SOLVENT EXTRACTION OF SOME TRANSITION METAL CHELATES

A THESIS
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CHAPTER I : INTRODUCTION

Historical

The development of solvent extraction of metals as a popular analytical technique began with the introduction of the selective and sensitive chelating agent 'dithizone' by H. Fischer in 1925.[1] Microgramme amounts of copper, zinc, mercury, etc. could be determined by extraction of their dithizonates into chloroform or carbon tetrachloride, followed by measurement of the optical absorbance of these extracts. Subsequently, a number of other chelating agents such as cupferron,[2] dimethylglyoxime,[3] 8-hydroxyquinoline,[4] and sodium diethyldithiocarbamate[5] were used in the extraction-photometric determination of several metals. The scope of solvent extraction in analysis is not, however, restricted to the extraction-photometry of chelate complexes. Many complexes other than chelates can also be used for this purpose: well-known examples are the thiocyanate complexes of iron, molybdenum and tungsten. Secondly, solvent extraction may be used merely as a pre-concentration step,[6-9] the final determination being made by techniques such as atomic absorption,[10] neutron activation or anodic stripping voltammetry. A widely used extractant for this purpose is APDC (ammonium pyrrolidine dithiocarbamate) with MIBK (methyl isobutyl ketone) as the solvent - a combination which is used for the determination of trace elements in waters. It is even possible to separate several elements as anionic complexes or solvated ion-pairs from mineral acid solutions.[13] This facilitates either the determination of the particular element so extracted, or of the elements remaining unextracted in the aqueous phase. A well-known and very early example is the separation of iron from hydrochloric acid solutions by extraction with diethyl ether.[14] A survey showed that solvent extraction is definitely the most popular separation method used in analytical work.[15] The modern developments in the field include the use of organo-phosphorus compounds,[16,17] crown ethers,[18,19] solvent-impregnated resins liquid membranes,[21,22] membrane filters[23] and organic-bonded beads impregnated with suitable complexing agents.[24]

The applications of solvent extraction are not confined to the analytical laboratory. The technique shot into the limelight during World War II in the extraction of uranium from nitric acid solutions with ether and other solvents.[25] Solvent extraction is one of those separation techniques which, originating in the domain of analytical chemistry, later found important commercial applications. Mention may be made of processes for extraction of uranium using high molecular weight amines[26] in nuclear-fuel reprocessing (Purex process) for separation of nickel and cobalt from copper,[27] and selective extraction of copper using the commercial extractant LIX 64N.[28]

Numerous monographs and review articles have been published[6,17,29-56] on both the analytical and the applied aspects of solvent extraction of metals.

Physico-Chemical Aspects of the Solvent Extraction of Metals

Definitions

If the concentrations of a given species in the organic and aqueous phases are C_o and C at equilibrium, the distribution law of Nernst is given by

$$K_d = \frac{C_o}{C} \qquad (1)$$

The equilibrium constant K_d is called the distribution constant for the given species for the given pair of solvents at a given temperature.

In the extraction of a metal into an organic phase, the metal may be present in different forms particularly in the aqueous phase (e.g. as hydroxy complexes, as charged, coordinatively unsaturated complexes etc.). A distribution ratio D is defined by

$$D = \frac{\text{Total concentration of the metal in the organic phase}}{\text{Total concentration of the metal in the aqueous phase}} \quad (2)$$

The distribution ratio is hence an experimental quantity. It is not a constant and varies with the extraction conditions. Often, the parameter of interest is the 'percent extraction' E which describes how much of the metal can be extracted under given conditions with given reagents. The relation between E and D is given by

$$E = \frac{100D}{D + (V_w/V_o)} \quad (3)$$

where V_w and V_o are the volumes of the aqueous and organic phases respectively. When the volumes are arranged to be equal

$$E = \frac{100D}{D + 1} \quad (4)$$

Nature of the Extracted Species

The most easily recognizable inorganic species extracted by an organic solvent are the following:

(i) Neutral molecules such as $HgCl_2$, I_2 and $SbCl_3$

These have a more or less molecular type of structure in the solid state.

(ii) Ion-association systems, which comprise

(a) non-solvated ion-pairs, particularly those involving large ions, such as rubidium polyiodide, caesium tetraphenyl borate or tetraphenylphosphonium tetrachloroaurate, i.e. $[P(C_6H_5)_4]^+ [AuCl_4]^-$;

(b) solvated ion-pairs, as in the extraction of the perchlorates of Co, Ni, Zn, etc. by higher alcohols or of metals such as U and Pu from nitric acid solutions with neutral solvents; (c) anionic complexes, as in the extraction of $FeCl_3$ from aqueous hydrochloric acid by diethyl ether, the extracted species probably being $[Et_2OH]^+ [FeCl_4(Et_2O)_2]^-$.

(iii) Uncharged coordination compounds

The species usually extracted is the uncharged complex in which all the coordinating positions are occupied by the ligand molecules. The most important type is the uncharged chelate; but mixed ligand complexes in which at least some of the coordinating positions are occupied by non-chelating ligands, may also be extractable. The formation of mixed ligand complexes generally leads to synergism in extraction and the subject is discussed later on in this summary.

Factors Governing the Extractability of Chelates

The most important factor governing the extractability of a chelate is its thermodynamic stability. This subject can be found extensively treated in standard texts.[57-60] The relevant information is summarised below.

The chelate stability depends on the nature of the metal atom, the nature of chelating reagent and the stereochemistry of the chelate, these factors being not totally independent of one another. With the same chelating ligand, the chelate stability increases with increasing 'acidity' of the metal ion. An approximate measure of this property is the value of Z^2/r where Z is the charge and r is the effective radius of the cation. Thus the more highly charged cations would in general, tend to form more stable chelates. Existence of inner bonding orbitals (such as the 3d orbitals for the first series of transitional elements) leads to greatly increased chelate stability.

This is often attributed to the higher polarizabilities of these cations. Thus the chelates formed by transitional elements are more stable than those formed by pre-transitional elements (i.e. the 'a' metals) with the same size and charge. A fairly satisfactory correlation for a number of transitional and non-transitional ions is that based on the ionization potential of the metal atom/ion corresponding to the last electron lost. On this basis, the well-known 'Irving-Williams' order of stabilities of the chelates of several divalent metals with EDTA has been drawn up: Ni(II) > Cu(II) > Pb(II) > Zn(II) ≃ Co(II) > Mn(II) > Ca(II) > Mg(II) ≃ Sr(II) > Ba(II). The relatively high stabilities of the EDTA complexes of the 'B' metals (e.g. Pb, Zn) in the above series is in agreement with the general observation that the properties of the B-metals (Zn, Cd, Hg, Cu, Tl, Pb) are intermediate between those of transitional metals on the one hand and the typical 'a' metals (pre-transitional metals) on the other. With a given ligand, the relative stabilities of transition metal complexes also depend on the crystal field stabilization energy (which itself depends on the nature of the cation and the ligand) as well as on the 'spin state' of the metal in the complex.

Thus we find that the ferrous complexes of dipyridyl, 1-10 phenanthroline and CN^- are more stable than the corresponding ferric complexes, whereas the reverse situation holds for the Fe(II) and Fe(III) complexes of citrate, tartrate, hydroxide, fluoride, etc.

The great, sometimes decisive, importance of the nature of the ligand, is also to be stressed. The important parameters here are the polarizability and basicity. Transitional elements and B-metals form stronger complexes with the more polarizable N as donor atom as compared to O, but this effect also depends on the metal. For instance, the difference in log K values of the Cu(II) and Mn(II) chelates of the three ligands oxalate, glycinate, and ethylenediamine are, respectively 3.2, 9.7 and 14.8 (the Cu chelate being more stable in all cases). The higher relative stabilities of chelates as compared to complexes with monodentate ligands is attributed to an enthalpy effect in the general case, but in the case of transition metal complexes there is an added enthalpy effect due to the higher crystal field stabilization energies of the chelating type of ligands (e.g. Dq for oxalate is greater than for formate and for ethylene diamine is greater than for ammonia). In sum, the more polarizable cations and ligands form stronger complexes than the less polarizable ones. The cations and ligands have been classified as 'hard', 'soft' and 'intermediate' acids (cations) and bases (ligands) respectively to enable qualitative prediction of the relative stabilities of complexes.[61,62]

Another weighty consideration in the solvent extraction of chelates is the stereochemistry of the chelate. For instance, Al(III) does not form an extractable complex with a 2-substituted 8-hydroxyquinoline. Owing to the steric hindrance from the 2-substituent, the small Al^{3+} ion cannot accommodate three such ligand moieties around itself. Another example is that, while ethylene diamine forms square planar complexes with Pt(II), Pd(II), Cu(II), Ni(II) and Co(II), cis-1,2-diaminocyclohexane does not form such complexes with Co(II) and trans-1,2-diaminocyclohexane forms chelates only with Pt(II) and Pd(II).

Other Factors Governing the Extractability of metal Complexes

(i) Nature of the solvent

The solvent does not, in general, play a purely passive role in the extraction of metals. It may directly coordinate with the metal ion, or it may be in the secondary coordination sphere as in true adducts. Even seemingly inert solvents such as benzene, hexane and chloroform, sometimes exhibit some specific effects.[63] The nature of the solvent is particularly important in the extraction of coordinatively unsaturated chelate complexes.[64,65] The efficacies of various solvents in this case can be arranged in decreasing order as: alcohols > ketones > complex ethers > simple ethers > halogen derivatives of hydrocarbons > hydrocarbons. On the other hand, coordinatively saturated chelates are better extracted with solvents such as benzene or carbon tetrachloride than with ethers or alcohols.[66]

(ii) Effect of pH

If the process of extraction is viewed as a chemical reaction it may be described by the equation

$$M^{n+} + nHA_{(o)} \rightleftharpoons MA_{n(o)} + nH^{+}$$

where M^{n+} is the metal ion, HA is the organic chelating agent and MA_n is the chelate. The subscript (o) refers to the non-aqueous phase. M^{n+} and H^{+}, being charged species, are assumed to exist only in the aqueous phase. The $HA_{(o)}$ is supposed to be in equilibrium with the aqueous phase as follows:

$$HA_{(o)} \rightleftharpoons HA \rightleftharpoons H^{+} + A^{-}$$

Similarly $MA_{n(o)} \rightleftharpoons MA_{n} \rightleftharpoons M^{n+} + nA^{-}$

The equilibrium constant for the extraction reaction is then given by

$$K_{ex} = \frac{[MA_{n}]_{o}\,[H^{+}]^{n}}{[M^{n+}]\,[HA]_{o}^{n}}$$

If no intermediate complexes of the metal, such as $(MA_{n-1})^{+}$ or $(MA_{n-2})^{2+}$ are formed, then the ratio $\frac{[MA]_{o}}{[M^{n+}]}$ gives the distribution ratio D, so that

$$K_{ex} = D\,\frac{[H^{+}]^{n}}{[HA]_{o}^{n}}$$

or $\log D = \log K_{ex} + n \log [HA]_{o} + n\,pH$ (5).

From this relation it follows that, if the concentration of the chelating agent in the organic phase is constant (as can be achieved by using a large total excess of the chelating agent) then log D increases linearly with pH, and the slope of this line gives the number of ligands n attached to an atom of the metal in the extracted chelate, i.e.

$$\frac{d \log D}{d \text{ pH}} = n \qquad (6)$$

These relations show that the percent extraction increases with pH. The situation is qualitatively similar to the conditions for formation of a soluble complex in the aqueous phase, where an increase in pH increases the concentration of the ligand species (A^-) and leads to higher concentration of the complex MA_n (or MA^+_{n-1}, MA^{2+}_{n-2} .....). The extraction equilibrium constant K_{ex} can be shown to be given by

$$K_{ex} = \frac{K_f \, K_{DX} \, K_i^n}{K_{DR}^n} \qquad (7)$$

where K_f = formation constant of the chelate MA_n

K_{DX} = distribution constant of the chelate

K_{DR} = distribution constant of the chelating reagent HA

and K_i = ionization constant of the reagent.

Thus, conditions are favourable for extraction (i.e. K_{ex} is high) if the chelate has high distribution and formation constants (K_{DX} and K_f). Generally, if the formation constant K_f of a metal complex with a given ligand is relatively high then the proton stability constant K_H of the ligand will also be relatively high, i.e. $K_i = \frac{1}{K_H}$ will be relatively low. Thus, in many cases, the distribution constant K_{DX} of the chelate has a dominant role in the extraction.

(iii) Effect of hydrolysis

It was mentioned in (ii) that the percent extraction would increase with increasing pH, but this is true only when the metal species in the aqueous phase is the cation M^{n+} or intermediate charged complex species such as $MA_m^{(n-m)+}$. But several metal ions react with hydroxyl ions in the aqueous phase to form hydroxy complexes, or mixed hydroxy chelates. These complexes are generally not extractable into organic solvents. Since the formation of such complexes is favoured by increasing pH, the extraction may actually decrease if the pH is sufficiently raised, and in the extreme case, the metal hydroxide may be precipitated.

(iv) Synergism[56,67-70]

This term describes the increase in extractability which a mixture of complexing agents (or solvents) produces, the enhancement being more than can be accounted for by the effects of the individual reagents or solvents as determined separately. The formation of mixed complexes is the commonest cause of synergism. For instance, the oxine complex of Sr[71,72] or the acetylacetone complex of U[73] can be made extractable only by addition of an excess of the neutral ligand. This was explained as due to the fact that the complexes were coordinatively unsaturated and the vacant positions are occupied by H_2O molecules. These H_2O molecules make the complexes more hydrophilic. Similarly, the extraction of thorium with thenoyltrifluoroacetone is enhanced by neutral ligands such as TBP.[74] The thorium complex which is extracted is commonly written as an adduct, viz. $Th(TTA)_4 \cdot TBP$; but, in reality, it is a mixed ligand complex. In fact, the differences in the effects of various types of solvents noted earlier are probably all due to synergistic effects of this type. The synergistic effect itself often depends on the type of inert solvent used. For instance, the synergic extraction of triply charged ions in a synergic system TTA/TBP/diluent increases in the order chloroform $<$ benzene $<$ carbon tetrachloride $<$ hexane $<$ cyclohexane.[74]

(v) Kinetic factors[75-78]

If either the rate of complex formation or the rate of transfer of the chelate from the aqueous layer is slow, the extractability is adversely affected. For instance, the extraction of Cr(III) with acetylacetone is satisfactory only when the solution containing the excess acetylacetone is boiled at pH 6.0. The rates of formation of dithizone with elements such as Ni(II) and Zn(II) are affected by anions such as acetate which are commonly added as buffer components. Equilibrium in extraction systems may be more speedily achieved if the reagent is added as a solution in a solvent miscible with water. On completion of the reaction, phase separation is achieved by adding a suitable electrolyte.[78]

(vi) Co-extraction[79]

Ions such as Ru(III), Cr(VI), Nb(V) and V(V) are not extracted with naphthenic acids; but in the presence of ferric salts they pass almost quantitatively into the organic phase. Co-extraction has been explained as due to sorption of the co-extracted element on the micelles of the complex extracted, or the formation of definite compounds. The co-extraction of Ca with lanthanide oxinates is assumed to be due to compounds such as $Ca(OX)_2 \cdot 2M(OX)_3$ where OX = 8-hydroxyquinoline. In addition to this type of co-extraction, a synergistic type of effect also is known - e.g. the extraction of the Cs - TTA complex is greatly enhanced if other alkali metals, and especially Ca, are present. The presence of neutral electrolytes of course leads to a slight increase in extractability due to the salting-out effect.

(vii) Suppression of extraction[80,81]

In the extraction of protonated anionic complexes with solvents of high dielectric constant or high basicity, it is found that the extraction of trace elements is suppressed in the presence of an extractable major component.

CHAPTER II : EXPERIMENTAL

2.1 Preparation of 2,4-dimethyl-6-hydroxyacetophenone (Reagent I).

(a) 3,5-Dimethyl anisole[82]

A solution of 3,5-dimethyl phenol (122 g, obtained from M/s. Fluka AG) and sodium hydroxide (40 g) in water (200 ml) was boiled under reflux for 3 hrs with frequent small additions of methyl sulphate (97 ml). The oil was separated and the aqueous layer extracted with ether. The oil and the ethereal extract were then washed with dilute sodium hydroxide solution and dried over calcium chloride. Ether was removed and the residue distilled, collecting the portion b.p. 190-200°C/740 mm. Redistillation gave 3,5-dimethyl anisole, b.p. 194°C/740 mm (118 g = 86.7%).

(b) 2,4-Dimethyl-6-hydroxyacetophenone[83] (Reagent I)

A mixture of 300 g of anhydrous aluminium chloride, 136 g of 3,5-dimethyl anisole and 400 g of carbondisulphide was heated to boiling and 82 g of acetic anhydride was added over a period of 30 minutes to the refluxing mixture. Refluxing was continued for an hour and the mixture was allowed to stand for 2 hrs. Ice-cold water was added and the oily layer separated. The aqueous layer was extracted with ether. The mixture of oil and ether extract was extracted with 5% NaOH solution. The alkaline aqueous layer was acidified and extracted with ether. The solid residue after the evaporation of ether was treated with charcoal and recrystallised from pet.ether (60-80°C) to give white crystals (m.p. 58°C).

Analysis: C, 73.40; H, 7.30; calculated for $C_{10}H_{12}O_2$; C, 73.20, H, 7.32.

The IR spectrum of the compound is given in Fig. 1 and the NMR spectrum in Fig. 2.

2.2 Preparation of 2,4-dimethyl-6-hydroxyacetophenone oxime[84] (Reagent II).

10 g of 2,4-dimethyl-6-hydroxyacetophenone, 25 g of hydroxylamine hydrochloride in 100 ml of water and 100 ml alcoholic sodium hydroxide (10 g NaOH dissolved in 20 ml of water and diluted to 140 ml with alcohol) were taken in a 500 ml flask, refluxed on a water bath for 20 minutes, cooled to room temperature, diluted to 400 ml and extracted with benzene. The benzene was evaporated and the residue was recrystallized from benzene - pet.ether mixture (1:1) to give colourless crystals. The oxime was dried at 90-100°C m.p. 142°C (reported value 143°C). The IR spectrum of the compound is given in Fig. 3.

Analysis: C, 66.85; H, 7.22; N, 7.73; calculated for $C_{10}H_{13}NO_2$; C, 67.02; H, 7.31; N, 7.82.

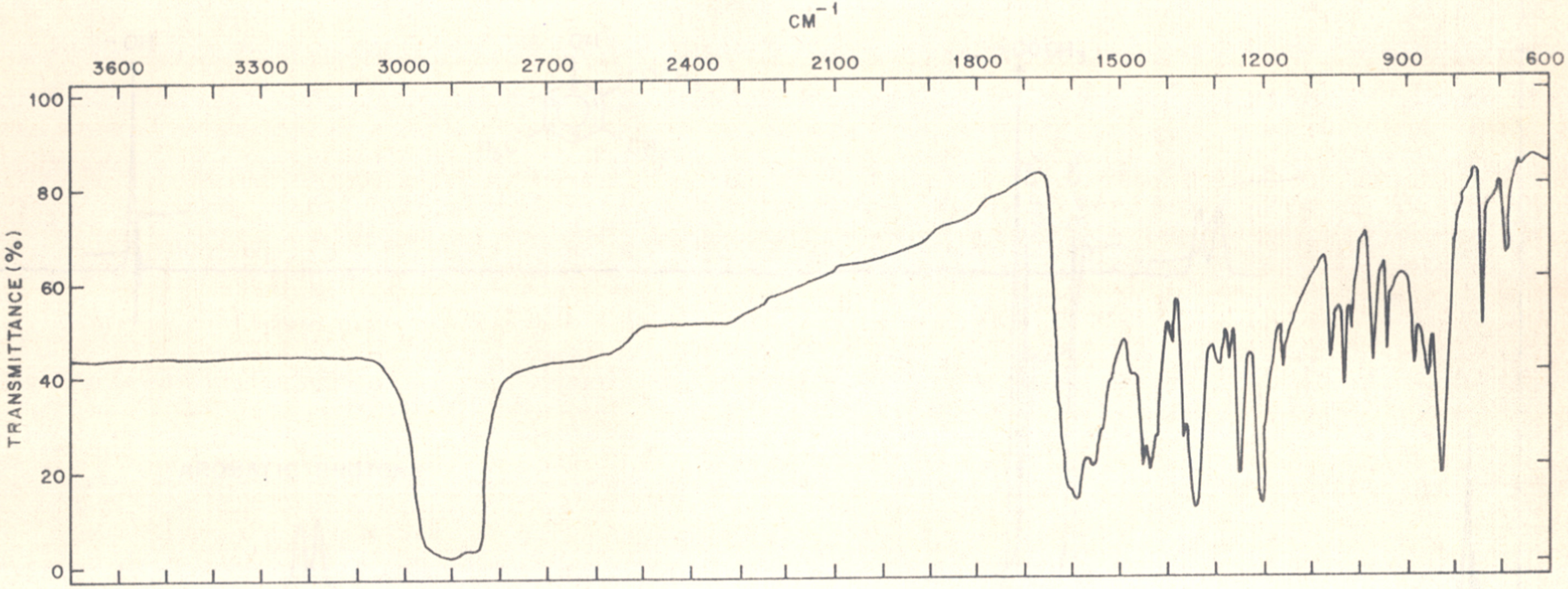


FIG. 1 : THE IR SPECTRUM OF 2,4-DIMETHYL-6-HYDROXY ACETOPHENONE IN NUJOL.

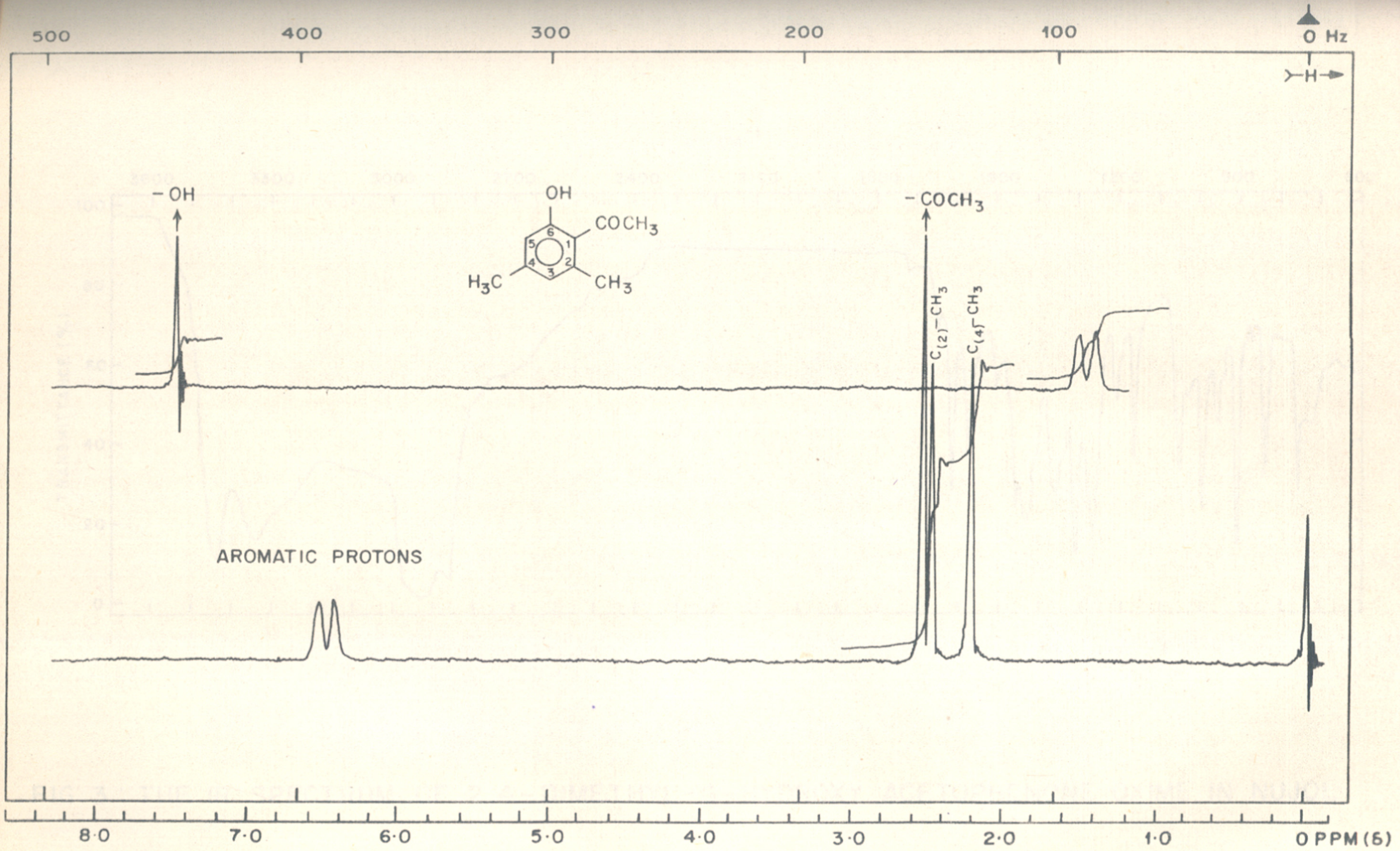


FIG. 2: THE NMR SPECTRUM OF 2,4-DIMETHYL-6-HYDROXY ACETOPHENONE IN CCl_4.

