)$	1:2
4.	9,a	$15.0(2.666 \times 10^{-3}M)$	$30(2.666 \times 10^{-3}M)$	1:2
5.	9,b	$15.2(5.333 \times 10^{-3}M)$	$30(5.333 \times 10^{-3}M)$	1:1.97

Structure of the complex :

The results of chemical analysis of the isolated yellow complex, for molybdenum and nitrogen contents revealed its composition as $(C_8H_8O_3N)_2MoO_2$.

On the basis of evidence derived from physico-chemical studies as well as the chemical analysis, the following structure may be assigned to the complex.



Composition and structure of Cu(II)-D.H.A.O.complex :

2,5-Dihydroxy-acetophenoneoxime forms insoluble, light brown coloured complex with copper ions in the pH range of 2.0-8.0.

Chemical analysis of the complex gave evidence for the formation of $(C_8H_8O_3N)_2Cu$ complex.

The composition of the complex was further studied by carrying out conductometric titrations (both direct and reverse) between the reactants. The results of all the titrations also revealed the formation of 1:2 (Cu:D.H.A.O.) complex. The results of the titrations are summarized below :

S.No.	Fig. & curve	Vol.of Copper sulphate (ml.)	Vol.of D.H.A.O. (ml.)	Mole ratio Cu/D.H.A.O.
1.	10,a	20.0($5x10^{-4}$M)	44.0($5x10^{-4}$M)	1:2.2
2.	10,b	20.0($1x10^{-3}$M)	41.0($1x10^{-3}$M)	1:2.05
3.	10,c	20.0($1.25x10^{-3}$M)	41.6($1.25x10^{-3}$M)	1:2.08
4.	11,a	9.6($2.5x10^{-3}$M)	20.0($2.5x10^{-3}$M)	1:2.08
5.	11,b	11.0($2x10^{-3}$M)	20.0($2x10^{-3}$M)	1:1.82

pH metric titrations were also carried out to determine the composition of the complex. The pH metric titrations of copper sulphate in presence of 0,1,2 and 3 moles of D.H.A.O. against standard KOH (Fig.15) provide the following information.

The titration curve(a) of copper sulphate alone against KOH has got only one inflexion point corresponding to the interaction of 2 moles of KOH with 1 mole of copper to give 1 mole of cupric hydroxide.

$$Cu^{++} + 2OH^- \longrightarrow Cu(OH)_2$$

On addition of 1 mole of the ligand to the copper-sulphate solution, the pH of the solution is lowered by about two units (curve b). This lowering in pH can only be attributed to the release of protons during complex formation. Two inflexion points are observed in curve (b), one corresponding to 1 mole and the other to 2 moles of KOH respectively. It may be assumed that 1 mole of KOH is required to neutralize a proton released during 1:2 complex (Cu : D.H.A.O) formation and the second mole of KOH is used for precipitating the remaining half of copper as the hydroxide.

$$\frac{1}{2} Cu^{++} + HL + OH^- \longrightarrow \frac{1}{2}\left[Cu(L)_2\right] + H_2O \quad \text{(HL stands for the ligand)}$$

$$\frac{1}{2} Cu^{++} + OH^- \longrightarrow \frac{1}{2}\left[Cu(OH)_2\right]$$

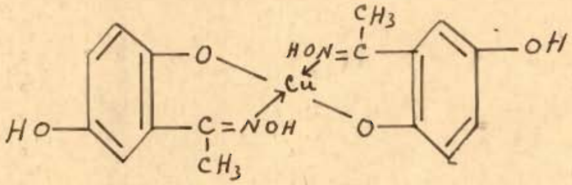
However, with the copper sulphate containing excess of the ligand (2 and 3 moles), only one inflexion point corresponding to 2 moles of KOH is realized (curves c,d). It is assumed that 2 moles of KOH may only be consumed for reacting with 2 H^+ released during complex formation. The reaction may be represented as follows :

$$Cu^{++} + 2HL + 2OH^- \longrightarrow Cu(L)_2 + 2H_2O$$

The pH metric titrations thus indicate that one mole of copper reacts with two moles of D.H.A.O. to form 1:2 complex.

The physico-chemical investigations as well as the results of chemical analysis provide evidence for the formation of 1:2 complex.

The infrared spectra show a lowering in the C=N- stretching frequency from 1590 cm^{-1} of free oxime (Fig.18) to 1550 cm^{-1} in the copper complex (Fig.19). It may thus be inferred that copper is coordinated to oxime through nitrogen of C=N-. The other group involved in chelation will then be phenolic(oH), the hydrogen of which is replaced by the metal. This is also confirmed on the basis of pH metric studies. The structure of the complex may be written as :



Composition and structure of Pd-D.H.A.O. complex :

2,5-Dihydroxy-acetophenoneoxime reacts with palladium ions to form yellow, insoluble complex in the pH range 2.5-6.0.

The results of estimation of palladium and nitrogen contents of the isolated complex corresponded to its molecular formula $(C_8H_8O_3N)_2Pd$.

The conductometric titrations carried out between palladium chloride and D.H.A.O. gave the combining ratio of 1:2 for metal and the ligand respectively. The results of the titrations are given below :

S.No.	Fig.& Curve	Volume of Palladium chloride (ml.)	Vol.of D.H.A.O. (ml.)	Mole ratio Pd/D.H.A.O.
1.	12,a	20.0(7.5×10^{-4}M)	42.7(7.5×10^{-4}M)	1:2.13
2.	12,b	20.0(1.5×10^{-3}M)	40.0(1.5×10^{-3}M)	1:2
3.	13,a	11.25(4×10^{-4}M)	20.0(4×10^{-4}M)	1:1.78
4.	13,b	10.0(6×10^{-4}M)	20.0(6×10^{-4}M)	1:2

pH metric titrations were also carried out to determine the composition of the complex.

Three sets of solutions were prepared as in the case of copper and were titrated against standard KOH solution (Fig.16). Since palladium chloride solution was prepared in 0.05N hydrochloric acid, necessary correction was, therefore, made while evaluating the composition. Curve(a) gives two inflexions corresponding to the consumption of 5 and 7 moles of KOH respectively. The first inflexion is due to complete neutralization of hydrochloric acid present in the solution, with KOH whereas the second inflexion indicates the complete precipitation of Pd as $Pd(oH)_2$;

$$5H^{+} + 5OH^{-} \longrightarrow 5H_2O$$

$$Pd^{++} + 2OH^{-} \longrightarrow Pd(oH)_2$$

$$\overline{Pd^{++} + 5H^{+} + 7OH^{-} \longrightarrow Pd(oH)_2 + 5H_2O}$$

On addition of the ligand to palladium solution, lowering in pH of the solution occurs as indicated by curve(b). This lowering of pH is attributed to chelation reaction resulting in the release of protons. Curve (b) records only one inflexion at 7 moles of KOH. Of the seven moles of KOH consumed, 5 moles are required to neutralize hydrochloric acid present in the solution. As the solution contains metal and ligand in the ratio of 1:1, it may be assumed that half of the palladium forms 1:2 complex with the ligand, with the release of one proton which reacts with one mole of KOH whereas the other half of palladium gets precipitated as hydroxide by another mole of KOH.

$$5H^+ + 5OH^- \longrightarrow 5H_2O$$

$$\frac{1}{2} Pd^{++} + HL + OH^- \longrightarrow \frac{1}{2}\left[Pd(L)_2\right] + H_2O$$

$$\frac{1}{2} Pd^{++} + OH^- \longrightarrow \frac{1}{2}\left[Pd(OH)_2\right]$$

Curve(c) is obtained on titrating the solution containing metal and the ligand in the ratio 1:2 respectively. There is only one inflexion corresponding to seven moles of KOH. Since five moles of KOH are consumed in the neutralization of the hydrochloric acid present in the solution, the remaining two moles are required to neutralize the two protons released during complex formation.

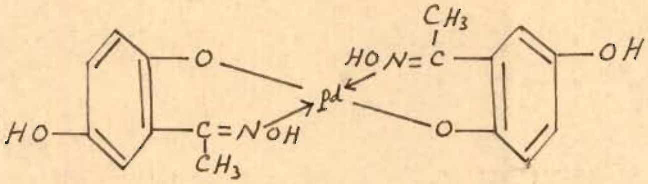
$$5H^+ + 5OH^- \longrightarrow 5H_2O$$

$$Pd^{++} + 2HL + 2OH^- \longrightarrow Pd(L)_2 + 2H_2O$$

Again with the solution containing metal and the ligand in the ratio 1:3 respectively, only one inflexion corresponding to seven moles of KOH, is observed (curve d).

From the pH metric titrations, it may, therefore, be concluded that for one mole of palladium, two moles of D.H.A.O are required to form the Pd-D.H.A.O.complex.

The structure of the complex was established by comparing the infrared spectra of the ligand (Fig.18) and the complex (Fig.20). The interesting feature of these spectra is the shifting of C=N- frequency from 1590 cm^{-1} (in the ligand) to 1560 cm^{-1} in the complex, pointing thereby coordination of the metal to the ligand through the nitrogen of C=N-. The other group responsible for chelation is the phenolic (oH), the hydrogen of which is replaced by the metal, as evidenced by pH metric titrations. The complex is, therefore, structurally represented as :



Composition and structure of Ni-D.H.A.O.complex :

The results of chemical analysis of the isolated complex corresponded to its formula $(C_8H_8O_3N)_2Ni$.

Conductometric titrations were carried out between nickel sulphate and D.H.A.O. The combining ratio of 1:2 for nickel and D.H.A.O. was evaluated from the titration curves. The results of the titrations are summarized as below:

S.No.	Fig.and curve	Vol.of $NiSo_4$ (ml.)	Vol.of D.H.A.O (ml.)	Mole ratio Ni/D.H.A.O
1.	14,a	10.0(5x10^{-3}M)	20.0(5x10^{-3}M)	1:2
2.	14,b	10.375(8x10^{-3}M)	20.0(8x10^{-3}M)	1:1.92

pH metric titrations were performed with the solutions containing nickel and D.H.A.O. in the ratio of 1:0, 1:1, 1:2 and 1:3 respectively against standard KOH (Fig.17).

In curve(a) there is only one inflexion corresponding to 2 moles of KOH, the whole quantity of KOH being consumed in precipitating nickel as hydroxide.

$$Ni^{++} + 2OH^{-} \longrightarrow Ni(OH)_2$$

Two inflexions are observed in curve(b) corresponding to 1 and 2 moles of KOH respectively. Since the solution contains metal and ligand in the ratio of 1:1, it may be concluded that half of the metal is consumed in the formation of 1:2 complex. The other half of the metal is precipitated as hydroxide by another mole of KOH

$$\frac{1}{2}\,Ni + HL + OH^{-} \longrightarrow \frac{1}{2}\left[Ni(L)_2\right] + H_2O$$

$$\frac{1}{2}\,Ni + OH^{-} \longrightarrow \frac{1}{2}\left[Ni(OH)_2\right]$$

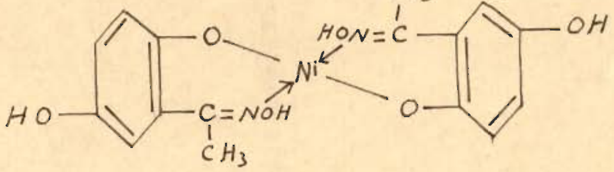
Curve(c) represents the titration of the solution containing metal and D.H.A.O. in the ratio of 1:2. Only one inflexion corresponding to 2 moles of KOH is realized. These two moles of KOH are consumed in reacting with two protons released during 1:2 complex formation

$$Ni^{++} + 2HL + 2OH^{-} \longrightarrow Ni(L)_2 + 2H_2O$$

In curve(d) representing the titration of the solution containing metal and ligand in the ratio of 1:3, there is also one inflexion corresponding to 2 moles of KOH, thus showing again 1:2 complex formation between nickel and D.H.A.O.

On comparison of the infrared spectra of D.H.A.O. and its nickel complex, it is found that the absorption band at 1590 cm^{-1} due to C=N- in the ligand (Fig.18) is shifted to 1550 cm^{-1} in the complex (Fig.21), showing thereby that the coordination of nickel takes place through nitrogen of the oxime group. The other group involved in chelation is the phenolic (OH), the hydrogen of which is replaced by the metal as evidenced by pH-metric titrations.

The nickel complex is, therefore, represented structurally as :



VOSBURGH COOPER'S METHOD

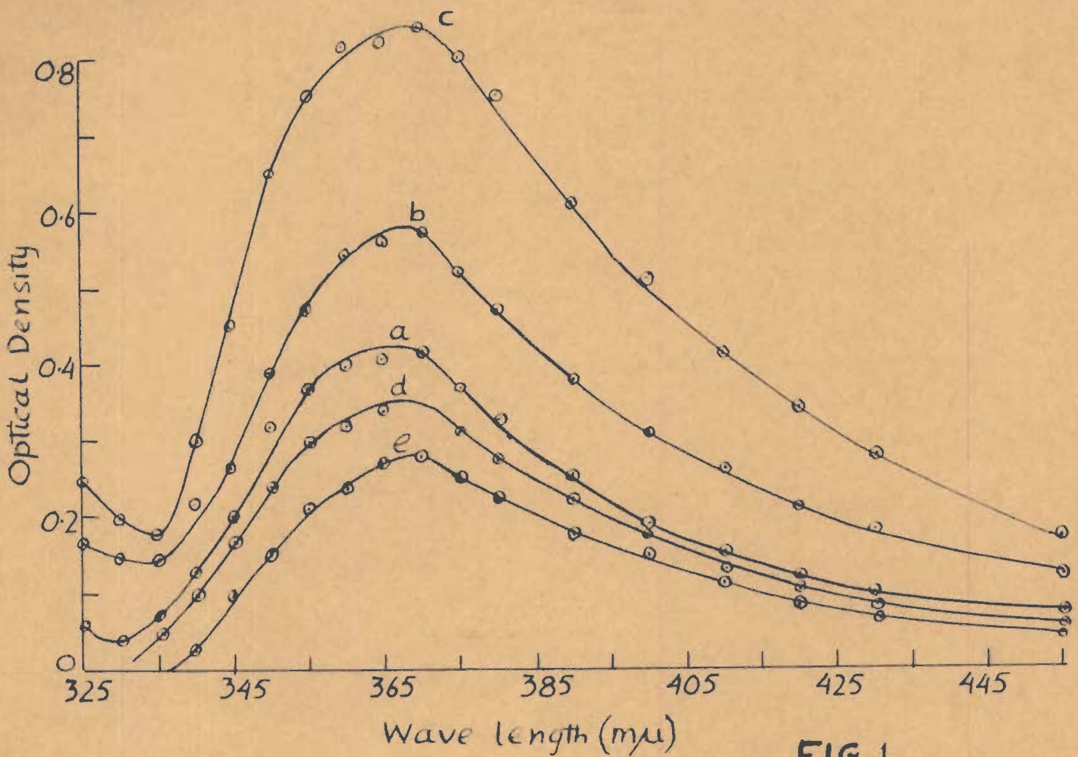


FIG. 1

INFLUENCE OF pH ON STABILITY OF COMPLEX

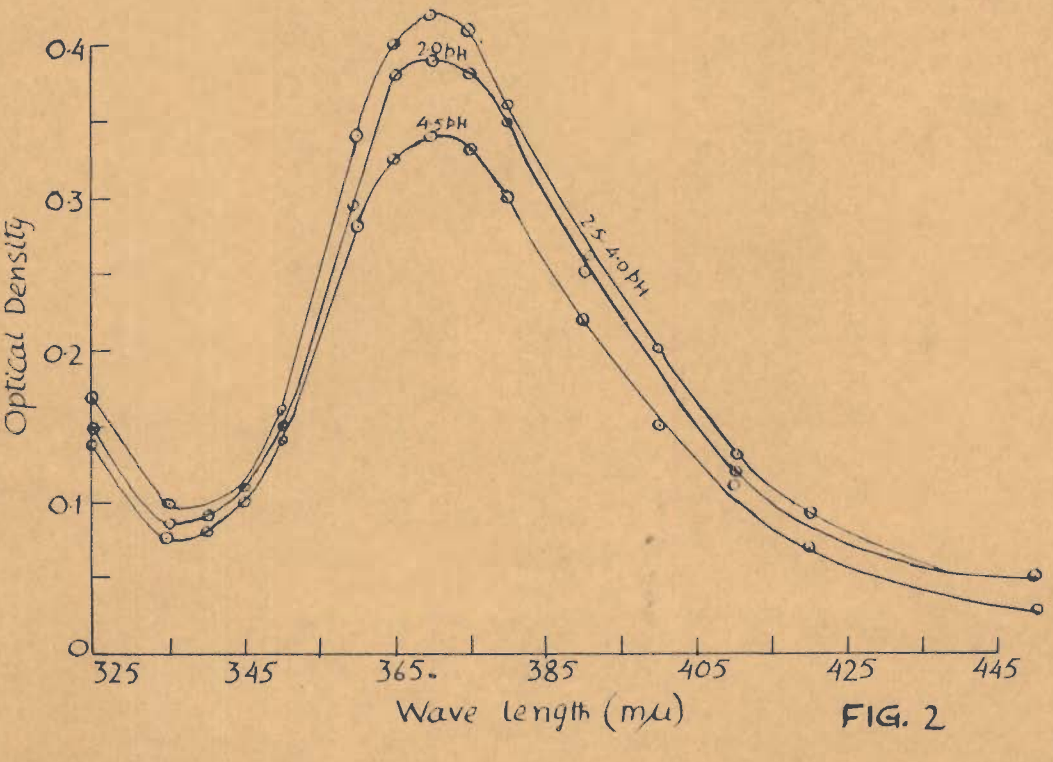


FIG. 2

JOB'S METHOD

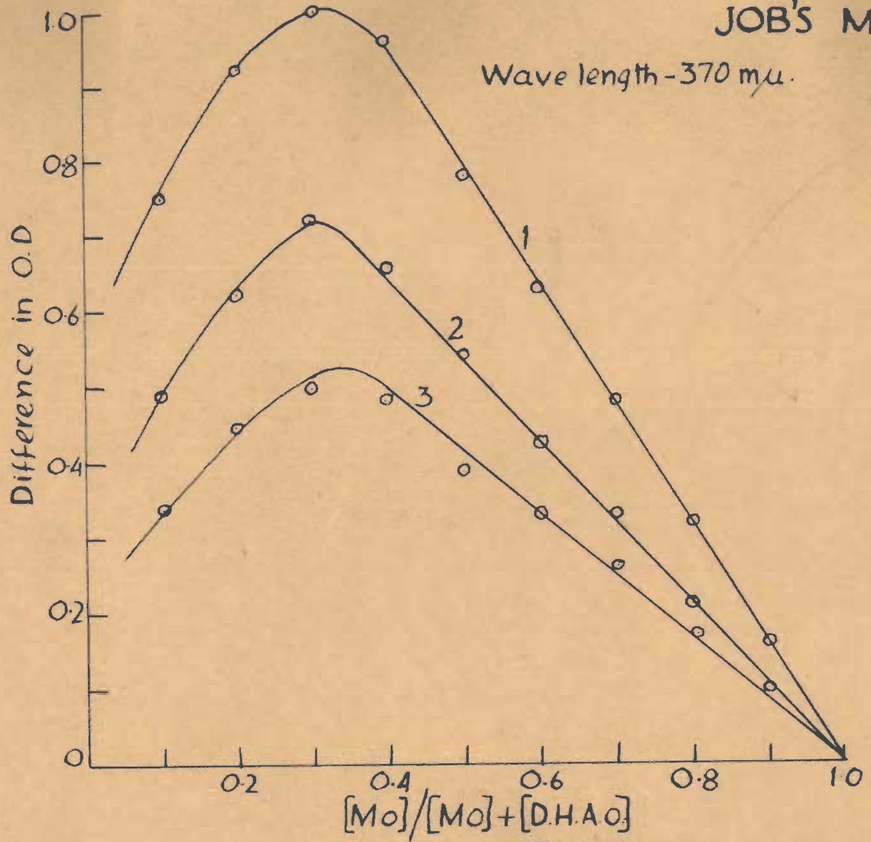


FIG. 3

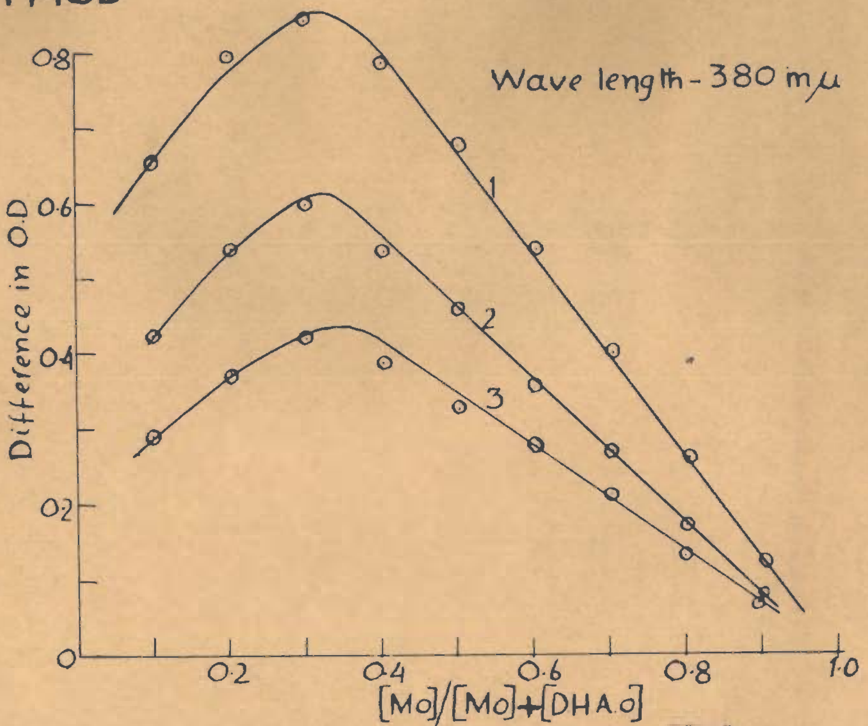


FIG. 4

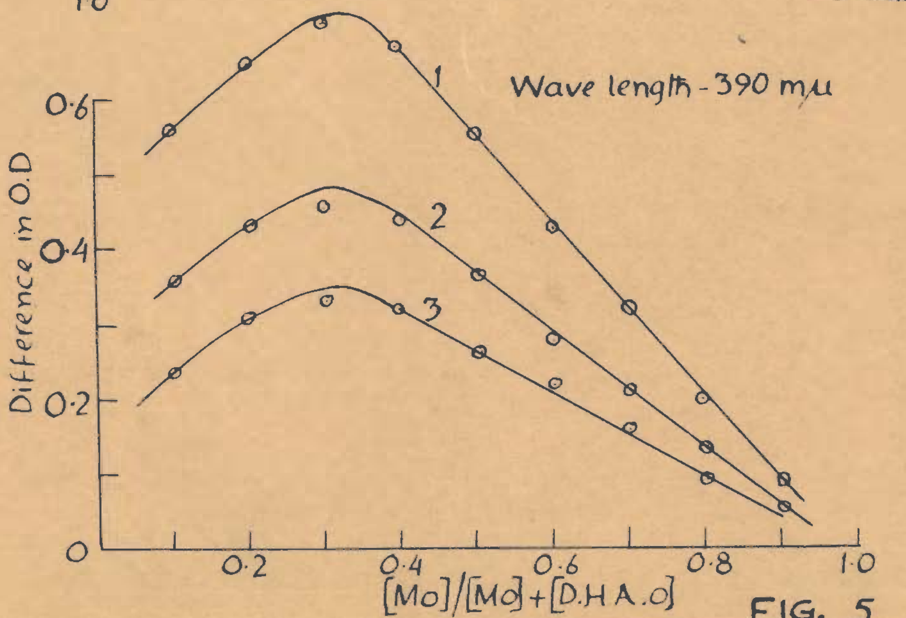


FIG. 5

SLOPE RATIO METHOD

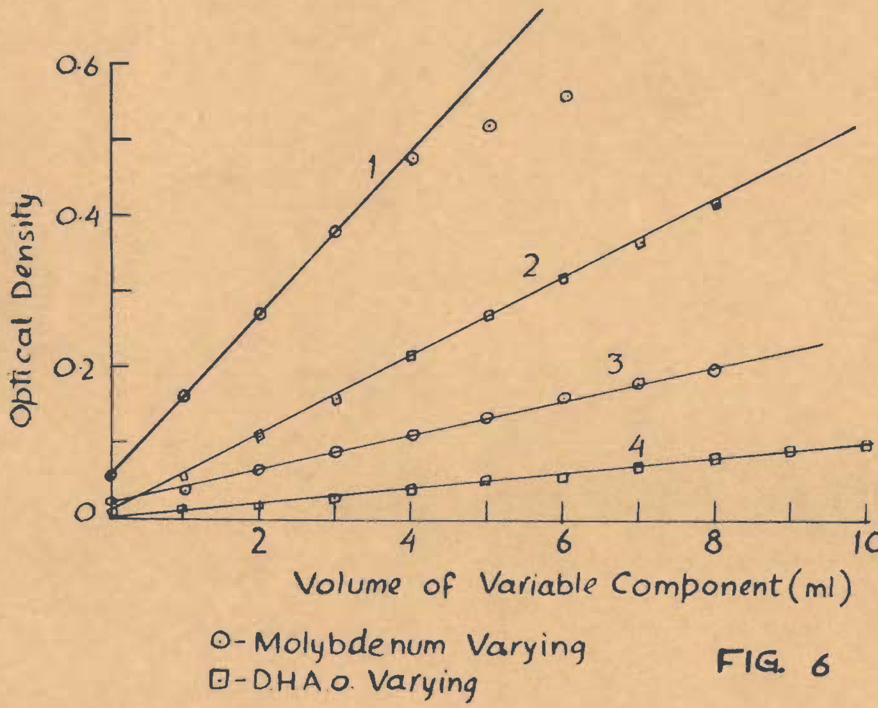


FIG. 6

FORMATION CONSTANT OF COMPLEX

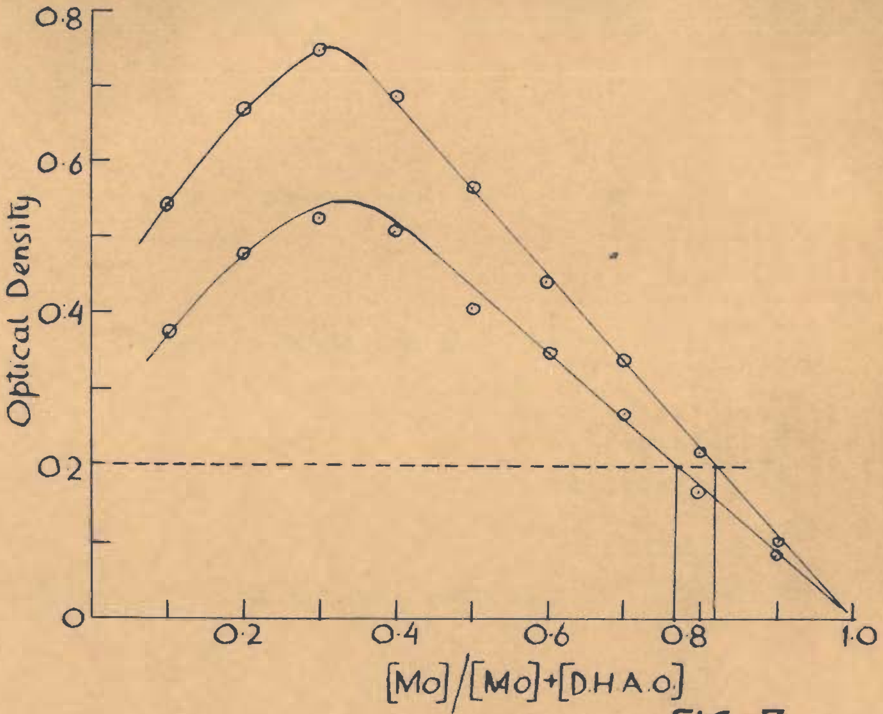


FIG. 7

CONDUCTOMETRIC TITRATIONS.

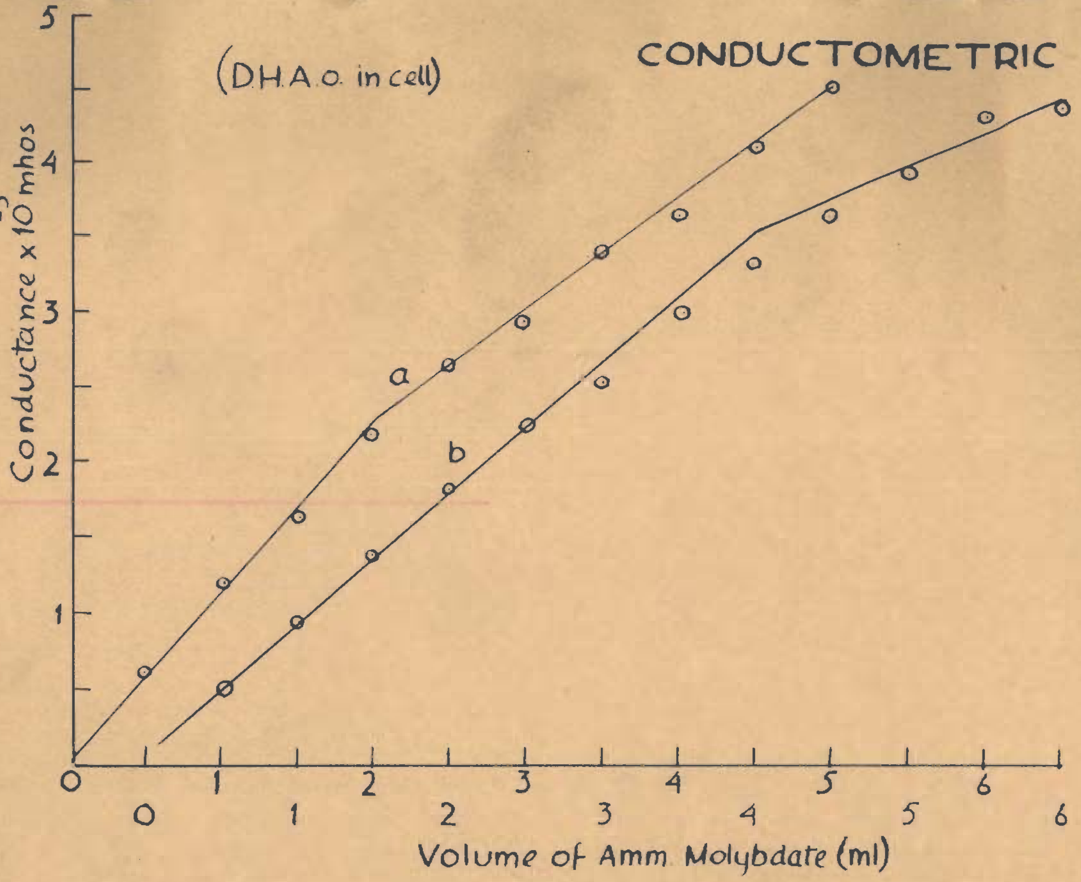


FIG. 9

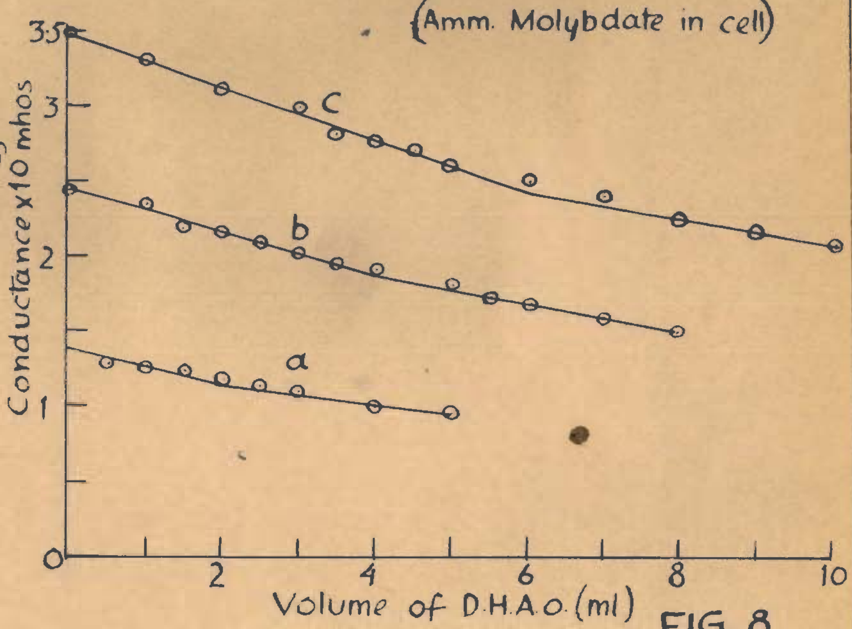


FIG. 8

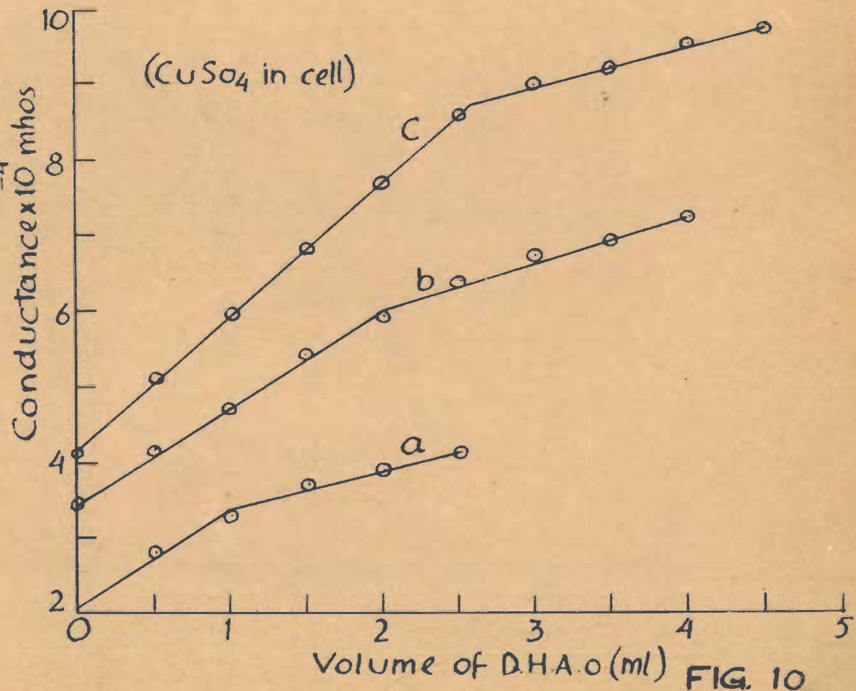


FIG. 10

CONDUCTOMETRIC TITRATIONS

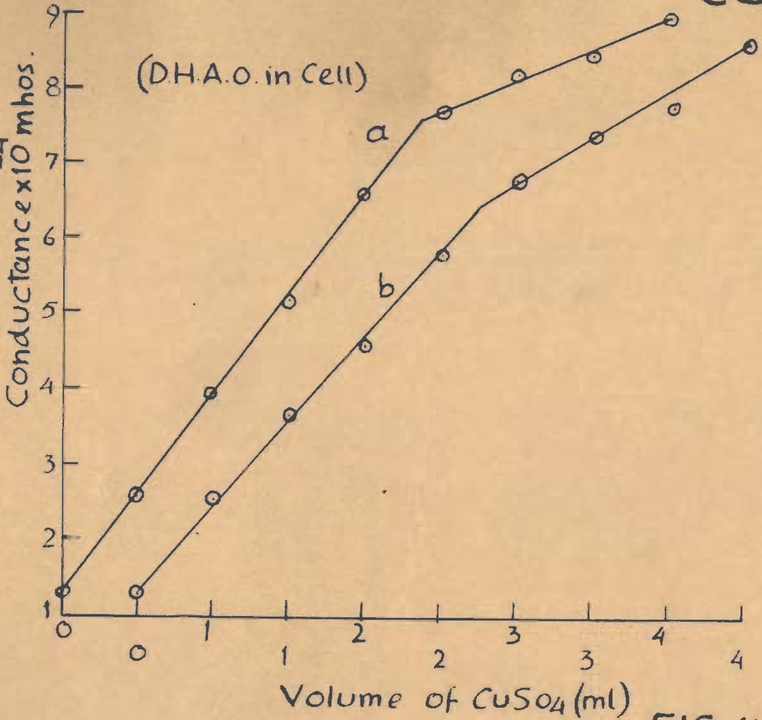


FIG. 11

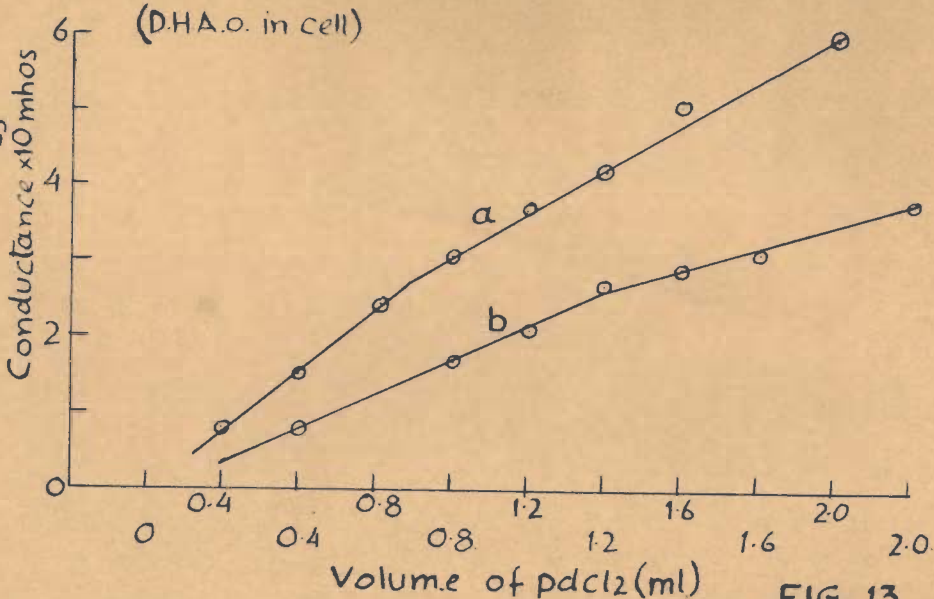


FIG. 13

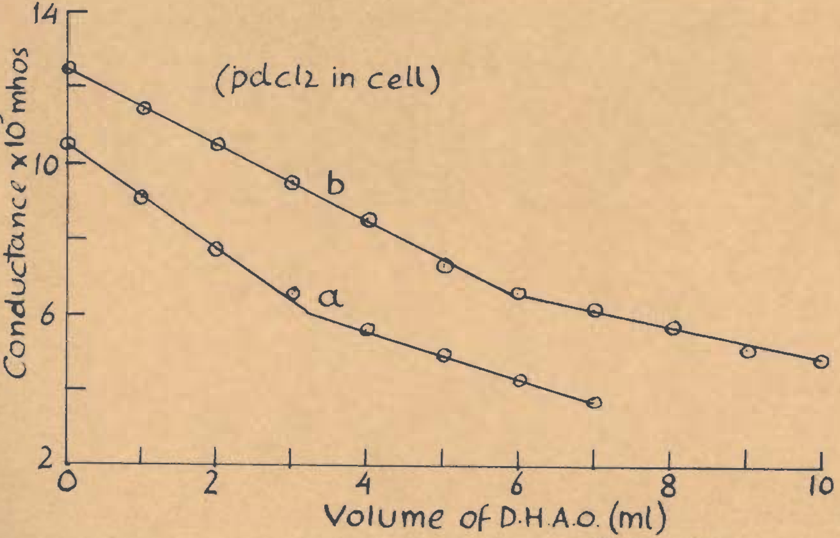


FIG. 12

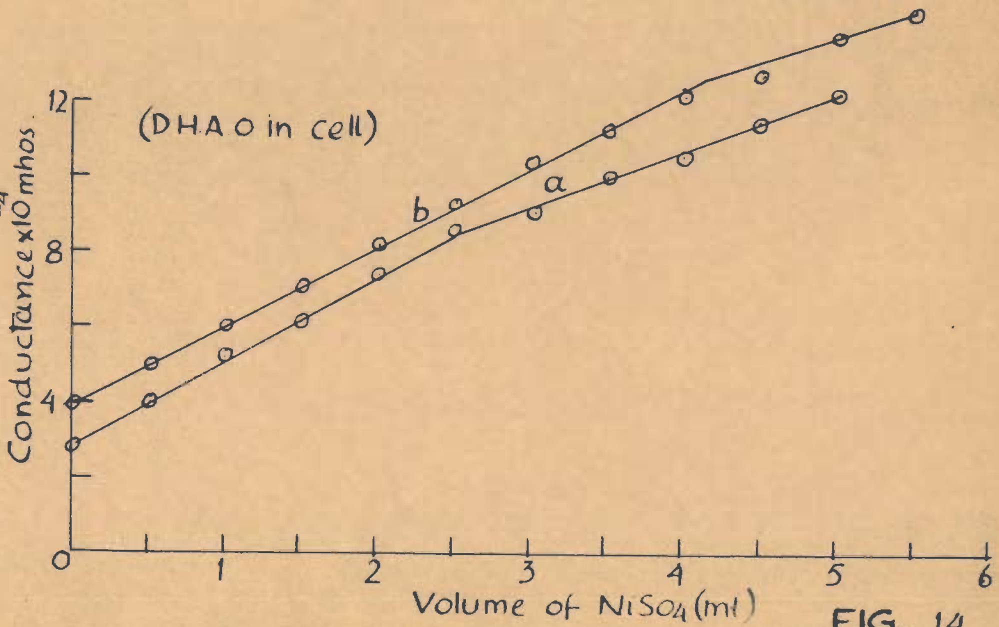


FIG. 14

pH-METRIC TITRATIONS

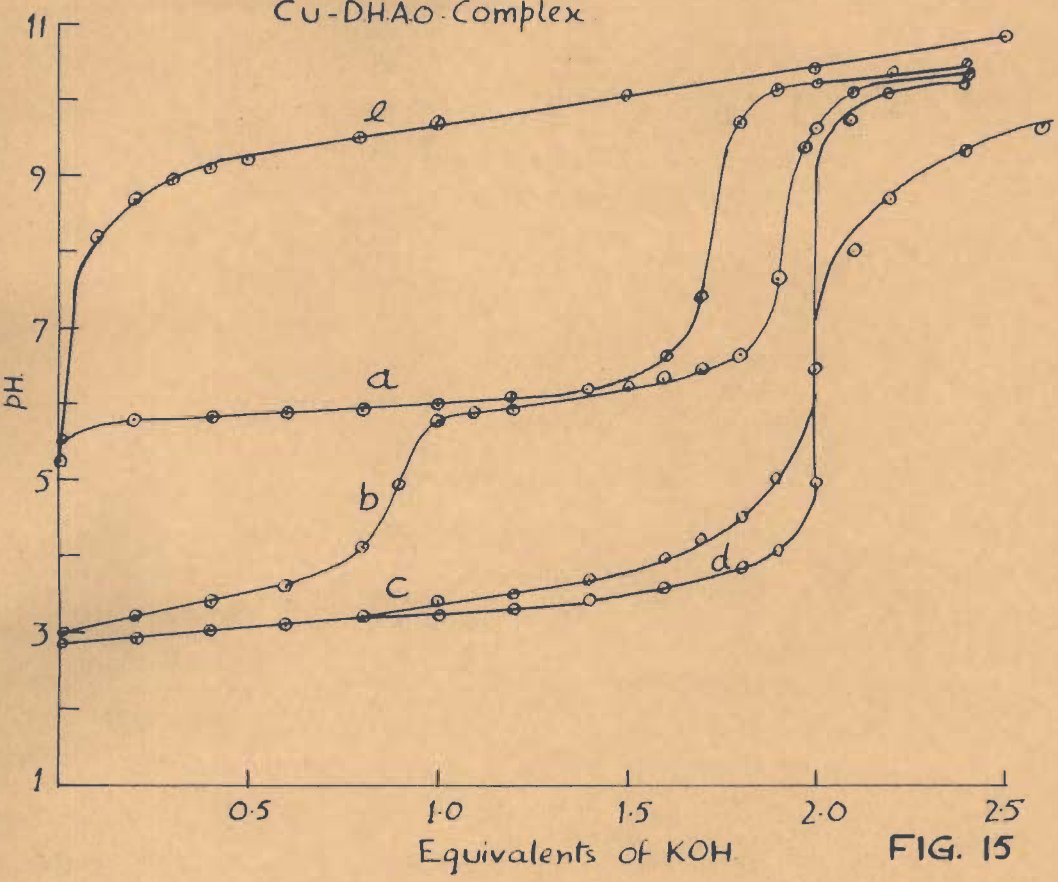


FIG. 15

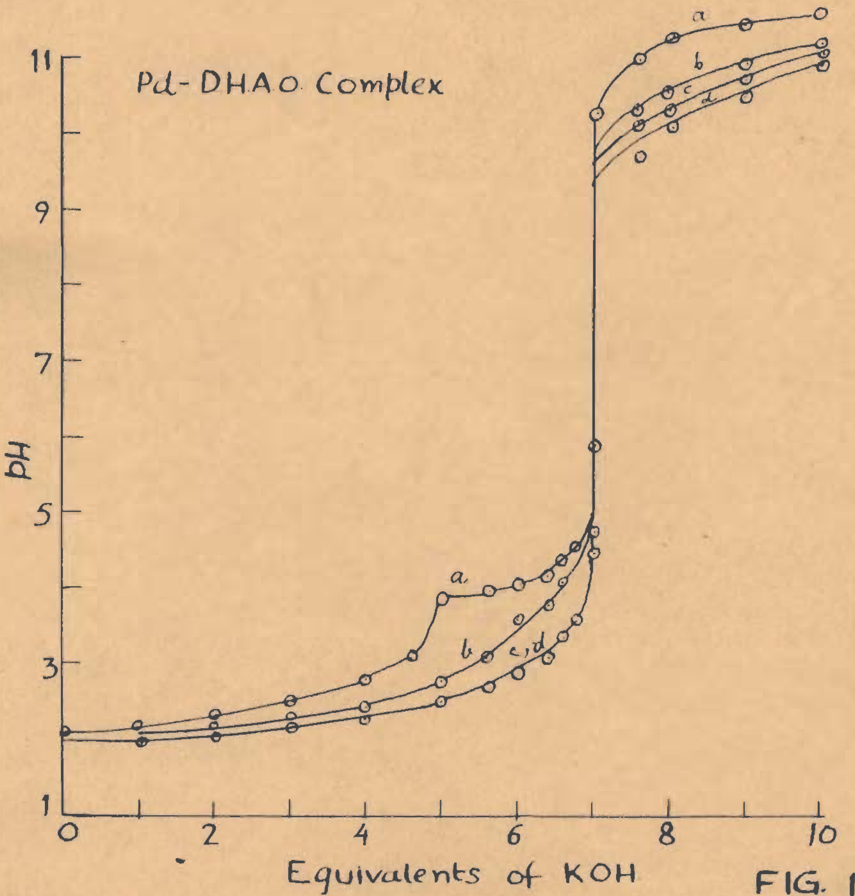


FIG. 16

þH-METRIC TITRATIONS

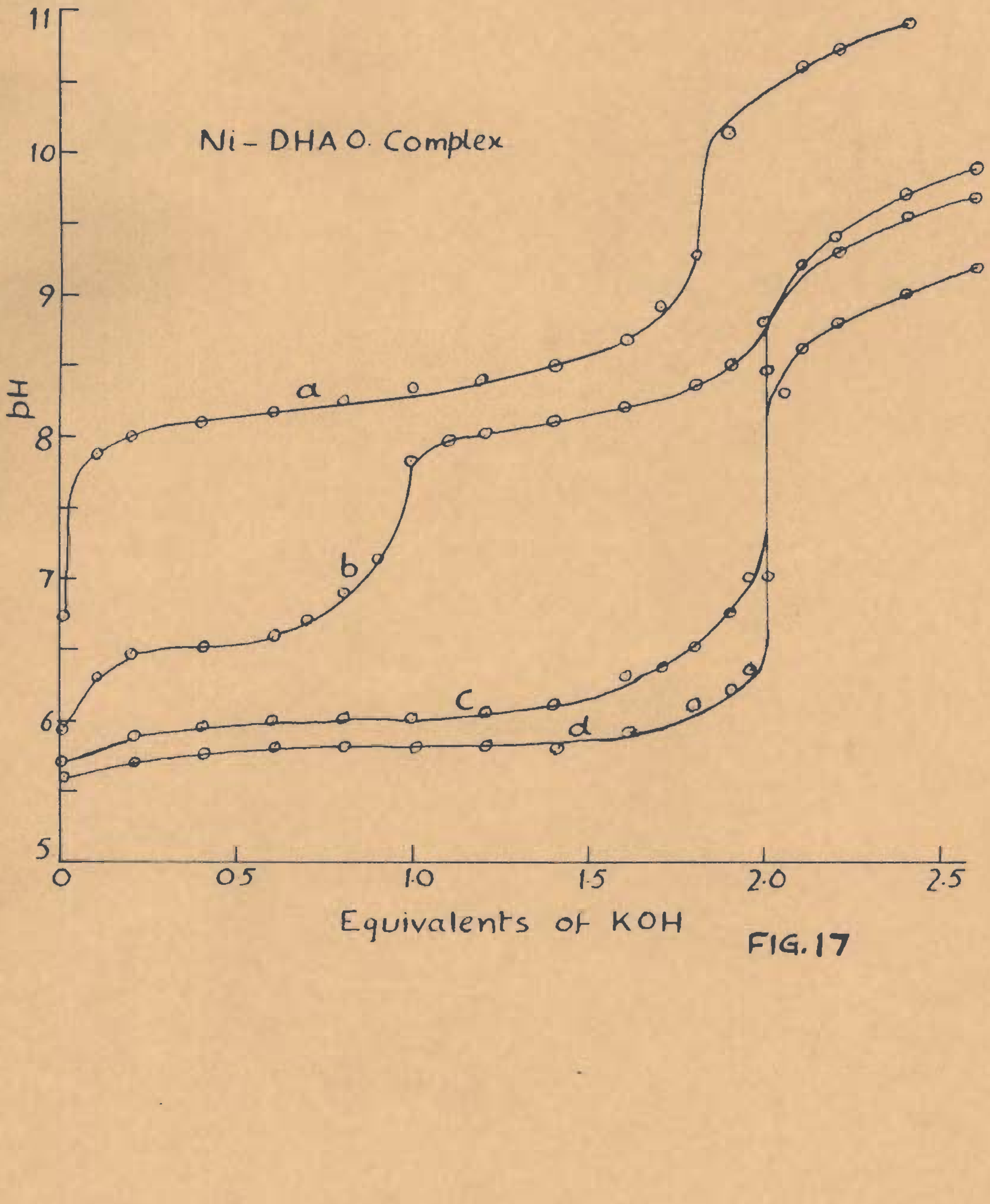
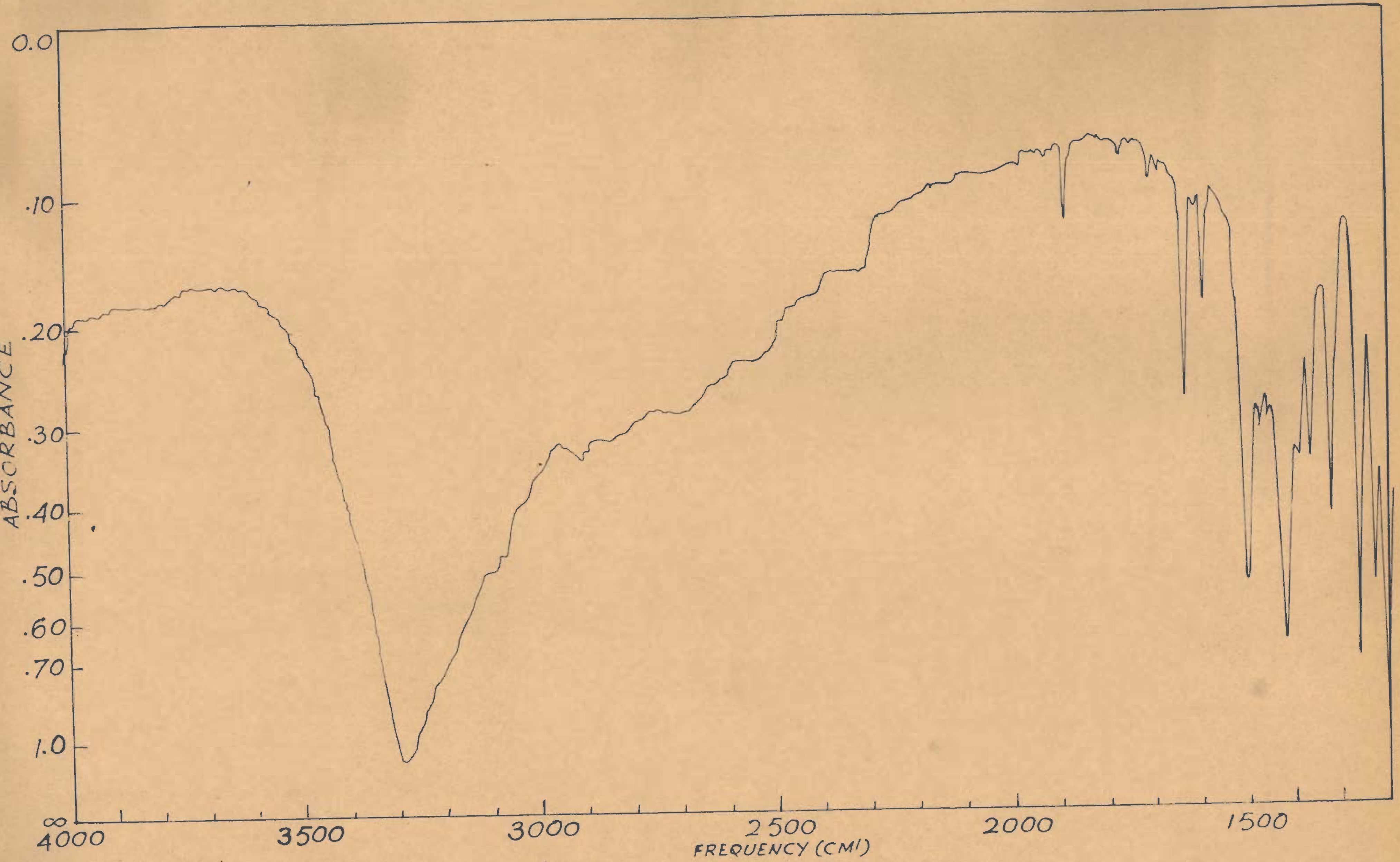
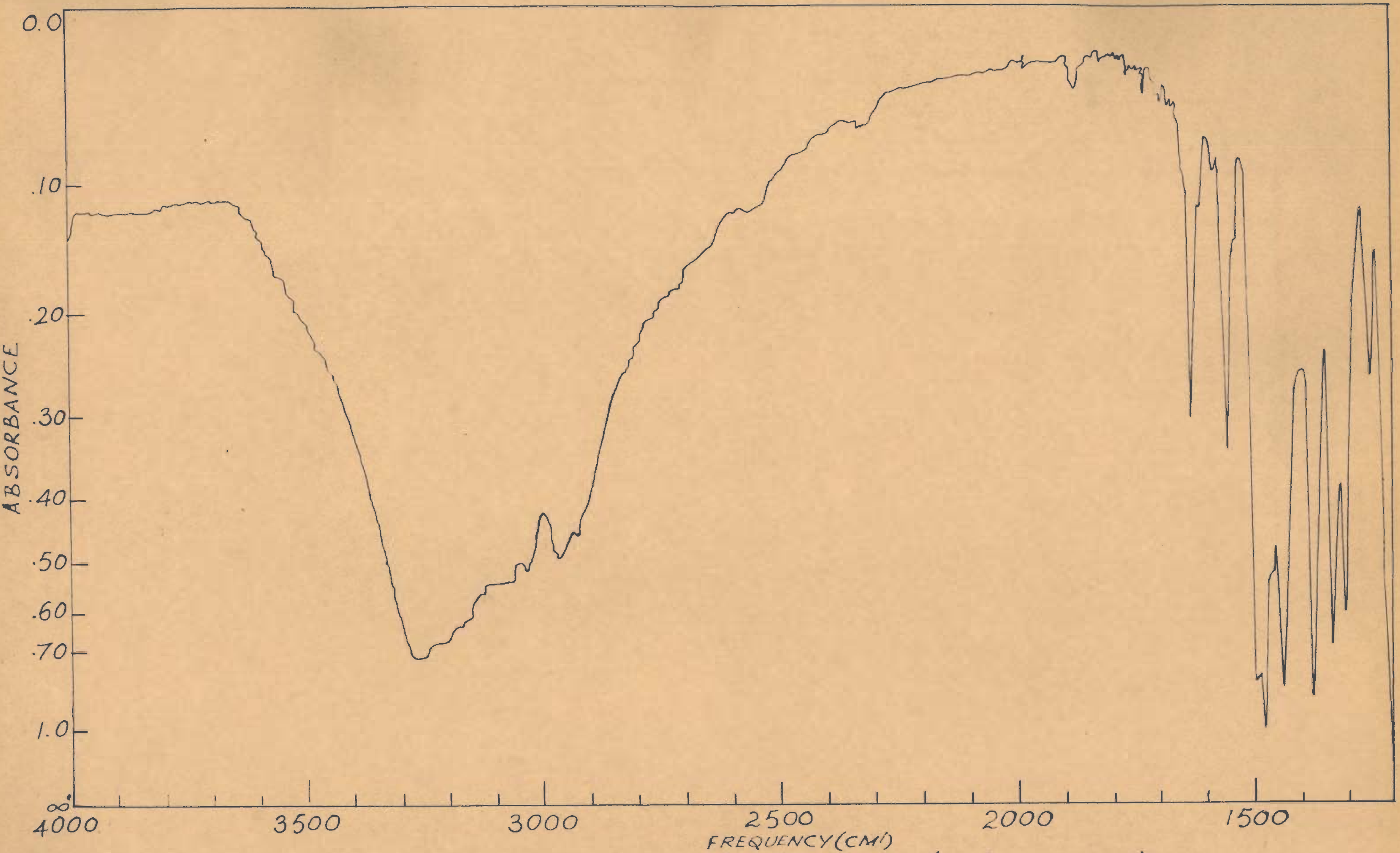