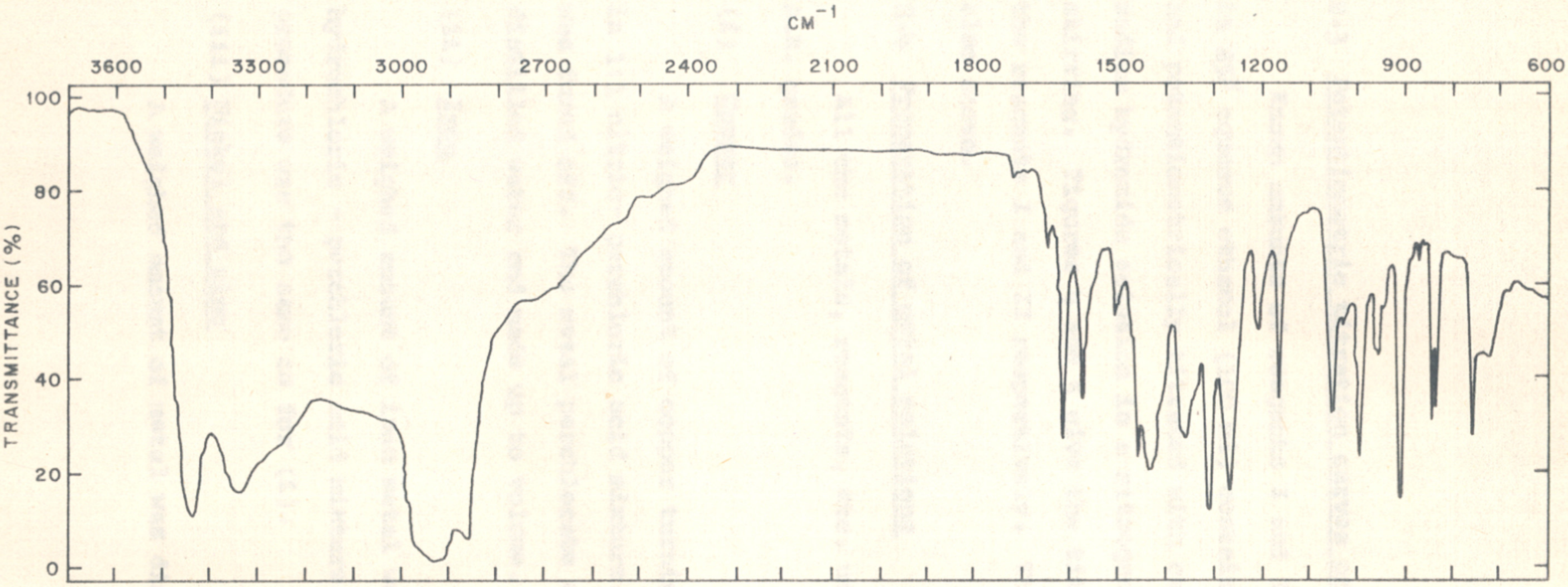


FIG. 3 : THE IR SPECTRUM OF 2,4-DIMETHYL-6-HYDROXY ACETOPHENONE OXIME IN NUJOL.

2.3 Potentiometric titration curves of the reagents

Known amounts of reagents I and II were dissolved in 25% aqueous ethanol (100 ml) containing 0.1 M $NaClO_4$ and potentiometrically titrated with carbonate-free sodium hydroxide solution in a nitrogen atmosphere with stirring. Figures 4 and 5 give the titration curves for the reagents I and II respectively. The $\Delta pH/\Delta V$ vs. V is also shown.

2.4 Preparation of metal solutions

All the metals, reagents, etc. used were of A.R. grades.

(i) Copper

A weighed amount of copper turnings was dissolved in 1:1 nitric- perchloric acid mixture. The excess acid was fumed off. The metal perchlorate was dissolved in distilled water and made up to volume.

(ii) Iron

A weighed amount of iron metal was dissolved in hydrochloric - perchloric acid mixture. The rest of the procedure was the same as for (i).

(iii) Nickel and zinc

A weighed amount of metal was dissolved in

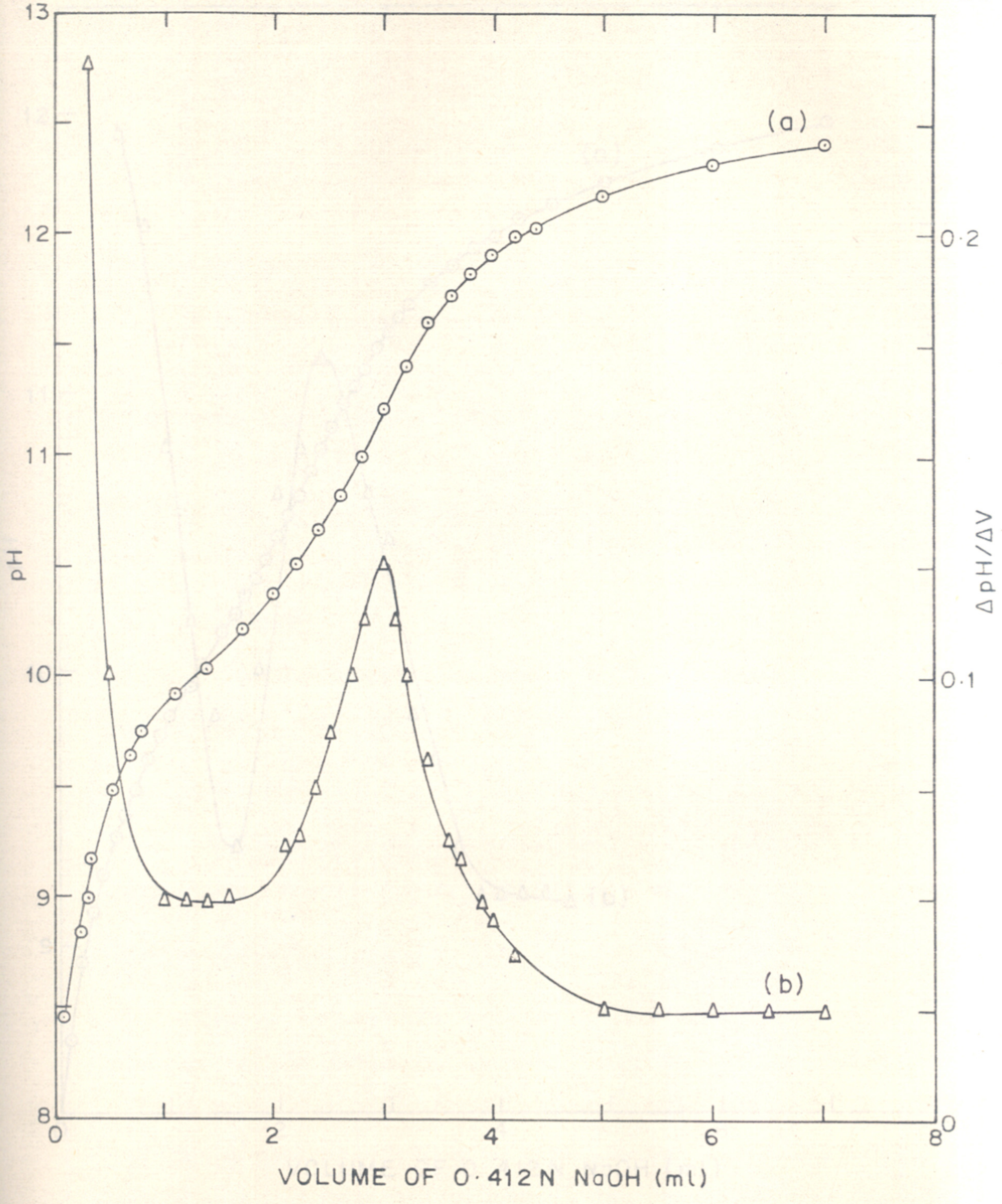


FIG. 4. POTENTIOMETRIC TITRATION CURVE OF REAGENT – I

(a) pH vs Vol. NaOH (ml) ⊙

(b) ΔpH/ΔV vs Vol. NaOH (ml) △

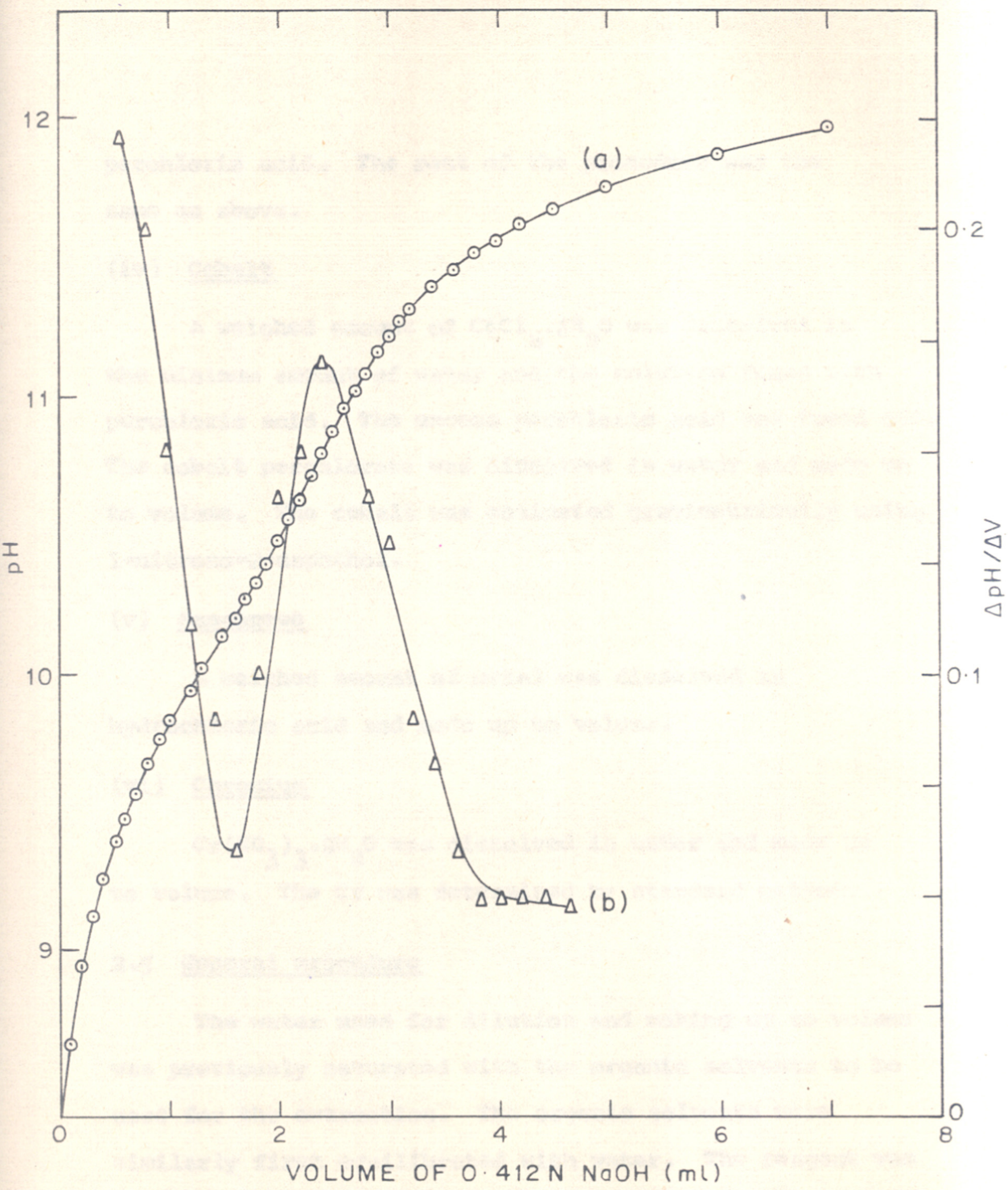


FIG. 5. POTENTIOMETRIC TITRATION CURVE OF REAGENT–II

(a) pH vs Vol. NaOH (ml) ⊙

(b) ΔpH/ΔV vs Vol. NaOH (ml) Δ

perchloric acid. The rest of the procedure was the same as above.

(iv) Cobalt

A weighed amount of $CoCl_2 \cdot 6H_2O$ was dissolved in the minimum amount of water and the solution fumed with perchloric acid. The excess perchloric acid was fumed off. The cobalt perchlorate was dissolved in water and made up to volume. The cobalt was estimated gravimetrically using 1-nitroso-2-naphthol.

(v) Manganese

A weighed amount of metal was dissolved in hydrochloric acid and made up to volume.

(vi) Chromium

$Cr(NO_3)_3 \cdot 9H_2O$ was dissolved in water and made up to volume. The Cr was determined by standard methods.

2.5 General procedure

The water used for dilution and making up to volume was previously saturated with the organic solvents to be used for the extraction. The organic solvents were similarly first equilibrated with water. The reagent was added as a solution in ethanol to the aqueous solution before the adjustment of pH. The pH of the aqueous layer was measured before and after extraction. The difference was less than 0.1. In this thesis, the pH measured after the extraction is reported as the pH of extraction. The solvent was run from a burette into a graduated pear-shaped separating funnel containing the aqueous phase and the contents were shaken together for a sufficiently long time to ensure attainment of equilibrium. The metal in the aqueous layer was directly estimated using AAS. The metal in the organic layer was first extracted into dilute acid and then determined by AAS. The absorbance of the organic extract was measured after drying it with AR anhydrous sodium sulphate.

2.6 Instruments used in the investigation

(1) 'Elico' digital pH meter model LI-120 reading to 0.01 pH unit with combined glass-calomel electrode.

(2) 'Pye Unicam SP-1900' Atomic absorption spectrophotometer for estimation of metals in the solutions.

(3) 'Pye-Unicam SP8-100' UV-Vis spectrophotometer for measurement/recording of optical absorbance.

(4) 'Princeton Applied Research (PAR) model 174-A' polarograph for experiments on polarographic reduction of ligands and metal complex solutions.

(5) 'Perkin Elmer 599B' I.R. spectrophotometer for recording IR spectra.

(6) 'Varian T-60' for recording NMR spectra.

2.7 Extraction of metals with 2,4-dimethyl-6-hydroxyacetophenone (reagent I) in the presence of ammonia

In all the extractions reported below involving reagent I, the following solution concentrations should be assumed:

(a) reagent: 820 mg of ligand I dissolved in 100 ml of ethanol

(b) sodium perchlorate: 1 M

(c) metal : 1 mM

To 1 ml of the metal solution taken in a 25 ml beaker were added 1.5 ml of the sodium perchlorate solution and 5 ml of the reagent. The solution was diluted to 10-12 ml and the pH adjusted to about 10.5 using 1:1 aqueous ammonia, with stirring. The solution was kept at room temperature ($30^{\circ} \pm 3^{\circ}C$) for 12 hrs, then transferred to a graduated separatory funnel, diluted to the 15 ml mark and extracted with 10 ml of chloroform. The chloroform layer was seperated and dried with anhydrous sodium sulphate. The absorption spectrum of the dried extract was recorded against a reagent blank. The metal concentrations in the two layers were determined as mentioned earlier and the percent extraction calculated. The results are given in Table 1 and the electronic absorption spectrum of the Cu-complex in Fig. 6.

When the pH was adjusted with sodium hydroxide instead of ammonia, the metal hydroxides were seen to precipitate and the extraction was very poor.

2.8 Extraction of metals with reagent I in the presence of diethylamine

Essentially the same procedure as in 2.7 was followed, but the pH was adjusted (10.0-10.5) with diethylamine. In the attempted separation of Cu(II) and Ni(II) a 1:1 molar mixture of the metal solutions was taken and the required amount of sodium tartrate added. Extractions were carried out with 2x10 ml and then with 1x5 ml chloroform. The values obtained for the percent extraction are given in Table 2. The electronic spectrum of the Cu complex is given in Fig. 7. Ni(II), Co(II) and Fe(III) gave very poor extraction; the absorbance of these extracts overlapped that of the blank. The values for the separation of Cu(II) and Ni(II) are given in Table 3.

Table 1

Extractions of metals with reagent - I
in the presence of ammonia

Metal	Percent extraction
Copper(II)	68
Nickel(II)	40
Cobalt(II)	42
Iron(III)	Hydroxide precipitated
Manganese(II)	Hydroxide precipitated
Zinc(II)	nil
Chromium(III)	nil

Table 2

Extraction of metals with reagent-I
in the presence of diethylamine.

Metal	Percent extraction	
	Single extraction	Triple extraction
Copper(II)	90	100
Nickel(II)	5	<10
Cobalt(II)	11	< 20
Iron(III)	7	< 10

Table 3

Separation of copper(II) from nickel(II)
with reagent-I, diethylamine and tartrate

No.	Sodium tartrate (mg)	Percent extracted in 3 extractions	
		Nickel(II)	Copper(II)
1	500	nil	42.0
2	250	nil	61.0
3	50	nil	81.0
4	10	nil	98.0
5	5	nil	100.0
6	nil	9	99.0

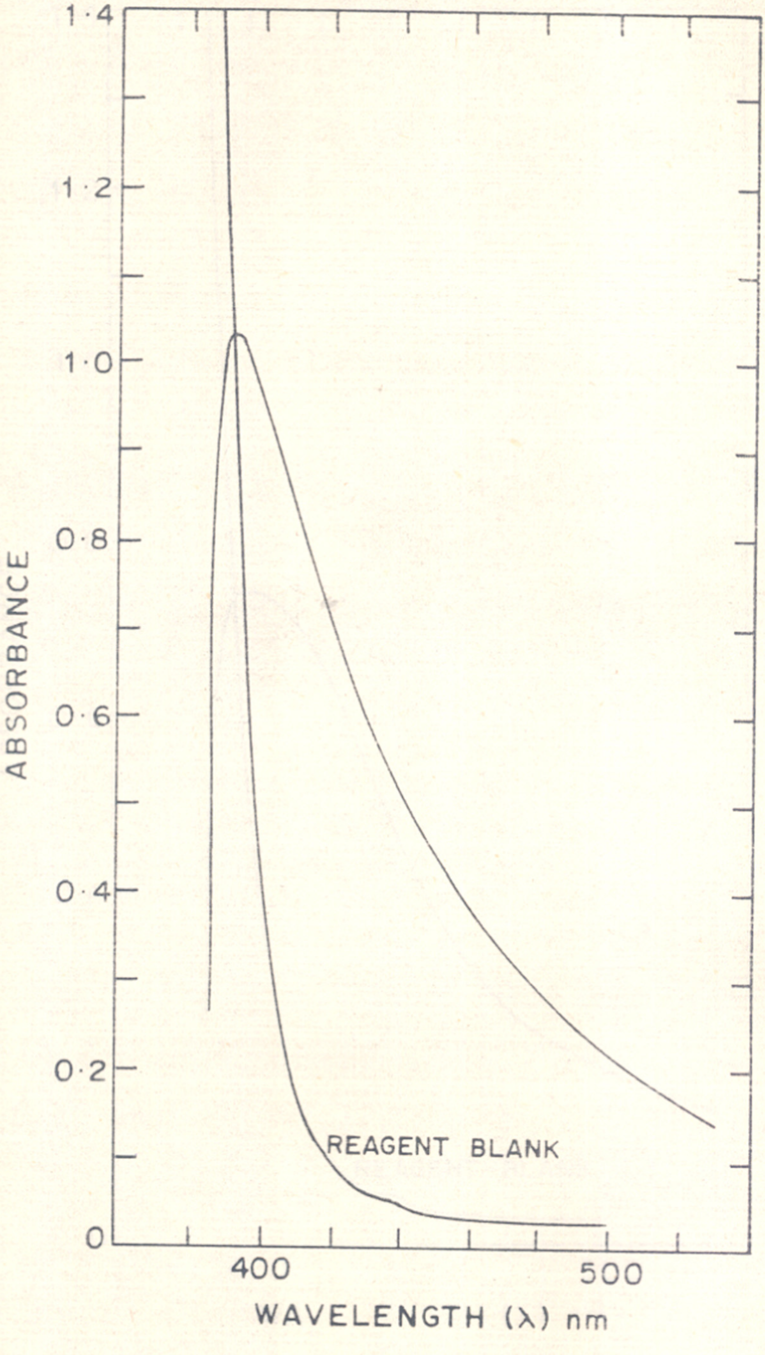


FIG. 6. ELECTRONIC ABSORPTION SPECTRUM OF REAGENT-I-COPPER (II) COMPLEX IN CHLOROFORM (EXTRACTED IN PRESENCE OF AMMONIA)

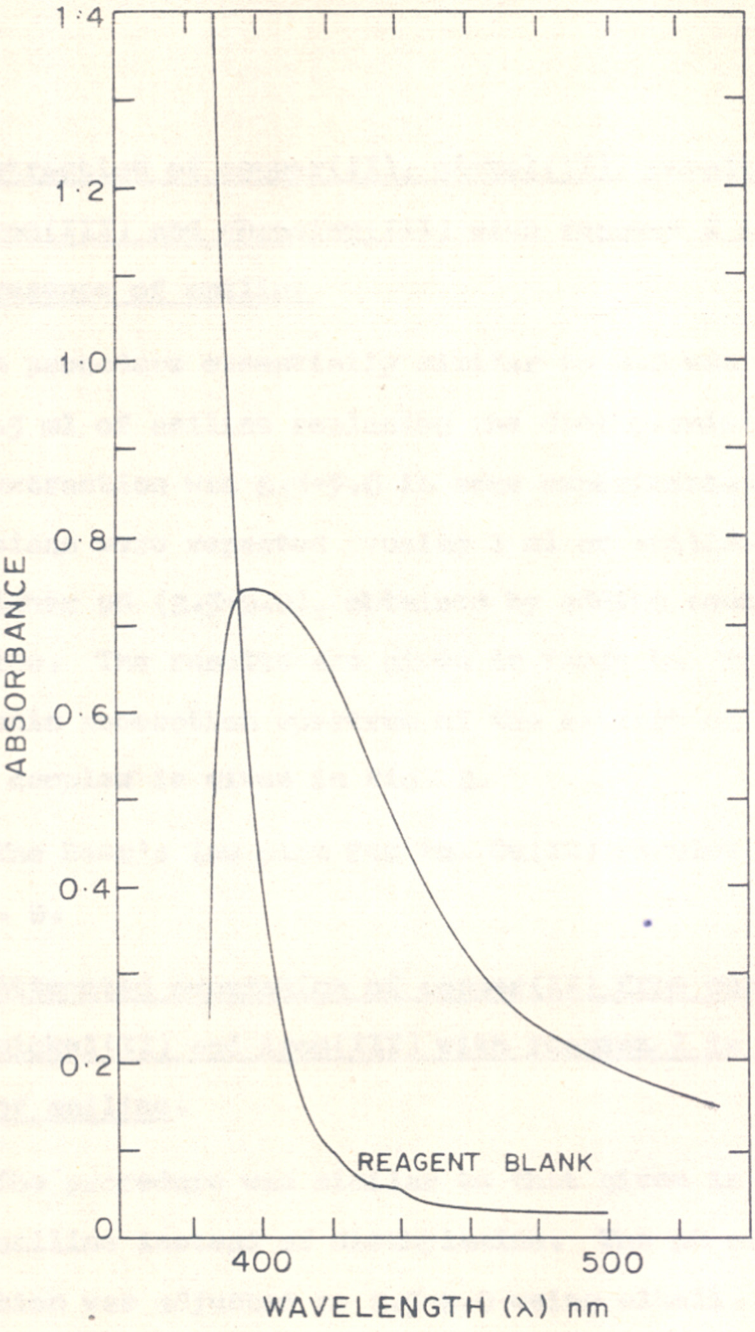


FIG. 7. ELECTRONIC ABSORPTION SPECTRUM OF REAGENT-I-COPPER (II) COMPLEX IN CHLOROFORM (EXTRACTED IN PRESENCE OF DI~~M~~ETHYLAMINE)

2.9 Extraction of copper(II), nickel(II), cobalt(II), iron(III) and chromium(III) with reagent I in presence of aniline

A procedure essentially similar to 2.8 was used, with 0.5 ml of aniline replacing the diethylamine. The pH of extraction was 6.5-7.0 in some experiments. The extractions were repeated by using 1 ml of aniline and also at a higher pH (8.5-9.0), obtained by adding sodium hydroxide. The results are given in Table 4. The electronic absorption spectrum of the extract of the Cu(II) complex is given in Fig. 8.

The Beer's law plot for the Cu(II) complex is given in Fig. 9.