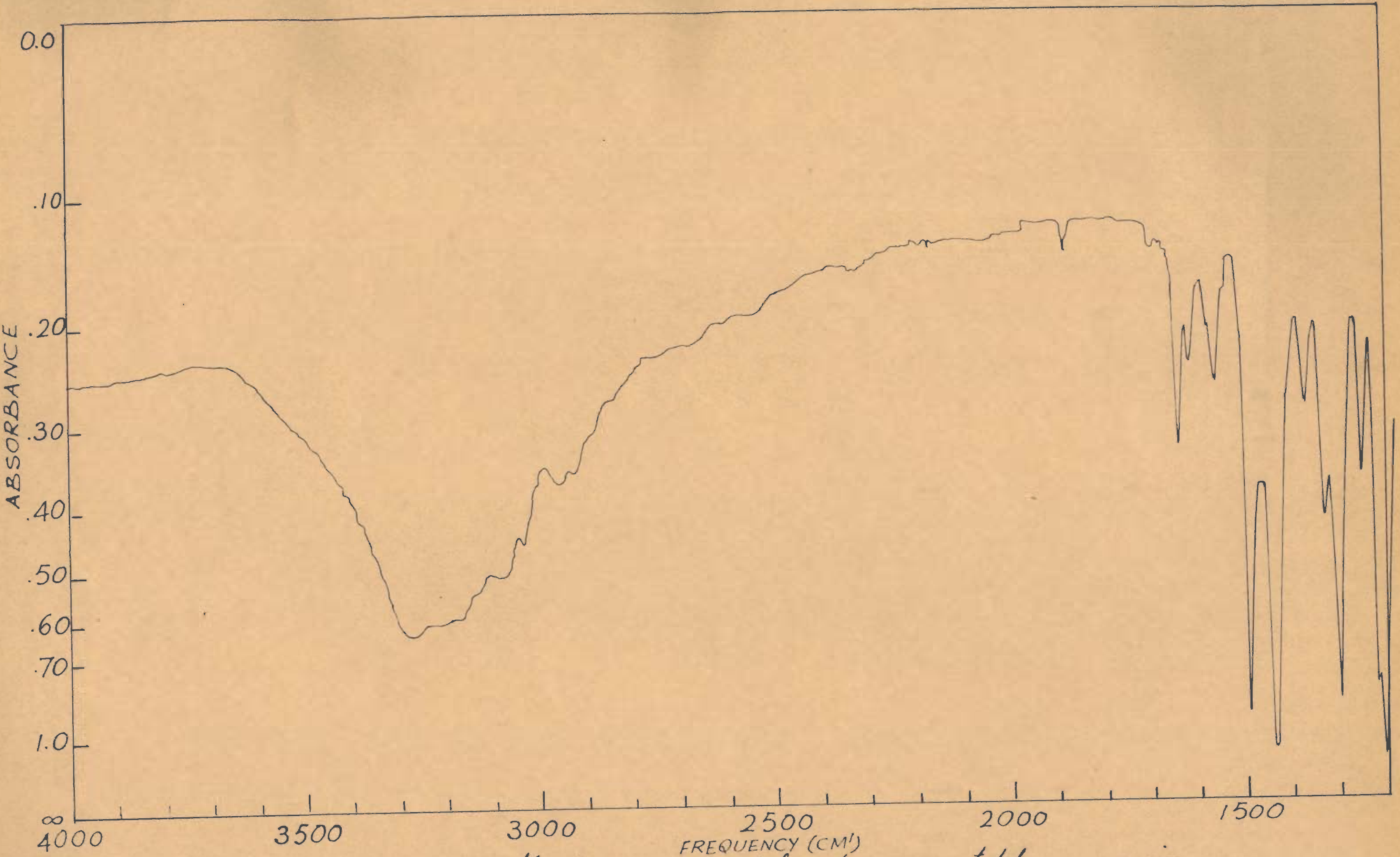
FIG. 17



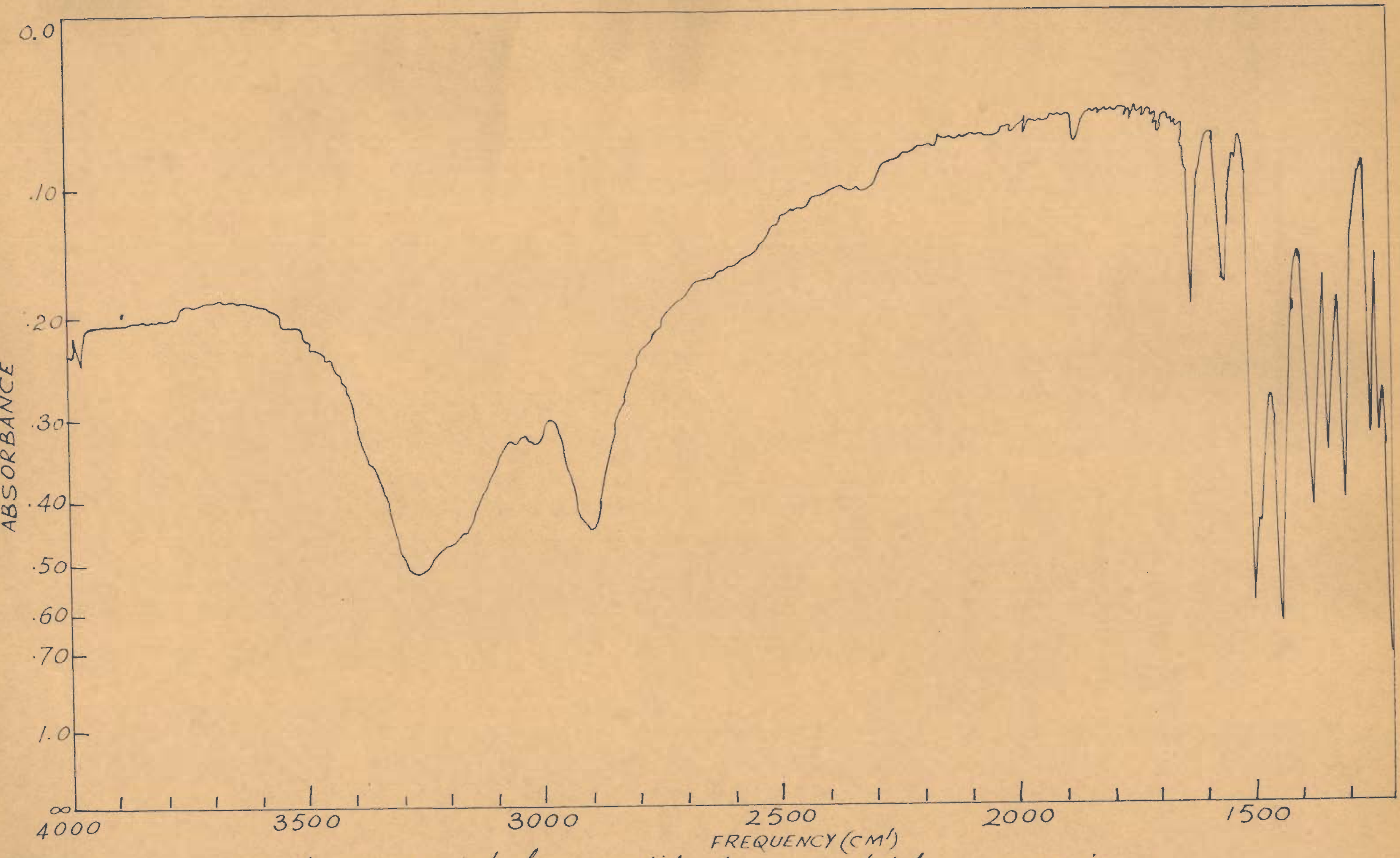
I.R. spectrum of 2,5-dihydroxy acetophenone oxime.
FIG. 18



I. R. spectrum of copper - 2,5 dihydroxy acetophenone oxime
FIG- 19



I.R. spectrum of palladium-2, 5 dihydroxy acetophenone oxime
FIG. 20



I.R. spectrum of nickel-2,5-dihydroxy acetophenone oxime.
FIG. 21

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CHAPTER IV

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" 2,5-Dihydroxyacetophenoneoxime as an analytical for copper, palladium, nickel and molybdenum "

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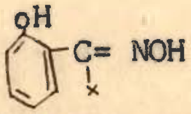
INTRODUCTION

2,5-dihydroxy-acetophenoneoxime as a colorimetric reagent for molybdenum :-

One of the earliest methods used for the colorimetric determination of molybdenum, is the thiocyanate method[1] which is still being used despite some of its limitations namely the poorer reduction of Mo(VI) to Mo(V), control of acidity, concentration of thiocyanate, fading of the colour on standing and the effect of the solvents.

Of the organic compounds recommended for the colorimetric estimation of molybdenum, pyrocatechol[2], phenyl-hydrazine[3], diphenylcarbazone[4], 8-hydroxyquinoline-5-sulphonic acid[5], chloranilic acid[6], thioglycollic acid[7] and toluene-3,4-dithiol[8] are worthmentioning.

The compounds containing 

(where X may be H, oH, NH_2 or alkyl group) have rarely been used as colorimetric reagents for the estimation of molybdenum The reactions of a few compounds of this series, viz., o-hydroxy-acetophenoneoxime, 2-hydroy-5-methyl-acetophenoneoxime and 2,5-dihydroxy-acetophenoneoxime with molybdenum have been described in the preceding Chapters. All these compounds give colour reactionswith molybdenum(VI). It has been found that out of these compounds, only 2,5-dihydroxy-acetophenoneoxime can be used as a colorimetric reagent for molybdenum due to its higher sensitivity and greater solubility in aquous-alcoholic medium.

Amperometric determination of copper, nickel and palladium with 2,5-dihydroxy-acetophenoneoxime :

The amperometric determination of copper has been studied by a number of workers. Amongst the reagents belonging to the oxime series, recommended for the estimation of the metal are salicylaldoxime[9], salicylamidoxime[10], α-benzoinoxime[11](cupron) and resacetophenoneoxime[12]. Neuberger estimated copper amperometrically by adding excess of salicylaldoxime to the copper solution and then back titrating the reagent with standard copper solution. Langer used α-benzoinoxime for the amperometric determination of copper but the method is not suitable as it involves the interference by a number of metals, e.g., Ni,Fe,Zn,Pb, etc. Salicylamidoxime is also recommended for the determination of copper amperometrically in the presence of Pb, Cd, Zn, Mn, Ni and Co. The interference due to Ag, Sb, Bi may be avoided by precipitating these metals as chloride and oxychlorides, prior to the addition of the acetate buffer solution.

Resacetophenoneoxime has recently been reported for copper determination in the presence of cadium and nickel; the interference due to other ions has not been studied by the authors.

A few references are available on the amperometric estimation of palladium; the reagents worthmentioning are salicylaldoxime[13], 1,2,3-benzotriazole[14], mercaptothiozole[15], dimethyl-glyoxime[16] and α-nitroso-β-naphthol[17].

1,2,3 benzotriazole has been recommended by Wilson and Wilson for the estimation of palladium amperometrically. The method fails in the presence of Os(VIII), Ru(III), Ni(II), Fe(III), Au(III), Co(II) and Ir.

A number of reagents have been investigated for the amperometric determination of nickel. The most extensively used reagent for the estimation of this metal is dimethyl-glyoxime[18].

The present investigations deal with the amperometric titrations of 2,5-dihydroxy-acetophenoneoxime with Cu(II), Ni(II) and Pd(II). The suitability of this compound as an analytical reagent for the amperometric determination of these metals, has also been explored.

EXPERIMENTAL

Solutions of the reagents, viz., 2,5-dihydroxyacetophenoneoxime, copper sulphate, palladium chloride, nickel sulphate and ammonium molybdate were prepared and standardized as described in the Chapter I.

Walpole buffers (sodium acetate-acetic acid) of pH 4.6 and 4.0 and ammonia-ammonium chloride buffer solution (pH 9.0) were prepared and their pH was checked in exactly the same manner as described earlier.

Gelatine solution of 0.1% was prepared in hot double distilled water.

Solutions of diverse ions were prepared from their suitable salts of A.R. quality.

Absorbance measurements were carried out with Bausch and Lomb 'Spectromic 20', using 1 cm. cells. All pH measurements were made with Beckman pH meter, model H.

Visual colour comparisons were made in 50 ml. Nessler cylinders.

A Toshniwal manual polarograph, type CLO-2(India), with Pye Scalamp galvanometer in external circuit, was employed for carrying out amperometric titrations. The polarographic cell was kept immersed in a water thermostat maintained at 30 ± 0.1°C. Fischer capillary was used for the dropping mercury electrode. A drop time of 3.5 secs. was maintained throughout the experiments.

2,5-dihydroxy-acetophenoneoxime as a colorimetric reagent for molybdenum:

Absorption spectrum of Mo(VI)-2,5-dihydroxy-acetophenoneoxime

In order to determine the wave length of maximum absorption, a solution of the complex was prepared by mixing 2.0 ml. of $1\times10^{-3}M$ ammonium molybdate with 10 ml. of $5\times10^{-3}M$ of 2,5-dihydroxy-acetophenoneoxime (D.H.A.O) and the final volume was made up to 25 ml. A reagent solution was also similarly prepared.

The absorbance of the orange-yellow solution was measured at different wave lengths, using reagent as blank.

Table - 1

Absorption spectrum of Mo(VI)-D.H.A.O. complex.

Concentration of ammonium molybdate $=8\times10^{-5}M$ (7.7 p.p.m)
Concentration of D.H.A.O $=2\times10^{-3}M$

Wave length (mμ)	Optical density
325	0.15
330	0.14
335	0.13
340	0.16
345	0.20
350	0.27
355	0.35
360	0.40
365	0.46
370	0.49
375	0.47
380	0.44
390	0.37
400	0.31
410	0.25
425	0.19
450	0.12

Fig. 1

The maximum absorbance of the complex lies at 370 mμ.

Effect of pH on the colour intensity of the complex solution :

The effect of pH on the colour reaction was studied by measuring the optical density, at 370 and 380 mμ, of the solutions containing the same concentrations of ammonium molybdate and the reagent and at different pH values.

Table - 2

Effect of pH on the colour intensity of the complex solution.

Concentration of ammonium molybdate = 8×10^{-5}M (7.7 p.p.m)
Concentration of D.H.A.O. = 2×10^{-3}M

pH of the solution	Optical density at	
	370 mμ	380 mμ
1.5	0.39	0.33
2.0	0.46	0.40
2.5	0.48	0.43
3.0	0.48	0.43
3.5	0.48	0.43
4.0	0.48	0.43
4.5	0.40	0.37
5.0	0.08	0.07
6.0	0.04	0.04

Fig. 2

Effect of reagent concentration :

Solutions containing 2.0 ml.of $1x10^{-3}$M ammonium molybdate and varying amounts of $1x10^{-2}$M D.H.A.O were prepared, the pH of each solution being 3.0-4.0 and total volume of 25 ml. The absorbance of these solutions was measured at 370, 380 and 390 mμ.

Table - 3

Effect of reagent concentration

Final concentration of ammonium molybdate =$8x10^{-5}$M(7.7 p.p.m
Initial concentration of the reagent added=$1x10^{-2}$M
Final volume = 25 ml.

Vol. of D.H.A.O. (ml.)	Optical density at		
	370 mμ	380 mμ	390 mμ
1.0	0.25	0.19	0.13
2.0	0.46	0.37	0.24
3.0	0.585	0.47	0.31
4.0	0.66	0.53	0.35
5.0	0.69	0.55	0.37
6.0	0.74	0.585	0.39
7.0	0.77	0.62	0.41
8.0	0.80	0.63	0.42
9.0	0.80	0.63	0.42
10.0	0.82	0.64	0.43

Fig. 3

Validity of Beer-Lambert's law :

In order to find out the concentration range of molybdenum over which Beer's law is obeyed, a series of solutions containing fixed concentration (6.4×10^{-3}M) of the reagent and the varying concentrations of ammonium molybdate were prepared and their absorbance was measured at 370 and 380 mµ, against reagent blank.

Table - 4

Validity of Beer-Lambert's law

Final concentration of reagent = 6.4×10^{-3}M
Initial concentration of amm.molybdate added= 1×10^{-3}M
Total volume = 25 ml.

Vol.of Amm.molybdate (ml.)	Optical density at 370 mµ	Optical density at 380 mµ
0.0	0.0	0.0
0.25	.04	0.04
0.5	0.11	0.10
1.0	0.23	0.20
1.5	0.36	0.30
2.0	0.48	0.42
2.5	0.57	0.52
3.0	0.72	0.64
3.5	0.81	0.74
4.0	0.91	0.84
4.5	1.03	0.93
5.0	1.11	1.035
5.5	1.19	1.1
6.0	1.23	1.16

Fig. 4

Visual sensitivity of the colour reaction :

50 ml. solutions containing 1×10^{-3}M of D.H.A.O and 0.5, 1.0 and 2.0 p.p.m. of molybdenum respectively were prepared. These solutions were observed against a blank (reagent) in Nessler cylinders.

Tolerance of foreign ions :

The solutions of diverse ions of varying concentrations were added to the 25 ml. flasks containing a fixed concentration of molybdenum (7.7 p.p.m) and to this was added the reagent (final concentration 4×10^{-3}M). The absorbance of these solutions was measured at 370 mμ against reagent blank.

Table - 5

Effect of Diverse ions

Final concentration of Amm.molybdate =8×10^{-5}M(7.7 p.p.m)
Final concentration of reagent =4×10^{-3}M
pH of the solutions =3.0-4.0
Wave length used =370 mμ

Ion	Added as	Conc.of ion (p.p.m)	Absorbance
-	-	-	0.48
Al^{+++}	$Al_2(So_4)_3$	0.5	0.46
		0.2	0.47
Be^{++}	$BeCl_2$	3.0	0.48
		6.0	0.478
		9	0.47
Cd^{++}	$Cd(No_3)_2$	25	0.48
		50	0.48
		100	0.472
Ce^{+++}	$Ce_2(So_4)_3$	1	0.478
		2	0.47

Ion	Added as	Conc. of ion (p.p.m)	Absorbance
Co^{++}	$CoSo_4$	50	0.48
		100	0.472
		150	0.465
Cr^{+++}	$Cr_2(So_4)_3$	0.2	0.47
Cu^{++}	$CuSo_4$	1	0.47
Fe^{++}	$FeSo_4(NH_4)_2So_4$	6	0.48
		12	0.47
Fe^{+++}	$FeCl_3$	1	0.59
Mg^{++}	$MgSo_4$	12	0.48
		24	0.475
		30	0.47
Mn^{++}	$MnCl_2$	100	0.48
		200	0.48
		300	0.472
Ni^{++}	$NiSo_4$	50	0.48
		100	0.49
Pb^{++}	$Pb(No_3)_2$	1	0.48
		2	0.47
Pd^{++}	$PdCl_2$	1	0.47
Ag^{+}	$AgNo_3$	1	0.47
Ti^{++++}	$TiCl_4$	1	0.485
		2	0.49
Uo_2^{++}	$Uo_2(No_3)_2$	100	0.48
		200	0.488
Vo^{++}	$VoSo_4$	0.5	0.53
Wo_4^{--}	Na_2Wo_4	2	0.48
		3	0.488
		4	0.50
Th^{++++}	$Th(No_3)_4$	5	0.48
		10	0.47
Zr^{++++}	$Zr(No_3)_4$	5	0.48
		10	0.465
Zn^{++}	$ZnSo_4$	100	0.48
		200	0.48
		400	0.472
$Ba^{++}, Sr^{++}, Ca^{++}$	Nitrate	1000	0.48

Ion	Added as	Conc.of ion (p.p.m)	Absorbance
Cl^-	KCl	1000	0.48
Br^-	KBr	1000	0.48
I^-	KI	1000	0.48
So_4^{--}	K_2So_4	1000	0.48
NO_3^-	KNo_3	1000	0.48
CH_3COO^-	CH_3COONa	1000	0.48
Oxalate	Potassium oxalate	1.0	0.47
Tartrate	Sodium tartrate	1.0 2.0	0.475 0.47
Citrate	Potassium citrate	1.0 2.0	0.475 0.472

Amperometric determination of copper, palladium and nickel with 2,5-dihydroxy-acetophenoneoxime.

Amperometric determination of copper(II):-

The amperometric titrations of Cu(II) were carried out at a potential of -0.15 volts vs S.C.E.

Titration procedure :-

An appropriate aliquot of the standard stock solution of copper(II), sufficient to give the desired concentration, was neutralized with dilute alkali and transferred to a 100 ml. flask; to it were added 50 ml. of 0.4N sodium acetate-acetic acid buffer solution (pH 4.6) and 10 ml. of 0.1% gelatine solution and the solution was diluted to the mark with double distilled water.

A 20 ml. aliquot of this solution was transferred to a titration cell, deaerated with purified hydrogen gas and was titrated against 40% alcoholic solution of 2,5-dihydroxy-acetophenoneoxime at a potential of -0.15 volts vs S.C.E., using dropping mercury indicator electrode. The current was recorded after each successive addition of the titrant. Volume correction was applied by multiplying the values of the current with $\frac{V+v}{V}$, where V was the initial volume of the solution taken in the cell and v, the volume of the titrant added. The extrapolation method was employed in ascertaining the volume of the titrant used in the titration.

Table -6

20 ml. of 2.5x10^{-3}M CuSo$_4$(in the cell) titrated against 2x10^{-2}M D.H.A.O.

Vol.of D.H.A.O. (ml.)	Current (2x10^{-7}amp)	Vol. of D.H.A.O. (ml.)	Current (2x10^{-7}amp.)
0.0	12.0	4.5	3.2
0.5	11.0	5.0	2.5
1.0	10.0	5.5	2.0
1.5	9.15	6.0	1.7
2.0	7.9	6.5	1.6
2.5	6.9	7.0	1.6
3.0	5.85	8.0	1.6
3.5	4.85		
4.0	4.0		

Fig.5, curve (a)

Table - 7

20 ml.of 2x10^{-3}M CuSo$_4$(in the cell)titrated against 2x10^{-2}M D.H.A.O.

0.0	10.05	3.5	2.8
0.5	9.0	4.0	2.4
1.0	8.0	4.5	1.8
1.5	7.05	5.0	1.6
2.0	5.9	5.5	1.6
2.5	4.7	6.0	1.6
3.0	3.65		

Fig.5, curve (b)

Table - 8

20 ml.of 1.5x10^{-3}M CuSo$_4$(in the cell) titrated against 2x10^{-2}M D.H.A.O.

0.0	8.1	3.5	1.4
0.5	7.0	4.0	1.25
1.0	6.0	4.5	1.2
1.5	4.6	5.0	1.2
2.0	3.5	5.5	1.2
2.5	2.2	6.0	1.2
3.0	1.7		

Fig.5, curve (c)

Table -9

20 ml.of 1x10^{-3}M $CuSo_4$(in the cell) titrated against 2x10^{-2}M D.H.A.O.

Vol.of D.H.A.O. (ml.)	Current (2x10^{-7}amp)	Vol.of D.H.A.O. (ml.)	Current (2x10^{-7}amp.)
0.0	5.9	2.0	1.2
0.2	5.4	2.2	1.0
0.4	4.9	2.4	0.7
0.6	4.3	2.6	0.7
0.8	3.75	2.8	0.7
1.0	3.3	3.0	0.7
1.2	2.8	3.2	0.7
1.4	2.3		
1.6	1.9		
1.8	1.45		

Fig.5, curve (d)

Table -10

20 ml.of 5x10^{-4}M $CuSo_4$(in the cell) titrated against 2x10^{-2}M D.H.A.O.

0.0	3.3	1.2	1.05
0.2	2.8	1.4	1.05
0.4	2.4	1.6	1.05
0.6	1.95	2.0	1.05
0.8	1.5		
1.0	1.2		

Fig.6, curve (a)

Table -11

20 ml.of 2.5x10^{-4}M $CuSo_4$(in the cell) titrated against 2x10^{-2}M D.H.A.O.

0.0	2.0	1.0	1.0
0.2	1.6	1.2	1.0
0.4	1.3	1.4	1.0
0.6	1.0		
0.8	1.0		

Fig.6, curve (b)

The reverse amperometric titrations, taking 2,5-dihydroxy-acetophenoneoxime in the cell, were carried out under similar conditions as in direct titrations.

Table - 12

20 ml. of $4x10^{-3}$M D.H.A.O. (in the cell) titrated against $1x10^{-2}$M $CuSo_4$

Vol.of $CuSo_4$ (ml.)	Current ($2x10^{-7}$amp.)	Vol.of $CuSo_4$ (ml.)	Current ($2x10^{-7}$amp.)
0.0	0.7	3.2	0.85
0.4	0.8	3.6	1.05
0.8	0.8	4.0	1.5
1.2	0.8	4.4	1.9
1.6	0.8	4.8	3.0
2.0	0.8	5.2	4.2
2.4	0.8	5.6	5.4
2.8	0.8		

Fig.7, curve (a)

Table - 13

20 ml.of $2x10^{-3}$M D.H.A.O. (in the cell)titrated against $1x10^{-2}$M $CuSo_4$

Vol.of $CuSo_4$ (ml.)	Current ($2x10^{-7}$amp.)	Vol.of $CuSo_4$ (ml.)	Current ($2x10^{-7}$amp.)
0.0	0.65	1.6	0.85
0.2	0.75	1.8	0.9
0.4	0.75	2.0	1.2
0.6	0.75	2.2	1.6
0.8	0.75	2.4	1.8
1.0	0.75	2.6	2.3
1.2	0.75	2.8	2.8
1.4	0.8	3.0	3.2
		3.5	4.5
		4.0	5.8

Fig.7, curve (b)

Table -14

20 ml.of 3×10^{-3}M D.H.A.O. (in the cell) titrated against 1×10^{-2}M $CuSo_4$

Vol.of $CuSo_4$ (ml.)	Current (2x10^{-7}amp.)
0.0	0.8
1.0	0.8
2.0	0.8
2.5	0.9
3.0	1.1
3.5	2.4
4.0	3.7
4.5	5.0
5.0	6.3

Fig. 7, curve (c)

Effect of diverse ions :

The effect of foreign ions on the amperometric determination of copper was studied by adding varying concentrations of the ions to the copper solution (fixed concentration 1.26 mg/20 ml.) and titrating the solution against the reagent under the conditions described during the amperometric titrations of copper. The results are summarized and given in the discussion part.

Amperometric determination of palladium :

Procedure :

An appropriate aliquot of the standard stock solution of palladium, to give the desired concentration, was transferred to a 25 ml. flask; to this were added 10 ml. of 0.5N sodium acetate-acetic acid buffer solution of pH 4.0 and 2.5 ml. of 0.1% gelatine solution and the solution was diluted to the mark with double distilled water.

A 20 ml. aliquot of this solution was transferred to a polarographic cell and the solution was deaerated by passing oxygen free nitrogen gas. The titration was carried out at -0.4 volts vs S.C.E., using dropping mercury indicator electrode. Small aliquots of the reagent were added to the palladium solution. After each addition, the solution was stirred with nitrogen gas and the current was measured after an interval of two minutes. The current values were corrected for dilution effect as described earlier. The end point was obtained graphically from the volume-current curve. The observations are tabulated below:

Table -15

20 ml. of 2.5×10^{-3}M $PdCl_2$(in the cell)titrated against 2×10^{-2}M D.H.A.O.

Vol.of D.H.A.O. (ml.)	Current (2×10^{-7}amp.)	Vol.of D.H.A.O. (ml.)	Current (2×10^{-7}amp.
0.0	7.6	3.5	2.6
0.5	6.9	4.0	1.9
1.0	6.2	4.5	1.3
1.5	5.5	5.0	0.95
2.0	4.75	5.5	0.7
2.5	4.05	6.0	0.5
3.0	3.4	6.5	0.5
		7.0	0.5

Fig.8, curve (a)

Table -16

20 ml.of $2x10^{-3}$M $PdCl_2$(in the cell) titrated against
$2x10^{-2}$M D.H.A.O.

Vol.of D.H.A.O. (ml.)	Current ($2x10^{-7}$amp.)	Vol.of D.H.A.O. (ml.)	Current ($2x10^{-7}$amp.)
0.0	6.2	3.5	1.25
0.5	5.5	4.0	0.7
1.0	4.9	4.5	0.5
1.5	4.1	5.0	0.4
2.0	3.2	5.5	0.4
2.5	2.6	6.0	0.4
3.0	1.9		

Fig.8, curve (b)

Table -17

20 ml.of $1.25x10^{-3}$M $PdCl_2$(in the cell)titrated against
$2x10^{-2}$M D.H.A.O.

0.0	4.2	3.0	0.55
0.5	3.5	3.5	0.45
1.0	2.7	4.0	0.40
1.5	1.9	4.5	0.40
2.0	1.2	5.0	0.40
2.5	0.8		

Fig.8, curve (c)

Table -18

20 ml.of $1x10^{-3}$M $PdCl_2$ (in the cell) titrated against
$2x10^{-2}$M D.H.A.O.

0.0	3.35	2.5	0.5
0.5	2.6	3.0	0.45
1.0	1.95	3.5	0.40
1.5	1.0	4.0	0.40
2.0	0.65		

Fig.8, curve (d)

Table -19

20 ml. of 5×10^{-4}M $PdCl_2$(in the cell) titrated against 2×10^{-2}M D.H.A.O.

Vol.of D.H.A.O. (ml.)	Current $\times 10^{-7}$amp.	Vol.of D.H.A.O. (ml.)	Current $\times 10^{-7}$amp.
0.0	3.2	1.2	0.5
0.2	2.7	1.4	0.4
0.4	2.1	1.6	0.4
0.6	1.5	1.8	0.4
0.8	0.95	2.0	0.4
1.0	0.6		

Fig.9, curve (a)

Table -20

20 ml.of 2.5×10^{-4}M $PdCl_2$(in the cell) titrated against 2×10^{-2}M D.H.A.O.

0.0	1.5	0.5	0.35
0.1	1.25	0.6	0.3
0.2	0.95	0.7	0.3
0.3	0.7	0.8	0.3
0.4	0.5		

Fig.9, curve (b)

Reverse titrations

Table - 21

20 ml.of 5×10^{-3}M D.H.A.O. (in the cell) titrated against 1×10^{-2}M $PdCl_2$

Vol.of $PdCl_2$ (ml.)	Current (2×10^{-7}amp.)	Vol.of $PdCl_2$ (ml.)	Current (2×10^{-7}amp.)
0.0	0.5	5.5	0.85
1.0	0.5	6.0	1.15
2.0	0.5	6.5	1.45
3.0	0.5	7.0	1.8
4.0	0.5	7.5	2.05
4.5	0.55	8.0	2.4
5.0	0.6		

Fig.10, curve (a)

Table -22

20 ml.of $2.5x10^{-3}$M D.H.A.O. (in the cell) titrated against $1x10^{-2}$M $PdCl_2$

Vol.of $PdCl_2$ (ml.)	Current ($2x10^{-7}$amp.)	Vol.of $PdCl_2$ (ml.)	Current ($2x10^{-7}$amp.)
0.0	0.5	3.5	1.15
1.0	0.5	4.0	1.5
2.0	0.5	5.0	2.2
2.5	0.6	6.0	2.9
3.0	0.8		

Fig.10, curve (b)

Table -23

20 ml.of $2x10^{-3}$M D.H.A.O. (in the cell) titrated against $1x10^{-2}$M $PdCl_2$

0.0	0.5	3.5	1.6
1.0	0.5	4.0	1.95
2.0	0.5	4.5	2.3
2.5	0.9	5.0	2.6
3.0	1.25	6.0	3.3

Fig.10, curve (c)

Effect of diverse ions :

Effect of diverse ions on the amperometric determination of palladium was studied in the same manner as described in the case of copper. The results are summarized and presented in the discussion part.

Amperometric determination of nickel(II):

Procedure :

A measured volume of standard nickel solution, to give the desired concentration, was introduced into 100 ml. flask; to this were added ammonia-ammonium chloride buffer (pH 9.0), 10 ml. of 0.1% gelatine solution and the solution was diluted to the mark with double distilled water.

A 20 ml. aliquot of this solution was transferred to a polarographic cell, deaerated with purified hydrogen gas and a potential of -1.2 volts was applied. Dropping mercury was used as an indicator electrode. Small aliquots of the reagent were added and after each addition, the solution was stirred by bubbling hydrogen gas and the current was measured after an interval of one minute. The observations are summarized in the following tables :

Table -24

20 ml. of 2.5×10^{-3}M $NiSo_4$(in the cell) titrated against 2×10^{-2}M D.H.A.O.

Vol. of D.H.A.O. (ml.)	Current (2×10^{-7}amp.)	Vol. of D.H.A.O. (ml.)	Current (2×10^{-7}amp.)
0.0	8.95	5.5	2.7
1.0	7.6	6.0	2.5
2.0	6.2	7.0	2.4
3.0	5.1	8.0	2.35
4.0	3.8	9.0	2.35
4.5	3.3	10.0	2.35
5.0	3.0		

Fig.11, curve (a)

Table -25

20 ml.of $2x10^{-3}$M NiSo$_4$ (in the cell) titrated against $2x10^{-2}$M D.H.A.O.

Vol.of D.H.A.O. (ml.)	Current ($2x10^{-7}$amp.)	Vol.of D.H.A.O. (ml.)	Current ($2x10^{-7}$amp.)
0.0	6.3	3.5	2.4
0.5	5.7	4.0	2.2
1.0	5.1	4.5	2.0
1.5	4.5	5.0	1.9
2.0	4.0	5.5	1.80
2.5	3.5	6.0	1.7
3.0	3.0	6.5	1.6
		7.0	1.5

Fig.11, curve (b)

Table -26

20 ml.of $1.5x10^{-3}$M NiSo$_4$ (in the cell) titrated against $2x10^{-2}$M D.H.A.O.

0.0	4.85	3.25	1.5
0.5	4.3	4.0	1.15
1.0	3.6	4.5	1.15
1.5	2.9	5.0	1.15
2.0	2.45	6.0	1.15
2.5	2.05		
3.0	1.6		

Fig.11, curve (c)

Table -27

20 ml.of $1x10^{-3}$M NiSo$_4$(in the cell) titrated against $2x10^{-2}$M D.H.A.O.

0.0	3.25	2.5	1.2
0.5	2.8	3.0	1.15
1.0	2.2	3.5	1.1
1.5	1.7	4.0	1.1
2.0	1.4	5.0	1.1

Fig.11, curve (d)

Table -28

20 ml.of $5x10^{-4}M$ $NiSo_4$ (in the cell) titrated against $2x10^{-2}M$ D.H.A.O.

Vol.of D.H.A.O. (ml.)	Current $(x10^{-7}amp)$	Vol.of D.H.A.O. (ml.)	Current $(x10^{-7}amp)$
0.0	3.05	0.7	2.0
0.1	2.9	0.8	1.85
0.2	2.75	0.9	1.75
0.3	2.6	1.0	1.7
0.4	2.45	1.1	1.7
0.6	2.15	1.4	1.7

Fig.12, curve (a)

Table -29

20 ml.of $7.5x10^{-4}M$ $NiSo_4$ (in the cell) titrated against $2x10^{-2}M$ D.H.A.O.

0.0	4.2	1.2	2.30
0.2	3.85	1.4	2.0
0.4	3.5	1.6	1.85
0.6	3.2	1.8	1.7
0.8	2.75	2.0	1.7
1.0	2.55		

Fig.12, curve (b)

Reverse titrations

Table 30

20 ml.of 5x10^{-3}M D.H.A.O.(in the cell) titrated against 1x10^{-2}M NiSo$_4$

Vol.of NiSo$_4$ (ml.)	Current (2x10^{-7}amp.)	Vol.of NiSo$_4$ (ml.)	Current (2x10^{-7}amp.)
0.0	0.8	5.0	1.05
1.0	0.8	5.5	1.3
2.0	0.8	6.0	1.6
3.0	0.8	6.5	2.0
4.0	0.8	7.0	2.5
4.5	0.9	7.5	3.0
		8.0	3.4
		9.0	4.35

Fig.13, curve (a)

Table -31

20 ml.of 4x10^{-3}M D.H.A.O. (in the cell) titrated against 1x10^{-2}M NiSo$_4$

0.0	0.8	4.5	1.5
1.0	0.8	5.0	1.95
2.0	0.8	5.5	2.45
3.0	0.8	6.0	3.0
3.5	0.85	7.0	4.05
4.0	1.1		

Fig.13, curve (b)

Table -32

20 ml.of 2x10^{-3}M D.H.A.O. (in the cell) titrated against 1x10^{-2}M NiSo$_4$

0.0	0.8	3.5	2.3
0.5	0.8	4.0	2.9
1.0	0.8	4.5	3.4
1.5	0.85	5.0	3.9
2.0	1.0		
2.5	1.2		
3.0	1.85		

Fig.13, curve (c)

DISCUSSION

2,5-dihydroxy-acetophenoneoxime as a colorimetric reagent for molybdenum:

2,5-dihydroxy-acetophenoneoxime forms an orange-yellow coloured, soluble, 2:1 complex with molybdenum in acidic medium. The complex is stable at room temperature and the intensity of the colour remains unchanged even on keeping for long period. The results of the spectrophotometric studies carried out under various conditions illustrate the applicability of 2,5-dihydroxy-acetophenoneoxime as a colorimetric reagent for molybdenum.

Determination of optimum conditions :

The orange-yellow coloured, soluble complex of molybdenum with 2,5-dihydroxy-acetophenoneoxime, shows maximum absorption at a wave length of 370 mμ (Fig.1) and this wave length was, therefore, selected for subsequent colorimetric studies. The maxima of the complex was realized by using reagent solution of the same concentration as blank due to the high absorption of the latter.

The absorption measurements recorded at various pH values show that the complex is stable in the pH range 2.0-4.5 (Fig.2, Chapter III) and from the subsequent spectral studies it is found that the complex acquires maximum colour intensity in the pH range 2.5-4.0 (Fig.2).

In order to assess the optimum conditions for attaining the maximum colour intensity of the complex, the absorption measurements were carried out with the solutions obtained by adding various concentrations (4x10^{-M}- 4x10^{-3}M) of the reagent to a fixed concentration (7.7 p.p.m) of the metal. It was found that 40-50 folds excess of the reagent were required to get maximum colour intensity of the solution (Fig.3).

The absorbance measurements carried out with the solutions containing fixed concentration of the reagent (6.4x10^{-3}M) and varying concentrations of the metal at 370 and 380 mu revealed that Beer's law was followed over the concentration range of 2-20 p.p.m of molybdenum (Fig.4).

Preliminary studies on the effect of temperature on the colour intensity of the solution showed that the colour was stable upto 40°C; beyond that temperature the colour started fading away. However, the solution regained its original colour intensity on cooling to temperature below 40°C.

The qualitative assessment of the colour intensity of the complex was studied by running a few experiments with Nessler cylinders. Visual colorimetry with the solutions containing 0.5, 1.0 and 2.0 p.p.m of molybdenum showed that only the solutions having concentrations of 1.0 p.p.m or above were visually distinguishable from the reagent.

The colorimetric estimations of molybdenum were studied in the presence of a number of foreign ions. Solutions having a fixed concentration of molybdenum (7.7 p.p.m) were taken and cations such as Al^{+++}, Be^{++}, Cd^{++}, Ce^{+++}, Co^{++}, Cr^{+++}, Cu^{++}, Fe^{++}, Fe^{+++}, Mg^{++}, Mn^{++}, Ni^{++}, Pb^{++}, Pd^{++}, Ag^{+}, Ti^{++++}, Vo^{++}, Wo_4^{--}, Th^{++++}, Zr^{++++}, Zn^{++}, Ca^{++}, Ba^{++}, Sr^{++} and anions such as Cl^-, Br^-, I^-, So_4^{--}, No_3^-, CH_3Coo^-, oxalate, citrate and tartrate were added in varying concentrations and absorbance measurements were carried out. Assuming ± 2% change in the observed absorbance of the solution containing foreign ion from that of the solution containing no foreign ion as an interference limit, it was found that Al^{+++}, Cr^{+++}, Fe^{+++}, Vo^{++} interferred strongly and must be eliminated prior to the estimation. Cu^{++}, Pd^{++}, Pb^{++}, Ti^{++++}, Wo_4^{--}, Ce^{+++}, oxalate, citrate and tartrate did not interfere if present upto 3.0 p.p.m., whereas other ions did not interfere at all with the estimation of molybdenum.

The tolerance limits of the various ions are summarized in the following table :

Concentration of Ammonium molybdate = 7.7 p.p.m
Concentration of reagent = 4×10^{-3}M

Ion	Added as	Tolerance limit (p.p.m)
Ag	$AgNo_3$	1
Al^{+++}	$Al_2(So_4)_3$	0.2
Be^{++}	$BeCl_2$	9.0
Cd^{++}	$Cd(No_3)_2$	100

Ion	Added as	Tolerance limit (p.p.m)
Ce^{+++}	$Ce_2(So_4)_3$	1
Co^{++}	$Co\ So_4$	100
Cr^{+++}	$Cr_2(So_4)_3$	0.2
Cu^{++}	$CuSo_4$	1
Fe^{++}	$FeSo_4(NH_4)_2So_4$	12
Fe^{+++}	$FeCl_3$	must be eliminated
Mg^{++}	$MgSo_4$	30
Mn^{++}	$MnSo_4$	300
Ni^{++}	$NiSo_4$	100
Pb^{++}	$Pb(No_3)_2$	2
Pd^{++}	$PdCl_2$	1
Ti^{++++}	$TiCl_4$	2
Uo_2^{++}	$Uo_2(No_3)_2$	200
Vo^{++}	$VoSo_4$	must be eliminated
Wo_4^{--}	Na_2Wo_4	3
Th^{++++}	$Th(No_3)_4$	10
Zn^{++}	$ZnSo_4$	400
Zr^{++++}	$Zr(No_3)_4$	7
$Ca^{++}, Ba^{++}, Sr^{++}$	Nitrate	>1000
Cl^-, Br^-, I^-	Potassium salts	>1000
So_4^{--}	K_2So_4	>1000
No_3^-	KNo_3	>1000
CH_3Coo^-	CH_3CooNa	>1000
Oxalate	Pot.oxalate	1
Tartrate	Sod.tartrate	2
Citrate	Pot.citrate	2

Recommended procedure for analysis:

Molybdenum can be determined in commercial samples, ores, minerals etc. by adopting the following procedure:

A solution of the weighed amount of the sample is prepared and treated to separate the other elements present as usual (Snell and Snell, Colorimetric methods of analysis, 3rd Edition, Vol. II A, page 364-69, D. Van Nostrand Co.,Inc., London; Sandell, " Colorimetric determination of traces of metals", 3rd Ed. page 654-63, Interscience Publishers, Inc.). The solution thus obtained, may be treated directly or in an aliquot portion with an excess (about fifty folds) of 2,5-dihydroxy-acetophenoneoxime solution. The pH of the solution is adjusted to 3-4 and then the solution be diluted to a requisite volume so that the molybdenum content lies between 2-20 p.p.m. The absorbance of the solution is measured at 370 mμ against reagent as blank. From the absorbance value, the concentration of the molybdenum can be found out with the help of the caliberation-curve.

From the above results it is concluded that 2,5-dihydroxy-acetophenoneoxime can be very well recommended as a colorimetric reagent for molybdenum. The reagent develops instantaneously a very stable orange-yellow colour over a fairly wide pH range of 2.5-4.0. Metals like berylium, nickel, cadmium, cobalt, ferrous iron, magnesium, manganese, uranium, zinc do not interfere even in large excess, with the estimation. Metals like copper, palladium, lead, titanium, thorium, zirconium, tungsten do not interfere if present in small amounts. The method is thus reliable and rapid as it does not involve the elimination of some of the common metallic impurities associated with molybdenum. Further, unlike the conventional thiocyanate method, it does not require the reduction of Mo(VI) to Mo(V) and the extraction of the complex with organic solvents and the colour intensity remains unchanged during the estimations.

Amperometric determination of copper(II), palladium(II) and Nickel(II) with 2,5-dihydroxy-acetophenoneoxime:

In the preceding chapter, the complexes of Cu(II), Ni(II) and Pd(II) with 2,5-dihydroxy-acetophenoneoxime have been described and their composition has been investigated by chemical analysis, conductometric and pH metric titrations. These metals form 1:2 complexes with the ligand. These complexes are very stable and insoluble in character.

Gravimetric analysis carried out with a few samples of these complexes shows that the reactions between metal ions (Cu^{++}, Ni^{++}, Pd^{++}) and the ligand take place quantitatively.

Amperometric determination of copper :

Amperometric titrations between copper and 2,5-dihydroxy-acetophenoneoxime were carried out using acetate buffer (4.6 pH) as supporting electrolyte and 0.01% gelatine solution as maximum suppressor at the reduction potential (-0.15 volts vs S.C.E) of copper.

Both direct (metal in the cell) and reverse (ligand in the cell) titrations were carried out. The current-volume curves (Figs.5-7) gave a stoichiometric ratio of 1:2 for the metal and the ligand respectively in all cases.

The results of these titrations are summarized below:

S.No.	Fig.& curve	Vol.of $CuSo_4$ (ml.)	Vol.of D.H.A.O. (ml.)	Molar ratio Cu/D.H.A.O.
1	5,a	20(2.5x10^{-3}M)	40.4(2.5x10^{-3}M)	1:2.02
2	5,b	20(2x10^{-3}M)	39.68(2x10^{-3}M)	1:1.985
3	5,d	20(1x10^{-3}M)	40.0(1x10^{-3}M)	1:2
4	7,a	10.2(4x10^{-3}M)	20(4x10^{-3}M)	1:1.96
5	7,b	10.0(2x10^{-3}M)	20(2x10^{-3}M)	1:2
6	7,c	9.87(3x10^{-3}M)	20(3x10^{-3}M)	1:2.02

During the course of amperometric titrations of copper(II) with 2,5-dihydroxy-acetophenoneoxime, it was observed that appreciable changes in the diffusion current of copper occurred on addition of the reagent. The reaction between copper and the reagent is also quantitative in the pH range 4.5-8.5. Keeping in view of the above observations it was proposed to investigate the possibility of employing amperometric titrations for the determination of copper.

The optimum conditions required for carrying out amperometric estimation of copper(II) with 2,5-dihydroxyacetophenoneoxime were found to be as follows:

(a) The pH of the medium was maintained at 4.6 by using sodium acetate-acetic acid buffer solution which also served as a supporting electrolyte.

(b) 0.01% gelatine solution was used as a maximum suppressor.

(c) A potential of -0.15 volts vs S.C.E. was applied during the course of titrations.

Copper solutions of varying concentrations (0.315-3.15 mg.) were titrated against reagent of a suitable concentration (at least 10 times the molar concentration of copper in the solution under titration). The results are summarized as follows :

S.No.	Vol.of solution (ml.)	Copper present (mg.)	Copper found (mg.)	% error
1	20.0	3.15	3.1815	+ 1
2	20.0	2.52	2.501	- 0.8
3	20.0	1.89	1.89	0.0
4	20.0	1.26	1.26	0.0
5	20.0	0.63	0.63	0.0
6	20.0	0.315	0.315	0.0

The amperometric estimations of copper were also carried out in the presence of foreign ions. To the solutions containing a fixed concentration of copper

(1.26 mg.), varying amounts of diverse ions were added and the amperometric titrations were performed, it was found that ions like Ag^{+}, Fe^{+++}, Pd^{++}, Ti^{++++}, Vo^{++} interferred strongly with the estimations and should be removed before carrying out the determinations. In the presence of other ions, the estimations can successfully be carried out. The results of the estimation of copper in the presence of other ions are summarized below:

Estimation of copper in the presence of other ions.

Ion	Added as	Concentration of ion (mg.)	Copper		% error
			present (mg.)	found (mg.)	
Ag^{+}	$AgNo_3$	1.0	1.26	1.35	+ 6.35
Al^{+++}	$Al_2(So_4)_3$	135	1.26	1.25	- 1.0
Be^{++}	$BeCl_2$	45	1.26	1.26	0.0
		90	1.26	1.248	- 1.0
Bi^{++}	$Bi(No_3)_3$	250	1.26	1.263	+ 0.25
Cd^{++}	$Cd(No_3)_2$	550	1.26	1.26	0.0
Co^{++}	$CoSo_4$	100	1.26	1.26	0.0
Cr^{+++}	$Cr_2(So_4)_3$	250	1.26	1.26	0.0
Fe^{++}	$FeSo_4(NH_4)_2So_4$	50	1.26	1.263	+ 0.25
Fe^{+++}	$FeCl_3$	0.5	1.26	1.51	+20.0
Hg^{++}	$Hg(No_3)_2$	200	1.26	1.248	- 1.0
Mg^{++}	$MgSo_4$	125	1.26	1.25	- 1.0
Mn^{++}	$MnCl_2$	200	1.26	1.25	- 1.0
Ni^{++}	$NiSo_4$	100	1.26	1.255	- 0.4
Pb^{++}	$Pb(No_3)_2$	1000	1.26	1.273	+ 1.0
Pd^{++}	$PdCl_2$	1.0	1.26	1.8	+42.8
Th^{++++}	$Th(No_3)_4$	500	1.26	1.26	0.0

Ion	Added as	Concentration of ion (mg.)	Copper present (mg.)	Found (mg.)	% error
Ti^{++++}	$TiCl_4$	0.5	1.26	1.4	+ 11.0
Uo_2^{++}	$Uo_2(No_3)_2$	200	1.26	1.265	+ 0.4
Vo^{++}	$VoSo_4$	1	1.26	1.28	+ 1.6
Wo_4^{--}	Na_2Wo_4	500	1.26	1.248	- 0.95
Zn^{++}	$ZnSo_4$	300	1.26	1.26	0.0
Zr^{++++}	$Zr(No_3)_4$	500	1.26	1.248	- 1.0
Ba^{++}	$BaCl_2$	500	1.26	1.26	0.0
Sr^{++}	$Sr(No_3)_2$	500	1.26	1.26	0.0
Ca^{++}	$Ca(No_3)_2$	500	1.26	1.26	0.0
Cl^-	KCl	1000	1.26	1.26	0.0
Br^-	KBr	1000	1.26	1.26	0.0
I^-	KI	1000	1.26	1.26	0.0
No_3^-	KNo_3	1000	1.26	1.26	0.0
So_4^{--}	K_2So_4	1000	1.26	1.26	0.0
Oxalate	Pot.oxalate	100	1.26	1.26	0.0
Citrate	Pot.citrate	200	1.26	1.25	- 0.8
Tartrate	Sod.tartrate	200	1.26	1.25	- 0.8

Amperometric determination of palladium :

The reaction between palladium and 2,5-dihydroxy-acetophenoneoxime proceeds quantitatively in the pH range 2.5-6.0.

Amperometric titrations between palladium and 2,5-dihydroxy-acetophenoneoxime were carried out at the potential -0.4 volts vs S.C.E., using sodium acetate-acetic acid buffer solution (pH 4.0) as supporting electrolyte and 0.01% gelatine solution as maximum suppressor. From the points of intersection on the current-volume curves a combining ratio of 1:2 for metal and ligand respectively was obtained. The results are summarized as follows:

S.No.	Fig.& curve	Vol.of $PdCl_2$ (ml.)	Vol.of D.H.A.O. (ml.)	Mole ratio Pd/D.H.A.O.
1	8,a	$20(2.5\times10^{-3}M)$	$39.2(2.5\times10^{-3}M)$	1:1.96
2	8,b	$20(2\times10^{-3}M)$	$40.5(2\times10^{-3}M)$	1:2.024
3	8,d	$20(1\times10^{-3}M)$	$40.0(1\times10^{-3}M)$	1:2
4	10,a	$10(5\times10^{-3}M)$	$20(5\times10^{-3}M)$	1:2
5	10,b	$10.2(2.5\times10^{-3}M)$	$20(2.5\times10^{-3}M)$	1:1.96
6	10,c	$10.0(2\times10^{-3}M)$	$20(1\times10^{-3}M)$	1:2

Like copper, it was found that amperometric titrations between palladium and 2,5-dihydroxy-acetophenoneoxime could also serve for the determination of the metal. The following conditions were maintained during the determination of palladium amperometrically:

(a) The pH of the solution was maintained at 4.0, using sodium acetate-acetic acid buffer solution which also served as the supporting electrolyte.

(b) Gelatine (0.01% solution) was used as a maximum suppressor.

(c) A potential of -0.4 volts vs S.C.E. was applied during the titration.

Solutions containing 0.532-5.32 mg. of palladium were used for the amperometric determination. The results are summarized in the following table :

S.No.	Fig.& curve	Vol.of solution (ml.)	Pd present (mg.)	Pd found (mg.)	% error
1	8,a	20	5.32	5.2136	- 2.0
2	8,b	20	4.256	4.309	+ 1.2
3	8,c	20	2.66	2.66	0.0
4	8,d	20	2.128	2.128	0.0
5	9,a	20	1.064	1.064	0.0
6	9,b	20	0.532	0.511	- 4.0

It is inferred that solutions containing 1.0-4.0 mg. of palladium can accurately be determined within ± 1% error.

The influence of foreign ions on the estimation of palladium was also studied in the usual manner. It was found that Ag^{+}, Fe^{+++}, Ti^{++++}, Vo^{++}, Cu^{++} interferred strongly. The presence of other ions did not hinder in the accurate determination of the metal.

The results of the amperometric titrations of palladium in the presence of other ions are summarized in the following table :

Ion	Added as	Conc. of ion (mg.)	Pd present (mg.)	Pd found (mg.)	% error
$\mathrm{Ag^{+}}$	$\mathrm{AgNo_3}$	0.2	1.064	1.12	-4.15
$\mathrm{Al^{+++}}$	$\mathrm{Al_2(So_4)_3}$	100	1.064	1.064	0.0
$\mathrm{Be^{++}}$	$\mathrm{BeCl_2}$	45	1.064	1.064	0.0
$\mathrm{Bi^{+++}}$	$\mathrm{Bi(No_3)_3}$	100	1.064	1.07	+0.65
$\mathrm{Cd^{++}}$	$\mathrm{Cd(No_3)_2}$	100	1.064	1.064	0.0
$\mathrm{Co^{++}}$	$\mathrm{CoSo_4}$	100	1.064	1.064	0.0
$\mathrm{Cr^{+++}}$	$\mathrm{Cr_2(So_4)_3}$	100	1.064	1.064	0.0
$\mathrm{Cu^{++}}$	$\mathrm{CuSo_4}$	0.5	1.064	1.9	+80.0
$\mathrm{Fe^{++}}$	$\mathrm{FeSo_4(NH_4)_2So_4}$	56	1.064	1.08	+1.5
$\mathrm{Fe^{+++}}$	$\mathrm{FeCl_3}$	0.5	1.064	1.5	+40.0
$\mathrm{Hg^{++}}$	$\mathrm{Hg(No_3)_2}$	200	1.064	1.06	-0.4
$\mathrm{Mg^{++}}$	$\mathrm{MgSo_4}$	100	1.064	1.064	0.0
$\mathrm{Mn^{++}}$	$\mathrm{MnCl_2}$	200	1.064	1.064	0.0
$\mathrm{Ni^{++}}$	$\mathrm{NiSo_4}$	100	1.064	1.07	+0.65
$\mathrm{Pb^{++}}$	$\mathrm{Pb(No_3)_2}$	200	1.064	1.06	-0.4
$\mathrm{Th^{++++}}$	$\mathrm{Th(No_3)_4}$	100	1.064	1.064	0.0
$\mathrm{Ti^{++++}}$	$\mathrm{TiCl_4}$	0.2	1.064	1.12	+6.0
$\mathrm{Uo_2^{++}}$	$\mathrm{Uo_2(No_3)_2}$	100	1.064	1.064	0.0
$\mathrm{Vo^{++}}$	$\mathrm{VoSo_4}$	1	1.064	1.09	+2.5
$\mathrm{Wo_4^{--}}$	$\mathrm{Na_2Wo_4}$	200	1.064	1.064	0.00
$\mathrm{Zn^{++}}$	$\mathrm{ZnSo_4}$	200	1.064	1.070	+0.65
$\mathrm{Zr^{++++}}$	$\mathrm{Zr(No_3)_4}$	200	1.064	1.064	0.0
$\mathrm{Ba^{++}}$	$\mathrm{BaCl_2}$	500	1.064	1.064	0.0

Ion	Added as	Conc.of ion (mg.)	Pd present (mg.)	Pd found (mg.)	% error
Sr^{++}	$Sr(No_3)_2$	500	1.064	1.064	0.0
Ca^{++}	$Ca(No_3)_2$	500	1.064	1.064	0.0
Cl^-	KCl	1000	1.064	1.064	0.0
Br^-	KBr	1000	1.064	1.064	0.0
I^-	KI	1000	1.064	1.064	0.0
So_4^{--}	K_2So_4	1000	1.064	1.064	0.0
No_3^-	KNo_3	1000	1.064	1.064	0.0
CH_3Coo^-	CH_3CooNa	1000	1.064	1.064	0.0
Oxalate	Pot.oxalate	100	1.064	1.064	0.0
Citrate	Pot.citrate	100	1.064	1.060	- 0.4
Tartrate	Sod.tartrate	100	1.064	1.060	- 0.4

Amperometric determination of Nickel :

The reaction between nickel and 2,5-dihydroxyacetophenoneoxime is quantitative in the pH range 6.0-10.0.

The amperometric titrations of nickel with the reagent were carried out at an applied potential of -1.2 volts vs S.C.E. in the presence of ammonia-ammonium chloride buffer solution (pH 9.0) as supporting electrolyte and 0.01% solution of gelatine as maximum suppressor. Both direct and reverse titrations were carried out and the combining ratio, from the points of intersection on the volume-current curves, was found to correspond to 1:2 complex for metal and ligand respectively. The results are summarized below :

S.No.	Fig.& curve	Vol.of $NiSo_4$ (ml.)	Vol.of D.H.A.O. (ml.)	Mole ratio Ni/D.H.A.O
1	11,a	20.0(2.5x10^{-3}M)	40.0(2.5x10^{-3}M)	1:2
2	11,b	20.0(2x10^{-3}M)	40.0(2.0x10^{-3}M)	1:2
3	11,c	20.0(1.5x10^{-3}M)	40.33(1.5x10^{-3}M)	1:2.017
4	13,a	10.4(5x10^{-3}M)	20.0(5x10^{-3}M)	1:1.92
5	13,b	10.0(4x10^{-3}M)	20.0(4x10^{-3}M)	1:2
6	13,c	10.5(2x10^{-3}M)	20.0(2x10^{-3}M)	1:1.9

The amperometric determination of nickel was carried out by titrating solutions containing (0.587-2.935 mg.) of nickel against 2,5-dihydroxy-acetophenoneoxime as titrant in the same manner as described above. The results of a few determination of nickel are tabulated below :

S.No.	Fig.& curve	Vol.of solution (ml.)	Ni present (mg.)	Ni found (mg.)	% error
1	11,a	20.0	2.935	2.935	0.0
2	11,b	20.0	2.348	2.348	0.0
3	11,c	20.0	1.761	1.7756	+ 0.83
4	11,d	20.0	1.174	1.1593	- 1.25
5	12,a	20.0	0.587	0.5166	- 12.0
6	12,b	20.0	0.8805	0.857	- 2.5

It is evident that the solutions containing 1.0-3.0 mg. of nickel can be accurately determined (± 2 % error).