2.10 Attempted separation of copper(II) from cobalt(II), nickel(II) and iron(III) with reagent I in presence of aniline.

The procedure was similar to that given in 2.8 using aniline instead of diethylamine. The pH of extraction was adjusted to 8.5-9.0 using alkali. The results are given in Table 5.

2.11 Extraction of metals with 2,4-dimethyl-6-hydroxyacetophenone oxime (reagent II)

In all the extractions with reagent II, the solutions

Table 4

Extraction of metals with reagent-I in the presence of aniline

Metal	Percent extraction		
	pH = 6.5 - 7.0 Aniline 0.5 ml	Aniline 1.0 ml	pH = 8.5 - 9.0 0.5 ml Aniline + sodium hydroxide solution
Copper(II)	70	73	100
Nickel(II)	nil	nil	3
Cobalt(II)	nil	2	5
Iron(III)	nil	nil	nil
Chromium(III)	nil	nil	nil

Table 5

Separation of copper(II) from nickel(II), cobalt(II), iron(III) and Cr(III) using reagent-I and aniline

Metals	pH	Sodium tartrate (mg)	Percent extracted in single extraction				
			Cu(II)	Ni(II)	Co(II)	Fe(III)	Cr(III)
Cu/Ni + Co + Fe	8·5	nil	37	14	17	17	-
"	9·5	5	41	6	10	nil	-
Cu/Ni	9·1	nil	35	19	-	-	-
Cu/Co	8·9	5	18	-	nil	-	-
Cu/Fe(III)	8·9	nil	38	-	-	17	-
Cu/Cr(III)	9·0	nil	30	-	-	-	nil

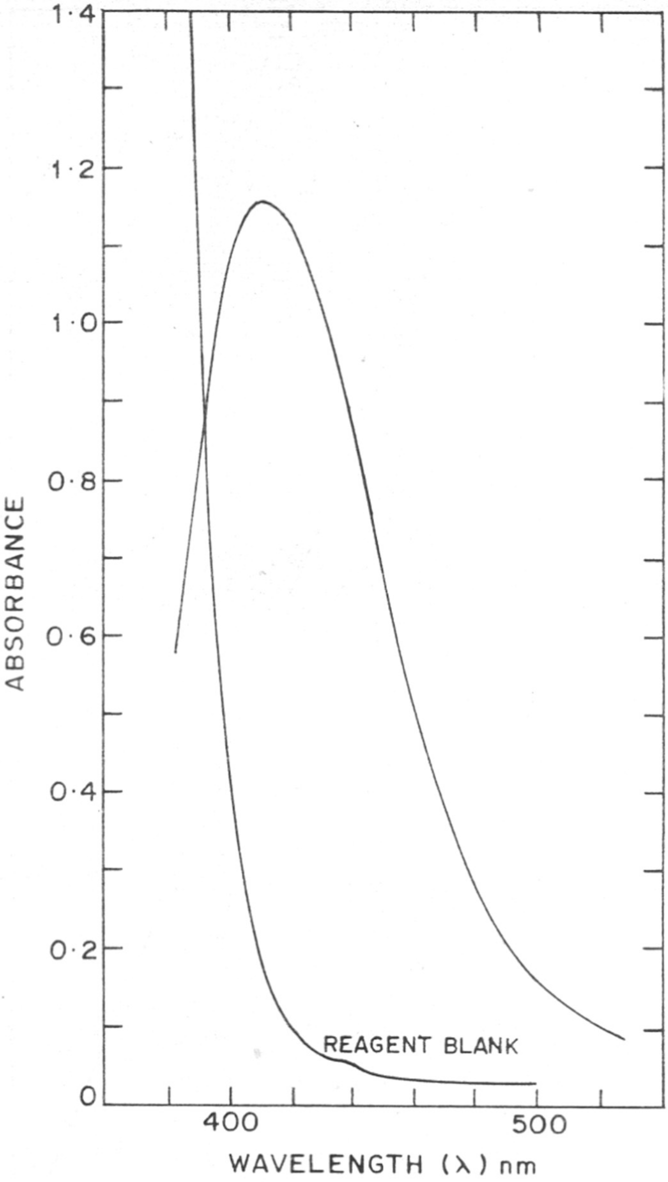


FIG. 8. ELECTRONIC ABSORPTION SPECTRUM OF REAGENT-I-COPPER (II) COMPLEX IN CHLOROFORM (EXTRACTED IN PRESENCE OF ANILINE)

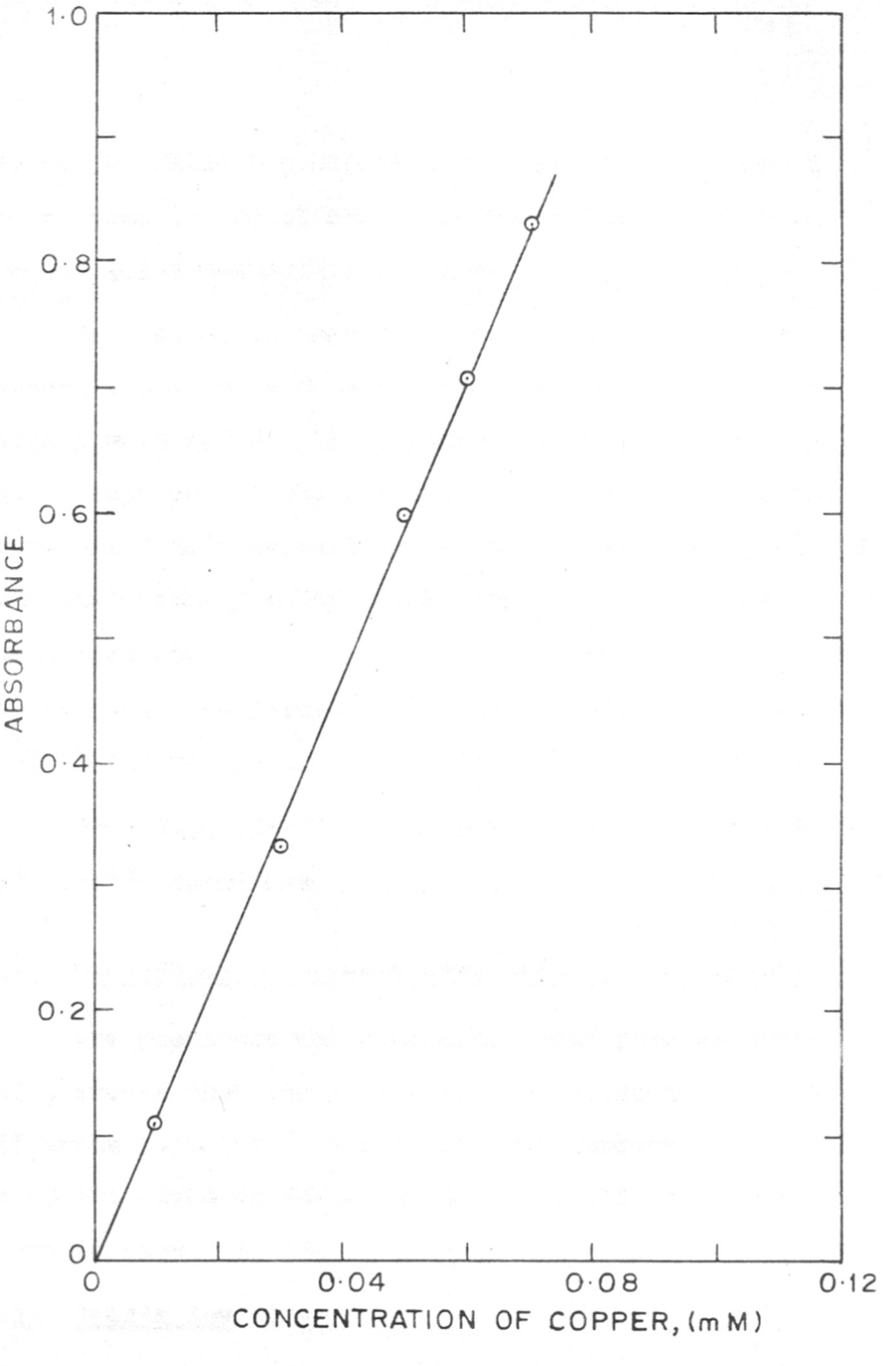


FIG. 9. BEER'S LAW PLOT OF COPPER (II)-REAGENT - I COMPLEX

(EXTRACTED IN PRESENCE OF ANILINE)

were of the following strength: (a) reagent: 900 mg of the reagent in 100 ml ethanol, (b) sodium perchlorate - 1 M and (c) metal solution - 1 mM.

To 1 ml of the metal solution taken in a 25 ml beaker, 1.5 ml of sodium perchlorate and 2.5 ml of the reagent were added. The solution was diluted to 12 ml, the pH adjusted to the required value and the solution transferred to a separatory funnel, diluted to 15 ml and extracted with 10 ml of chloroform. The electronic absorption spectra of the dried chloroform layer are given in Fig. 10. The percent extraction values are given in Table 6 and the molar absorbance values in Table 7.

Iron(II), zinc(II) and chromium(III) did not form extractable complexes.

2.12 Dependence of percent extraction by reagent-II on pH

The procedure was essentially the same as given in 2.11, except that the extractions were carried out at different pH values. The values for percent extraction vs pH are given in Tables 8, 9, 10 and 11. The plots are given in Figs. 11, 12, 13 and 14.

2.13 Beer's law plots

Beer's law plots for the extraction of copper(II), nickel(II), cobalt(II) and iron(III) in the optimum pH range are given in Figs. 15, 16, 17 and 18.

Table 6

Extraction of metals using reagent-II

Metal	pH	Percent extraction
Copper(II)	5.0 - 6.0	100
Nickel(II)	8.0 - 8.5	100
Cobalt(II)	8.5 - 9.0	100
Iron(III)	5.0 - 6.0	100
Manganese(II)	8.5 - 9.0	100
Zinc(II)	7.0 - 8.0	nil
Chromium(III)	8.0 - 9.0	nil

Table 7

Molar absorbance value and λ_{max} of metal complexes of reagent-II

Metal	λ_{max} (nm)	Molar absorbance ϵ_M
Copper(II)	336	$(7 \cdot 3 \pm 0 \cdot 1) \times 10^3$
Nickel(II)	360	$(6 \cdot 2 \pm 0 \cdot 1) \times 10^3$
Cobalt(II)	340	$(7 \cdot 7 \pm 0 \cdot 1) \times 10^3$
Iron(III)	334	$(5 \cdot 1 \pm 0 \cdot 1) \times 10^3$
Manganese(II)	342	$(6 \cdot 25 \pm 0 \cdot 1) \times 10^3$

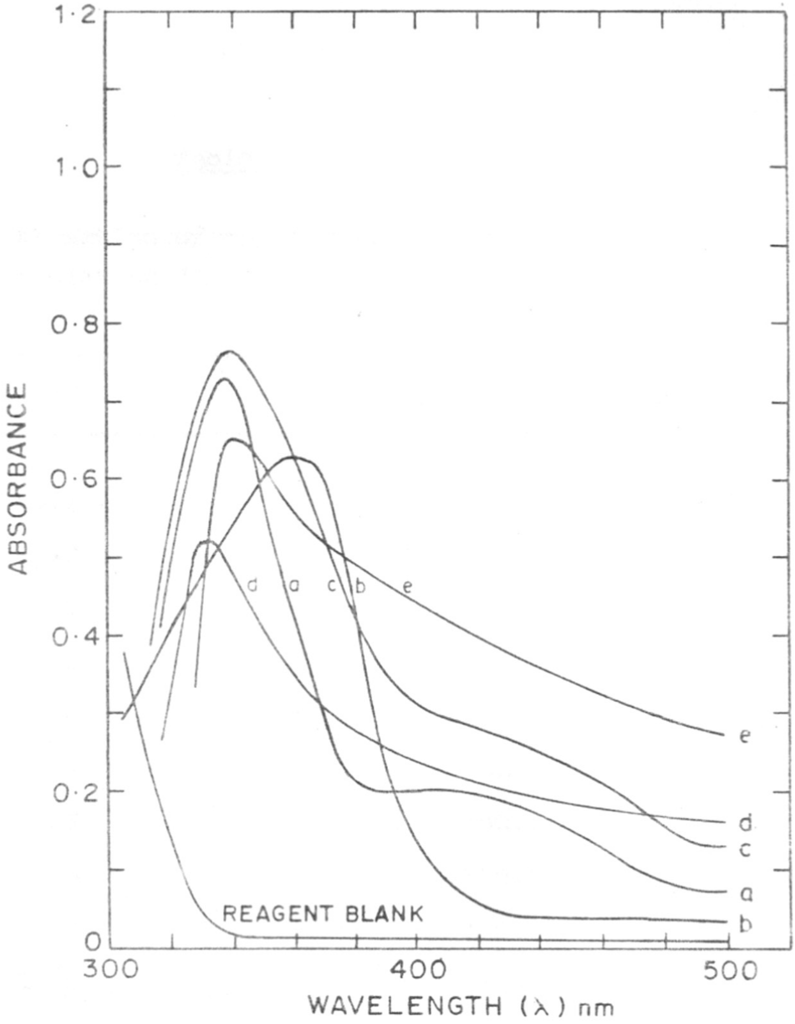


FIG. 10. ELECTRONIC ABSORPTION SPECTRA OF THE REAGENT-II COMPLEXES IN CHLOROFORM OF (a) COPPER (II), (b) NICKEL (II), (c) COBALT (II), (d) IRON (III) AND (e) MANGANESE (II)

Table 8

Extraction of copper(II) - reagent-II complex at different pHs

pH	Percent extraction
2.8	3.0
3.0	10.0
3.5	36.0
3.8	69.0
4.0	88.0
4.3	98.5
4.5	100.0
5.0	100.0
9.0	100.0
10.0	98.0

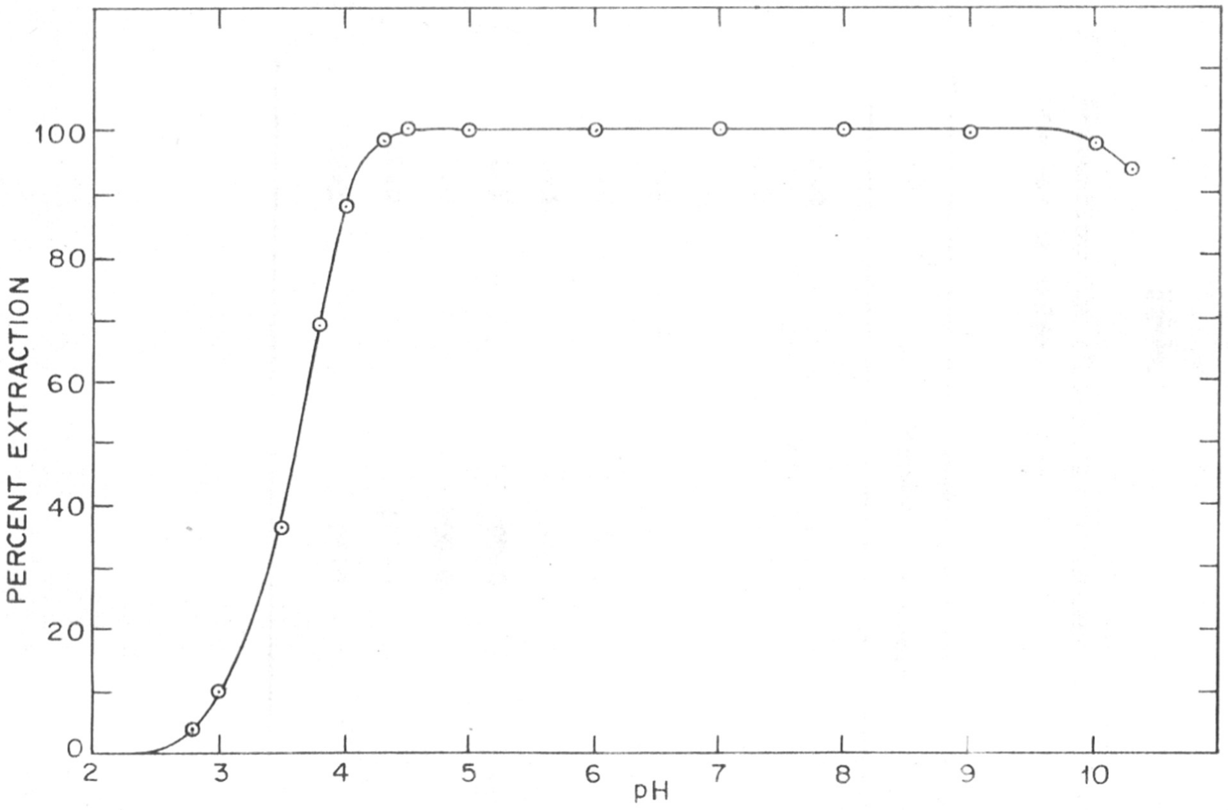


FIG. 11. pH vs PERCENT EXTRACTION: COPPER (II) – REAGENT – II COMPLEX

Table 9

Extraction of nickel(II) - reagent-II complex at different pHs

pH	Percent extraction
6.0	nil
6.5	nil
7.0	11.0
7.5	47.0
8.0	88.0
8.3	98.0
8.5	99.0
9.0	100.0
10.0	100.0
10.5	95.0

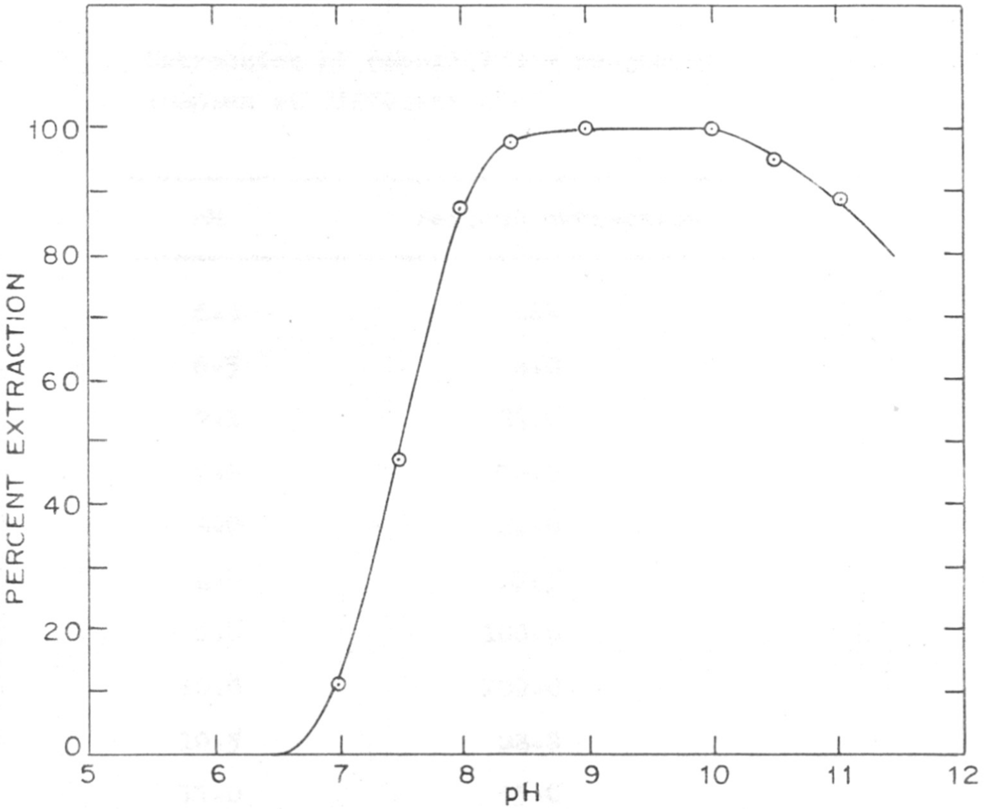


FIG. 12. pH vs PERCENT EXTRACTION: NICKEL (II)-REAGENT-II COMPLEX

Table 10

Extraction of cobalt(II) - reagent-II complex at different pHs

pH	Percent extraction
6.2	nil
6.5	2.0
7.1	23.0
7.6	58.0
8.0	89.0
8.4	97.5
9.0	100.0
10.0	100.0
10.5	98.0
11.0	85.0

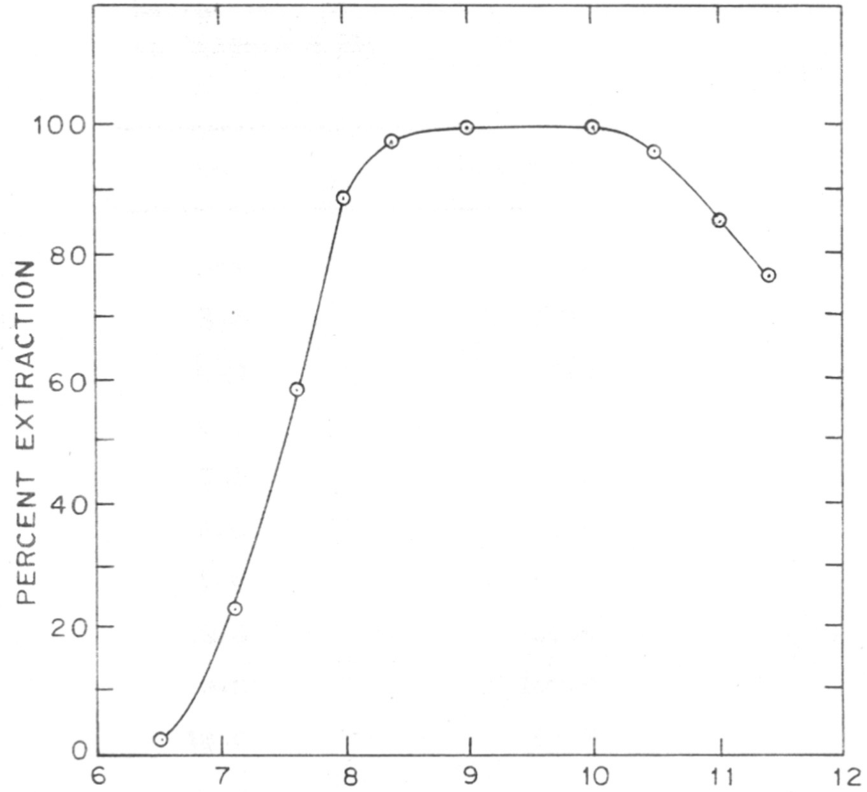


FIG. 13. pH vs PERCENT EXTRACTION: COBALT (II)-REAGENT-II COMPLEX

Table 11

Extractions of iron(III) - reagent-II complex at different pHs

pH	percent extraction
3.4	18.0
3.8	57.0
4.2	86.0
4.6	97.5
5.0	100.0
6.0	100.0
7.0	100.0
8.0	100.0
9.0	100.0
10.0	91.0