The effect of diverse ions on the determination of nickel could not be studied due to the formation of their hydroxides or insoluble chelates with the reagent in the basic medium.

From the above results, a conclusion may be drawn that 2,5-dihydroxy-acetophenoneoxime may be used for the amperometric determination of Cu, Ni and Pd. Copper and palladium can be accurately estimated in the presence of a number of other ions. Nickel can also be estimated in a wide range of concentrations, though the presence of foreign ions interfere with the estimation.

ABSORPTION CURVE OF Mo-D.H.A.o. COMPLEX

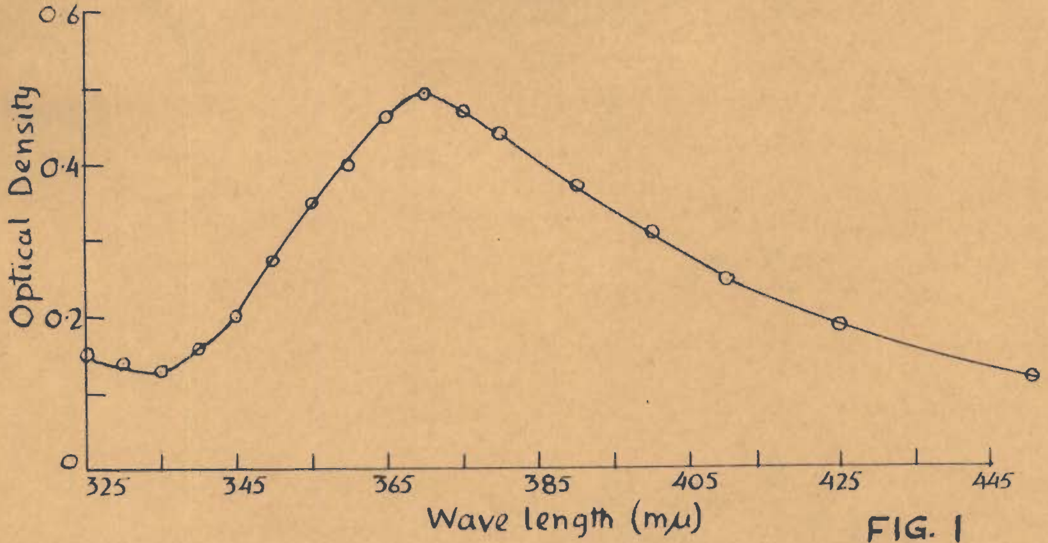


FIG. 1

EFFECT OF pH ON COLOUR INTENSITY

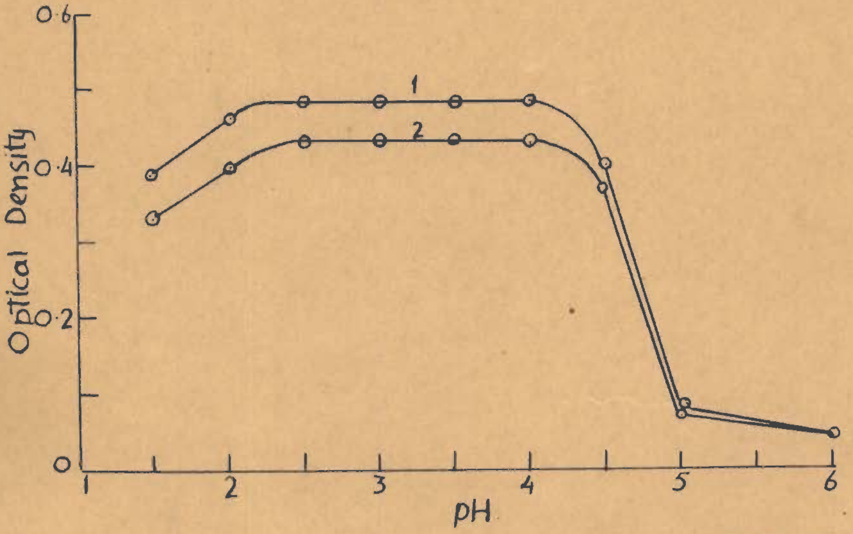


FIG. 2

1- O.D. at 370 mµ

2- O.D. at 380 mµ

EFFECT OF REAGENT CONCENTRATION

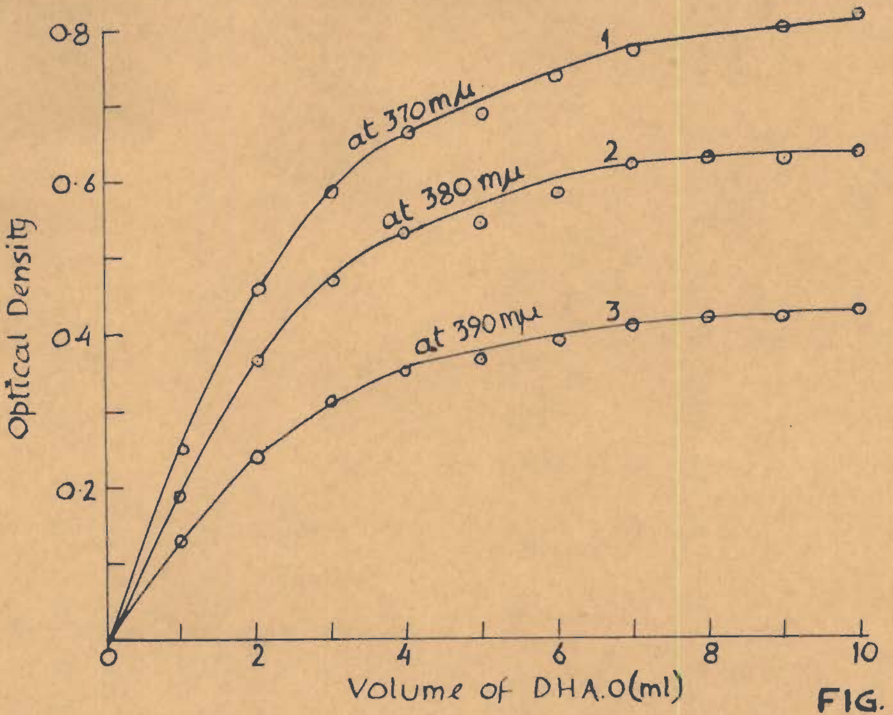


FIG. 3

BEER-LAMBERT'S LAW

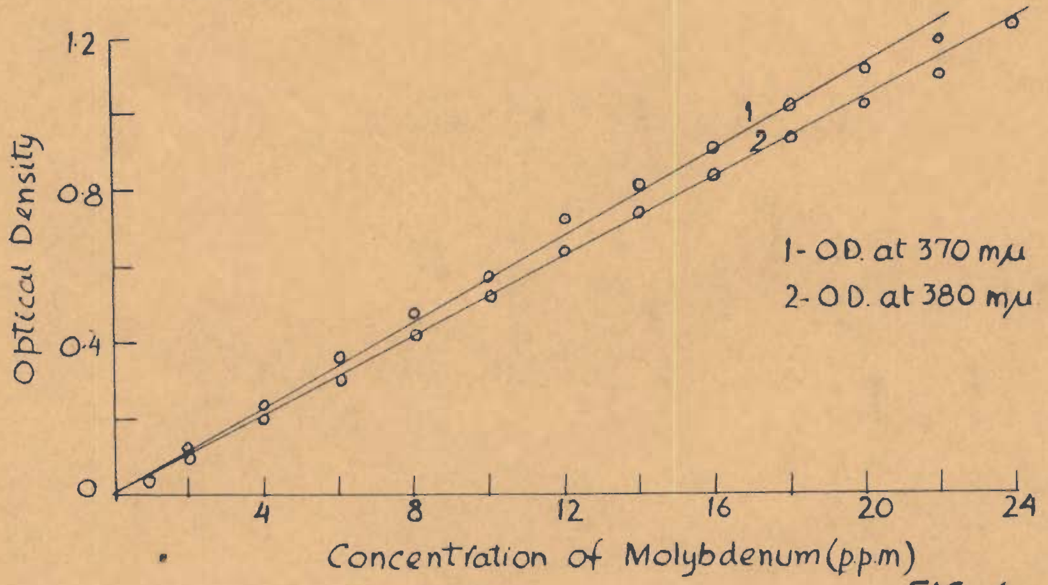


FIG. 4

AMPEROMETRIC TITRATIONS

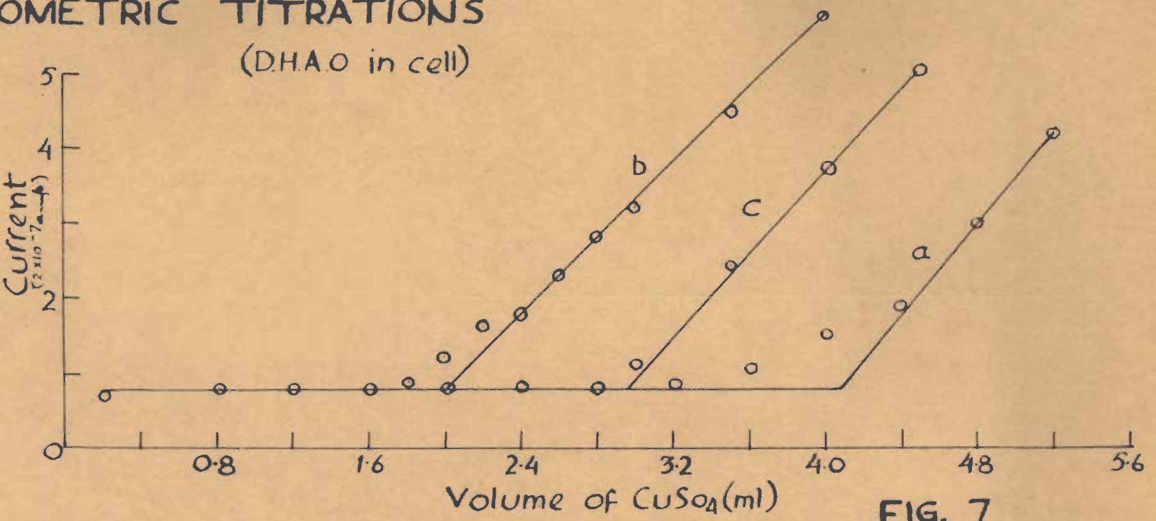


FIG. 7

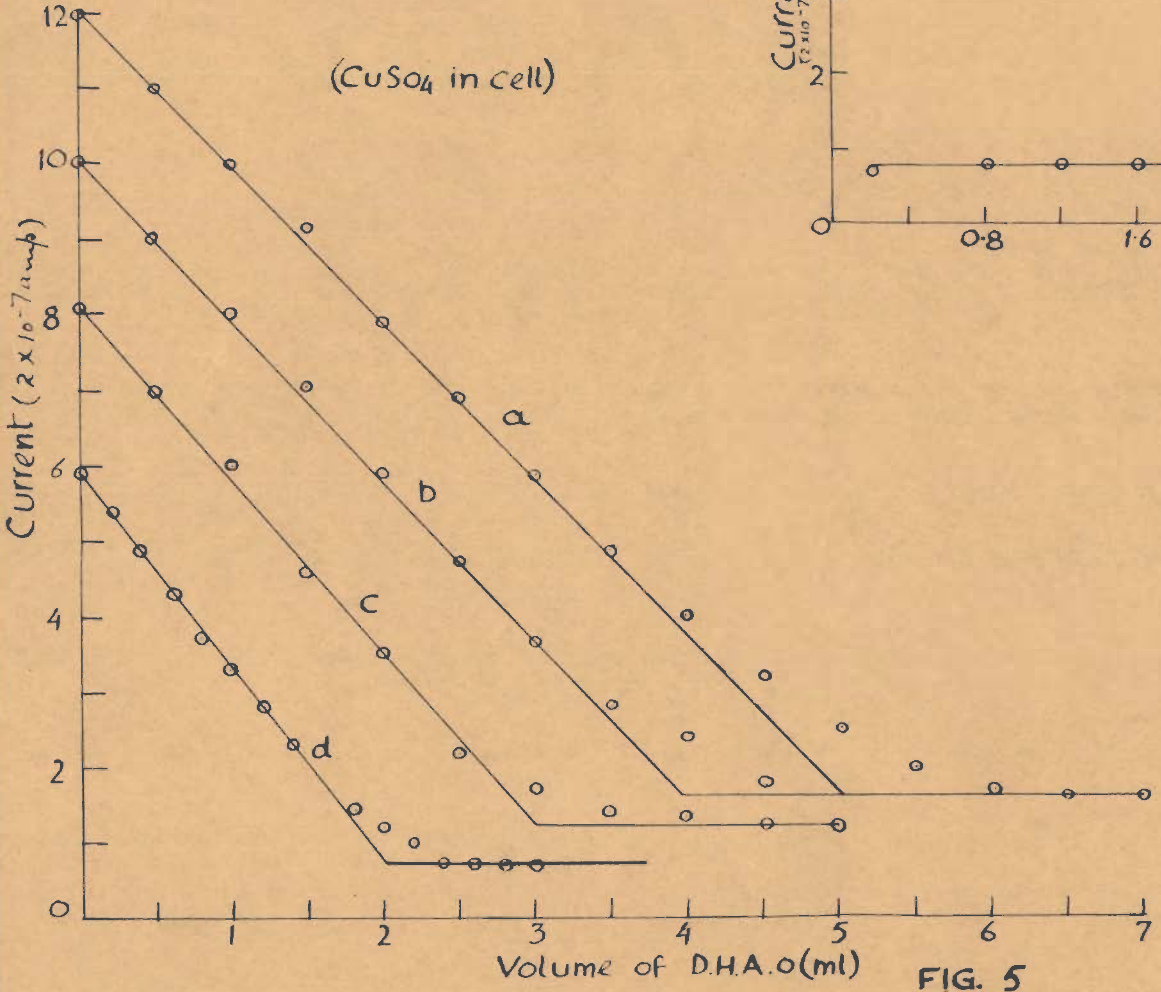


FIG. 5

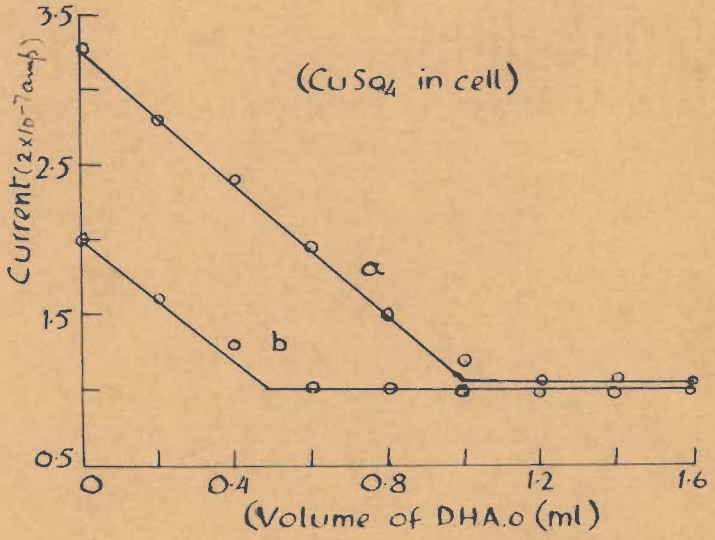


FIG. 6

AMPEROMETRIC TITRATIONS

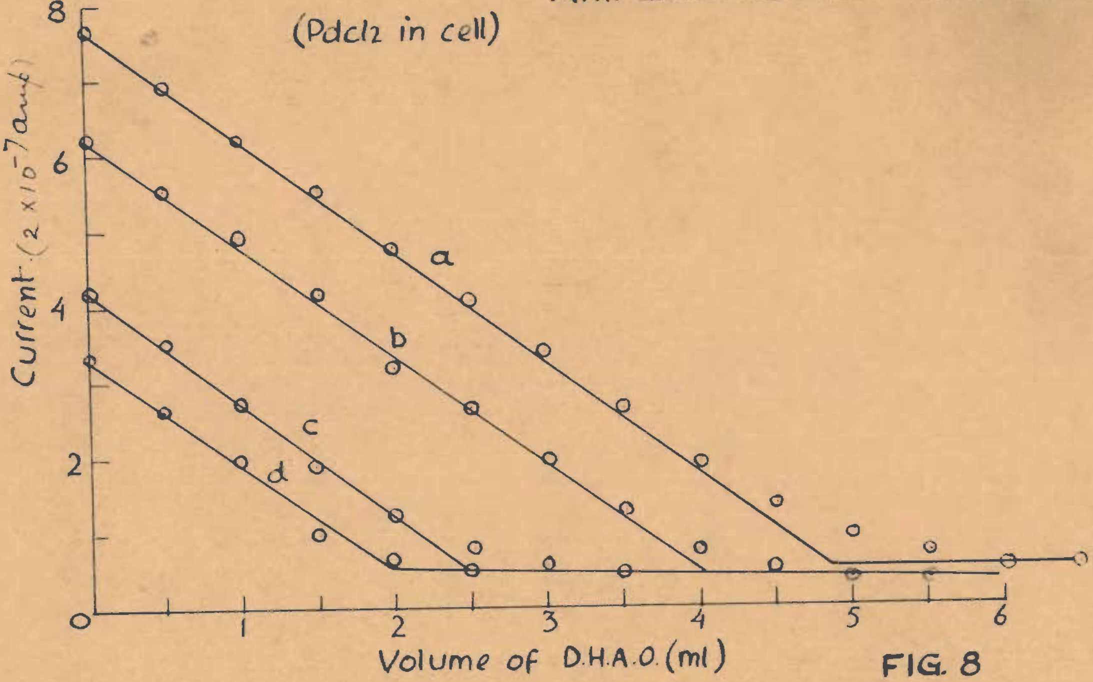


FIG. 8

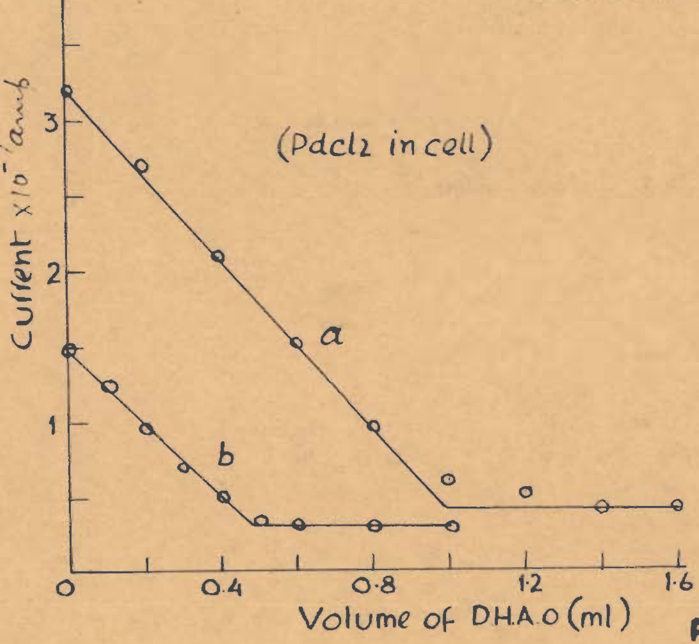


FIG. 9

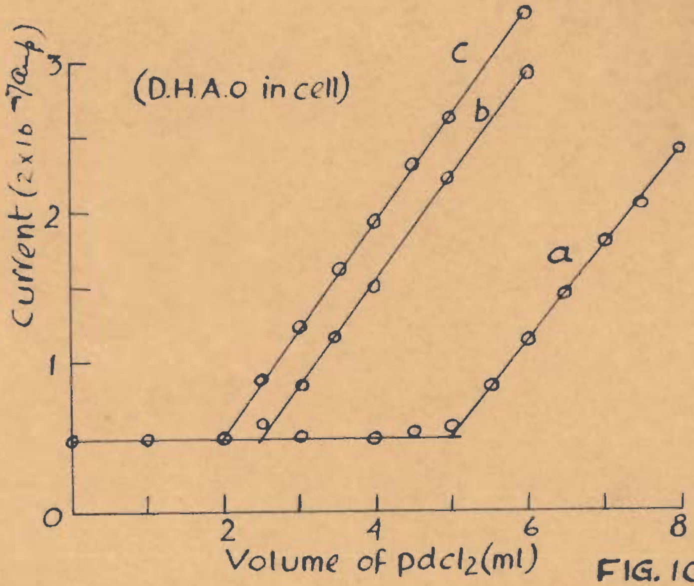


FIG. 10

AMPEROMETRIC TITRATIONS

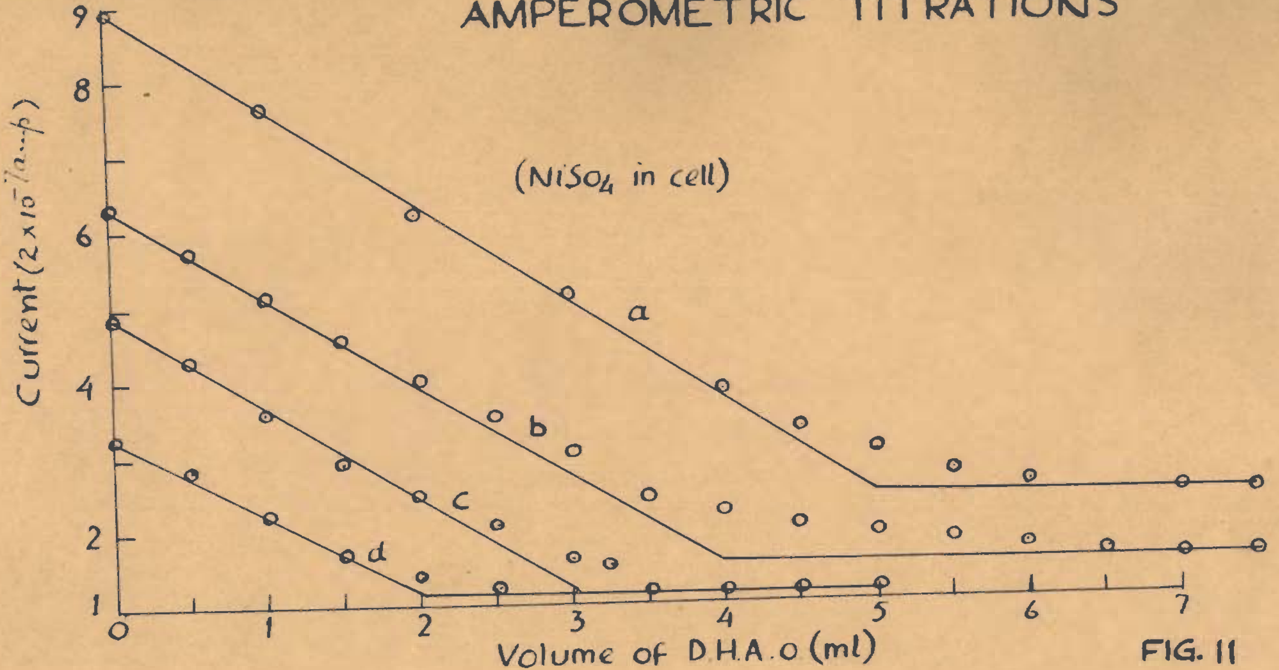


FIG. 11

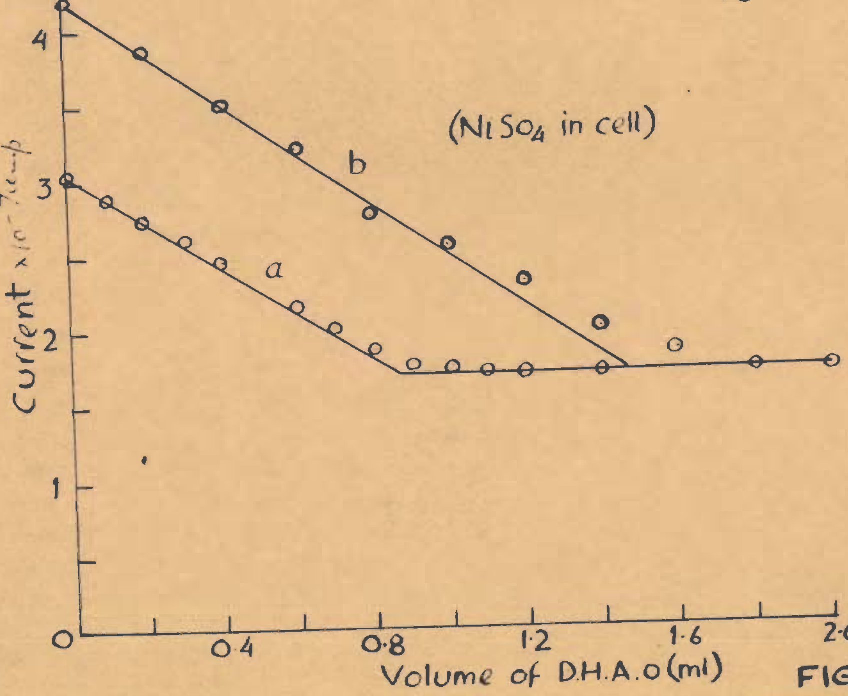


FIG. 12

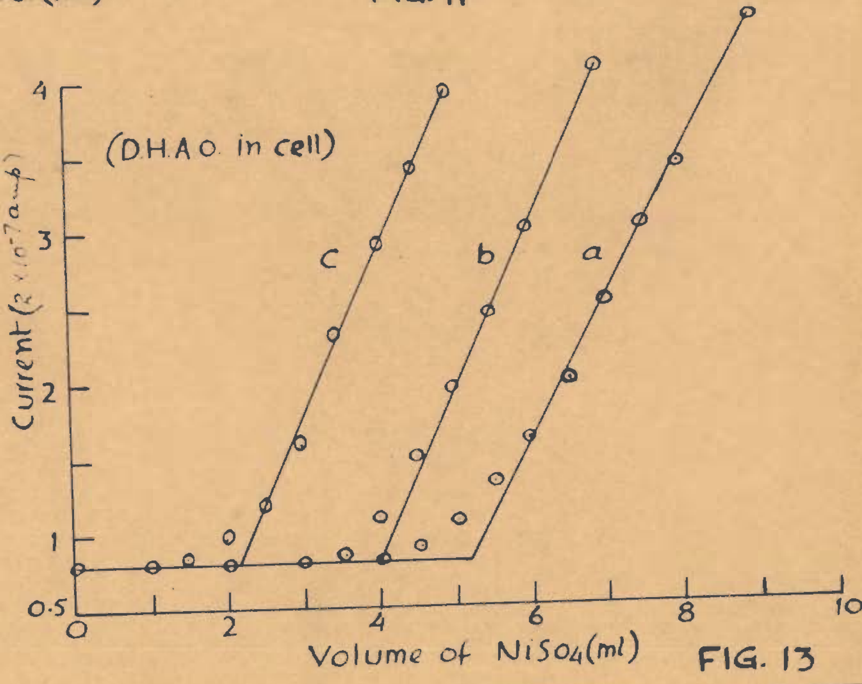


FIG. 13

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CHAPTER V

****

" Uranyl and thorium(IV) complexes of 2-hydroxy-5-methyl acetophenone "

***

INTRODUCTION

The metal chelates of hydroxyaldehydes and ketones have mainly been used for the detection and estimation of metal ions. The precipitates formed by the interaction of copper, nickel and ferric iron with salicylaldehyde[1] in ammoniacal medium, have been found suitable for their gravimetric estimations. Another aldehyde namely pyrogallol aldehyde[2,3] has been employed by Kaserer for the detection of thorium and zirconium.

Amongst the aromatic hydroxy ketones, 2,4-dihydroxyacetophenone (resacetophenone) has been reported for the detection of iron[4] and boron[5].

From the structural point of view, a little attention has been paid to the studies of the metal chelates of these reagents. Mostly the work has been done by Wilson and Calvin[6,7] who have studied the stability of Cu, Ni, Co and Zn complexes of salicylaldehyde and its derivatives potentiometrically. A few references of the chelates of copper, nickel and cobalt with p-methoxy-o-hydroxyacetophenone[8] have also been reported in the literature. Reactions of metals with 2-hydroxy-5-methyl acetophenone have, however, not been studied so far. It was, therefore, considered worthwhile to study its reactions with few metals. For this purpose two metals namely uranium and thorium were chosen. These metals gave soluble complexes whose composition was determined by spectro-photometric and conductometric methods.

EXPERIMENTAL

SOLUTIONS;

Uranyl nitrate :-

Uranyl nitrate (B.D.H. Analar) was dissolved in double distilled water. The strength of the solution was determined gravimetrically as uranyl oxinate.