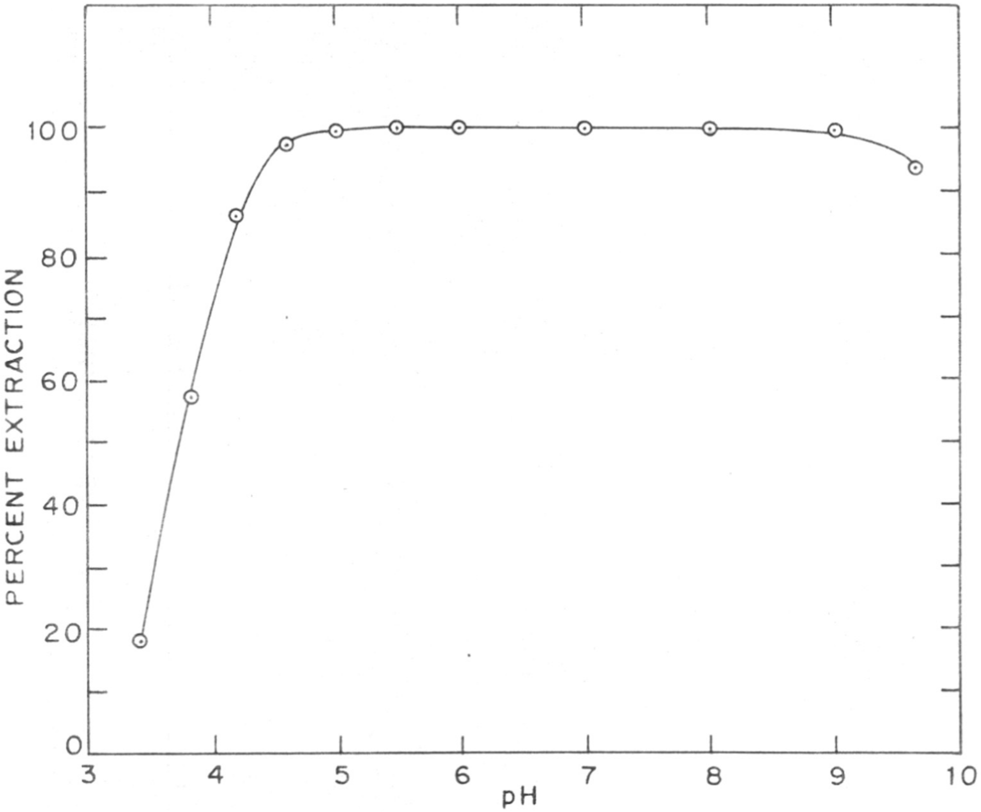


FIG. 14. pH vs PERCENT EXTRACTION: IRON (III)-
REAGENT-II COMPLEX

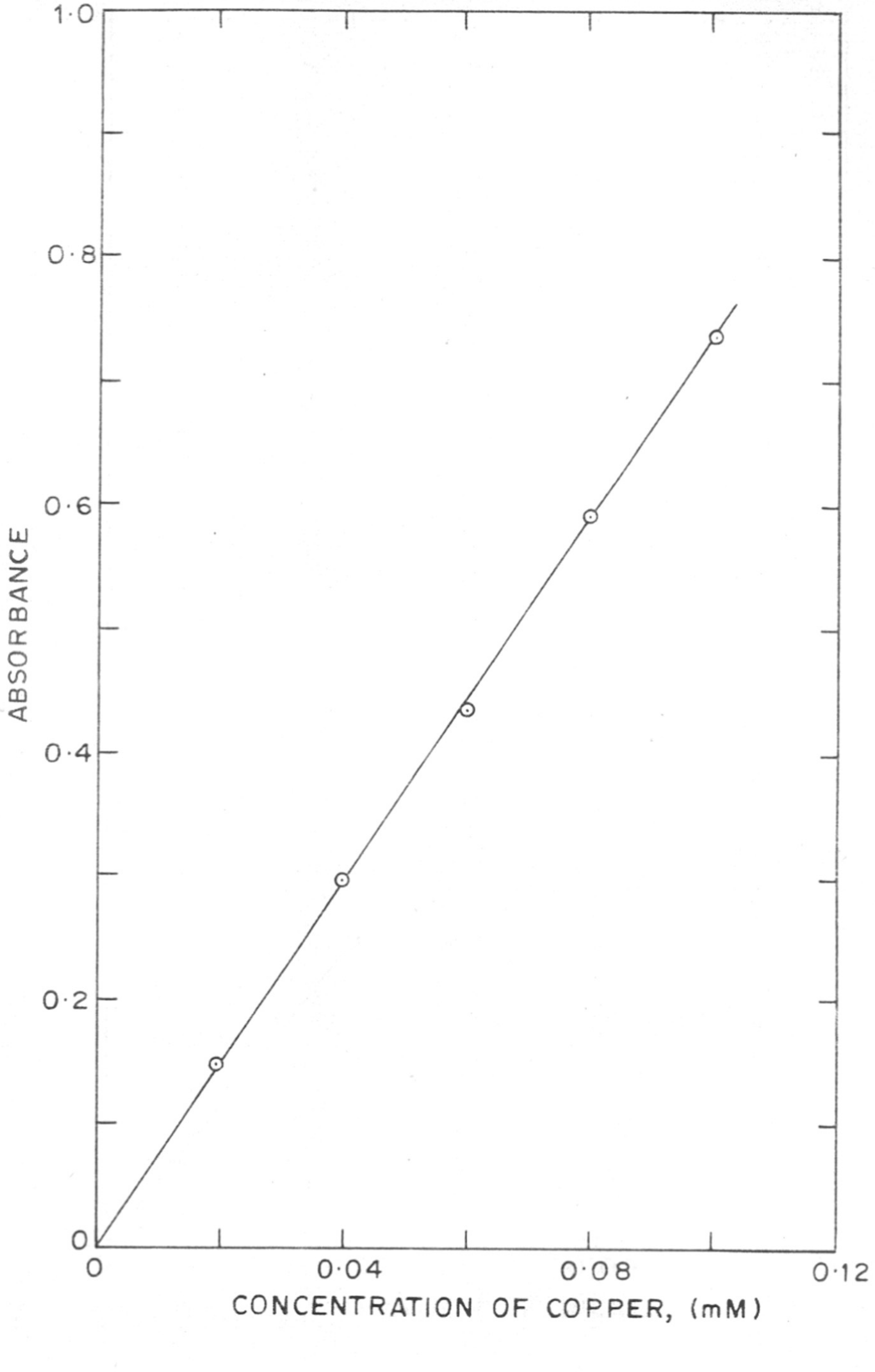


FIG. 15. BEER'S LAW PLOT OF COPPER (II)-REAGENT-II COMPLEX

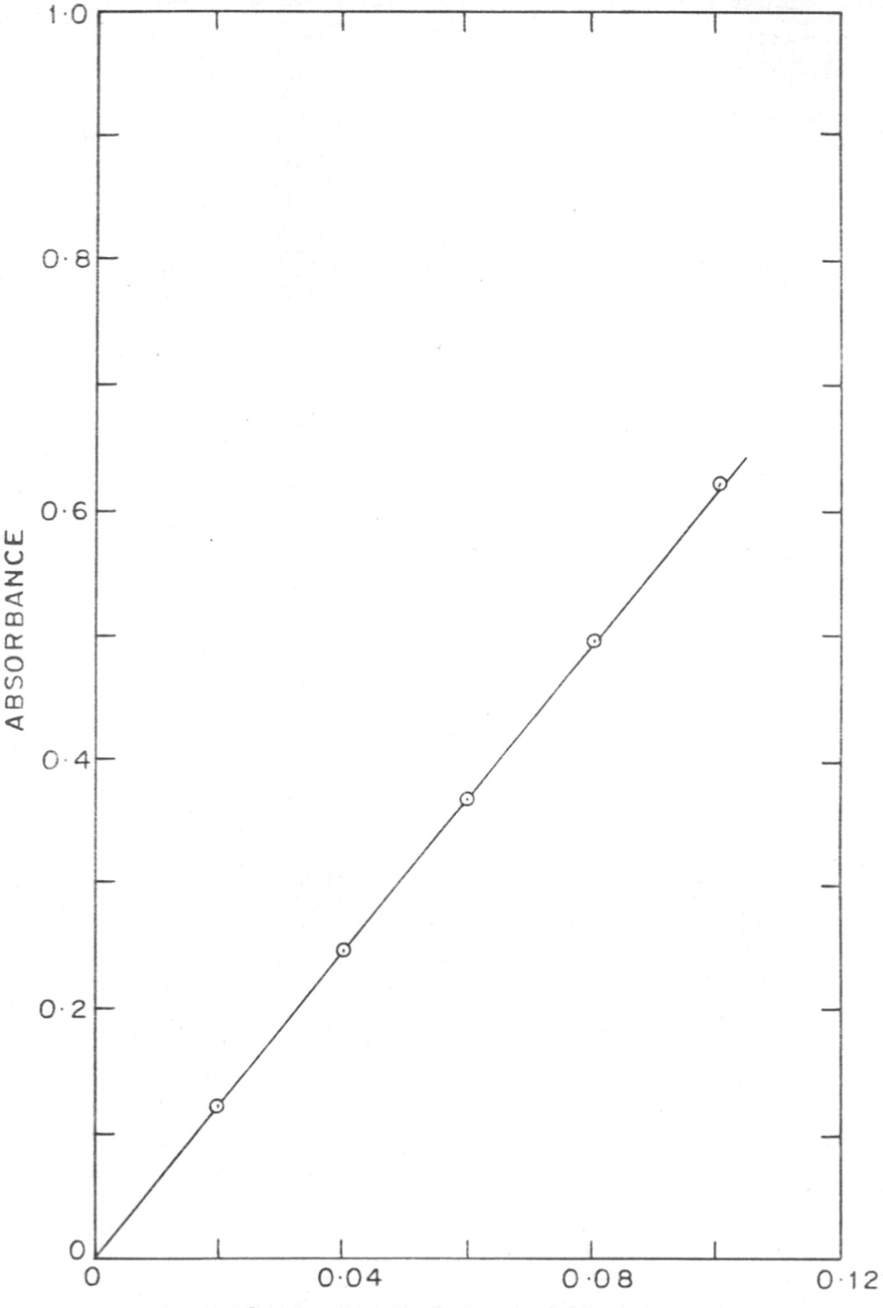


FIG. 16. BEER'S LAW PLOT OF NICKEL (II)-REAGENT-II COMPLEX

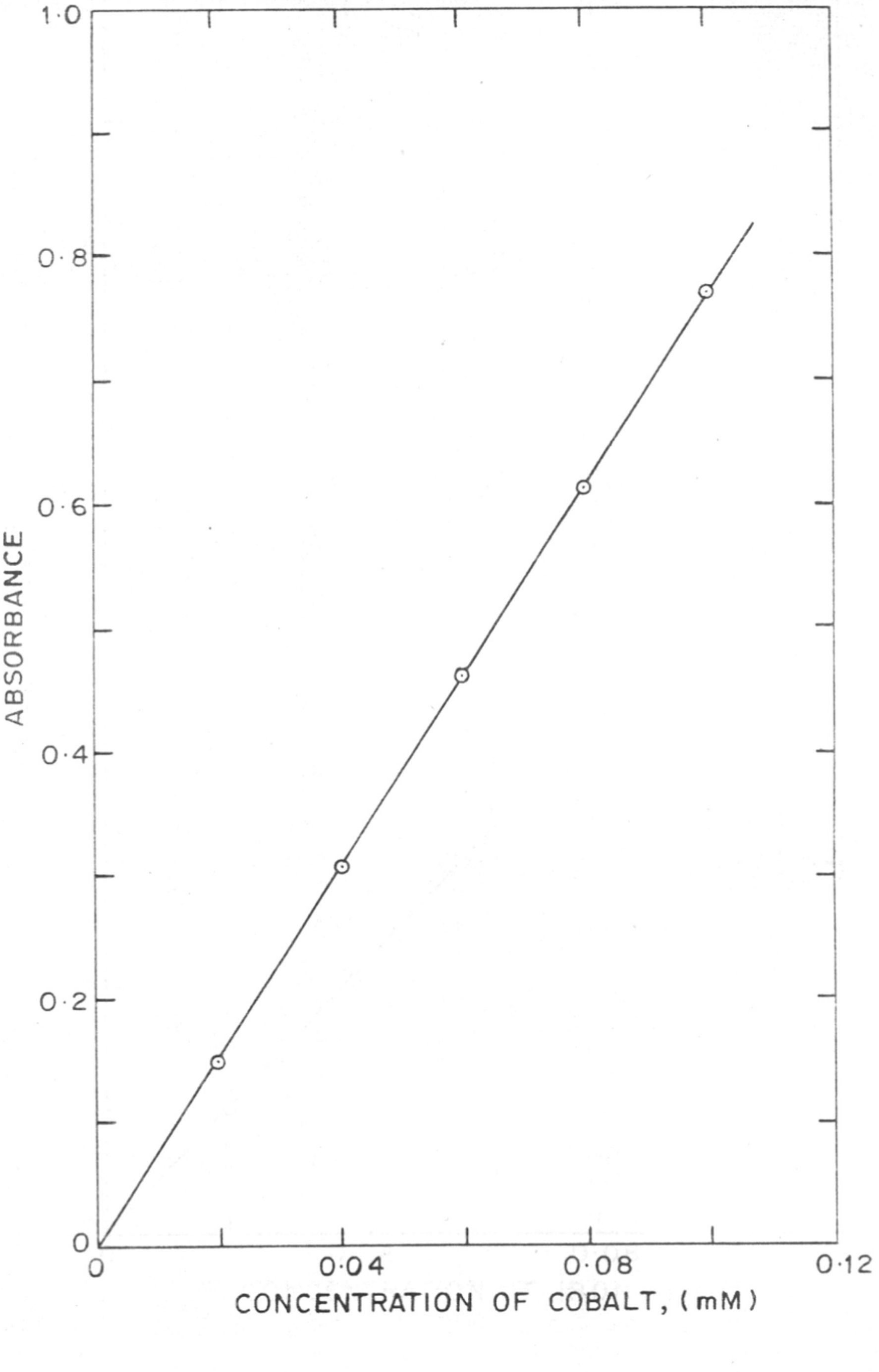


FIG. 17. BEER'S LAW PLOT OF COBALT (II)-REAGENT -II COMPLEX

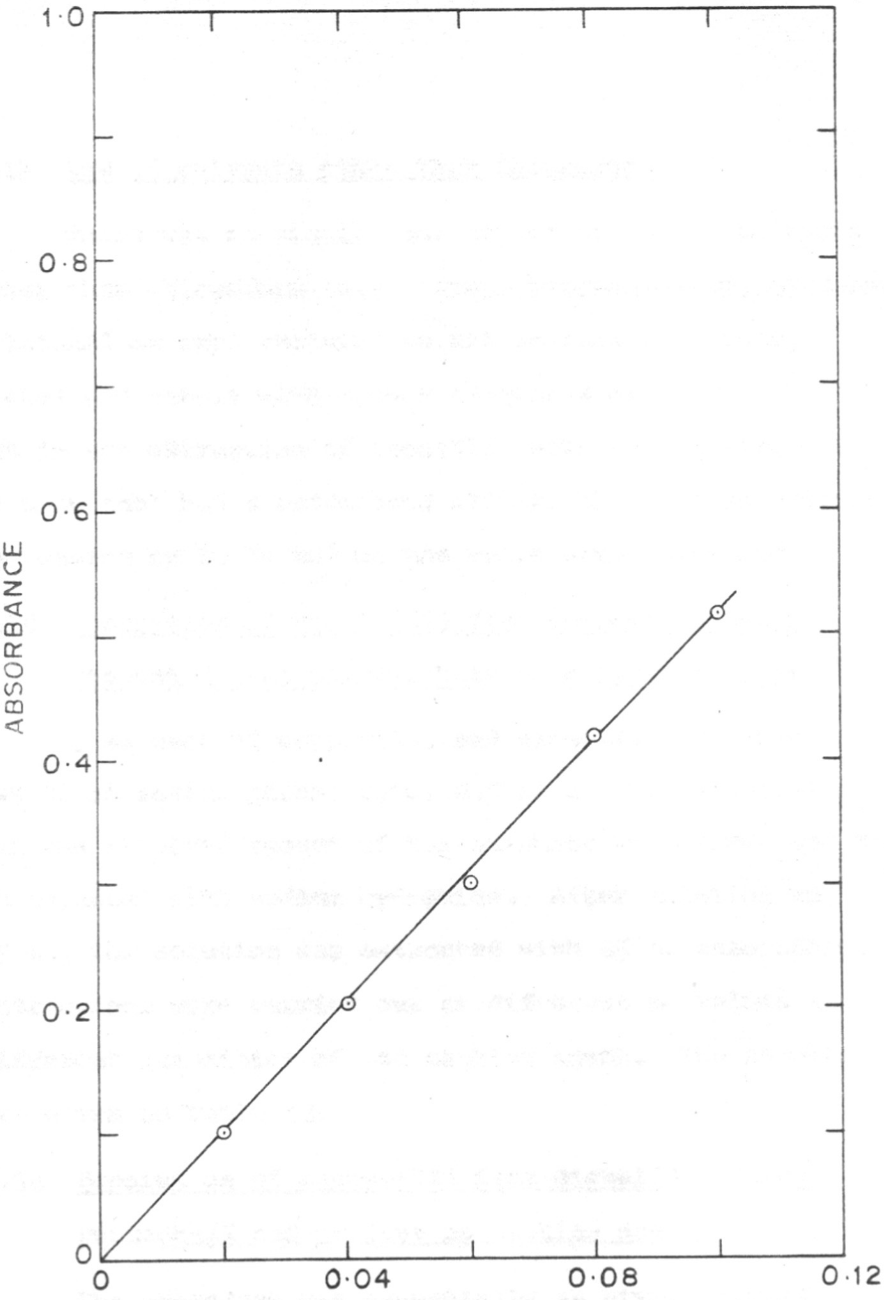


FIG. 18. BEER'S LAW PLOT OF IRON (III)-
REAGENT-II COMPLEX

2.14 Use of solvents other than chloroform

There was no significant effect of use of solvents other than chloroform (e.g. carbon tetrachloride, benzene, n-butanol or amyl acetate) in the extractions of copper, nickel and cobalt with either reagent-I or reagent-II. But in the extraction of iron(III) with reagent-II, use of n-butanol had a pronounced effect, the percent extraction increasing by 10 to 40% of the value with chloroform.

2.15 Separation of nickel(II) from copper(II) using reagent-II and thiosulphate as a masking agent

1 ml each of copper(II) and nickel(II) solutions, 2.5 ml of sodium perchlorate, 2.5 ml of the reagent-II and the required amount of thiosulphate were mixed and the pH adjusted with sodium hydroxide. After dilution to 25 ml, the solution was extracted with 25 ml chloroform. Extractions were carried out at different pH values and different quantities of the masking agent. The results are given in Table 12.

2.16 Separation of copper(II) from nickel(II) using reagent-II and oxalate as masking agent

The procedure was essentially as given in 2.15. Extractions were carried out using different quantities of oxalate, at different pH values, and also using aqueous

Table 12

Separation of nickel(II) from copper(II) using reagent-II and thiosulphate as a masking agent

pH	Sodium thiosulphate (mg)	Percent extraction	
		Copper(II)	Nickel(II)
5•1	100	2	nil
6•9	100	23	20
8•2	100	73	93
8•5	500	56	95
9•5	500	61	96

diethylamine (1:5) in place of sodium hydroxide for adjustment of the pH. The percent extractions in these experiments are given in Table 13.

2.17 Separation of copper(II) from nickel(II) using reagent-II and tartrate as masking agent

The investigations given in 2.16 were repeated using tartrate instead of oxalate as masking agent. The results obtained are given in Table 14.

2.18 Separation of copper(II) from iron(III) using reagent-II and tartrate as masking agent

Extractions were carried out using 1 ml each of copper(II) and iron(III) in 0.1 molar tartrate at different pH values. The results are given in Table 15.

2.19 Separation of copper(II) from both nickel(II) and iron(III) using reagent-II and tartrate as masking agent

The Fe/Cu and Ni/Cu molar ratios in these experiments both varied from 1:1 to 100:1. The pH varied from 8.50 - 8.90. The results obtained are given in Table 16.

2.20 Interference of ions in the extraction-photometric determination of copper using reagent-II

Various ions were examined for their effect on the extraction photometric determination of copper. Extractions

Table 13

Separation of copper(II) from nickel(II) using reagent-II and oxalate as masking agent

No.	pH	Weight of sodium oxalate (mg)	Percent extraction Copper(II)	Percent extraction Nickel(II)
1	7.2	10	86	nil
2	7.8	10	99	19
3	8.6	25	95	9
4	8.6	35	93	5
5	6.0	10	95	5
6	6.5	10	100	12
7	6.5	25	97	6
8	7.0	35	95	2

In experiments 5 to 8, the pH was adjusted with diethylamine.

Table 14

Separation of copper(II) from nickel(II) using reagent-II and tartrate as masking agent

No.	pH	Weight of sodium tartrate (g)	Percent extraction	
			Copper(II)	Nickel(II)
1	8•0	0•500	96	nil
2	8•3	0•500	99	nil
3	8•5	0•500	100	nil
4	8•5	0•250	100	7
5	8•7	0•500	100	nil
6	8•9	0•500	100	3
7	9•5	0•500	100	27

Table 15

Separation of copper(II) from iron(III)
using reagent-II and tartrate as masking agent

pH	Percent extraction of metals	
	Copper(II)	Iron(III)
3.00	nil	nil
4.00	nil	nil
5.00	nil	nil
6.00	15	nil
7.00	81	nil
8.00	100	nil
9.00	100	nil
10.00	100	nil

Table 16

Separation of copper(II) from nickel(II) and iron(III) using reagent-II and tartrate as masking agent

No	Cu = 0.04 mM		Concentration of sodium tartrate (Molar)	pH	Percent extraction of metals		
	Fe/Cu ratio	Ni/Cu ratio			Copper(II)	Nickel(II)	Iron(III)
1	1	1	0.1	8.5	100	nil	nil
2	1	10	0.1	8.55	99.0	5	nil
3	1	10	0.3	8.65	100	nil	nil
4	1	100	0.6	8.50	98.0	nil	nil
5	1	100	0.6	8.60	100	nil	nil
6	1	100	0.6	8.9	100	nil	nil
7	10	1	0.1	8.4	99	nil	nil
8	10	1	0.1	8.5	99	1	nil
9	10	1	0.2	8.5	100	nil	nil
10	10	100	0.6	8.5	98	nil	nil
11	10	100	0.6	8.8	100	nil	nil
12	100	1	0.3	8.8	100	nil	nil
13	100	10	0.6	8.8	100	nil	nil

were carried out with different concentrations of ions and the tolerance limit for each ion was determined.

1.0 ml of copper solution (1 mM) was taken in a 25 ml beaker. 2.5 ml of the reagent-II solution and the required amount of the ion to be tested were added and diluted to 20 ml. The pH of the solution was adjusted to 8.5 - 9.0 with dilute NaOH, the solution diluted to 25 ml and extracted with 25 ml of chloroform. The extract was dried and the absorbance was measured at 336 nm against a reagent blank. The aqueous layer was also analysed for copper. The results obtained for various ions are given in Table 17.

2.21 Interference of ions in the extraction photometric determination of nickel using reagent-II

The tolerance limits for various ions in the extraction photometric determination of nickel(II) with reagent-II was found out exactly as in the case of copper. The results obtained are given in Table 18.

2.22 Separation of nickel(II) from iron(III) using reagent-II in presence of hydroxylamine hydrochloride

From a mixed solution containing 1 ml each of nickel(II) and iron(III) solutions, extractions were performed at different pH values after the addition of reagent-II and different amounts of hydroxylamine

Table 17

Tolerance limit for various ions in the extraction photometric determination of copper(II) using reagent-II.

Copper taken for determination - 63.54 µg

Tolerance limit upto - µg	Foreign ion
3×10^6	Na^+, K^+, NH_4^+, Cl^-, NO_3^- ClO_4^-, tartrate, NH_2OH
1×10^6	Sr^{2+}, Zn^{2+}, Mg^{2+}, acetate, CO_3^{2-}, HCO_3^- oxalate, SO_4^{2-}, Br^-, F^-.
5×10^4	Ba^{2+}, Ca^{2+}, Mo(IV), VO_3^-, Bi^{3+}, Ag^+
1×10^4	Cd^{2+}, PO_4^{3-}, Al^{3+}, SCN^-, pb^{2+}
1×10^3	Sn(II), Ti(IV), Zr(IV)
< 50	Sn^{4+}, Cr(III)
Absent	Fe(III), Co(II), Mn(II), citrate $S_2O_3^{2-}$, EDTA, CN^-, Ni(II)

Table 18

Tolerance limit for various ions in the extraction photometric determination of nickel(II) using reagent-II

Nickel taken for determination - 58.69 µg

Tolerance limit upto - µg	Foreign ion
3×10^6	Na^+, K^+, Mg^{2+}, Cl^-, NO_3^- SO_4^{2-}, ClO_4^-, NH_4^+
1×10^6	Br^-, acetate, Zn^{2+}, Sr^{2+}, NH_2OH, CO_3^{2-}, HCO_3^-
5×10^5	F^-, SCN^-, Mo(IV)
1×10^5	Ca^{2+}, Ag^+, Ba^{2+}
3×10^4	Pb^{2+}, $S_2O_3^-$, Al^{3+}, Cd^{2+}
1×10^4	PO_4^{3-}, Bi^{3+}
1×10^3	Vanadate, Ti^{4+}, Zr^{4+}, Sn^{2+}, tartrate
< 50	Cr^{3+}, Sn^{4+}
Absent	EDTA, oxalate, citrate, CN^-, Fe(III), Co(II), Cu(II), Mn(II).

hydrochloride. The results obtained are given in Table 19.

2.23 Separation of nickel(II) from chromium(III) by extraction with reagent-II

To 1 ml of nickel(II) solution were added 2.5 ml of reagent II, 0.25 - 0.50 g of solid sodium perchlorate or acetate and varying amounts of chromium(III). The pH was adjusted to 9.0 - 9.5 and extractions carried out as before. The results are given in Table 20.

2.24 Simultaneous extraction-photometric determination of nickel(II) and copper(II) using reagent-II

An aliquot containing 10-60 µg each of nickel(II) and copper(II), 2.5 ml of the reagent and 1.5 ml of sodium perchlorate solution were taken in a 25 ml beaker, diluted to 10 ml and the pH of solution adjusted to 8.5 - 9.0. It was transferred to a separatory funnel, diluted to 15 ml and extracted with 10 ml of chloroform.