Thorium nitrate :-

Thorium nitrate of A.R. quality (B.D.H) was dissolved in double distilled water and the strength of the solution was determined gravimetrically.

2-Hydroxy-5-methyl acetophenone :-

It was prepared by the method described in Chapter II. Its solution was prepared in 50% alcohol.

Apparatus :-

The details of the apparatus employed are the same as described in the preceding Chapters.

Spectrophotometric studies on the nature, composition and stability of uranyl-2-hydroxy-5-methyl acetophenone :

Uranyl ions react with 2-hydroxy-5-methyl acetophenone (designated as H.A.O) forming an orange, water soluble and stable complex.

Vosburgh and Cooper's method was employed to determine the number of complexes formed in solution. Equimolar solutions were prepared by mixing the reactants in the same manner as described earlier.

The absorbance of all these solutions was measured at different wave lengths (350-450 mμ), using reagent solution as blank.

Table -1

Absorption spectrum of uranyl nitrate solution

Wave length (mμ)	O.D. of $Uo_2(No_3)_2$ solutions of concs.		
	0.1M	0.05M	0.025M
350	0.37	0.20	0.09
360	0.32	0.17	0.075
370	0.35	0.19	0.09
380	0.46	0.25	0.12
390	0.62	0.34	0.17
400	0.77	0.42	0.21
410	0.80	0.43	0.23
420	0.66	0.36	0.175
430	0.46	0.25	0.12
450	0.16	0.08	0.04
	Curve(a)	Curve(b)	Curve (c)

Fig. 1

λmax lies at 410 mμ

Table -2

Absorption spectrum of H.M.A. solution

Wave length	O.D. of H.M.A. solutions of concs.	
(mμ)	2.5×10^{-4}M	1.25×10^{-4}M
325	0.53	0.30
330	0.64	0.38
335	0.75	0.42
340	0.81	0.47
345	0.86	0.48
350	0.88	0.49
355	0.84	0.46
360	0.78	0.42
365	0.68	0.36
370	0.58	0.29
375	0.43	0.23
380	0.30	0.16
385	0.20	0.12
390	0.135	0.085
400	0.05	0.035
	Curve (a)	Curve (b)

Fig. 2

The maximum absorption of the solution occurs at 350 mμ

Table -3

Vosburgh and Cooper's method applied to UO_2-H.M.A

Concentration of uranyl nitrate = $2x10^{-3}M$

Concentration of H.M.A = $2x10^{-3}M$

Wave length (mμ)	Optical density of solutions Ratio of uranyl nitrate to H.M.A 1:1	1:2	1:3	2:1	3:1
350	0.065	0.09	0.12	0.065	0.065
355	0.09	0.12	0.14	0.09	0.095
360	0.11	0.15	0.18	0.11	0.11
365	0.13	0.18	0.21	0.13	0.13
370	0.17	0.20	0.25	0.16	0.15
375	0.20	0.24	0.28	0.185	0.17
380	0.22	0.26	0.29	0.20	0.19
385	0.21	0.25	0.28	0.19	0.18
390	0.19	0.24	0.26	0.18	0.17
400	0.17	0.21	0.22	0.16	0.15
410	0.15	0.18	0.20	0.14	0.12
420	0.13	0.16	0.18	0.12	0.11
Curves	(a)	(b)	(c)	(d)	(e)

Fig. 3

The λmax of the solution lies at 380 mμ.

In order to study the influence of pH on the colour reaction of uranium with H.M.A, the absorbance of equimolar solutions containing $8x10^{-4}M$ uranyl nitrate and $4x10^{-3}M$ H.M.A. and adjusted to different pH values (3.0-5.0), was measured at different wave lengths (350-450 mμ).

Table -4

Influence of pH on the of stability Uo_2 - H.M.A

Concentration of uranyl nitrate = $8x10^{-4}M$

Concentration of H.M.A = $4x10^{-3}M$

Wave length (mμ)	O.D. of solutions at different pH values			
	3.0	3.5	4.0	4.5
350	0.04	0.07	0.16	0.08
360	0.08	0.12	0.22	0.15
370	0.11	0.17	0.31	0.21
380	0.12	0.19	0.41	0.29
390	0.08	0.17	0.38	0.25
400	0.05	0.14	0.35	0.21
410	0.035	0.10	0.31	0.18
420	0.02	0.08	0.26	0.14
430	0.01	0.06	0.225	0.115
450	0.0	0.03	0.16	0.07
Curves	(a)	(b)	(c)	(d)

Fig. 4

The λmax of the solutions lies at 380 mμ in the pH range 3.0-4.5.

For determining the composition of the complex, Job's method of continued variation was employed.

Equimolar solutions were prepared by mixing the reactants in the same manner as described earlier.

The difference between the optical density of the mixture and that of uranyl nitrate and H.M.A. was plotted against the ratio $(Uo_2^{++})/(Uo_2^{++}) + (H.M.A)$. The absorbance data at 390 mu are given in the following tables while those at 380 and 400 mu are depicted in Figs.5,7 :

Table-5

Wave length 390 mu

Final concentration of the reactants = $8x10^{-3}M$

Vol.of $Uo_2(No_3)_2$ (ml.)	Vol.of H.M.A (ml.)	Optical density			
		Mixture	$Uo_2(No_3)_2$	H.M.A	Difference
1.0	9.0	0.745	0.01	0.34	0.395
2.0	8.0	0.81	0.02	0.32	0.47
3.0	7.0	0.825	0.02	0.30	0.505
4.0	6.0	0.775	0.025	0.26	0.49
5.0	5.0	0.72	0.03	0.23	0.46
6.0	4.0	0.64	0.035	0.20	0.405
7.0	3.0	0.54	0.04	0.17	0.33
8.0	2.0	0.41	0.04	0.12	0.25
9.0	1.0	0.26	0.045	0.06	0.155

Fig.6, curve 1

Table -6

Wave length 390 mμ

Final concentration of the reactants = $4x10^{-3}M$

Vol.of $Uo_2(No_3)_2$ (ml.)	Vol.of H.M.A (ml.)	Optical density			
		Mixture	$Uo_2(No_3)_2$	H.M.A	Difference
1.0	9.0	0.41	-	0.195	0.215
2.0	8.0	0.43	-	0.18	0.25
3.0	7.0	0.44	-	0.17	0.27
4.0	6.0	0.39	-	0.14	0.25
5.0	5.0	0.36	-	0.12	0.24
6.0	4.0	0.31	-	0.10	0.21
7.0	3.0	0.25	-	0.08	0.17
8.0	2.0	0.19	-	0.05	0.14
9.0	1.0	0.12	-	0.025	0.095

Fig.6, curve 2

Table -7

Wave length 390 mμ

Final concentration of the reactants = $2x10^{-3}M$

Vol.of $Uo_2(No_3)_2$	Vol.of H.M.A	Optical density			
		Mixture	$Uo_2(No_3)_2$	H.M.A	Difference
1.0	9.0	0.20	-	0.11	0.09
2.0	8.0	0.215	-	0.10	0.115
3.0	7.0	0.21	-	0.085	0.125
4.0	6.0	0.19	-	0.07	0.12
5.0	5.0	0.17	-	0.06	0.11
6.0	4.0	0.15	-	0.05	0.10
7.0	3.0	0.12	-	0.04	0.08
8.0	2.0	0.09	-	0.03	0.06
9.0	1.0	0.06	-	0.015	0.045

Fig.6, curve 3

The formation constant of the complex was calculated from the absorbance values of Job's method at 390 mu (tables 6,7). The uranyl ions are colourless at the given concentrations. For arbitrary absorbance value of 0.15, the initial concentrations of the reactants were found :

Solution I:
Conc.of $Uo_2(No_3)_2(a_1) = 3.44x10^{-3}M$
Conc.of H.M.A.$(b_1) = 0.56x10^{-3}M$

Solution II:
Conc.of $Uo_2(No_3)_2(a_2) = 1.2x10^{-3}M$
Conc.of H.M.A $(b_2) = 0.8x10^{-3}M$

Conductometric studies on the composition of the complex :

Both direct (metal in the cell) and reverse (ligand in the cell) titrations were carried out to determine the composition of the complex.

The observations of the titrations are tabulated below :

Table -8

Direct titration (uranyl nitrate in the cell)

Vol.of uranyl nitrate = 20.0 ml.

Concentration of uranyl nitrate = 1.25×10^{-3}M (Set I)
= 2×10^{-3}M (Set II)
= 0.75×10^{-3}M (Set III)

Initial concentration of H.M.A. added = 1×10^{-2}M

Vol.of H.A.O.	I Corrected conductance $\times 10^{-4}$(mhos)	II Corrected conductance $\times 10^{-4}$(mhos)	III Corrected conductance $\times 10^{-4}$(mhos)
0.0	7.4	8.3	6.5
0.5	-	-	6.2
1.0	6.7	7.65	5.8
2.0	6.1	7.2	5.1
2.5	-	-	4.8
3.0	5.3	6.6	4.4
3.5	-	-	4.1
4.0	4.7	6.06	3.8
5.0	4.05	5.4	3.4
6.0	3.6	4.9	2.8
7.0	3.2	4.4	2.3
8.0	2.9	4.0	
9.0	2.5	3.7	
10.0	2.1	3.4	
11.0		3.2	
12.0		3.0	
	Curve(a)	Curve(b)	Curve(c)

Fig.9

Curve (a)

20.0 ml.of 1.25×10^{-3}M $Uo_2(No_3)_2$ ≡ 5.2 ml.of 1×10^{-2}M H.M.A
≡41.6 ml.of 1.25×10^{-3}M H.M.A

Curve (b)

20.0 ml.of 2×10^{-3}M $Uo_2(No_3)_2$ ≡ 7.7 ml.of 1×10^{-2}M H.M.A
≡38.5 ml.of 2×10^{-3}M H.M.A

Curve (c)

20.0 ml.of 0.75×10^{-3}M $Uo_2(No_3)_2$ ≡ 3.4 ml.of 1×10^{-2}M H.M.A
≡45.4 ml.of 0.75×10^{-3}M H.M.A

Table -9

Reverse titrations (H.M.A. in the cell)

Volume of H.M.A. = 20.0 ml.
Concentration of H.M.A = $7.5\text{x}10^{-3}$M (Set I)
= $1\text{x}10^{-2}$M (Set II)

Initial concentration of $Uo_2(No_3)_2$ added = $2\text{x}10^{-2}$M

Vol.of $Uo_2(No_3)_2$ (ml.)	I Corrected conductance $\text{x}10^{-4}$ (mhos)	II Corrected conductance $\text{x}10^{-4}$(mhos)
0.0	1.6	0.7
1.0	2.25	1.25
1.5	3.0	1.8
2.0	3.6	2.3
2.5	4.1	2.8
3.0	4.35	3.2
3.5	4.8	3.7
4.0	5.0	4.25
4.5	5.9	4.7
5.0	6.3	5.1
5.5	6.7	5.5
6.0	7.1	5.95
6.5		6.3
7.0		6.7
8.0		7.3
	Curve(a)	Curve(b)

Fig.10

Curve (a)

20.0 ml.of $7.5\text{x}10^{-3}$M H.M.A. ≡ 3.85 ml.of $2\text{x}10^{-2}$M $Uo_2(No_3)_2$
≡ 10.3 ml.of $7.5\text{x}10^{-3}$M $Uo_2(No_3)_2$

Curve (b)

20.0 ml. of $1\text{x}10^{-2}$M H.M.A. ≡ 4.85 ml.of $2\text{x}10^{-2}$M $Uo_2(No_3)_2$
≡ 9.7 ml.of $1\text{x}10^{-2}$M $Uo_2(No_3)_2$

Thorium(IV)-2-hydroxy-5-methyl acetophenone:

Thorium nitrate reacts with 2-hydroxy-5-methyl acetophenone forming stable, water soluble, yellow complex in the acidic medium. The colour develops instantaneously.

Vosburgh and Cooper's method was applied to determine the nature and the number of complexes formed by the interaction between thorium ions and H.M.A. Thorium nitrate and H.M.A solutions were mixed in different proportions, viz., 1:1, 1:2, 1:3, 2:1, 3:1 and the absorption spectra of these solutions were taken, using reagent as blank.

Table -10

Vosburgh and Cooper's method applied to Th(IV)-H.M.A

Concentration of thorium nitrate = 8×10^{-4}M
Concentration of H.M.A. = 8×10^{-4}M

Wave length	Optical density of solutions				
	Ratio of thorium ions to H.M.A				
(mμ)	1:1	1:2	1:3	2:1	3:1
350	0.21	0.22	0.34	0.175	0.145
355	0.30	0.32	0.45	0.265	0.185
360	0.42	0.44	0.54	0.39	0.27
365	0.51	0.53	0.63	0.45	0.33
370	0.58	0.59	0.70	0.51	0.37
375	0.59	0.635	0.74	0.53	0.38
380	0.58	0.615	0.73	0.52	0.36
390	0.49	0.52	0.64	0.42	0.30
400	0.35	0.37	0.46	0.30	0.21
410	0.21	0.22	0.28	0.17	0.12
425	0.055	0.07	0.09	0.05	0.035
Curves	(a)	(b)	(c)	(d)	(e)

Fig.11

λmax of all the solutions lies at 375 mμ

The influence of pH on the complex was studied by measuring the absorbance at different wave lengths (350-425 mμ) of equimolar solutions (conc. 4×10^{-4}M) containing thorium nitrate and H.M.A in the 1:1 ratio and adjusted to different pH values.

Table -11

Influence of pH on the stability of the complex

Concentration of thorium nitrate = 4×10^{-4}M
Concentration of H.M.A. = 4×10^{-4}M

Wave length (mμ)	O.D.of solutions at different pH values					
	2.0	2.5	3.0	3.5	4.0	4.5
350	0.0	0.01	0.09	0.13	0.04	0.0
355	0.0	0.035	0.14	0.21	0.06	0.0
360	0.0	0.06	0.19	0.27	0.11	0.03
365	0.02	0.08	0.25	0.34	0.14	0.05
370	0.025	0.08	0.26	0.365	0.16	0.06
375	0.02	0.095	0.28	0.38	0.17	0.07
380	0.02	0.09	0.27	0.37	0.16	0.06
390	0.01	0.07	0.23	0.31	0.13	0.05
400	0.01	0.05	0.16	0.22	0.10	0.03
410	0.01	0.03	0.09	0.13	0.05	0.02
425	0.0	0.01	0.02	0.04	0.015	0.01
Curves	(a)	(b)	(c)	(d)	(e)	(f)

λmax of the complex lies at 375 mμ in the pH range 2.5-4.5

The composition of the complex was determined by applying Job's method of continued variation. The solutions were mixed in the same manner as described earlier. The absorbance data taken at 375 mμ are given below while those at 380 and 390 mμ are depicted in Figs.14,15 :

Table -12

At 375 mμ

Concentration of the reactants = 1.6×10^{-3}M

Vol.of $Th(No_3)_4$ (ml.)	Vol.of H.M.A. (ml.)	Optical density of		
		Mixture	H.M.A.	Difference
1.0	9.0	0.64	0.36	0.28
2.0	8.0	0.96	0.34	0.62
3.0	7.0	1.1	0.31	0.79
4.0	6.0	1.15	0.25	0.90
5.0	5.0	1.155	0.225	0.930
6.0	4.0	1.0	0.19	0.81
7.0	3.0	0.825	0.135	0.690
8.0	2.0	0.62	0.10	0.52
9.0	1.0	0.35	0.06	0.29

Fig.13, curve (1)

Table -13

At 375 mμ

Concentration of the reactants $= 8\times10^{-4}M$

Vol. of thorium nitrate (ml.)	Vol. of H.M.A. (ml.)	Optical density of		
		Mixture	H.M.A.	Difference
1.0	9.0	0.31	0.22	0.09
2.0	8.0	0.43	0.19	0.24
3.0	7.0	0.51	0.18	0.33
4.0	6.0	0.52	0.14	0.38
5.0	5.0	0.50	0.11	0.39
6.0	4.0	0.46	0.10	0.36
7.0	3.0	0.38	0.07	0.31
8.0	2.0	0.27	0.05	0.22
9.0	1.0	0.15	0.03	0.12

Fig. 13, curve (2)

Table -14

At 375 mμ

Concentration of the reactants $= 4\times10^{-4}M$

Vol. of thorium nitrate (ml.)	Vol. of H.M.A. (ml.)	Optical density of		
		Mixture	H.M.A.	Difference
1.0	9.0	0.15	0.11	0.04
2.0	8.0	0.18	0.09	0.09
3.0	7.0	0.19	0.07	0.12
4.0	6.0	0.21	0.07	0.14
5.0	5.0	0.19	0.05	0.14
6.0	4.0	0.16	0.035	0.125
7.0	3.0	0.15	0.025	0.125
8.0	2.0	0.09	0.02	0.07
9.0	1.0	0.04	0.01	0.03

Fig. 13, curve (3)

The results of Job's method were further confirmed by the method of slope ratio. The method was performed at two different concentrations of the solutions. The results are depicted in Fig.16.

The formation constant of the complex was determined by Anderson's modified method. For the reaction :

$$Th^{+4} + H.M.A \longrightarrow Th^{+3} - H.M.A. + H^{+}$$

if x represents the concentration of the complex at equilibrium, a and b, the initial concentrations of the metal ions and the ligand respectively, the formation constant is given by

$$K = \frac{x}{(a-x)(b-x)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Taking two concentrations a_1, a_2 and b_1, b_2 of the reactants in the solutions having the same optical density i.e. the same value of x, we have

$$K = \frac{x}{(a_1-x)(b_1-x)} = \frac{x}{(a_2-x)(b_2-2)} \;\ldots\ldots \quad (2)$$

$$\text{or} \qquad x = \frac{a_1b_1 - a_2b_2}{(a_1+b_1)-(a_2+b_2)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Thus from equation(3), the value of x and subsequently the value of K by substituting x in equation(1) can be calculated.

The absorbance data (tables 12,13) of Job's method was used for the calculation of the value of K.

The conductance data of the conductometric titrations between thorium nitrate and H.M.A., are depicted in Figs.18,19.

DISCUSSION

Uranyl-2-hydroxy-5-methyl acetophenone complex :

Uranyl ions form instantaneously soluble, orange coloured complex with 2-hydroxy-5-methyl acetophenone (designated as H.M.A). The complex is highly stable and its colour intensity remains unchanged even on keeping for a week or so. The change of temperature (upto 80°C) has no effect on its colour intensity.

Vosburgh and Cooper's method showed the existence of only one complex having maximum absorption at 380 mμ (Fig.3). Since the reagent absorbs heavily in this spectral range, viz., upto 400 mμ, therefore, the reagent solution instead of water was used as blank in all these absorbance measurements.

The absorption spectra of the solutions having the same concentration of the reactants but at different pH values, exhibited only one maxima at 380 mμ (Fig.4), showing thereby the stability of the complex in the pH range 3.0-4.5; above 4.5 pH, the complex got hydrolysed resulting in the precipitation of uranium hydroxide. The solution attained maximum colour intensity at 4.0 pH.

From the Job's method of continued variation (Figs.5-7) the composition of the complex was found to be 1:2 (Uo_2:H.M.A).

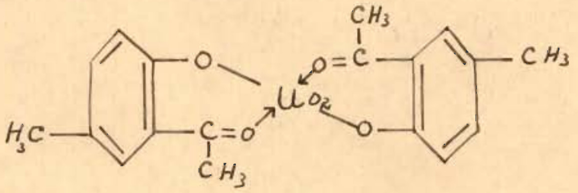
The value of formation constant K of the complex was calculated from the absorbance data (tables 6-7, Fig.8) and found to be 1.49×10^7. The free energy of formation-$\triangle$F was worked out to be 9.91 KCals at 30°C from the relation -$\triangle$F = RT lnk.

The conductometric titrations between uranyl nitrate and H.M.A also confirmed the same composition of the complex. The results of the titrations are summarized below :

S.No.	Fig.& curve	Vol.of $Uo_2(No_3)_2$ (ml.)	Vol.of H.M.A (ml.)	Mole ratio Uo_2^{++}/H.M.A
1	9,a	$20.0(1.25\times10^{-3}M)$	$41.6(1.25\times10^{-3}M)$	1:2.08
2	9,b	$20.0(2\times10^{-3}M)$	$38.5(2\times10^{-3}M)$	1:1.925
3	9,c	$20.0(0.75\times10^{-3}M)$	$45.33(0.75\times10^{-3}M)$	1:2.25
4	10,a	$10.3(7.5\times10^{-3}M)$	$20.0(7.5\times10^{-3}M)$	1:1.94
5	10,b	$9.7(1\times10^{-2}M)$	$20.0(1\times10^{-2}M)$	1:2.06

Structure of the complex :

The structure of Uo_2-2-hydroxy-5-methyl acetophenone may be written as :



on the assumption that there is coordination through the carbonyl oxygen and replacement of the phenolic hydrogen by the uranyl ion.

Th(IV)-2-hydroxy-5-methyl acetophenone complex :

2-Hydroxy-5-methyl acetophenone reacts with thorium(IV) ions in aquous medium to give instantaneously a yellow coloured, soluble complex.

Application of Vosburgh and Cooper's method demonstrated the existence of only one complex having λmax at 375 mμ (Fig.11).

The complex was found to be stable in the pH range 2.5-4.5 and the solution attained the maximum colour intensity at pH 3.5 (Fig.12).

From both Job's method of continued variation (Figs.13-15) and slope ratio method (Fig.16), the composition of the complexes was found to be 1:1 (Th(IV):H.M.A).

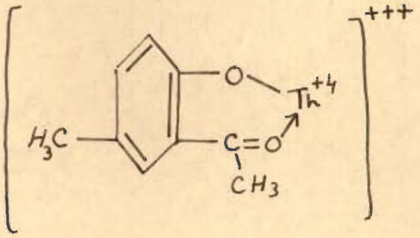
The value of formation constant K was found to be 2.66×10^2. The free energy of formation $-\Delta F$ was calculated to be 3.351 Kcals at 30°C.

Conductometric titrations (both direct and reverse) were also carried out to investigate the composition of the complex. The points of intersection in the conductance curves (Figs.18,19) gave a ratio of 1:1 for thorium and H.M.A in the complex, thereby confirming the results of spectrophotometry. The results of the titrations are summarized below :

S.No.	Fig.& curve	Vol.of $Th(No_3)_4$ (ml.)	Vol.of H.M.A (ml.)	Mole ratio Th/H.M.A
1	18,a	20.0(1.25×10^{-3}M)	18.88(1.25×10^{-3}M)	1:0.94
2	18,b	20.0(2×10^{-3}M)	19.2 (2×10^{-3}M)	1:0.96
3	19,a	19.0(4×10^{-3}M)	20.0 (4×10^{-3}M)	1:1.05
4	19,b	19.7(6×10^{-3}M)	20.0 (6×10^{-3}M)	1:1.002

Structure of the complex :

The structure of the thorium(IV)-2-hydroxy-5-methyl acetophenone complex may be written as :



ABSORPTION CURVES OF $UO_2(NO_3)_2$

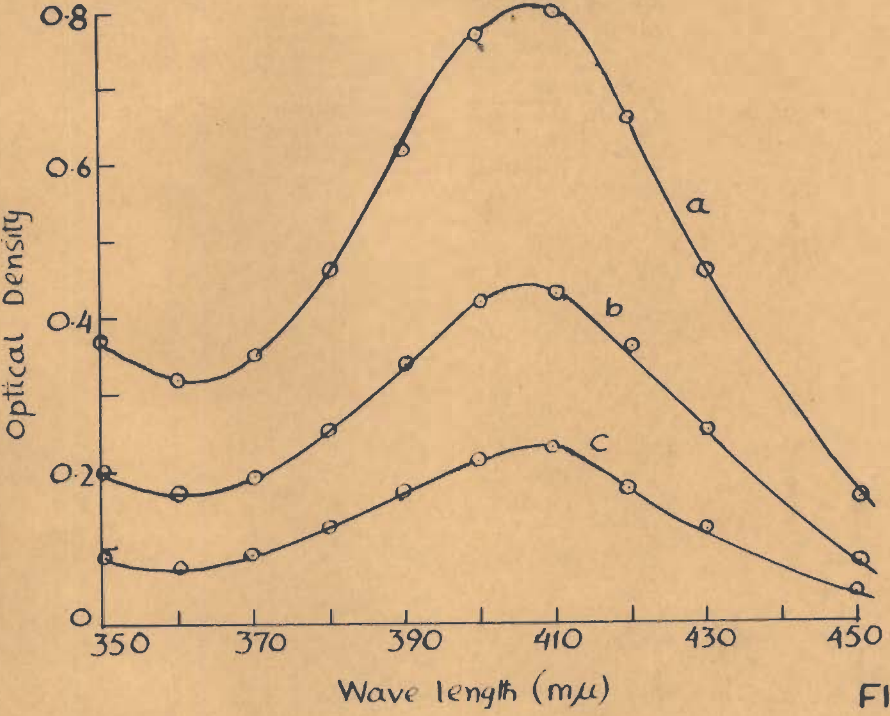


FIG. 1

ABSORPTION CURVES OF H.M.A.O.

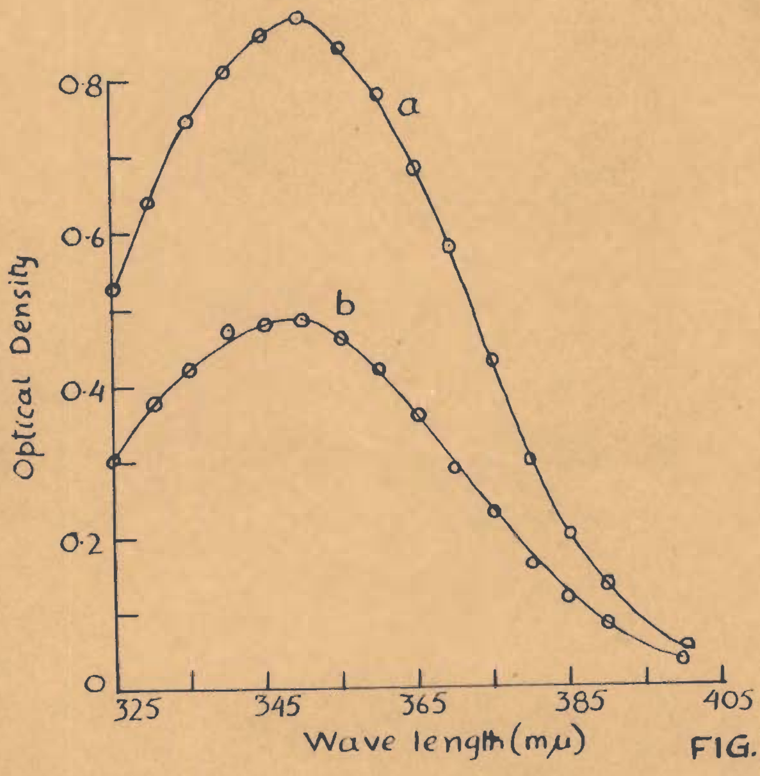


FIG. 2

UO_2-H.M.A. COMPLEX.

VOSBURGH COOPER'S METHOD

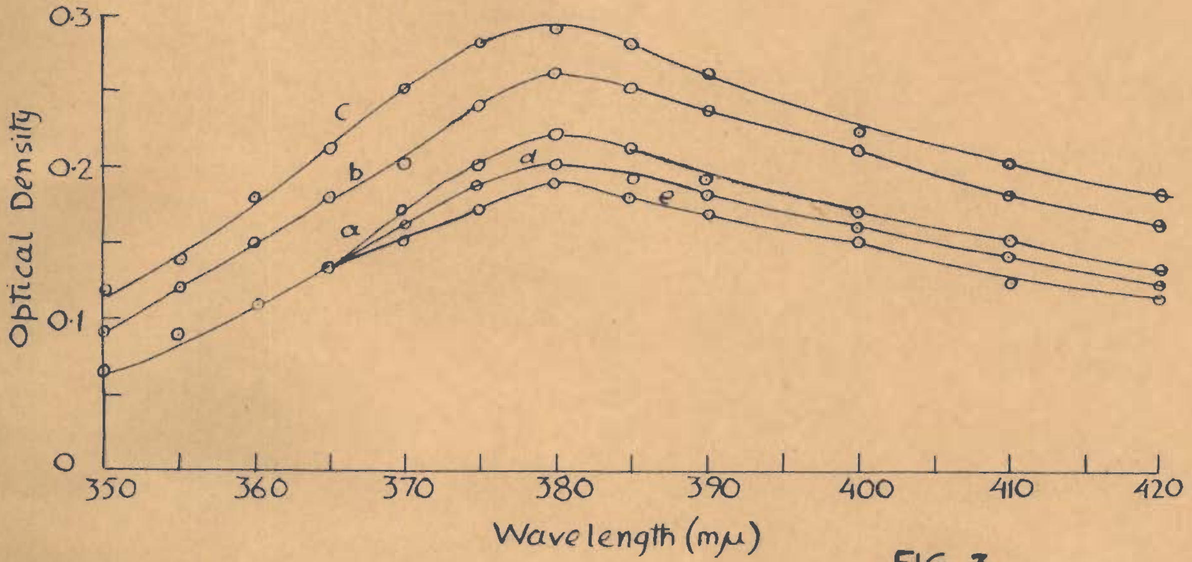


FIG. 3

INFLUENCE OF pH ON STABILITY OF COMPLEX

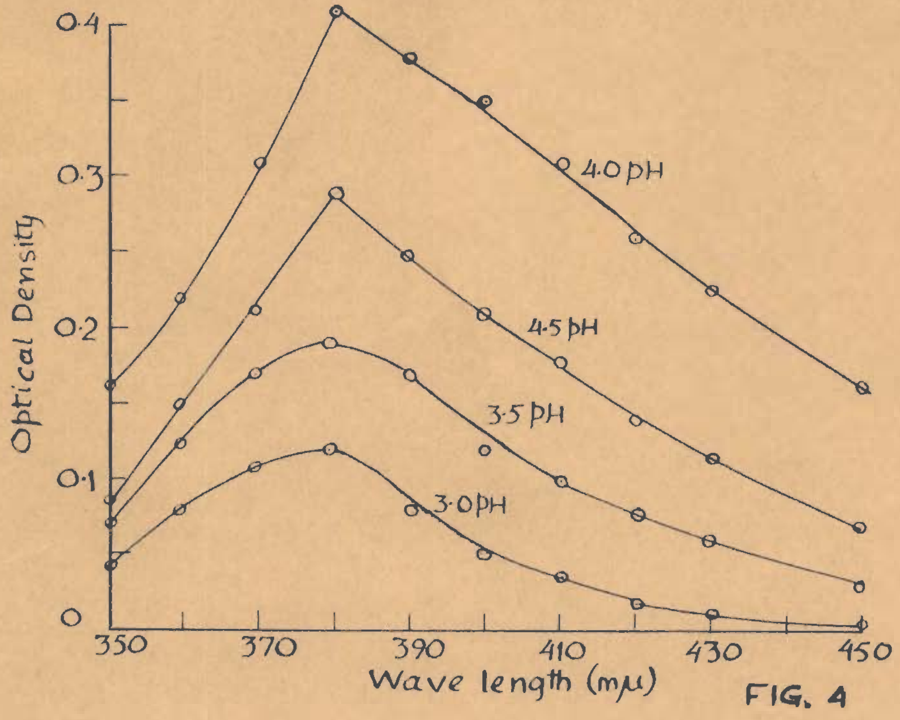


FIG. 4

JOB'S METHOD

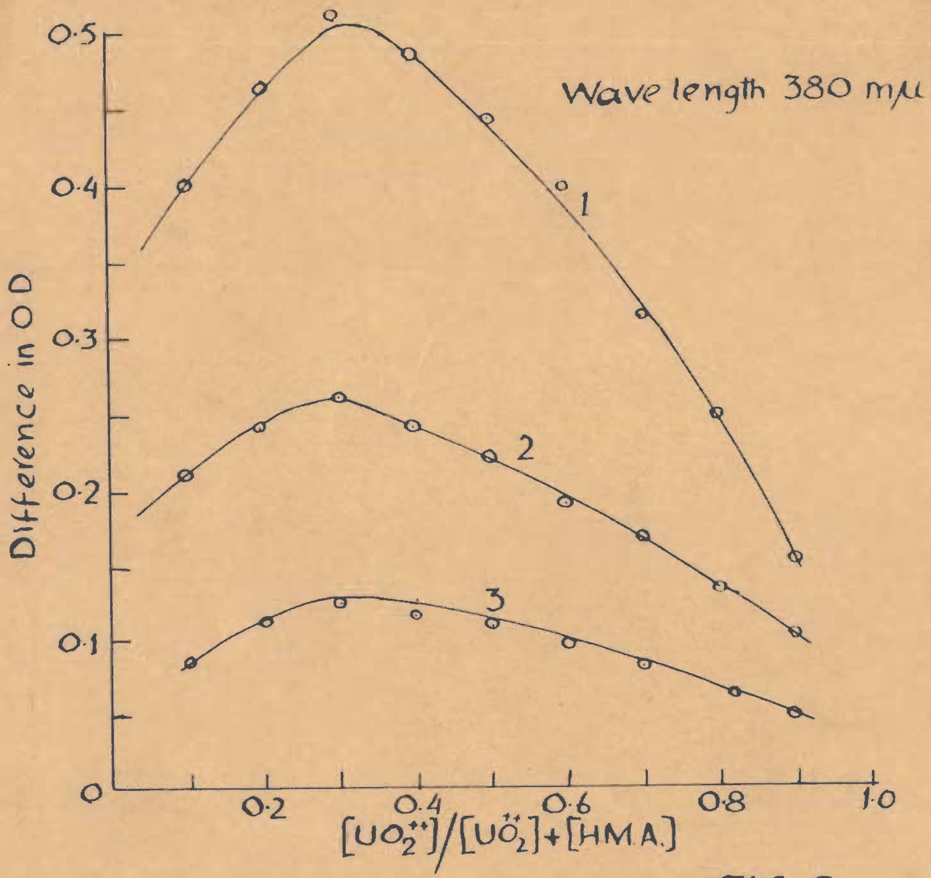


FIG. 5

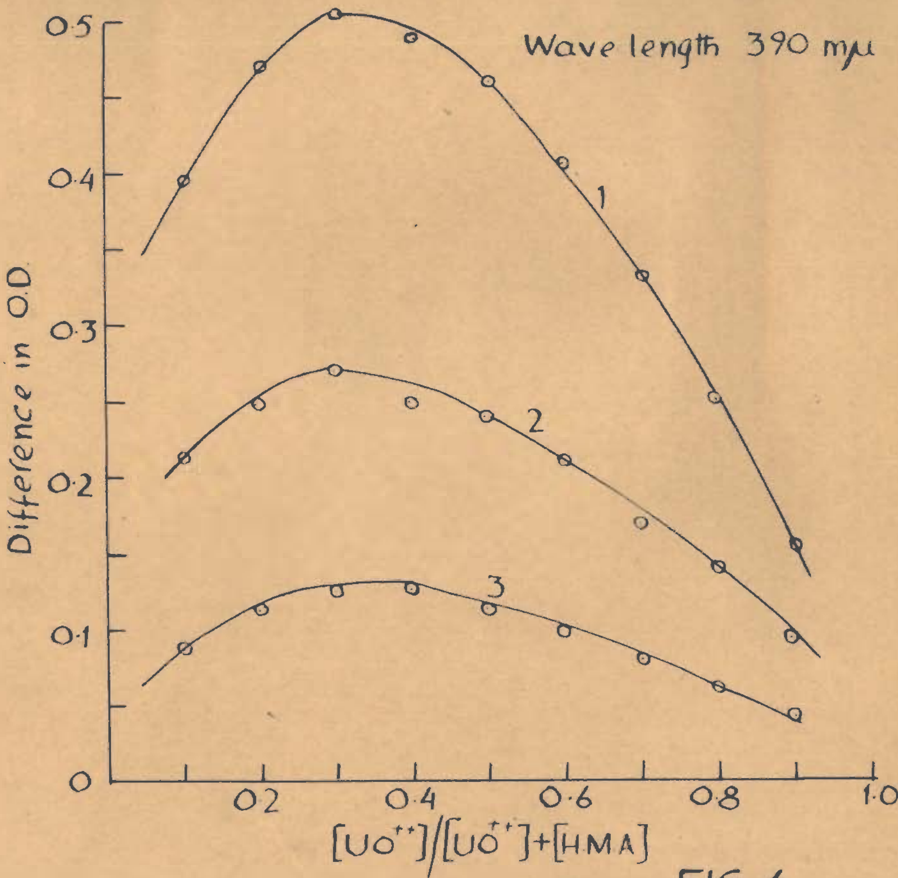


FIG. 6

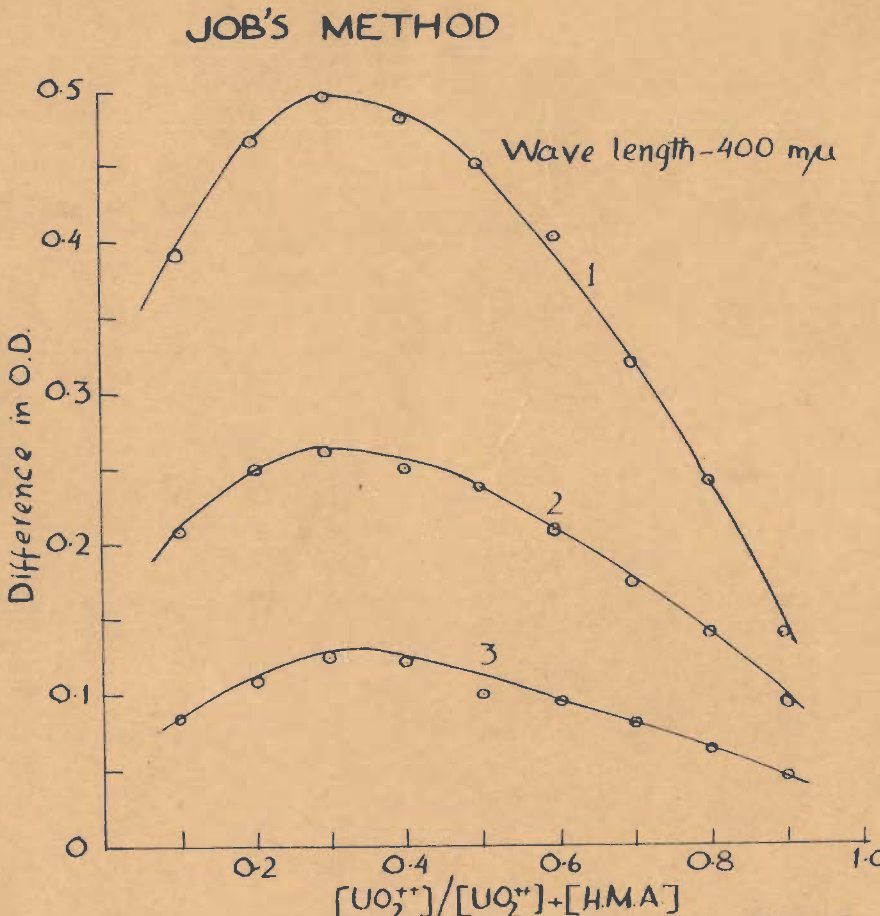

JOB'S METHOD

FIG. 7

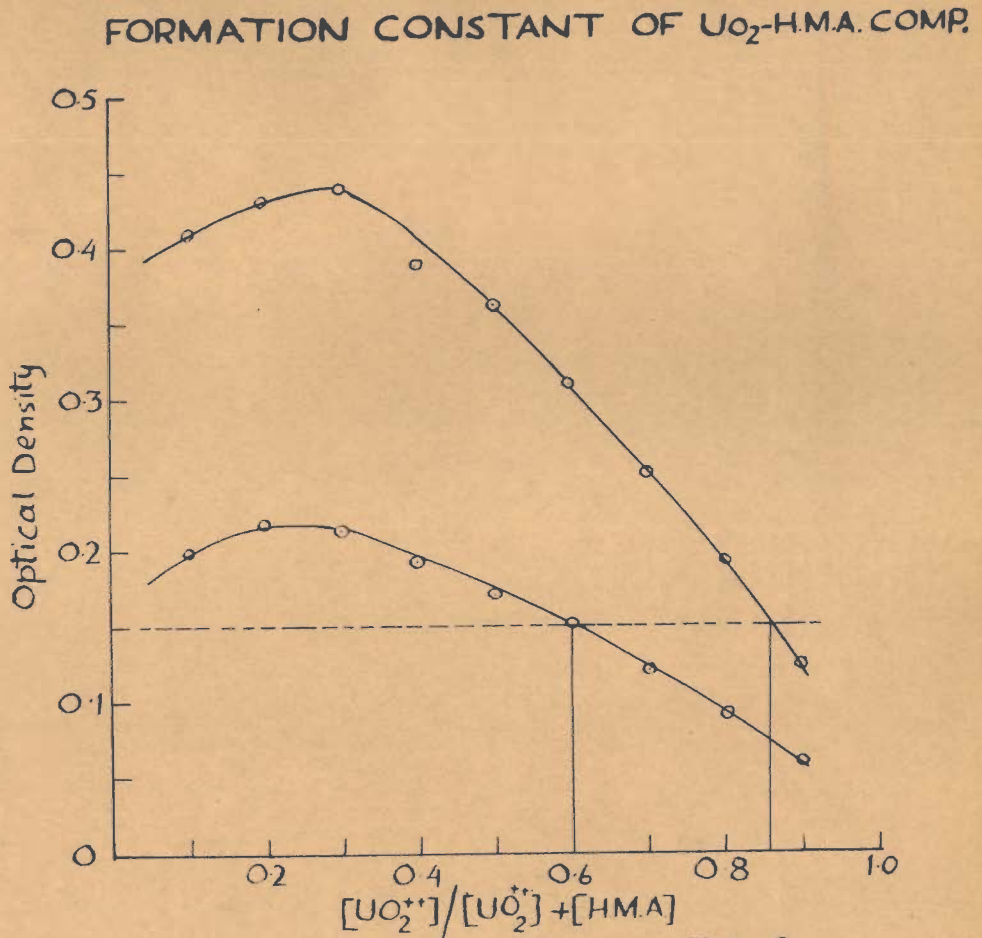

FORMATION CONSTANT OF UO$_2$-H.M.A. COMP.

FIG. 8

CONDUCTOMETRIC TITRATIONS

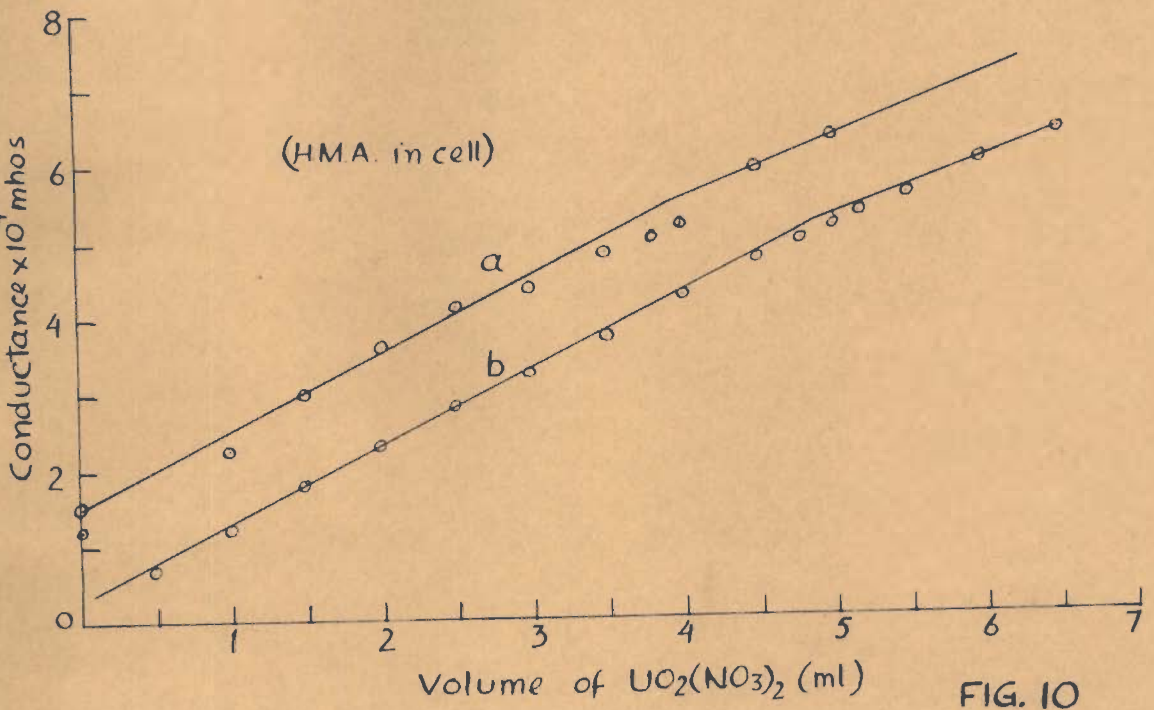


FIG. 10

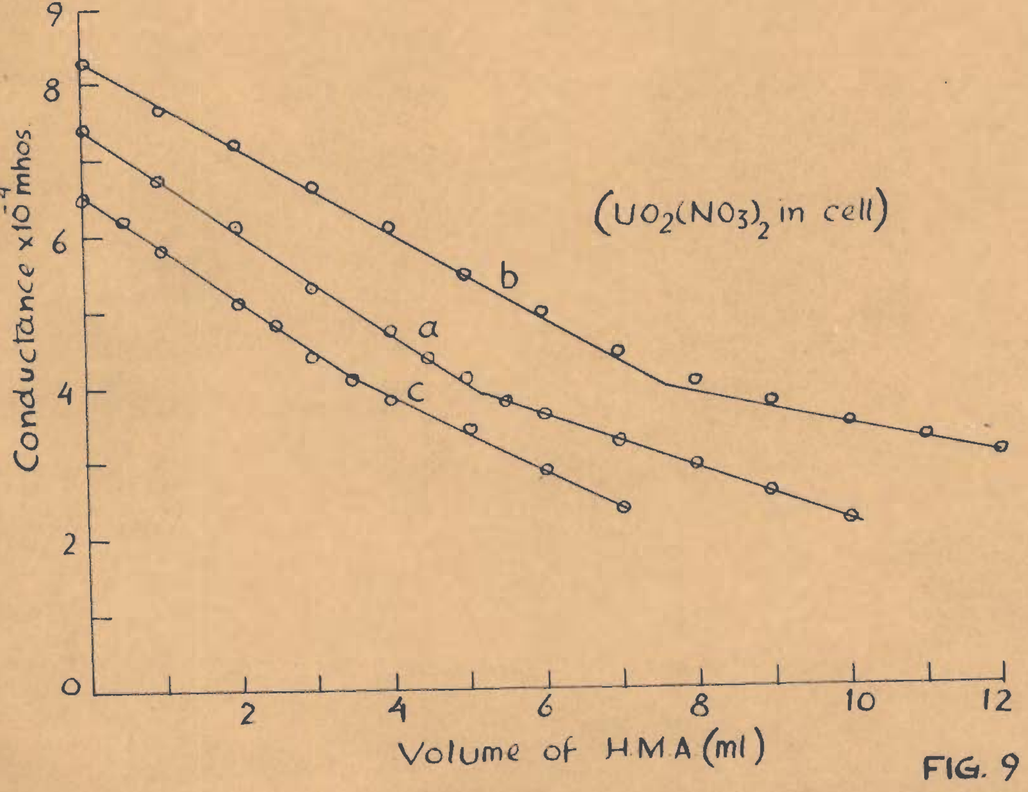


FIG. 9

Th-H.M.A. COMPLEX.