The extract was dried and the absorbance measured at 360 nm (λ_{max} of nickel-complex) and 336 nm (λ_{max} of copper complex). The amounts of the two metals in the 10 ml chloroform extract were found by solving the equations

Table 19

Separation of nickel(II) from iron(III) using reagent-II in the presence of hydroxylamine hydrochloride

pH	Hydroxylamine hydrochloride (g)	Percent extraction Ni(II)	Percent extraction Fe(III)
7.6	0.10	46.0	nil
8.0	0.10	81.0	nil
8.7	0.10	100.0	5.0
8.7	0.25	100.0	nil
9.5	0.25	100.0	nil
10.0	0.25	-	Part of the Fe(III) precipitated as hydroxide

Table 20

Separation of nickel(II) from chromium(III) using reagent-II

58.7 µg of nickel(II) was taken for each extraction.

Cr(III) taken (µg)	Percent extraction	
	nickel(II)	chromium(III)
30	90.0	nil
45	84.0	nil
60	70.0	nil
100	49.0	nil
300	23.0	nil

$$\mathrm{Ni} = \frac{A_{360}\,\epsilon_{336}^{\mathrm{Cu}} - A_{336}\,\epsilon_{360}^{\mathrm{Cu}}}{\epsilon_{360}^{\mathrm{Ni}}\,\epsilon_{336}^{\mathrm{Cu}} - \epsilon_{336}^{\mathrm{Ni}}\,\epsilon_{360}^{\mathrm{Cu}}} \times 0.587\ \mathrm{g}$$

$$\mathrm{Cu} = \frac{A_{336}\,\epsilon_{360}^{\mathrm{Ni}} - A_{360}\,\epsilon_{336}^{\mathrm{Ni}}}{\epsilon_{360}^{\mathrm{Ni}}\,\epsilon_{336}^{\mathrm{Cu}} - \epsilon_{336}^{\mathrm{Ni}}\,\epsilon_{360}^{\mathrm{Cu}}} \times 0.635\ \mathrm{g}$$

where A_{336} and A_{360} are the absorbances of the sample extract at 336 nm and 360 nm and ϵ values are the molar absorptivities for the nickel and copper complexes of reagent-II at the above wavelengths. The results obtained are given in Table 21.

2.25 Simultaneous extraction-photometric determination of nickel(II) and copper(II) in presence of iron(III) using reagent-II and hydroxylamine hydrochloride

For the simultaneous extraction-photometric determination of copper(II) and nickel(II) in presence of iron(III), 0.2 g of the hydroxylamine hydrochloride was added to the solution. The extractions were carried out at pH 8.5 - 9.0 with different quantities of copper(II) and nickel(II) as before. The results obtained are given in Table 21.

Table 21

Simultaneous extraction-photometric determination of copper(II) and nickel(II) using reagent-II

No.	Taken, ug		Found, ug		Error %	
	Copper(II)	Nickel(II)	Copper(II)	Nickel(II)	Copper(II)	Nickel(II)
1	50.8	46.9	51.0	46.6	0.4	0.6
2	12.7	58.7	12.5	58.6	1.6	0.2
3	25.4	29.3	25.7	29.4	1.2	0.3
4	38.1	17.6	38.3	17.2	0.5	2.3
5	31.8	23.5	31.9	24.0	-	2.1
6	18.9	11.7	18.7	11.9	1.0	1.7
7*	15.8	14.7	16.0	14.8	1.3	0.7
8*	18.9	11.7	19.3	11.5	2.1	1.7
9*	50.8	35.1	50.7	34.9	0.2	0.6
10**	63.5	58.7	63.1	58.0	0.6	1.2

* in presence of iron(III) (56 ug)

** in presence of iron(III) and chromium(III) by the method given in 2.36.

2.26 Interference of ions in the simultaneous extraction-photometric determination of copper(II) and nickel(II) using reagent-II

A solution containing 15-50 µg of copper and nickel each were taken for extraction. The required amount of the ion to be tested was added. The simultaneous determination was carried out as in 2.24 and 2.25. The tolerance limits of various ions are given in Table 22.

2.27 Separation of cobalt(II) from copper(II) using reagent-II and thiosulphate as masking agent

These extractions were carried out exactly as for separation of nickel(II) from copper(II) described in 2.15. The results obtained are given in Table 23.

2.28 Separation of copper(II) from cobalt(II) using reagent-II and sodium tartrate

The procedure was as given in 2.18. Results are given in Table 24.

2.29 Effect of diethylamine in the extraction of metals using reagent-II

The procedure was essentially as given in 2.11. The pH was adjusted to 8.0 - 8.5 with aqueous diethylamine (1:1) before extraction. The absorption spectra are given in Figs. 19-23 and the λ_{max} and ϵ_M in Table 25-A. Table 25-B shows the increase in percent extraction when diethylamine is used. Diethylamine by itself does not lead to any significant degree of extraction.

Table 22

Tolerance limit for various ions in the simultaneous extraction-photometric determination of copper(II) and nickel(II) using reagent-II

50 µg each of the metals were used for each extraction.

Tolerance limit (µg)	Foreign ion
1×10^6	Na^+, K^+, NH_4^+, NO_3^-, ClO_4^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-, Cl^-, NH_2OH.
5×10^5	Zn^{2+}, Mg^{2+}, acetate, Br^-
3×10^4	Ba^{2+}, Ca^{2+}, F^-, Ag^+
1×10^4	Cd^{2+}, Al^{3+}, Pb^{2+}, Sr^{2+}, SCN^-, Mo(IV)
10^3	Vanadate, PO_4^{3-}, Bi^{3+}, Sn^{2+}
1×10^2	Ti(IV), Zr(IV)
< 50	Cr^{3+}, Sn^{4+}, tartrate
Absent	S_2O_3, CN^-, EDTA, oxalate citrate, Fe(III), Co(II), Mn(II).

Table 23

Separation of cobalt(II) from copper(II)
using reagent-II and thiosulphate as masking agent

pH	Sodium thiosulphate (g)	Percent extraction	
		Copper(II)	Cobalt(II)
8.5	0.1	47.0	87.0
8.5	0.2	39.0	83.0
8.5	0.3	28.0	80.0
8.5	0.5	26.0	80.0
9.0	0.5	51.0	89.0
9.5	0.5	71.0	93.0

Table 24

Separation of copper(II) from cobalt(II) using reagent-II and sodium tartrate as masking agent

pH	Sodium tartrate (g)	Percent extraction	
		Copper	Cobalt
6.5	0.05	86	56
8.0	0.25	96	31
9.0	1.0	100	19
9.0	1.50	98	15
9.5	1.50	100	29

Table 25-A

Effect of diethylamine on the absorption spectra of metal-reagent(II) complexes

Metal	Ligand-II		Ligand II + Diethylamine	
	λ_{max} nm	ϵ_M ± 100	λ_{max} nm	ϵ_M ± 100
Copper(II)	336	7300	336	7700
Nickel(II)	360	6200	360	9200
Cobalt(II)	338	7700	344	8400
Iron(III)	334	5080	334	6600
Manganese(II)	342	6250	338	9000

Table 25-B

Effect of diethylamine on the percent extraction of metals

Metal	pH	Percent extraction without diethylamine	Percent extraction with diethylamine
Copper(II)	3.6	45.0	80.0
Nickel(II)	6.6	nil	16.0
Cobalt(II)	6.7	10.0	68.0
Iron(III)	3.8	57.0	55.0

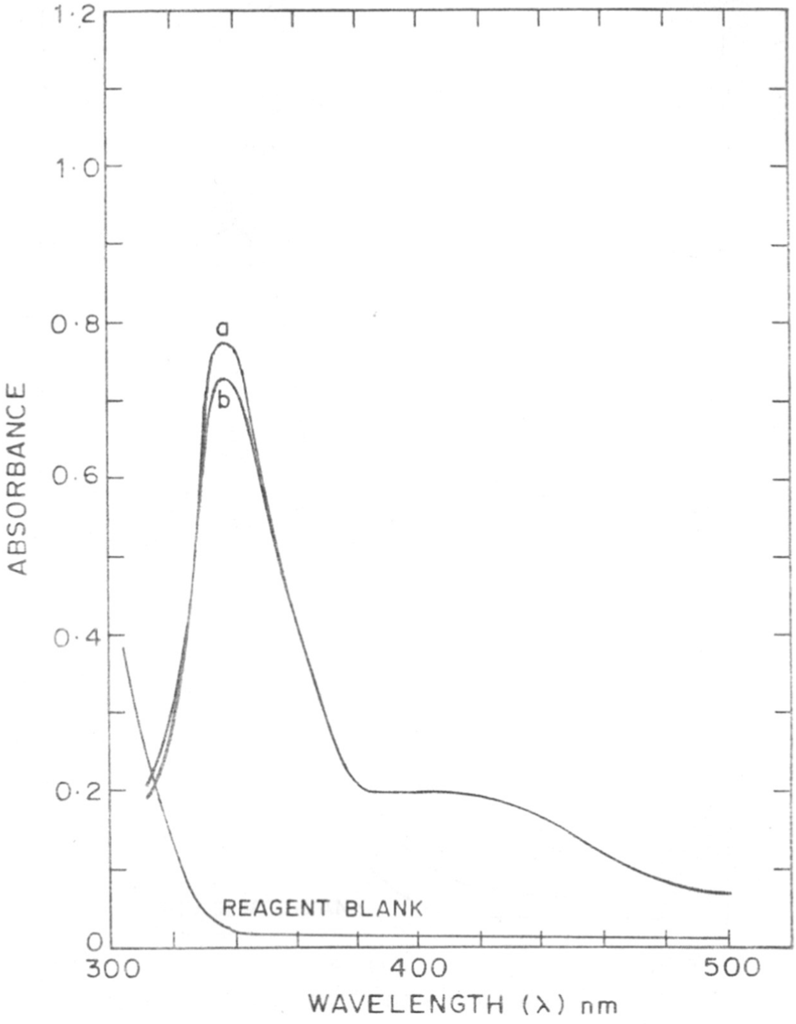


FIG. 19. ELECTRONIC ABSORPTION SPECTRA OF COPPER (II)-REAGENT-II COMPLEX IN CHLOROFROM,
(a) WITH DIETHYLAMINE
(b) WITHOUT DIETHYLAMINE

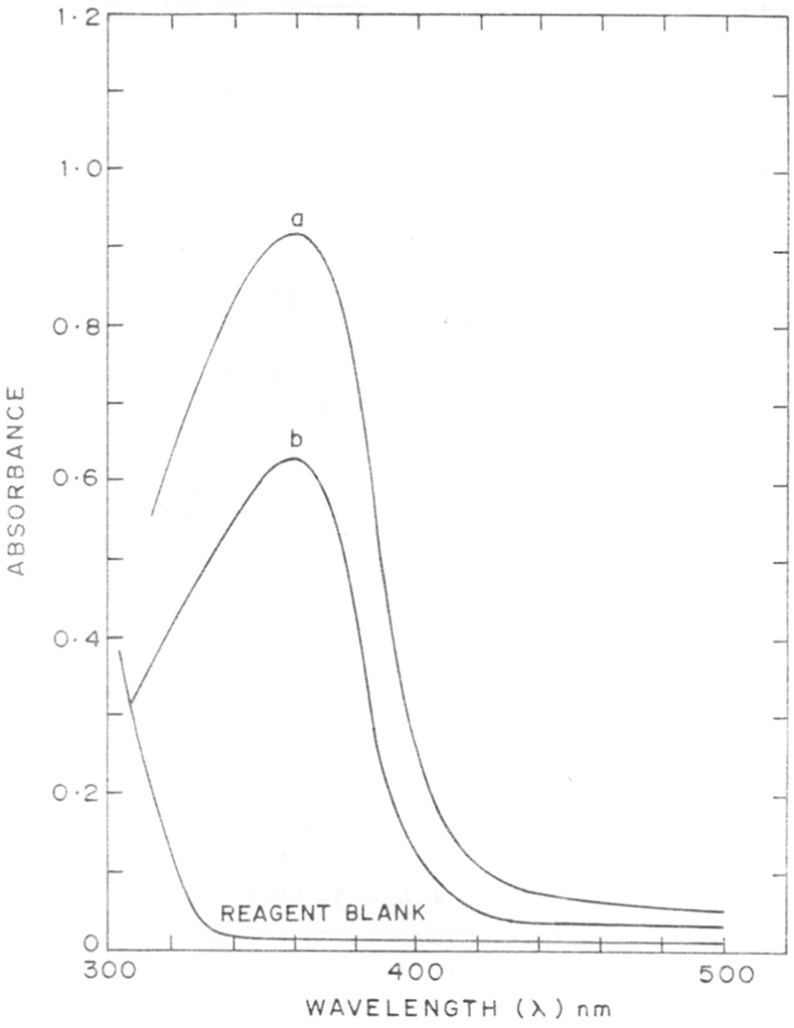


FIG. 20. ELECTRONIC ABSORPTION SPECTRA OF NICKEL-(II)-REAGENT-II COMPLEX IN CHLOROFORM,

(a) WITH DIETHYLAMINE

(b) WITHOUT DIETHYLAMINE

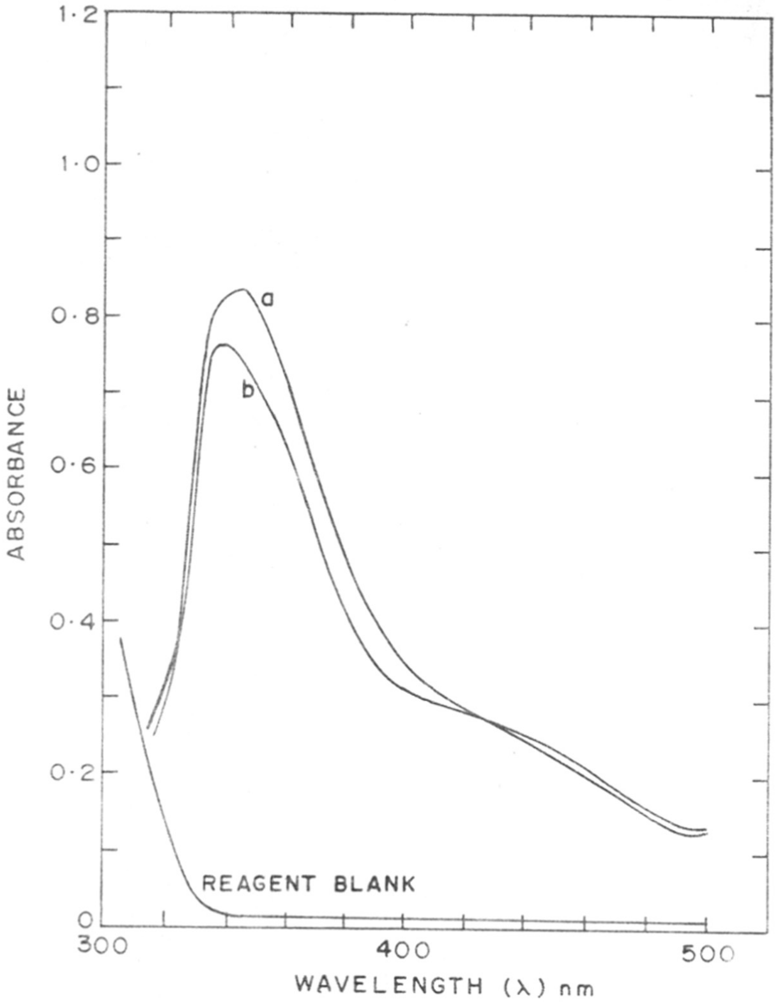


FIG. 21. ELECTRONIC ABSORPTION SPECTRA OF COBALT (II)-REAGENT II COMPLEX IN CHLOROFORM,

(a) WITH DIETHYLAMINE

(b) WITHOUT DIETHYLAMINE

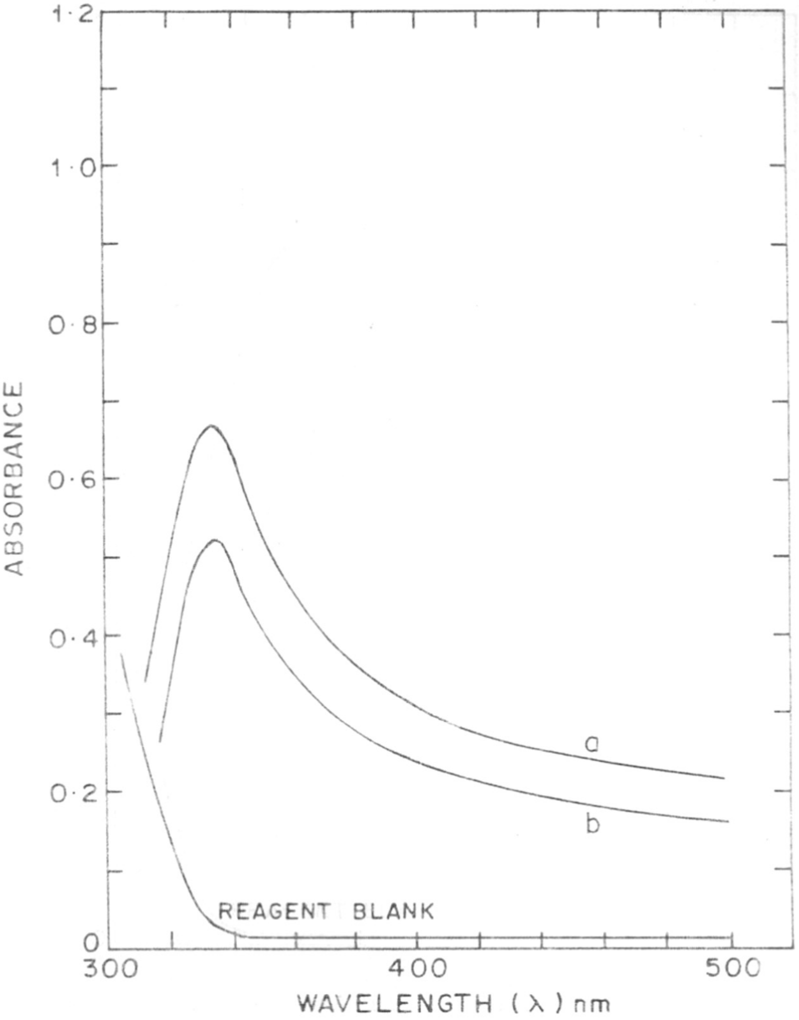


FIG. 22. ELECTRONIC ABSORPTION SPECTRA OF IRON (III)-REAGENT-II COMPLEX IN CHLOROFORM
(a) WITH DIETHYLAMINE
(b) WITHOUT DIETHYLAMINE

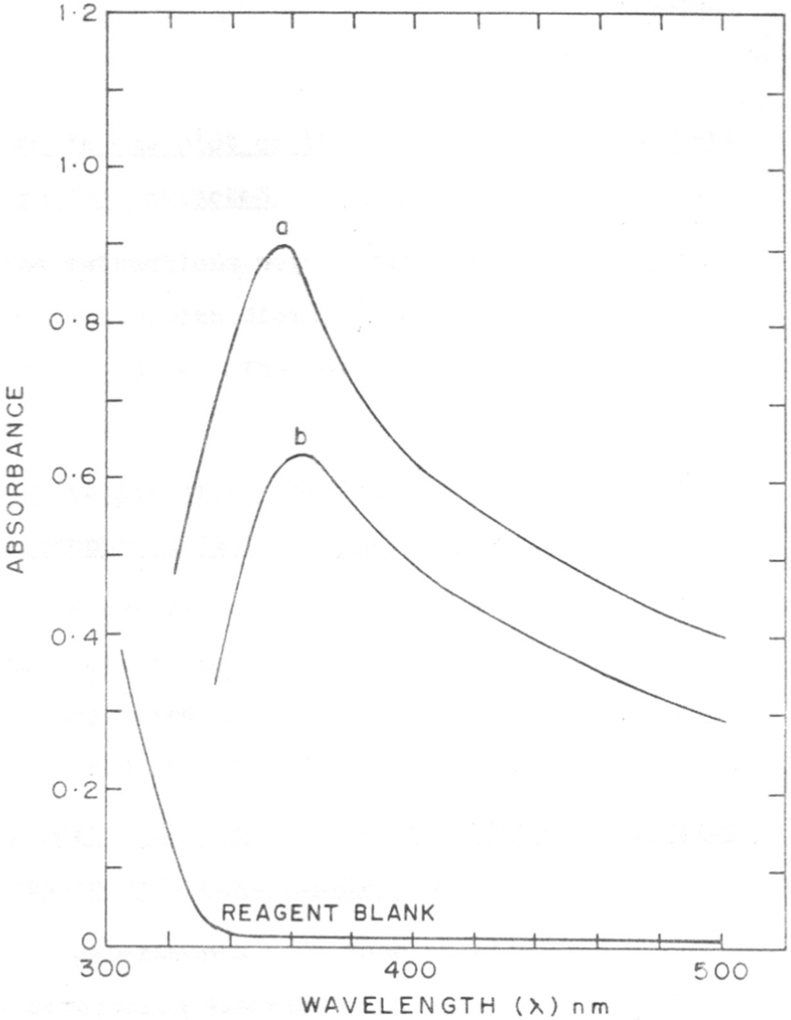


FIG. 23. ELECTRONIC ABSORPTION SPECTRA OF MANGANESE-(II)-REAGENT-II COMPLEX

(a) WITH DIETHYLAMINE

(b) WITHOUT DIETHYLAMINE

2.30 Beer's Law plot of the copper(II) - reagent-II complex extracted in presence of diethylamine

The extractions were done after adjusting the pH to 8.0 - 9.0 with diethylamine. Absorbances were measured at 336 nm. The Beer's Law plot is given in Fig. 24.

2.31 Separation of copper(II) from nickel(II) using reagent-II, diethylamine and tartrate

These experiments were carried out with different quantities of sodium tartrate and at different pH's using diethylamine to adjust the pH. The results are given in Table 26.

2.32 Separation of copper(II) from cobalt(II) using reagent-II, diethylamine and tartrate

The experiments were done exactly as for copper, nickel separation described in 2.31. The results obtained are given in Table 27.

2.33 Separation of copper(II) from chromium(III) using reagent-II and sodium tartrate

The procedure was the same as for the copper-iron separation described in 2.18 except that the reagent was first dissolved in chloroform instead of being added to

Table 26

Separation of copper(II) from nickel(II) using reagent-II, diethylamine and tartrate

pH	Sodium tartrate (mg)	Percent extraction of metals	
		Copper(II)	Nickel(II)
4.4	5	98	nil
4.6	5	100	nil
4.6	10	97	nil
5.5	5	100	nil
6.0	5	100	1
6.0	10	100	nil
7.0	10	100	15

Table 27

Separation of copper(II) from cobalt(II) using reagent-II, diethylamine and tartrate

pH	Sodium tartrate (mg)	Percent extraction	
		Copper(II)	Cobalt(II)
7•1	25	100	12
7•1	100	100	nil
7•1	250	95	nil
7•6	75	100	nil
8•1	100	100	7
8•1	250	98	3

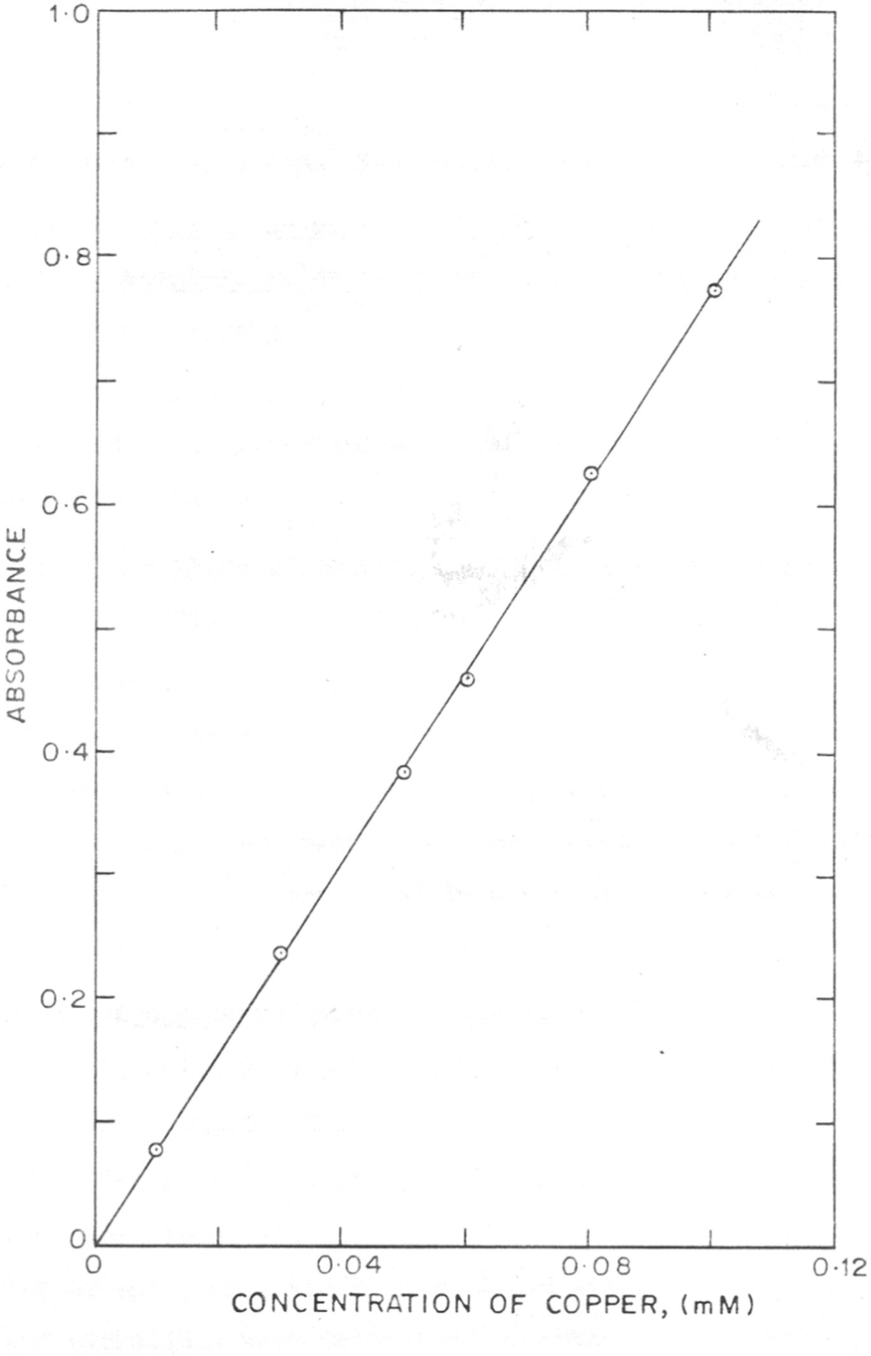


FIG. 24. BEER'S LAW PLOT OF COPPER (II)-
REAGENT-II COMPLEX IN
PRESENCE OF DIETHYLAMINE

the aqueous solution. The results are given in Table 28.

2.34 Separation of copper(II) from chromium(III) using reagent-II in presence of diethylamine (or aniline) and tartrate

The procedure was as in 2.33 except that the pH was adjusted with diethylamine or aniline. The results are given in Table 29.

2.35 Separation of copper(II), niciel(II) and iron(III) together from chromium(III) using reagent-II

The solution contained 1 micromole each of copper(II), nickel(II), iron(III) and chromium(III). Extraction was carried out as in 2.11, without the addition of any masking agent. Copper and nickel were completely extracted with partial (60%) extraction of iron and nil extraction of chromium.

2.36 Simultaneous determination of copper(II) and nickel(II) in presence of iron(III) and chromium(III) using reagent-II

The extraction of copper(II) and nickel(II) along with some iron(III) was carried out as given in 2.35. The organic layer was then stripped with acid and the copper(II) and nickel(II) were determined by extraction-photometry

Table 28

Separation of copper(II) from chromium(III) using reagent-II in chloroform with sodium tartrate

pH	Percent extraction		No. of extractions
	Copper(II)	Chromium(III)	
8.0 - 8.5	51	nil	1
9.0 - 9.5	70	nil	1
9.0 - 9.5	90	nil	2
9.5 - 10.0	78	nil	1
9.5 - 10.0	99	nil	3

Table 29

Separation of copper(II) from chromium(III) using reagent-II in chloroform, with sodium tartrate and diethylamine or aniline

pH	Percent extracted in single extraction	
	Copper(II)	Chromium(III)
8.0 - 8.5	85.0	nil
8.5 - 9.0	89.0	nil
9.0 - 9.5	93.0	nil
*9.0 - 9.5	85.0	nil
9.5 - 10.0	98.0	nil

* Aniline was used instead of diethylamine

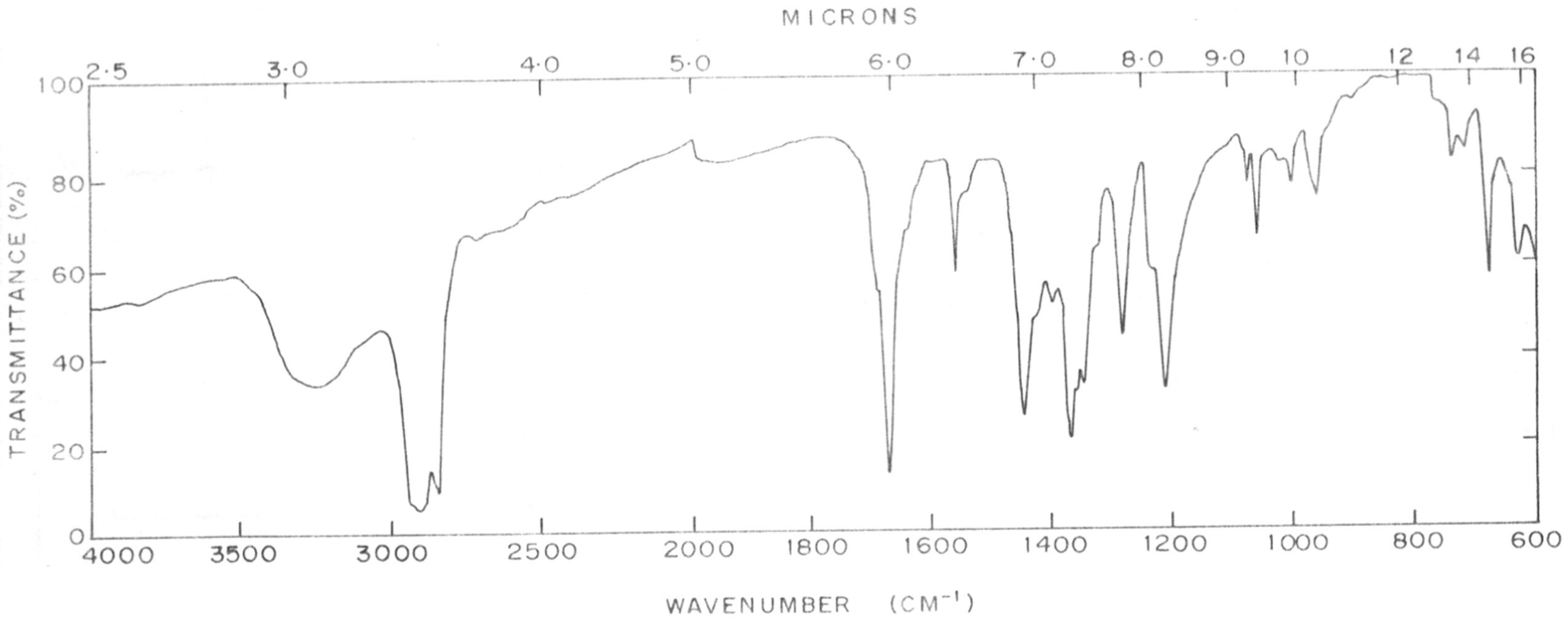


FIG. 25 THE IR SPECTRUM OF 3, 5—DIBROMO-2,4-DIMETHYL-6-HYDROXYACETOPHENONE IN NUJOL

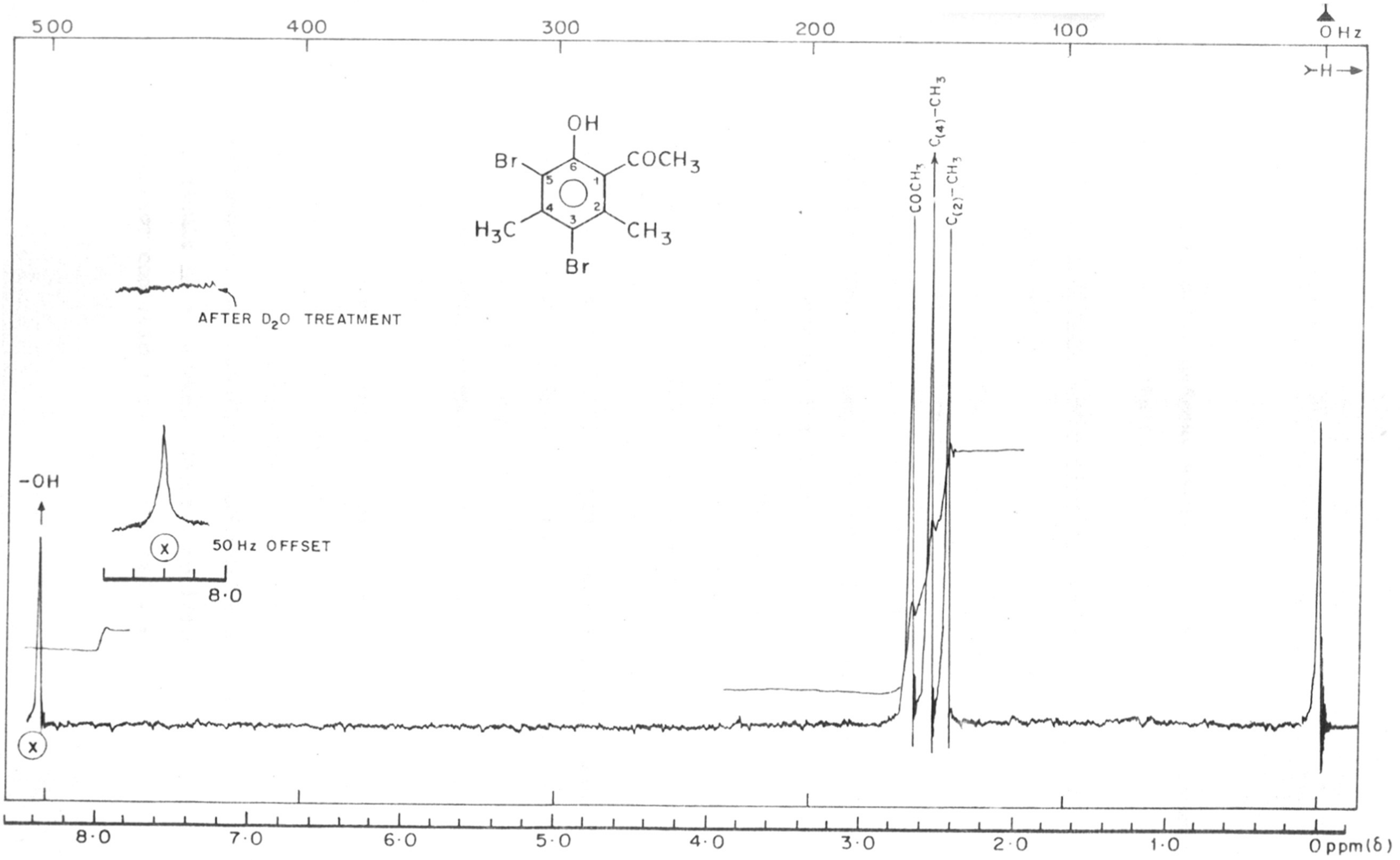


FIG. 26. NMR SPECTRUM OF 3,5–DIBROMO–2,4–DIMETHYL–6–HYDROXY–
–ACETOPHENONE IN CCl_4

as in 2.25 using hydroxylamine to suppress the extraction of iron. The results is given in Table 21.

2.37 3,5-Dibromo-2,4-dimethyl-6-hydroxyacetophenone (reagent-III)

1.0 g of reagent-I and 25 ml of 50 percent aqueous acetic acid were taken in a 100 ml beaker. 2.4 g of bromine in 9.5 ml of 80 percent acetic acid was added dropwise with stirring. The reaction mixture was kept at room temperature for 2 hrs. It was then diluted with water and extracted twice with chloroform. The chloroform extract was washed with water several times to remove the acetic acid. The chloroform was removed and the product obtained was recrystallized from chloroform-pet.ether (60-80°C) mixture (1:5) to give white crystals, m.p. 123°C. Analysis: Found C, 37.29; H, 3.15; Br, 49.70 percent. Required for $C_{10}H_{10}Br_2O_2$; C, 37.30; H, 3.13; Br, 49.63 percent. The IR and the NMR spectra are given in Figs. 25 and 26 respectively.

Attempts to prepare a pure monobromo product from reagent-I using the procedure recommended in literature[85] for 3,5-dimethyl-6-hydroxyacetophenone were unsuccessful. The product was probably a mixture of isomers which was difficult to separate. Several modifications of the reaction conditions were also tried without success.

2.38 3,5-Dibromo-2,4-dimethyl-6-hydroxyacetophenone oxime (Reagent-IV)

3.0 g of reagent-III, 4.5 g of hydroxylamine hydrochloride and 22 ml of water were taken in a 250 ml round bottomed flask. 22 ml of alcoholic sodium hydroxide (2.5 ml of sodium hydroxide in 5 ml water diluted to 35 ml with alcohol) was added. It was refluxed on the water bath for 30 minutes, cooled, diluted to 100-150 ml with water and extracted with benzene. The benzene was evaporated and the solid residue obtained was recrystallized from benzene-pet. ether (60-80°C fraction) mixture (1:10) to give white crystals, m.p. 137°C.

Analysis: Found C, 36.0; H, 3.55; Br, 46.93; N, 4.17 percent. Required for $C_{10}H_{11}Br_2O_2N$; C, 35.63; H, 3.29; Br, 47.42; N, 4.15 percent.

The IR spectrum of the compound is given in Fig. 27.

2.39 Potentiometric titration of reagents-III and IV in 50% aqueous ethanol

1 millimole of the reagent was dissolved in 50 ml of ethanol in a 250 ml beaker. 1 ml of standard hydrochloric acid (0.862 N) was added and the solution diluted with deionised water to 100 ml. It was potentiometrically titrated against carbonate-free standard sodium

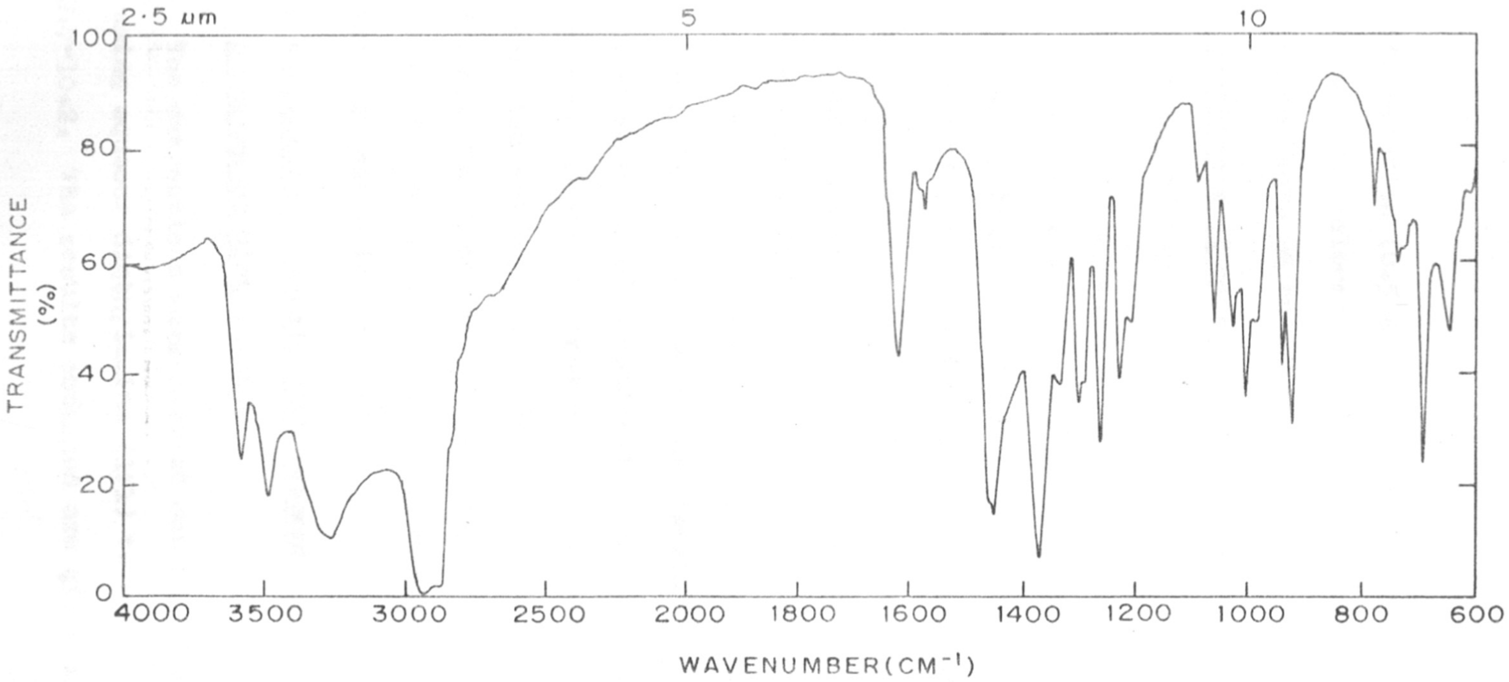


FIG. 27 THE IR SPECTRUM OF 3,5-DIBROMO-2,4-DIMETHYL-6-HYDROXYACETOPHENONE OXIME IN NUJOL

hydroxide solution (0.588 N) with stirring, in nitrogen atmosphere. The relevant portions of the titration curves are given in Figs. 28 and 29.

2.40 Extractions of metals using reagent-III in presence of ammonia

To 1 ml of the metal solution (1 mM) were added 2.5 ml of sodium perchlorate solution (1 M) and 2.5 ml of the ligand solution (0.8 g in 100 ml ethanol). The solution was diluted to around 18 ml and the pH adjusted with aqueous ammonia solution (1:1) to 9.5 - 10.0. The solution was allowed to stand for 2 hrs at room temperature and then transferred to the separatory funnel. It was diluted to 25 ml and extracted with 25 ml of chloroform. Extractions were also carried out using an ammoniacal solution of ligand-III (0.8 g in 100 ml 1:1 aqueous ammonia) instead of an alcoholic solution. This solution was kept for several hours at room temperature before use. The metal in both the layers was estimated by AAS and the percent extraction calculated. The results obtained are given in Table 30.

2.41 Extraction of metals with reagent-III in presence of diethylamine

The extractions were carried out as given above but using aqueous diethylamine (1:1) to adjust the pH to 9.7-10.2. The results obtained are given in Table 31.

Table 30

Extraction of metals with reagent-III in presence of ammonia

Metal	Percent extraction	
	Using alcoholic solution of reagent-III	Using ammoniacal solution of reagent-III
Copper(II)	87	99
Nickel(II)	58	97
Cobalt(II)	44	89
Iron(III)	98	100
Manganese(II)	45	81

Table 31

Extraction of metals with reagent-III in presence of diethylamine

Metal	Percent extraction
Copper(II)	96
Nickel(II)	60
Cobalt(II)	32
Iron(III)	55
Manganese(II)	18

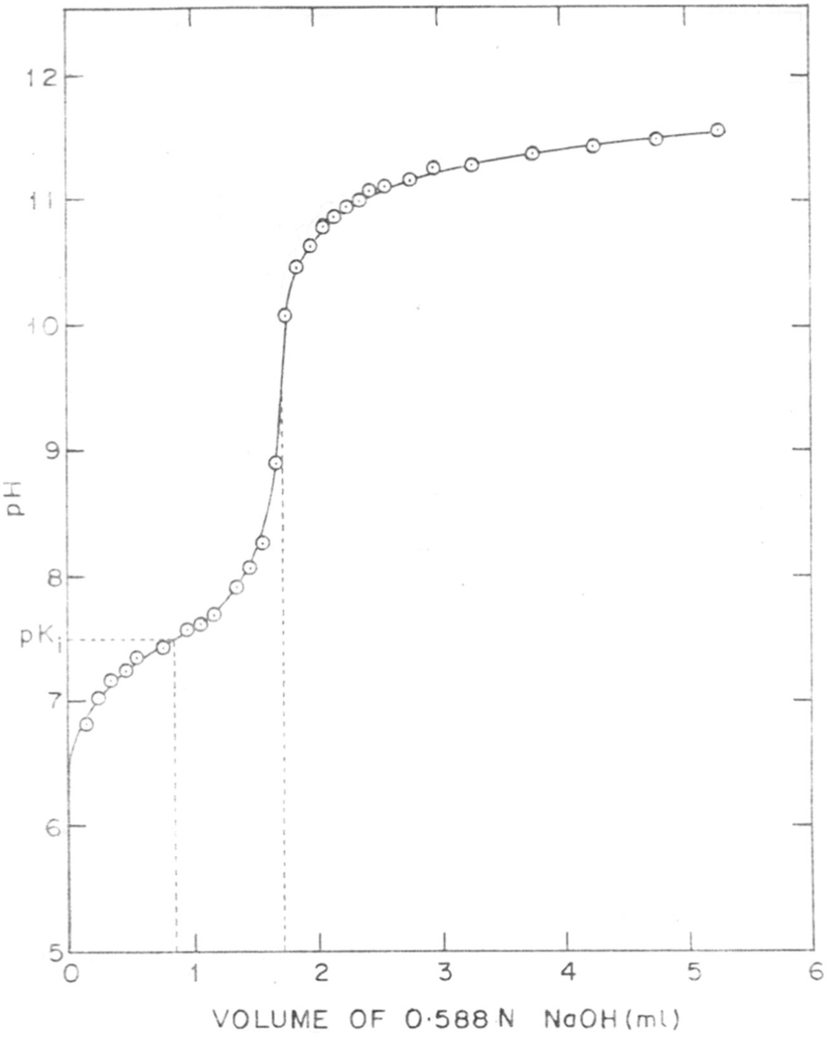


FIG. 28. POTENTIOMETRIC TITRATION CURVE OF REAGENT-III

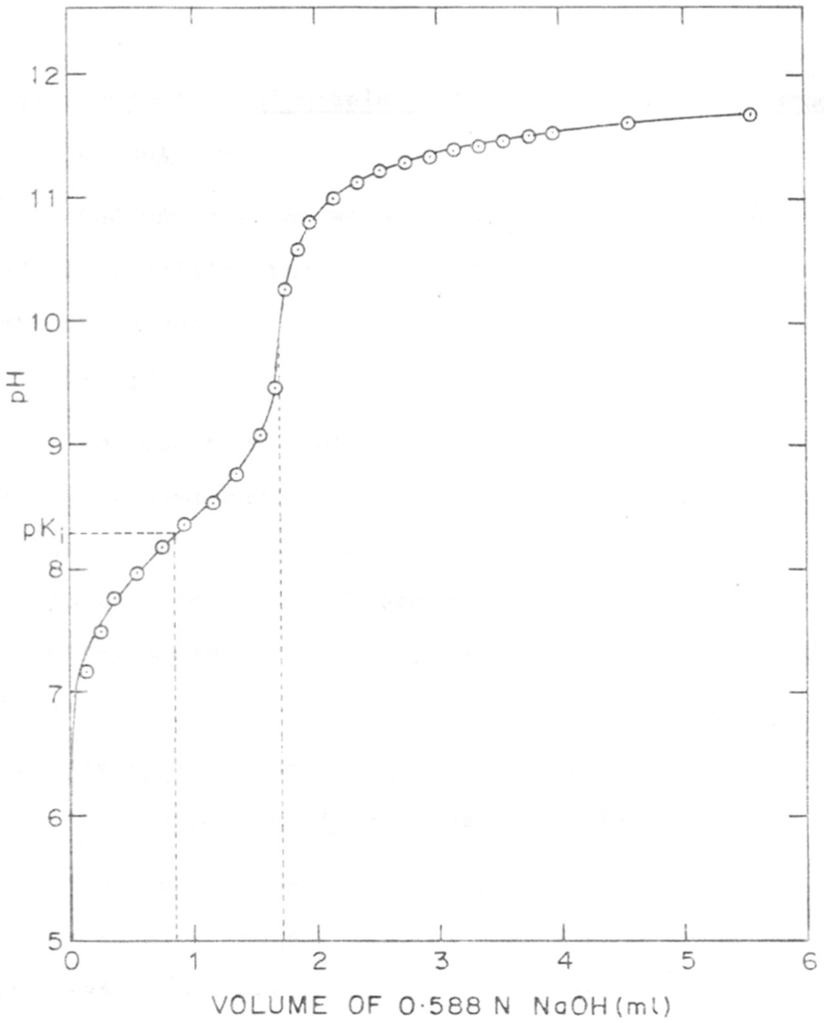


FIG. 29. POTENTIOMETRIC TITRATION CURVE OF REAGENT – IV

2.42 Extraction of metals with reagent-III in presence of aniline

The extractions were carried out as above but using 0.5 ml of aniline instead of diethylamine. The pH of the extraction was 6.5 - 7.0. The results obtained are given in Table 32.

The electronic absorption spectra of the complexes (in 2.40, 2.41 and 2.42) in chloroform were recorded. It was found that the metal complexes absorbed in the region in which blank absorbance was very high. So reagent-III was not used further for extraction-photometric study.