VOSBURGH COOPER'S METHOD

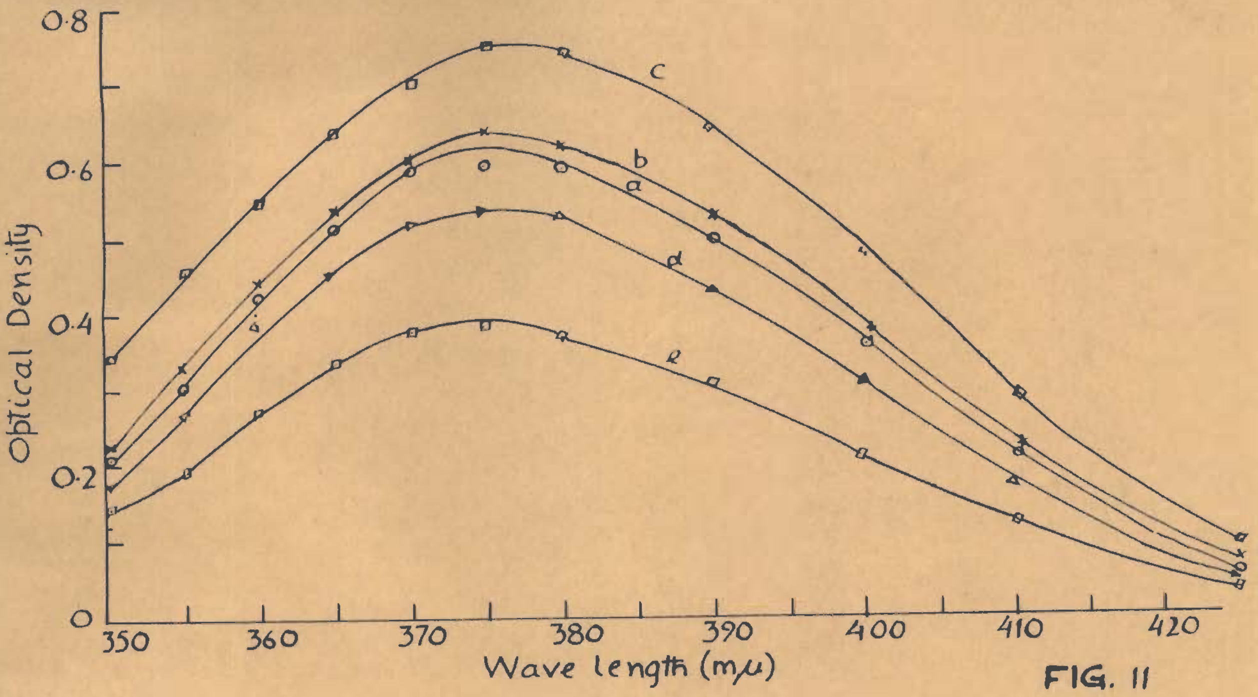


FIG. 11

INFLUENCE OF pH ON STABILITY OF COMPLEX

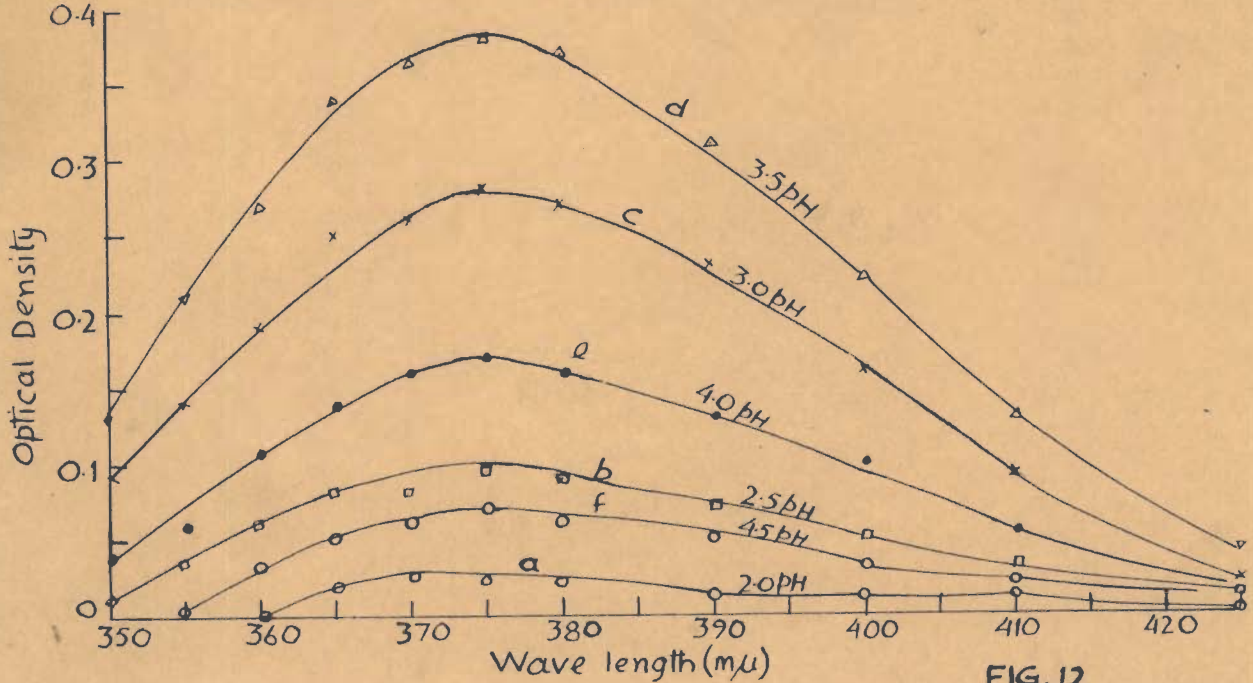


FIG. 12

JOB'S METHOD

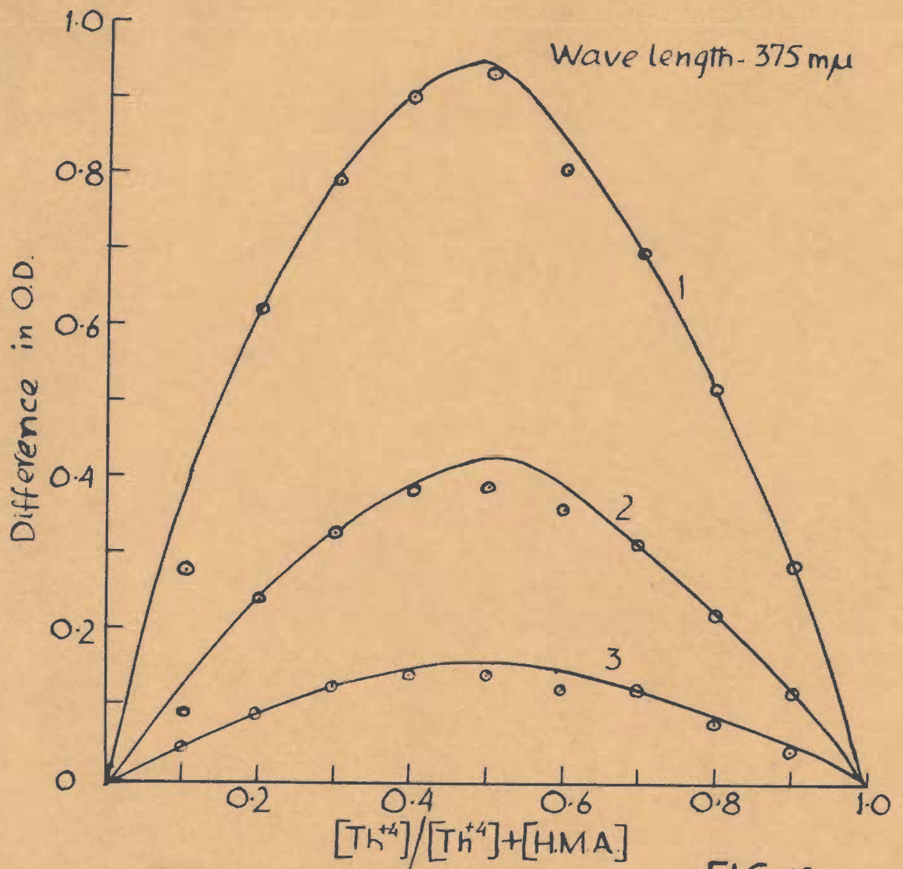


FIG. 13

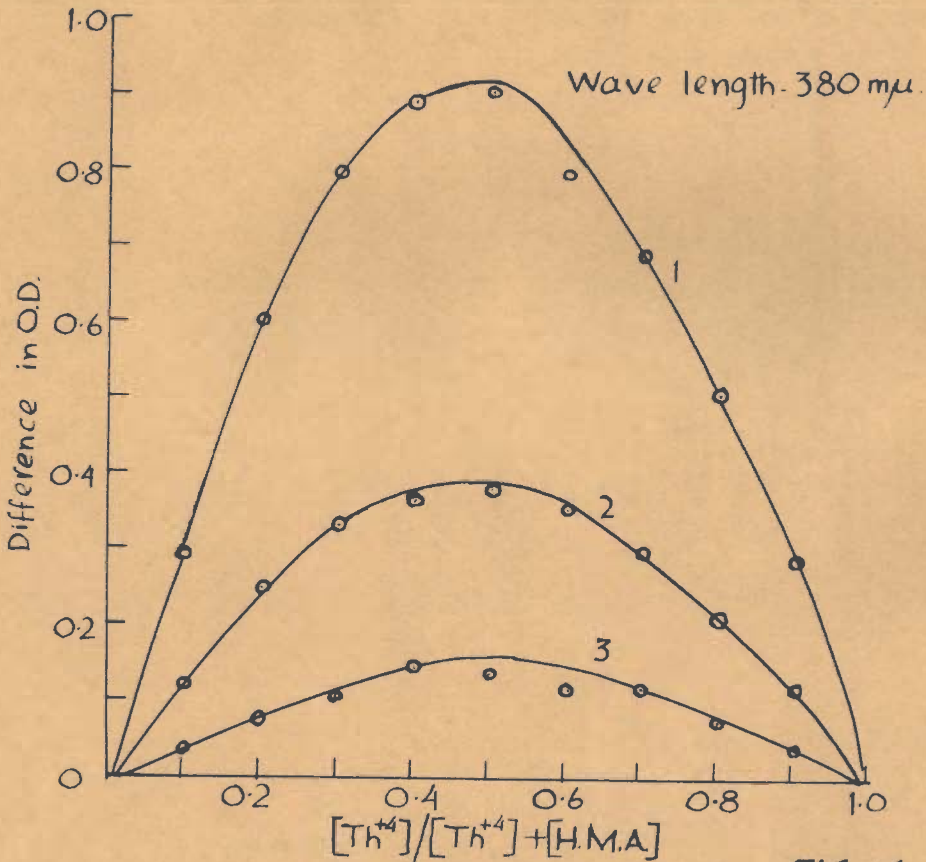
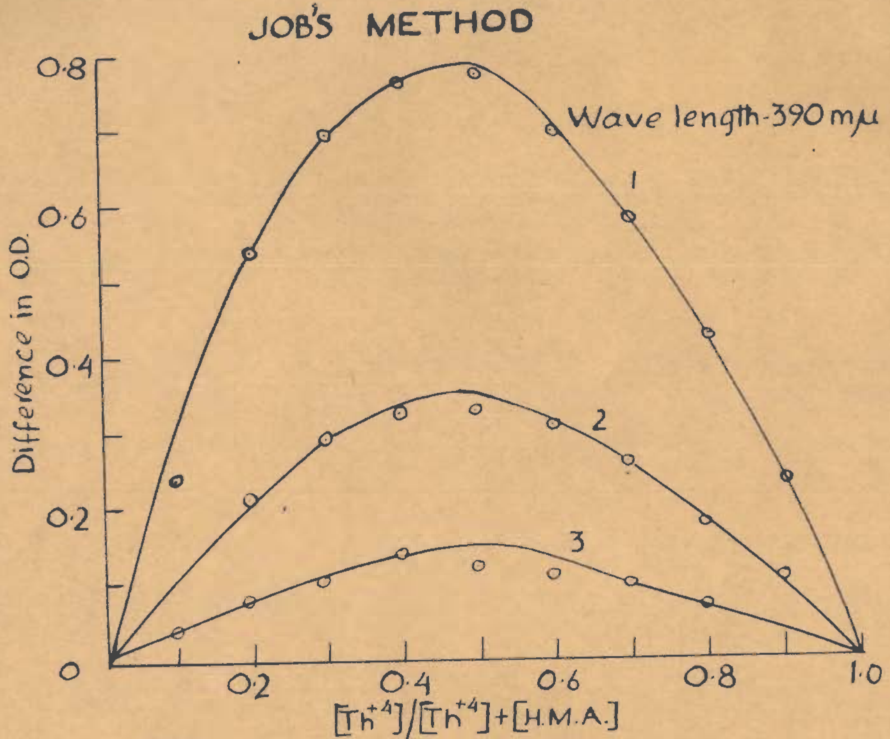
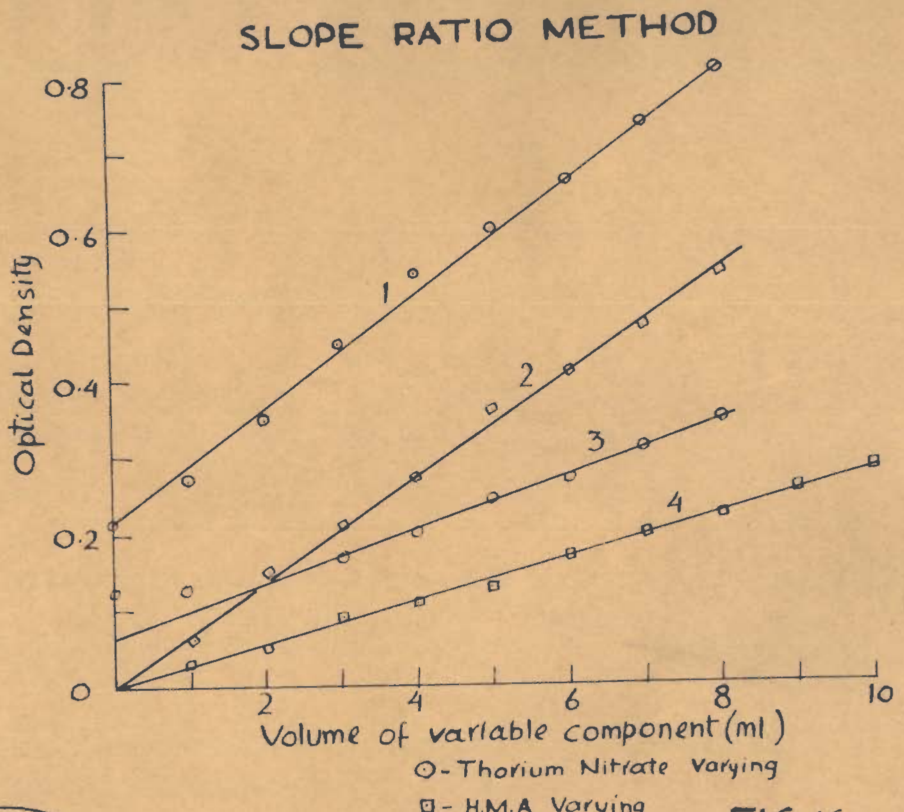


FIG. 14



JOB'S METHOD

FIG. 15



SLOPE RATIO METHOD

FIG. 16

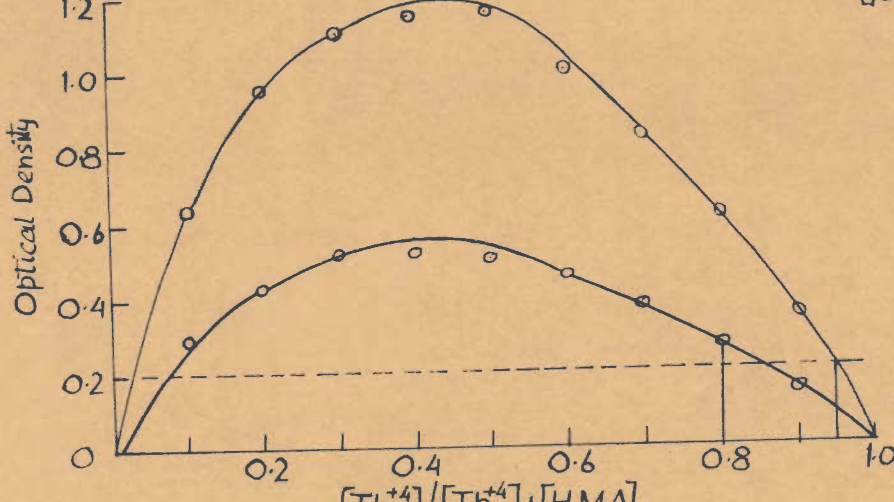


FIG 17

FORMATION CONSTANT OF Th-H.M.A. COMPLEX

CONDUCTOMETRIC TITRATIONS

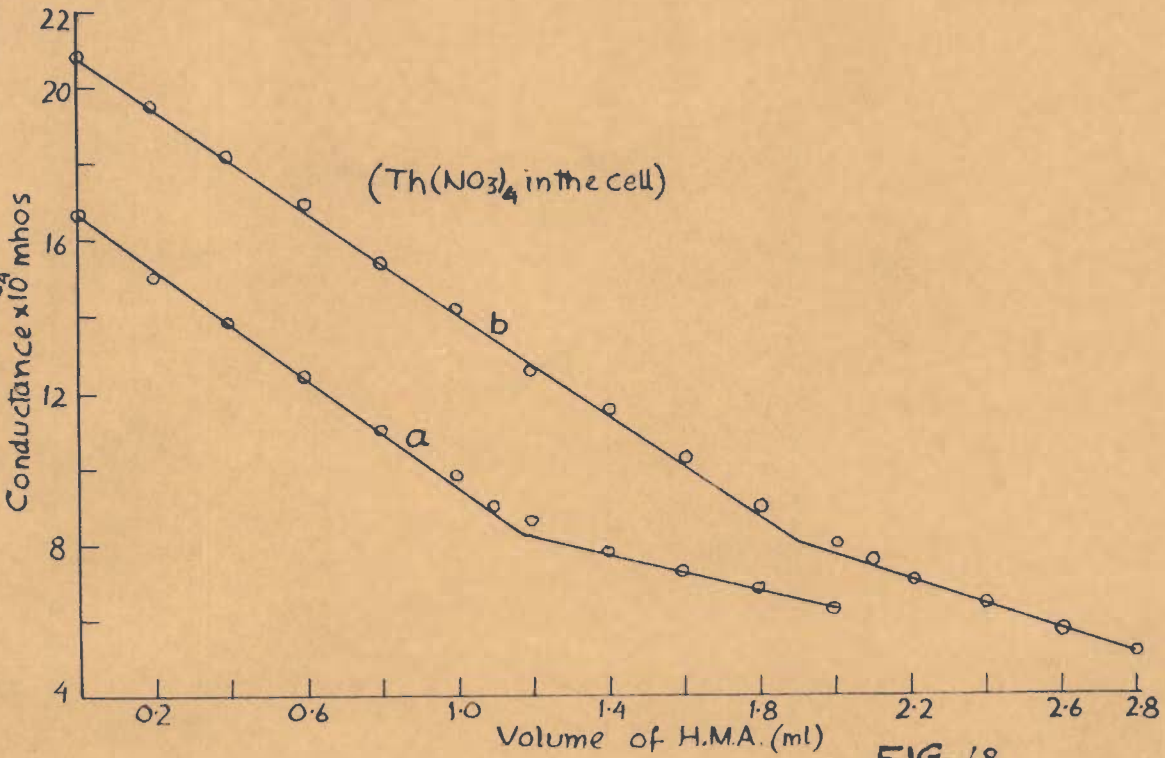


FIG. 18

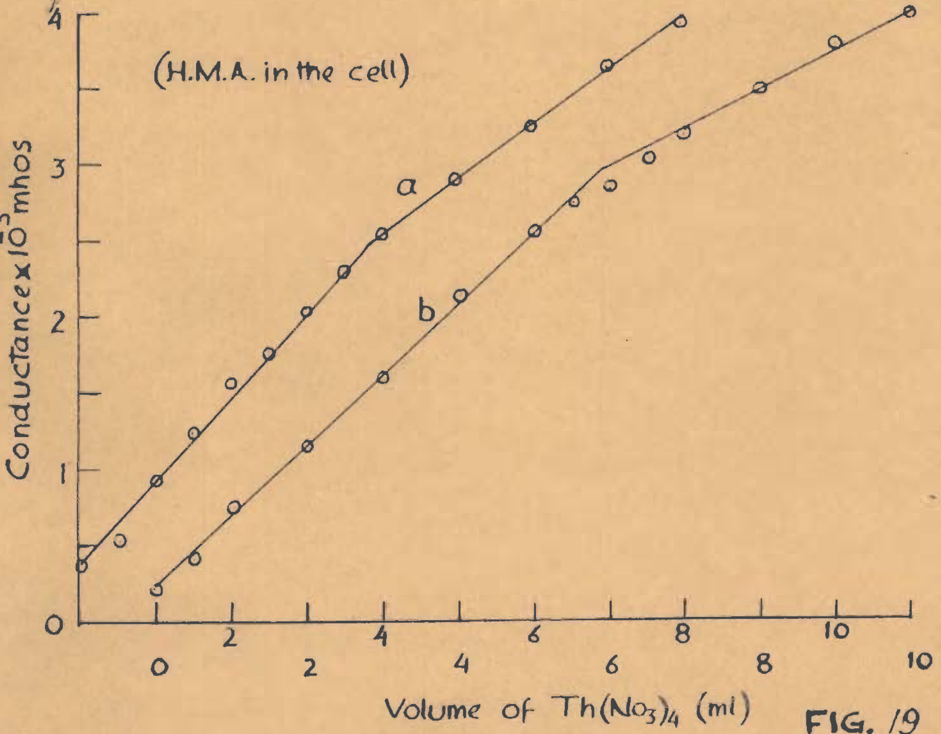


FIG. 19

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RESUME

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RESUME

Amongst the nitrogen bearing ligands offering sites simultaneously for salt formation and coordination, hydroxyaldoximes deserve special mention. In these compounds, the hydroxyl group is so located with respect to the nitrogen atom of the oxime group that six-membered rings are formed with metals. Many of these metallic salts are insoluble in water and consequently adaptable to the detection and determination of numerous cations. In order to increase the selectivity and the sensitivity of these reactions, many derivatives have been prepared and studied.

In the existing literature, the applications of such compounds as analytical reagents have been cited but very little attention has been paid towards the study of their chelation reactions.

In this thesis, the reactions of aromatic hydroxy ketoximes with metals have been discussed. The compounds chosen for such studies were the oximes of o-hydroxy - acetophenone, 2-hydroxy-5-methyl acetophenone and 2,5-dihydroxy-acetophenone and the metallic ions were MoO_4^{--}, Cu^{++}, Pd^{++} and Ni^{++}.

The chelation reactions of the hydroxyketone, viz., 2-hydroxy-5-methyl acetophenone with radioactive elements like uranium and thorium(IV) were also investigated. The interesting aspect about the choice of these metals was that soluble as well as insoluble complexes were

available, thereby offering a wide range of physico-chemical methods which could be employed for investigating their nature and composition.

Mo(VI)-hydroxy-acetophenoneoximes :-

The reactions of Mo(VI) with hydroxy-acetophenoneoximes have not been investigated so far, either from the structural or analytical point of view. The reactions of this metal with the oximes of o-hydroxy-acetophenone, 2-hydroxy-5-methyl-acetophenone and 2,5-dihydroxy-acetophenone were considered as typical cases for investigations.

The following colour reactions were obtained on mixing the reactants :

(i) Mo(VI)+ o-hydroxy-acetophenoneoxime - bright yellow solution.

(ii) Mo(VI)+ 2-hydroxy-5-methyl-acetophenoneoxime - bright yellow solution.

(iii) Mo(VI)+ 2,5-dihydroxy-acetophenoneoxime - orange-yellow solution.

Spectrophotometric methods were employed to determine their nature, composition and stability. Vosburgh and Cooper's method demonstrated the formation of only one complex (pp.54,97,130) in all these cases. The complexes of o-hydroxy-acetophenoneoxime and 2-hydroxy-5-methyl-acetophenoneoxime had maximum absorption at 345 mµ while that of 2,5-dihydroxy-acetophenoneoxime had maximum absorption at 370 mµ.

Job's method of continued variation and slope ratio method showed the composition of these complexes as 1:2 (MoO_4^{--}: the complexing agent) (pp.55,97,98,130).

Further confirmation of their composition was obtained from both direct (MoO_4^{--} in the cell) and reverse (complexing agent in the cell) conductometric titrations. In all cases the plots of conductance against volume of the titrant, gave inflexion points (pp.56,98,131) corresponding to the combining ratio of 1:2 for MoO_4^{--} and the complexing agent.

The complexes were also isolated through crystallization and analysed for their molybdenum and nitrogen contents. The results of the analysis corresponded to their molecular formulae :

$(C_8H_8O_2N)_2MoO_2$....for Mo(VI)-o-hydroxyacetophenoneoxime.

$(C_9H_{10}O_2N)_2MoO_2$...for Mo(VI)-2-hydroxy-5-methyl acetophenoneoxime.

$(C_8H_8O_3N)_2MoO_2$....for Mo(VI)-2,5-dihydroxy-acetophenoneoxime.

The formation constants of these complexes were determined from the absorbance data of Job's method using the modified Anderson's method. The values of K and those of free energy of formation -△F were found to be :

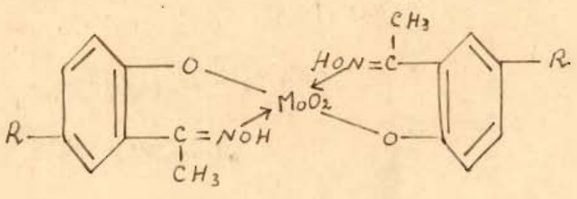
Complex	Value of K	-△F
Mo(VI)-o-hydroxyacetophenoneoxime	9.3×10^{8}	12.39 KCals at30°
Mo(VI)-2-hydroxy-5-methyl-acetophenoneoxime	4.87×10^{8}	12.0 KCals at 30°
Mo(VI)-2,5-dihydroxy-acetophenoneoxime	1.39×10^{10}	14.02 KCals at 30°

Mo(VI)-2,5-dihydroxy-acetophenoneoxime should, therefore, be the most stable of all of them.

Since in all these cases 1:2 complexes were formed, the molybdenum complex of the parent member, viz., o-hydroxy-acetophenoneoxime, was therefore, subjected to infrared studies (pp.58) in order to know the structure of these complexes.

The infrared spectrum of the complex had shown complete absence of the phenolic (OH) band as against that of o-hydroxy-acetophenoneoxime at 3350 cm^{-1}. This observation provided enough evidence of the fact that the phenolic hydrogen was replaced by the metal. Furthermore the stretching frequency of C=N- of the oxime group got shifted from 1620 cm^{-1} (for the ligand) to 1550 cm^{-1} in the complex. From this marked shift in the C=N- stretching frequency, it was concluded that the metal was also coordinated to the ligand through the nitrogen of C=N-.

The above mechanism, viz., the replacement of phenolic hydrogen by molybdenum which in turn is coordinated through the nitrogen of C=N-, resulting in chelate formation, should also hold good in the molybdenum complexes of the other two compounds. The following structure was, therefore, assigned to these complexes.



[R = H, OH, CH$_3$]

2,5-dihydroxy acetophenoneoxime as a colorimetric reagent for the estimation of molybdenum :

o-Hydroxy-acetophenoneoxime and its methyl derivative namely 2-hydroxy-5-methyl-acetophenoneoxime can be used as colorimetric reagents for the estimation of molybdenum as both these compounds give stable, bright yellow solutions with molybdenum. But 2,5-dihydroxy - acetophenoneoxime has been found to be more suitable for this purpose, due to its greater solubility in aquous - alcoholic medium and higher sensitivity in comparison to the corresponding o-hydroxy-acetophenoneoxime and its methyl derivative.

The orange-yellow solution showed maximum absorption at 370 mμ(pp.165) and this wave length was, therefore, chosen for colorimetric measurements. The complex was found to be stable in the pH range 2.0-4.5 (pp.130) and the solution acquired the maximum colour intensity in the pH range 2.5-4.0 (pp.165).

In order to obtain maximum colour intensity of the solution, about 40-50 folds excess of the reagent were required (pp.166). The colour system obeyed Beer's law over the concentration range of 2-20 p.p.m of molybdenum (pp.166). The colour was found to be stable upto 40°C; beyond this temperature the colour started fading away. However, the solution regained its original colour intensity when cooled to the temperature below 40°C.

Visual colorimetry showed that solutions having molybdenum concentration of 1.0 p.p.m or above were visually distinguishable from the reagent.

The effect of foreign ions on the estimation of molybdenum was also investigated. Assuming ± 2 % change in the observed absorbance of the solution containing foreign ion from that of the solution containing no foreign ion as interference limit, it was found that Al^{+++}, Cr^{+++}, Fe^{+++} and Vo^{++} interferred strongly and must be eliminated prior to estimation. Ions like Cu^{++}, Pd^{++}, Pb^{++}, Ti^{++++}, Wo_4^{--}, Ce^{+++}, oxalate, tartrate and citrate did not interfere when present within 1-3 p.p.m whereas the other ions showed no interference at all (pp.167,168).

Molybdenum(VI) may thus be determined in commercial samples, ores, minerals etc. by this method (pp.169). This method has the advantage that it neither requires the reduction of Mo(VI) to Mo(V) nor extraction of the complex with organic solvents and the colour intensity of the solution does not change for long periods.

Reactions of Cu(II), Pd(II) and Ni(II) with hydroxy - acetophenoneoximes :

Poddar (Z.Anal.Chem. 154, 254, 1957) drew attention to the possible use of o-hydroxy-acetophenoneoxime as a precipitating reagent for the gravimetric estimation of heavy metals. The structures of the resulting complexes have not, so far, been investigated. Besides, the reactions of the metal ions with 2,5-dihydroxy-acetophenoneoxime, have not yet been studied either from the chemical or analytical point of view. Investigations in these directions were, therefore, undertaken.

The reactions of Cu(II), Pd(II) and Ni(II) with o-hydroxy-acetophenoneoxime and its derivatives are given below :

Reaction	Colour of the precipitate	Incipient pH
(i) Cu^{++}+ o-hydroxyacetophenoneoxime	dirty-white	2.1-8.0
(ii) Pd^{++}+ "	yellowish	1.0-4.5
(iii) Ni^{++}+ "	green	5.0-9.0
(iv) Cu^{++}+ 2-hydroxy-5-methyl-acetophenoneoxime	dirty-white	1.5-8.0
(v) Pd^{++}+ "	yellow	1.0-5.0
(vi) Ni^{++}+ "	light-green	4.5-9.0
(vii) Cu^{++}+ 2,5-dihydroxy-acetophenoneoxime	light-brown	2.0-8.0
(viii) Pd^{++}+ "	yellow	2.5-6.0
(ix) Ni^{++}+ "	green	6.0-10.0

Composition and structure of the complexes :

Evidence of 1:2 complex (metal: the complexing agent) formation in all these reactions, was available on the basis of the results of conductometric (pp.60,99,101, 103,132,135,138) and amperometric (pp.61,100,102,103,171, 175,179) (both direct and reverse) titrations between the metal solutions and the complexing agents. Their composition was further confirmed on the basis of the determination of their metal and nitrogen contents. They were found to have the following molecular formulae :

$(C_8H_8O_2N)_2M$ ....for metal complexes of o-hydroxy-acetophenone-oxime.

$(C_9H_{10}O_2N)_2M$....for metal complexes of 2-hydroxy-5-methyl-acetophenoneoxime.

$(C_8H_8O_3N)_2M$ ....for metal complexes of 2,5-dihydroxy -acetophenoneoxime.

(M = Cu, Pd, Ni)

The structures of these complexes were established by studying their infrared spectra (pp.62,100,102, 104,134,137,139). Some of the important stretching frequencies of the complexing agents and their metal complexes are enlisted below :

Compound	ν OH(phenolic) (cm^{-1})	νC=N- (cm^{-1})
o-hydroxyacetophenoneoxime	3350	1620
Cu(II)-o-hydroxyacetophenoneoxime	-	1560
Pd(II)-o-hydroxyacetophenoneoxime	-	1540
Ni(II)-o-hydroxyacetophenoneoxime	-	1550

Compound	νOH (phenolic) (cm^{-1})	νC=N- (cm^{-1})
2-hydroxy-5-methyl-acetophenoneoxime	3340	1590
Cu(II)-2-hydroxy-5-methylacetophenone-oxime	-	1540
Pd(II)-2-hydroxy-5-methylacetophenone-oxime	-	1535
Ni(II)-2-hydroxy-5-methylacetophenone-oxime	-	1545
2,5-dihydroxy-acetophenoneoxime	3290	1590
Cu(II)-2,5-dihydroxy-acetophenoneoxime	3260	1550
Pd(II)-2,5-dihydroxy-acetophenoneoxime	3270	1560
Ni(II)-2,5-dihydroxy-acetophenoneoxime	3260	1550

The complete absence of the phenolic(OH) band in the metal complexes of o-hydroxy-acetophenoneoxime and 2-hydroxy-5-methyl acetophenoneoxime, points to the replacement of the phenolic hydrogen by the metal. From the lowering in the C=N- frequencies in all the metal complexes against those in the complexing agents, it can be inferred that the metal is also coordinated through the nitrogen of C=N-.

The above mechanism involving the removal of proton from the phenolic (OH) group of the hydroxy-acetophenon oximes was also confirmed on the basis of the results of the pH metric titrations. 2,5-dihydroxy-acetophenoneoxime was taken as a typical case for carrying out these titrations (pp.132,135,138) using KOH as the titrant. It was observed that with the metal solutions containing 2 equivalents of the ligand, only one inflexion point corresponding to 2 equivalents of KOH, was obtained, indicating thereby that

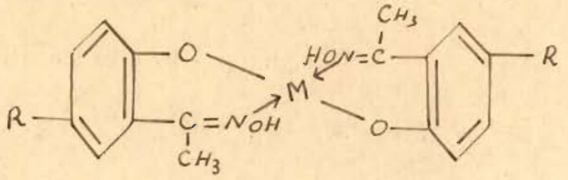
2 H^+ were evolved during the reaction.

$$M^{++} + 2HL + 2OH^- \longrightarrow M(L) + 2H_2O$$

(HL stands for the ligand)

The inflexion point was found to be independent of the amount of the ligand beyond 2 equivalents.

On the basis of the above physico-chemical evidence, the following structure may be assigned to these metal complexes :



[R = H, OH, CH3
M = Cu, Pd, Ni]

Amperometric determination of copper :

During the course of amperometric titrations of copper(II) against 2,5-dihydroxy-acetophenoneoxime(pp.153), it was observed that appreciable changes in the diffusion current of copper occurred on addition of the titrant. Gravimetric estimations of a few samples of copper with this compound also showed that the reaction was quantitative in the pH range 4.5-8.5. In view of the above observations, it was proposed to explore the possibility of employing amperometric titrations for the determination of copper.

The optimum conditions required for carrying out such amperometric determinations were kept as follows :

(i) The pH of the medium was maintained at 4.6 by using 0.2N sodium acetate-acetic acid buffer which also served as supporting electrolyte.

(ii) 0.01% gelatine solution was used as maximum suppressor.

(iii) A potential of -0.15 volts vs.S.C.E. was applied during the titration.

Copper solutions of varying concentrations (0.315-3.15 mg.) were successfully titrated within ± 1 % error (pp.172).

The estimations of copper (1.26 mg.) were also carried out in the presence of foreign ions. It was found that ions like Ag^{+}, Fe^{+++}, Pd^{++}, Ti^{++++}, Vo^{++} interferred strongly while the others did not hinder (pp.173).

Amperometric determination of palladium :

The reaction between palladium and 2,5-dihydroxyacetophenoneoxime proceeds quantitatively in the pH range 2.5-6.0. During preliminary experiments, it was found that amperometric titrations of palladium against 2,5-dihydroxyacetophenoneoxime could also be used for the determination of the metal.

The following conditions were maintained during the titrations :

(i) The solution of sodium acetate-acetic acid buffer (pH 4.0) was used as a supporting electrolyte.

(ii) Gelatine (0.01%) solution was used as maximum suppressor.

(iii) A potential of -0.4 volts vs.S.C.E. was applied during the titrations.

Solutions containing 0.532-5.32 mg. of palladium were titrated. It was found that solutions containing 1-4.0 mg. of the metal could be accurately determined within ± 1 % error (pp.176).

The influence of foreign ions on the estimation of the metal (1.064 mg.) was also studied. It was found that Ag^{+}, Fe^{+++}, Ti^{++++}, Vo^{++}, Cu^{++} interferred strongly whereas the presence of other ions did not hinder in the accurate determination of the metal (pp.177).

Amperometric determination of nickel :

The quantitative precipitation of the metal as nickel-2-5-dihydroxy-acetophenoneoxime occurs in the pH range 6.0-10.0.

Amperometric determination of nickel was carried out by titrating solutions (containing 0.587-2.935 mg.) of nickel against 2,5-dihydroxy-acetophenoneoxime.

The pH of the solution was maintained at 9.0 by using ammonia-ammonium chloride buffer which also served as a supporting electrolyte. A solution of 0.01% gelatine was used as a maximum suppressor. A potential of -1.1 volts vs.S.C.E. was applied during the titrations. It was found that the solutions containing 1-3.0 mg. of nickel may be accurately determined within ± 2 % error (pp.179).

The effect of diverse ions on the estimation of nickel could not be studied due to the formation of their hydroxides or insoluble chelates with the reagent in the basic medium.

Uranium and thorium complexes of 2-hydroxy-5-methylacetophenone :

Uranyl and thorium ions react instantaneously with 2-hydroxy-5-methyl acetophenone to give soluble, orange and yellow coloured complexes respectively. The complexes are highly stable and their colour intensity does not fade even on keeping for longer periods.

The composition of these complexes was determined by both spectrophotometric and conductometric methods.

Vosburgh and Cooper's method demonstrated the existence of only one complex in both the cases (pp.198,200).

The uranyl complex was found to be stable in the pH range 3.0-4.5 (pp.198) while the Th(IV) complex in the pH range 2.5-4.5 (pp.200).

Job's method of continued variation revealed the existence of 1:2 (pp.198) and 1:1 (pp.200) complexes in the case of uranyl and thorium(IV) respectively.

Conductometric titrations, both direct(metal solution in the cell) and reverse (ligand in the cell) also gave inflexion points corresponding to 1:2 (pp.199) and 1:1 (pp.201) (metal:ligand) combining ratios in uranyl and thorium(IV) complexes respectively.

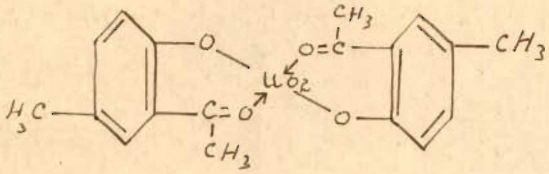
The formation constants of the complexes were determined by Anderson's modified method. The values of K and - △F, the free energy of formation, were found to be :

Uo$_2$-2-hydroxy-5-methyl-acetophenone: $K = 1.49 \times 10^{7}$, - △F=9.91 KCals at 30°C.

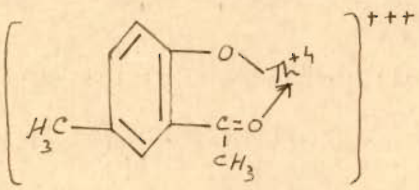
Th(IV)-2-hydroxy-5-methylacetophenone: $K = 2.66 \times 10^{-2}$, - F=3.351 KCals at 30°C.

The complexes could not be isolated and hence their chemical analysis and I.R. spectra could not be recorded.

The following structures may be suggested to these complexes :



Uo$_2$-2-hydroxy-5-methyl-acetophenone



Th(IV)-2-hydroxy-5-methyl-acetophenone.