2.43 Extractions with 3,5-dibromo-2,4-dimethyl-6-hydroxyacetophenone oxime (reagent-IV)

The extractions were carried out essentially as in the case of reagent-III, as described above. Reagent-IV was used as a solution in ethanol (0.85 g in 100 ml). The pH of the solutions, prior to extraction, was adjusted with sodium hydroxide, except in the case of copper in which case aqueous diethylamine (1:1) was used. The copper complex was extracted into benzene, as it was not extractable into chloroform and most other usual solvents. The solid copper complex was also soluble in diethylamine.

Table 32

Extraction of metals with reagent-III in presence of aniline.

Metal	Percent extraction
Copper(II)	89
Nickel(II)	9
Cobalt(II)	14
Iron(III)	65
Manganese(II)	nil

The electronic absorption spectra of the organic extracts are given in Fig. 30. The values for λ_{max}, ϵ_M and percent extraction are given in Table 33.

2.44 Beer's Law plots of the complexes of copper(II), nickel(II) and cobalt(II) with reagent-IV

The absorbances of the extracts were measured for nickel(II), cobalt(II) and copper(II) at 372 nm, 356 nm and 350 nm respectively. The extraction of copper was carried out with the addition of diethylamine as mentioned above. The Beer's Law plots are given in Figs. 31, 32 and 33.

2.45 Beer's Law plots of the complexes of iron(III) and manganese(II)

The absorbances were measured at 336 nm for iron(III) and 346 nm for manganese(II). The plot for the iron(III) complex is given in Fig. 34. The values for the manganese-complex were too scattered for plotting.

2.46 Extraction of metal-reagent-IV complexes at different pHs

The variation of percent extraction with pH for the complexes of copper(II), nickel(II), cobalt(II) and iron(III) at different pHs are given in Tables 34, 35, 36 and 37. The pH vs extraction plots are given

Table 33

λ_{max} (nm) and ϵ_M of metal-reagent-IV complexes

Metal	λ_{max} (nm)	ϵ_M
Copper(II)	350	$(7{\cdot}7 \pm 0{\cdot}1) \times 10^3$
Nickel(II)	372	$(7{\cdot}8 \pm 0{\cdot}1) \times 10^3$
Cobalt(II)	356	$(10{\cdot}5 \pm 0{\cdot}1) \times 10^3$
Iron(III)	336	$(10{\cdot}6 \pm 0{\cdot}1) \times 10^3$
Manganese(II)	346	$(7{\cdot}8 \pm 0{\cdot}1) \times 10^3$

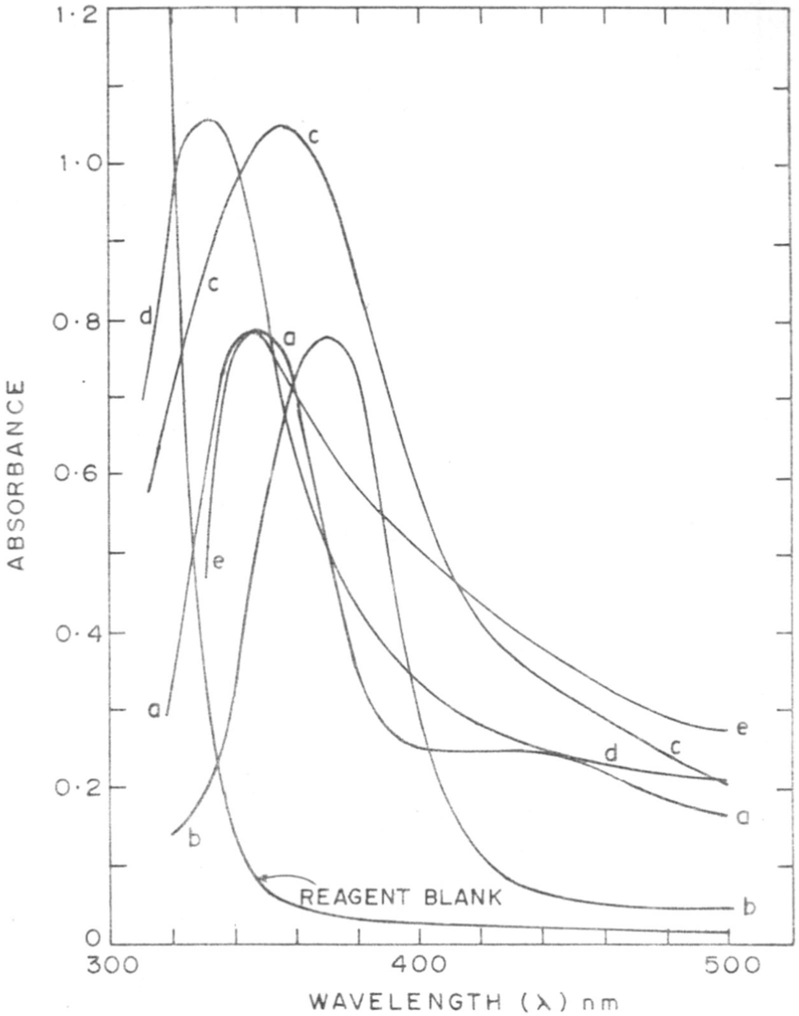


FIG. 30. ABSORPTION SPECTRA OF THE REAGENT-IV-COMPLEXES IN CHLOROFORM (IN BENZENE FOR COPPER) OF (a) COPPER(II), (b) NICKEL(II), (c) COBALT(II), (d) IRON(III) AND (e) MANGANESE(II)

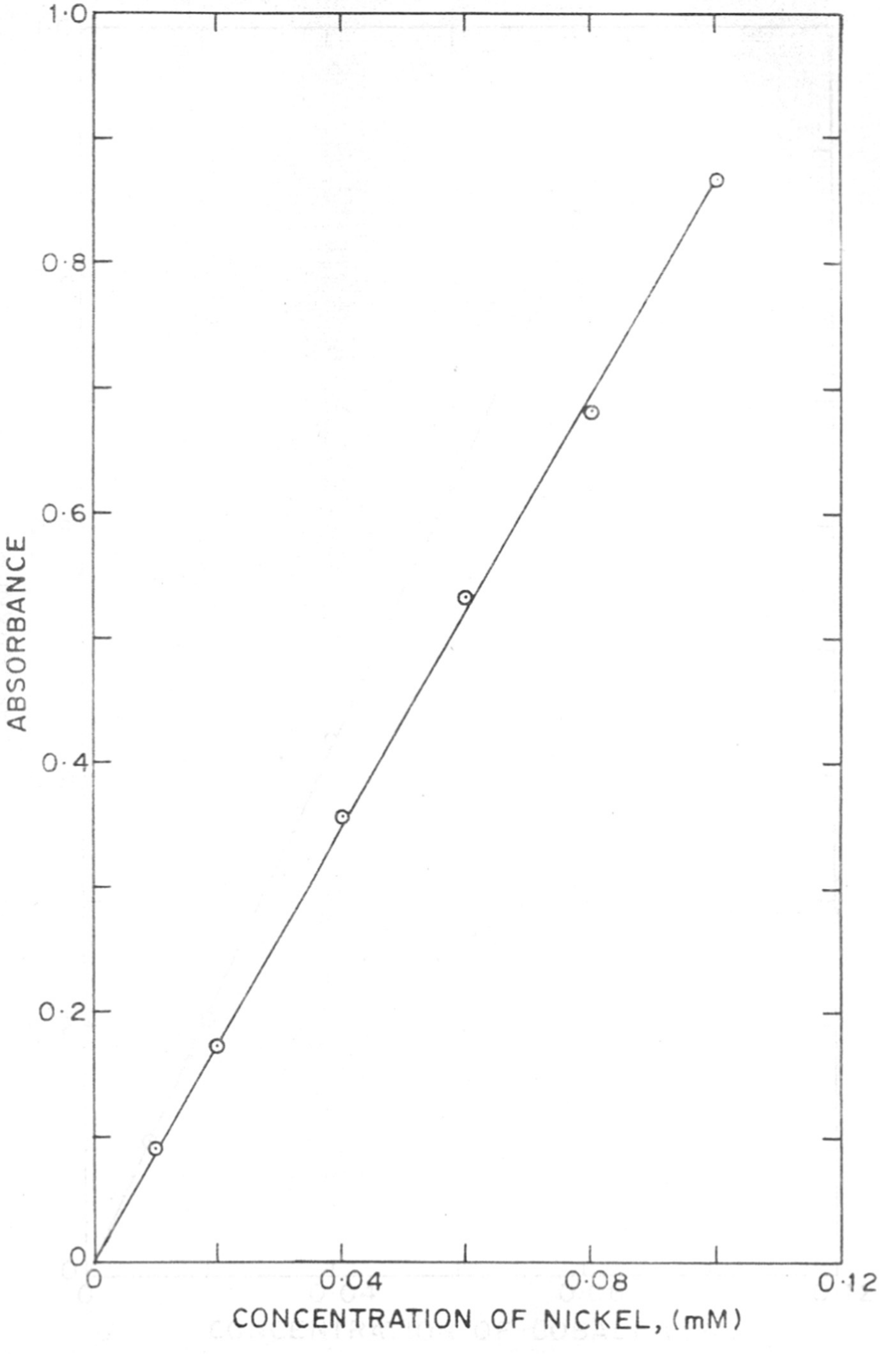


FIG. 31. BEER'S LAW PLOT OF NICKEL (II)-
REAGENT-IV COMPLEX

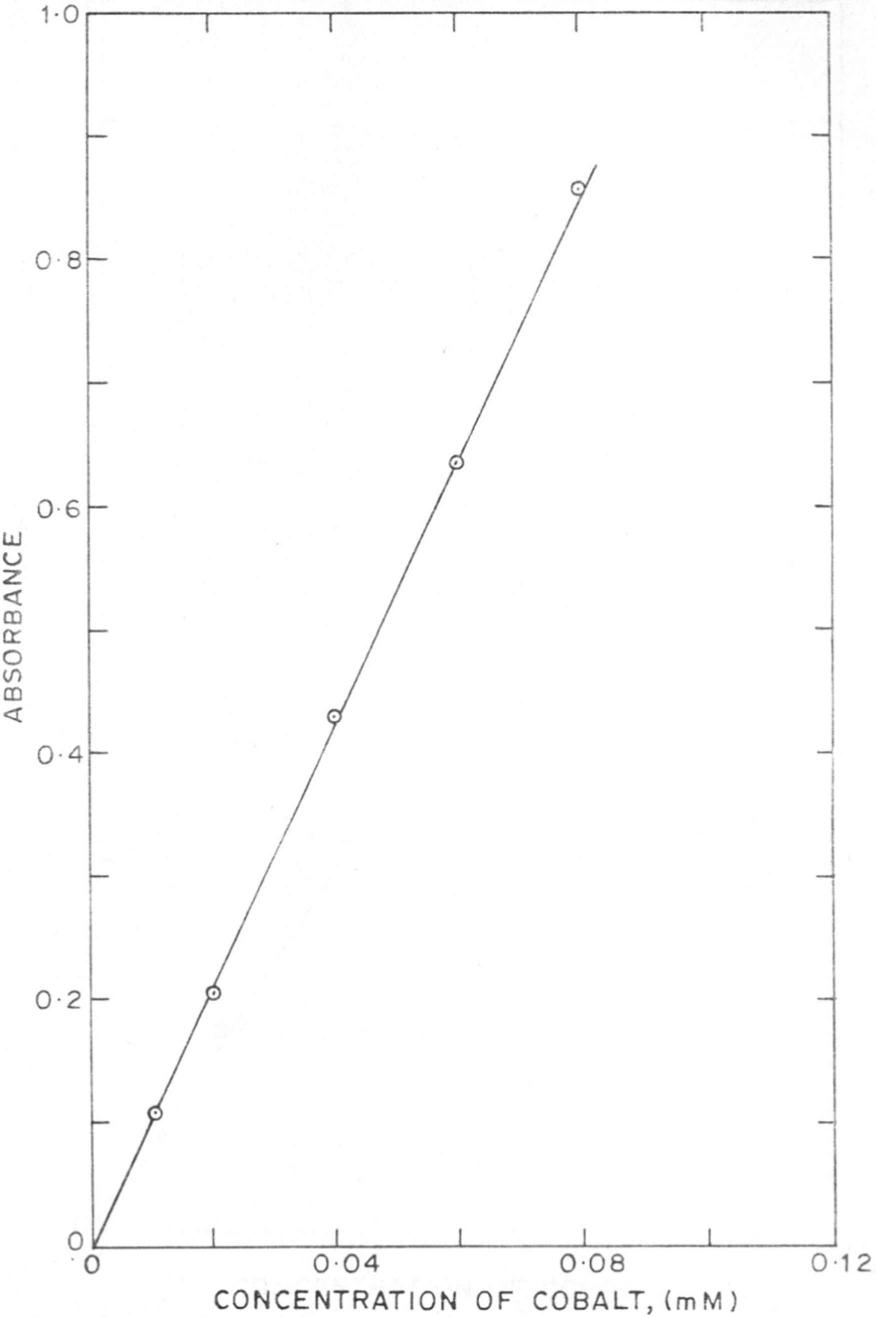


FIG. 32: BEER'S LAW PLOT OF COBALT (II)-REAGENT-IV COMPLEX

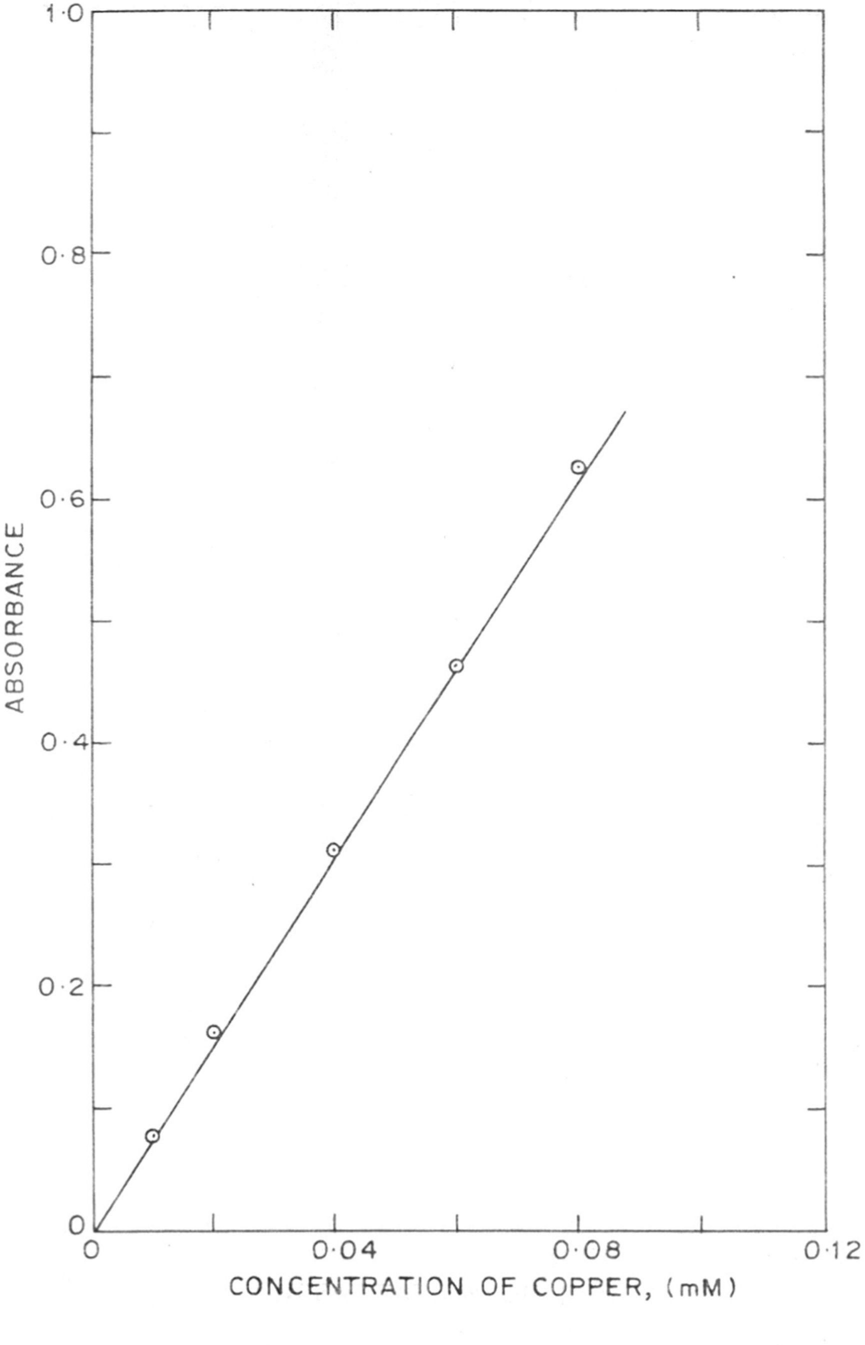


FIG. 33. BEER'S LAW PLOT OF COPPER (II)-
REAGENT-IV COMPLEX IN
PRESENCE OF DIETHYLAMINE

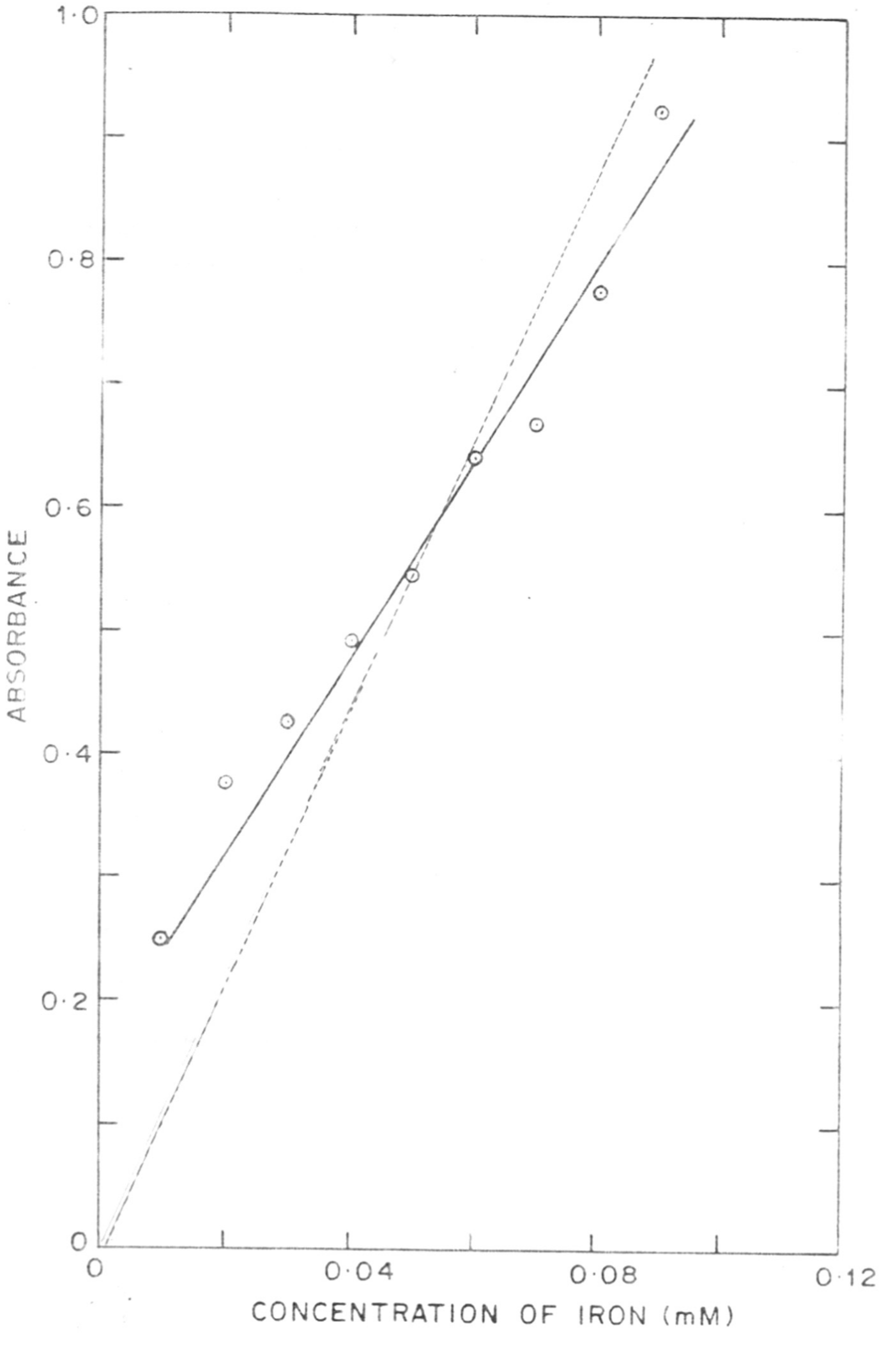


FIG. 34. BEER'S LAW PLOT OF IRON-(III)-
REAGENT-IV COMPLEX

Table 34

Extraction of copper(II) - reagent IV complex at different pHs.

pH	Percent extraction
1.97	2
2.49	27
3.17	81
3.58	96
3.90	100
5.0	100
7.0	100
9.0	100
10.0	100
11.0	100

Table 35

Extraction of nickel(II) - reagent-IV complex at different pHs

pH	Percent extraction
3.6	nil
5.1	5.3
5.7	51.0
6.2	85.0
6.5	97.0
7.0	100.0
8.0	100.0
9.0	100.0
10.0	97.0
10.5	87.0

Table 36

Extraction of cobalt(II)-reagent-IV complex at different pHs

pH	Percent extraction
3·7	nil
5·4	2·0
6·0	25·0
6·6	82·0
7·2	99·0
9·0	100·0
10·9	100·0
10·5	96·0
11·0	83·0

Table 37

Extraction iron(III)-reagent-IV complex at different pHs

pH	Percent extraction
2.1	1.5
2.5	12.0
2.9	31.0
3.3	82.0
3.7	94.5
4.0	99.0
4.5	100.0
5.0	100.0
9.0	99.0
10.0	92.0

in Figs. 35, 36, 37 and 38. The copper complex was extracted in presence of diethylamine.

2.47 Effect of diethylamine on the extraction of metals with reagent-IV

The values for molar absorbance ϵ_M and λ_{max} of the complexes of nickel(II), cobalt(II), iron(III) and manganese(II) extracted with and without the addition of diethylamine are given in Table 38. The absorption spectra are given in Figs. 39, 40, 41 and 42.

The values for copper (necessarily with addition of diethylamine) are included in Table 38. Without the addition of diethylamine, very little (5-10%) extraction was observed. The complex precipitated from the extract on standing for a few minutes. The percent extraction and stability of the extract increased sharply with the addition of diethylamine but a quantitative relation could not be found between the percent extraction and the concentration of diethylamine.

2.48 Separation of copper(II) from nickel(II) using reagent-IV, diethylamine and sodium tartrate as masking agent

The procedure was essentially the same as for reagent-II (2.17), except that the pH was adjusted with diethylamine. Results are presented in Table 39.

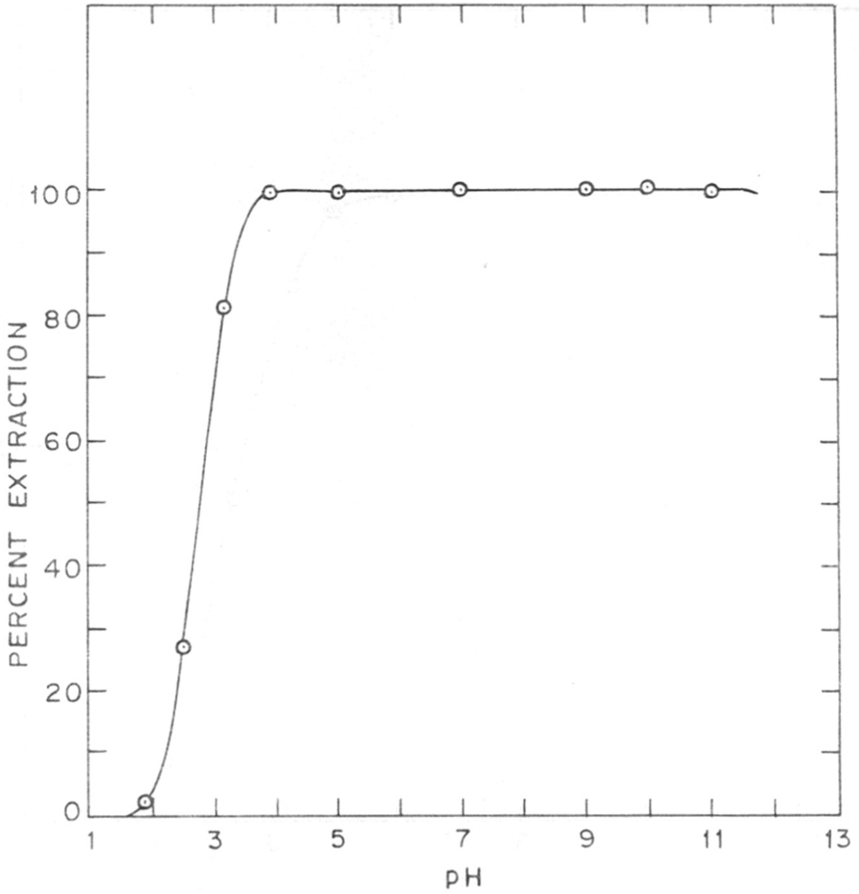


FIG. 35. pH vs PERCENT EXTRACTION OF COPPER (II)-REAGENT-IV COMPLEX IN PRESENCE OF DIETHYLAMINE

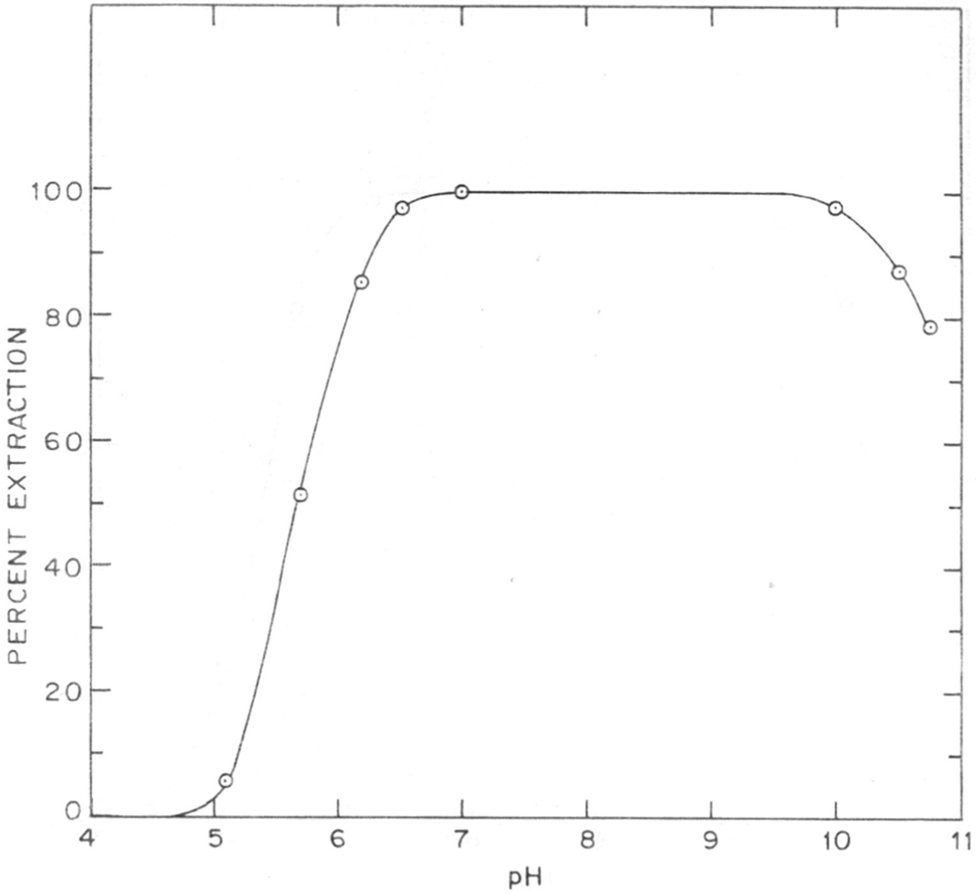


FIG. 36. pH vs PERCENT EXTRACTION OF NICKEL (II)-REAGENT-IV COMPLEX

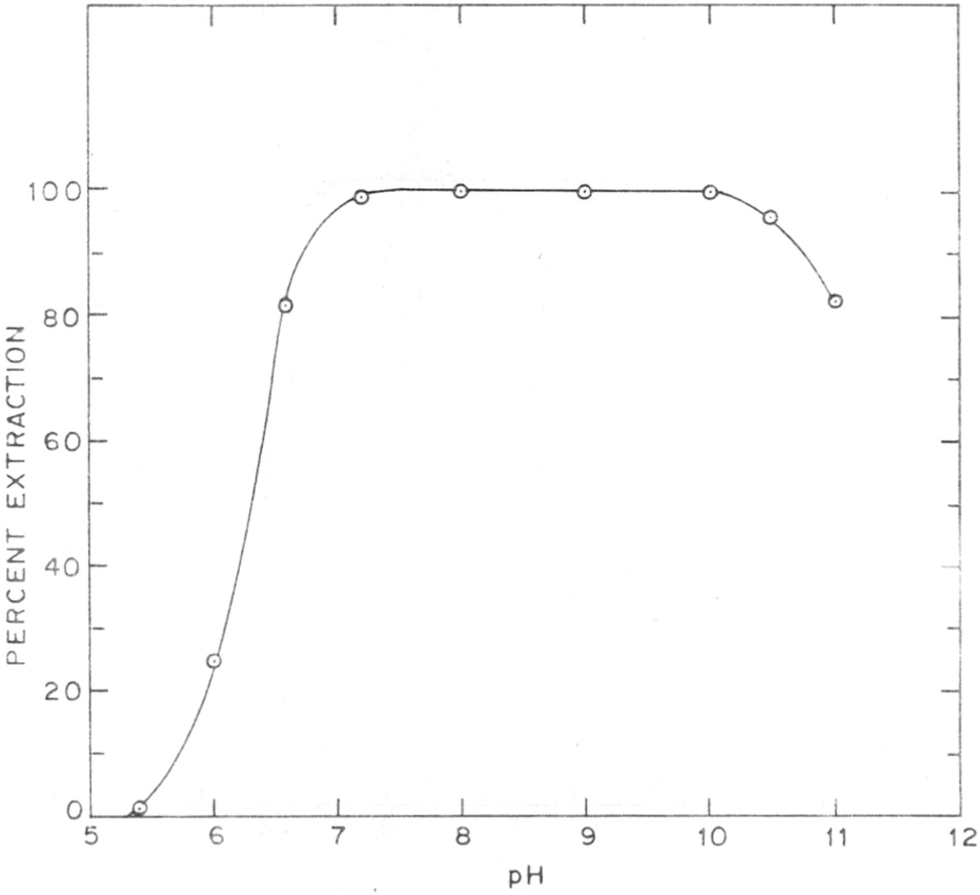


FIG. 37. pH vs PERCENT EXTRACTION OF COBALT (II)-REAGENT-IV COMPLEX

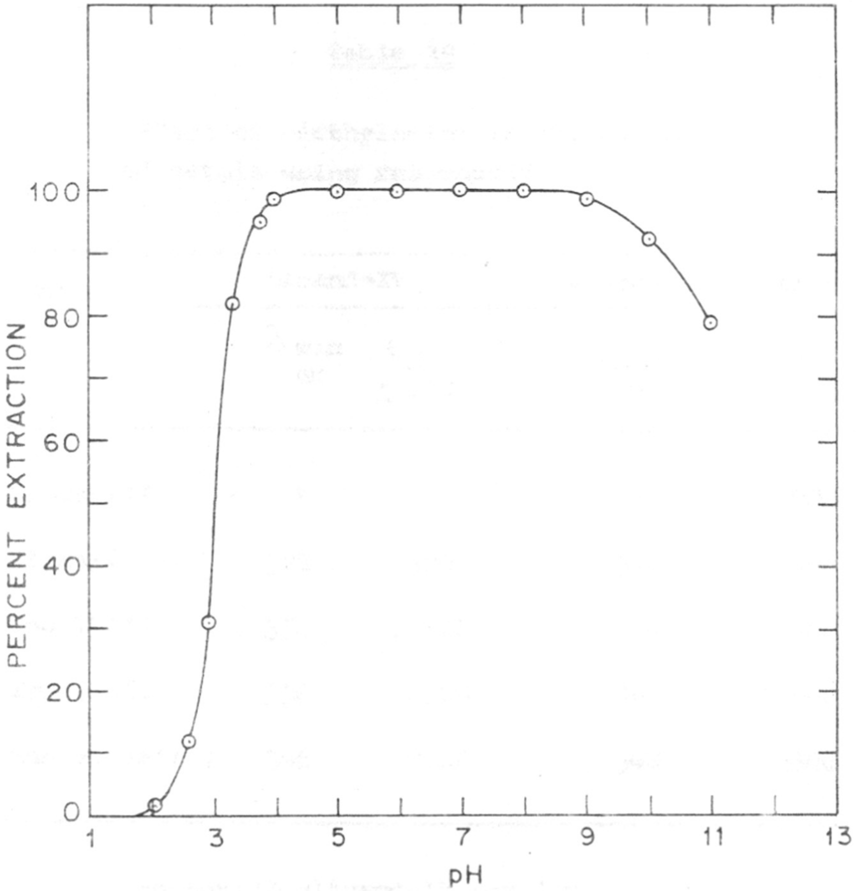


FIG. 38. pH vs PERCENT EXTRACTION OF IRON (III)-REAGENT-IV COMPLEX

Table 38

Effect of diethylamine in the extraction of metals using reagent-IV

Metal	Ligand-IV		Ligand-IV + diethylamine	
	λ_{max} nm	ϵ_M ± 100	λ_{max} nm	ϵ_M ± 100
Copper(II)	*	*	350	7700
Nickel(II)	372	7800	344	9600
Cobalt(II)	356	10500	344	8900
Iron(III)	336	10600	340	10000
Manganese(II)	346	7800	342	8800

* The copper(II)-ligand-IV complex is insoluble (or unstable) in solvents in the absence of diethylamine.

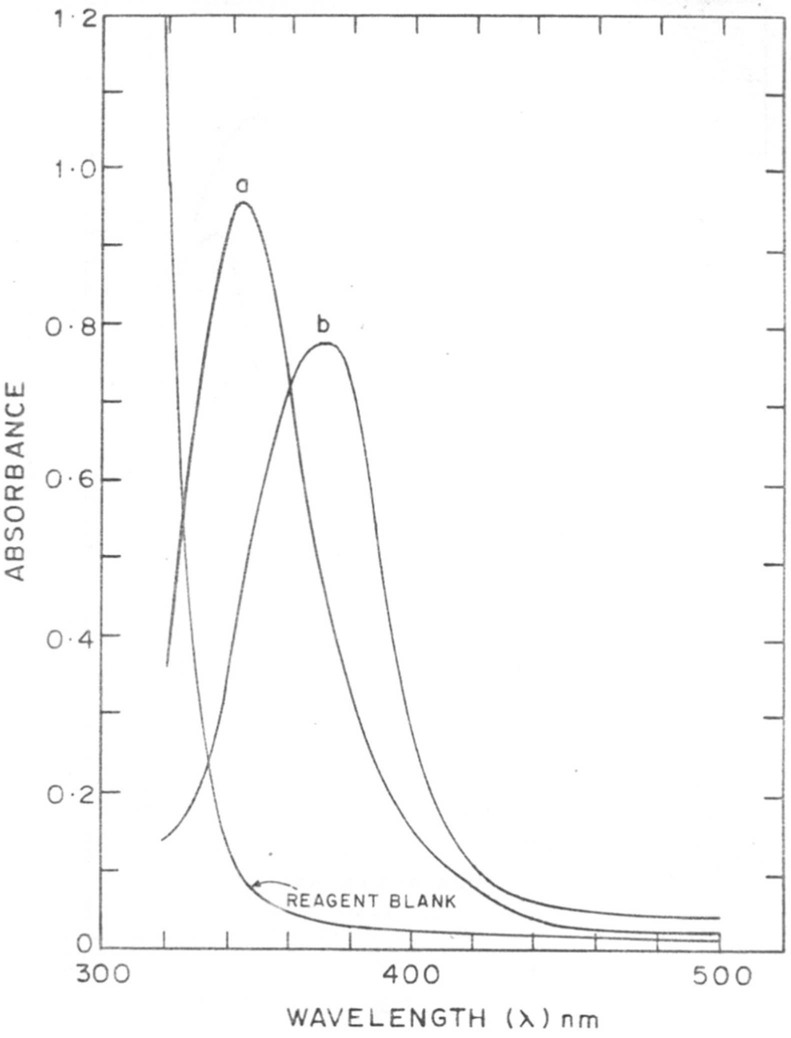


FIG. 39. ABSORPTION SPECTRA OF NICKEL-(II)-REAGENT-IV COMPLEX IN CHLOROFORM:

(a) WITH DIETHYLAMINE

(b) WITHOUT DIETHYLAMINE

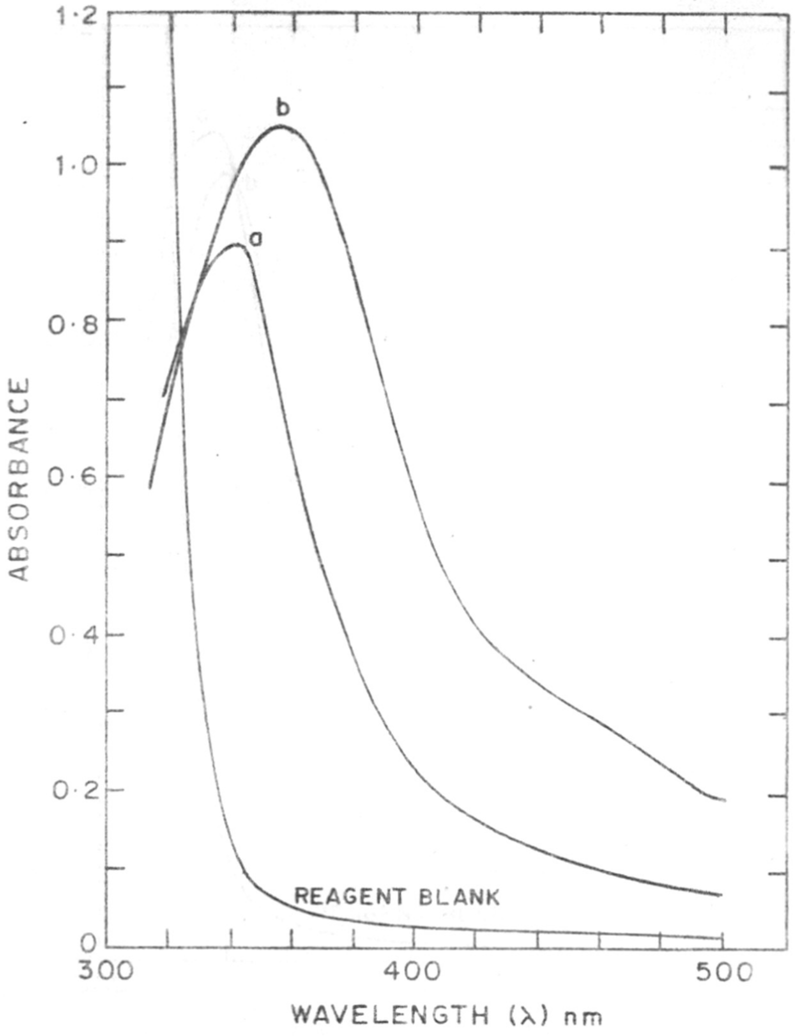


FIG. 40. ABSORPTION SPECTRA OF COBALT-(II)-REAGENT-IV COMPLEX IN CHLOROFORM:
(a) WITH DIETHYLAMINE
(b) WITHOUT DIETHYLAMINE

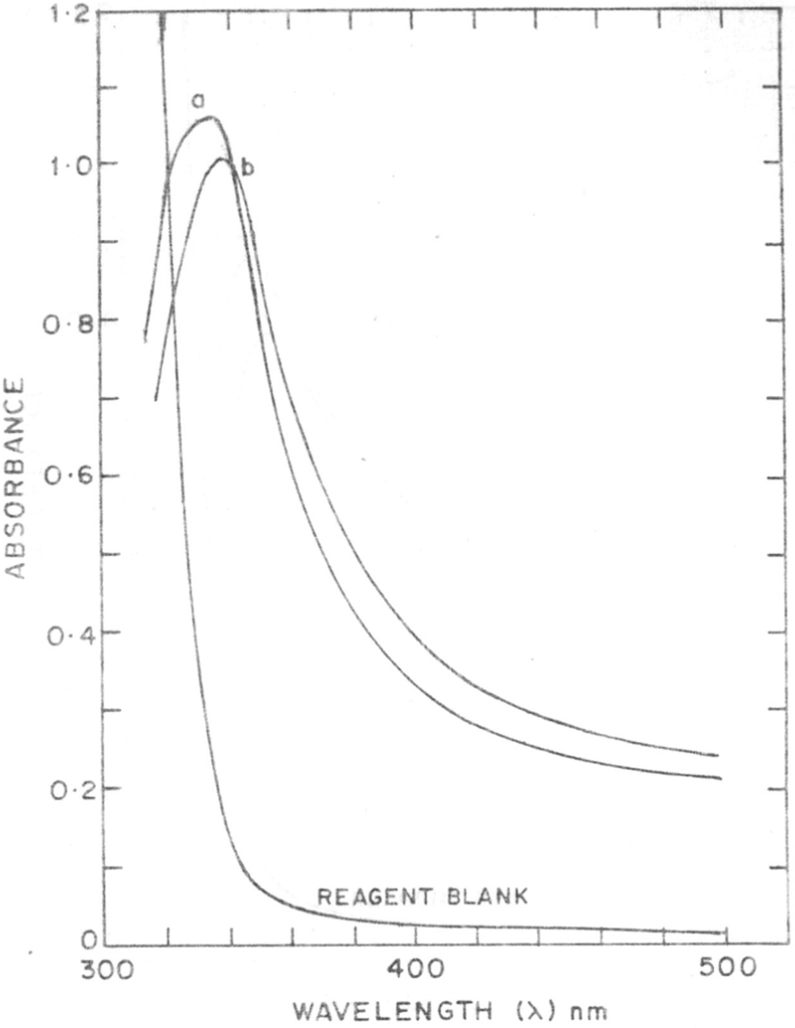


FIG. 41. ABSORPTION SPECTRA OF IRON (III)-REAGENT-IV COMPLEX IN CHLOROFORM:
(a) WITH DIETHYLAMINE
(b) WITHOUT DIETHYLAMINE

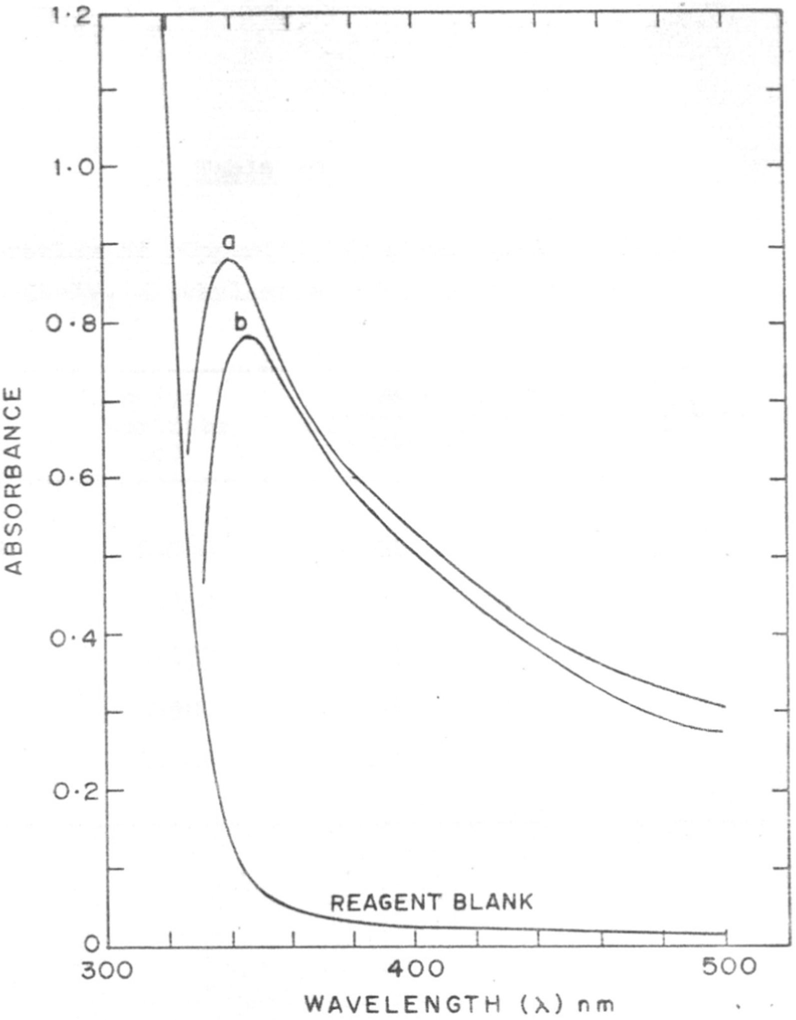


FIG. 42. ABSORPTION SPECTRA OF MANGANESE-(II)-REAGENT-IV COMPLEX IN CHLOROFORM:
(a) WITH DIETHYLAMINE
(b) WITHOUT DIETHYLAMINE

Table 39

Separation of copper(II) from nickel(II) using reagent-IV, diethylamine and sodium tartrate.

pH	Sodium tartrate (g)	Percent extraction	
		Copper(II)	Nickel(II)
3.3	0.010	61	13
3.3	0.250	45	nil
5.6	0.250	85	34
7.5	0.500	99	81
9.5	1.000	100	90

2.49 Separation of nickel(II) from copper(II) using reagent-IV and sodium thiosulphate as masking agent

The procedure was essentially the same as for reagent-II (2.15). Results are presented in Table 40.

2.50 Separation of copper(II) from nickel(II) using reagent-IV, diethylamine and sodium oxalate as masking agent

The procedure was similar to the corresponding experiments with reagent-II (2.16) except that the pH was adjusted with diethylamine. The results obtained are given in Table 41.

2.51 Separation of cobalt(II) from copper(II) using reagent-IV and thiosulphate as masking agent

The procedure was the same as in the corresponding trials with reagent-II (2.27). The results obtained are presented in Table 42.

2.52 Separation of copper(II) from chromium(II) using reagent-IV and diethylamine

From a solution containing 1 micromole each of copper(II), chromium(III), the copper could be completely separated in a single extraction at pH 6.0 - 7.0, using diethylamine, but no tartrate unlike the experiment in section 2.33.

Table 40

Separation of nickel(II) from copper(II) using reagent-IV and sodium thiosulphate

pH	Sodium thiosulphate	Percent extraction	
		Nickel(II)	Copper(II)
8.0	30	89	nil
8.1	10	98	5
8.1	20	96	nil
8.3	20	100	nil
8.6	25	100	nil
9.0	25	100	nil
9.5	25	100	nil
9.5	30	99	nil
9.5	50	79	nil
10.0	20	100	18
10.5	10	100	53
*8.4	10	97	24

* Aqueous diethylamine (1:1) was used to adjust the pH of the solution.

Table 41

Separation of copper(II) from nickel(II) using reagent-IV, diethylamine and sodium oxalate

pH	Sodium oxalate (mg)	Percent extraction	
		Copper(II)	Nickel(II)
4.1	25	35.0	nil
6.8	25	97.0	3.0
6.8	50	91.5	nil
7.5	50	100.0	6.5
8.5	50	100.0	21.0

More than 50 mg of sodium oxalate cannot be used in 25 ml aqueous layer.

Table 42

Separation of cobalt(II) from copper(II) using reagent-IV and sodium thiosulphate

pH	Sodium thiosulphate (mg)	Percent extraction	
		Cobalt(II)	Copper(II)
8.0	30	89	21
8.1	50	93	7
9.0	50	95	23
9.8	50	99	64
10.5	50	100	67

2.53 Separation of nickel(II) from chromium(III) using reagent-IV and diethylamine

Using the procedure given in section 2.23 it was seen that 85% of the nickel could be extracted from a mixed nickel(II)-chromium(III) solution at pH 8.0-8.5 without extracting any of the chromium. Without diethylamine the extraction of nickel was suppressed.

2.54 Log D vs pH plots of metal-reagent-II complexes of copper(II), nickel(II), cobalt(II) and iron(III).

The log D values calculated at different pHs are given in Tables 43, 44, 45 and 46. The log D values were plotted against pH and are given in Figs. 43, 44, 45 and 46 for copper(II), nickel(II), cobalt(II) and iron(III) respectively.

2.55 Log D vs log L plots of the reagent-II complexes of copper(II) and iron(III)

The calculated values of log D and log L at different reagent concentrations for the complexes of copper(II) and iron(III) are given in Tables 47 and 48. The log D vs log L plots are given in Figs. 47 and 48.

2.56 Log D vs pH plots of copper(II), nickel(II), cobalt(II) and iron(III) complexes of reagent-IV

The log D values calculated at different pHs are

Table 43

Log D vs pH of copper(II)-reagent-II complex

pH	Percent extraction	D	Log D
2.8	3.5	0.036	-1.440
3.0	10.2	0.113	-0.947
3.5	36.0	0.562	-0.250
3.8	69.0	2.030	+0.308
4.0	88.0	7.330	+0.865
4.3	98.5	65.660	+1.817

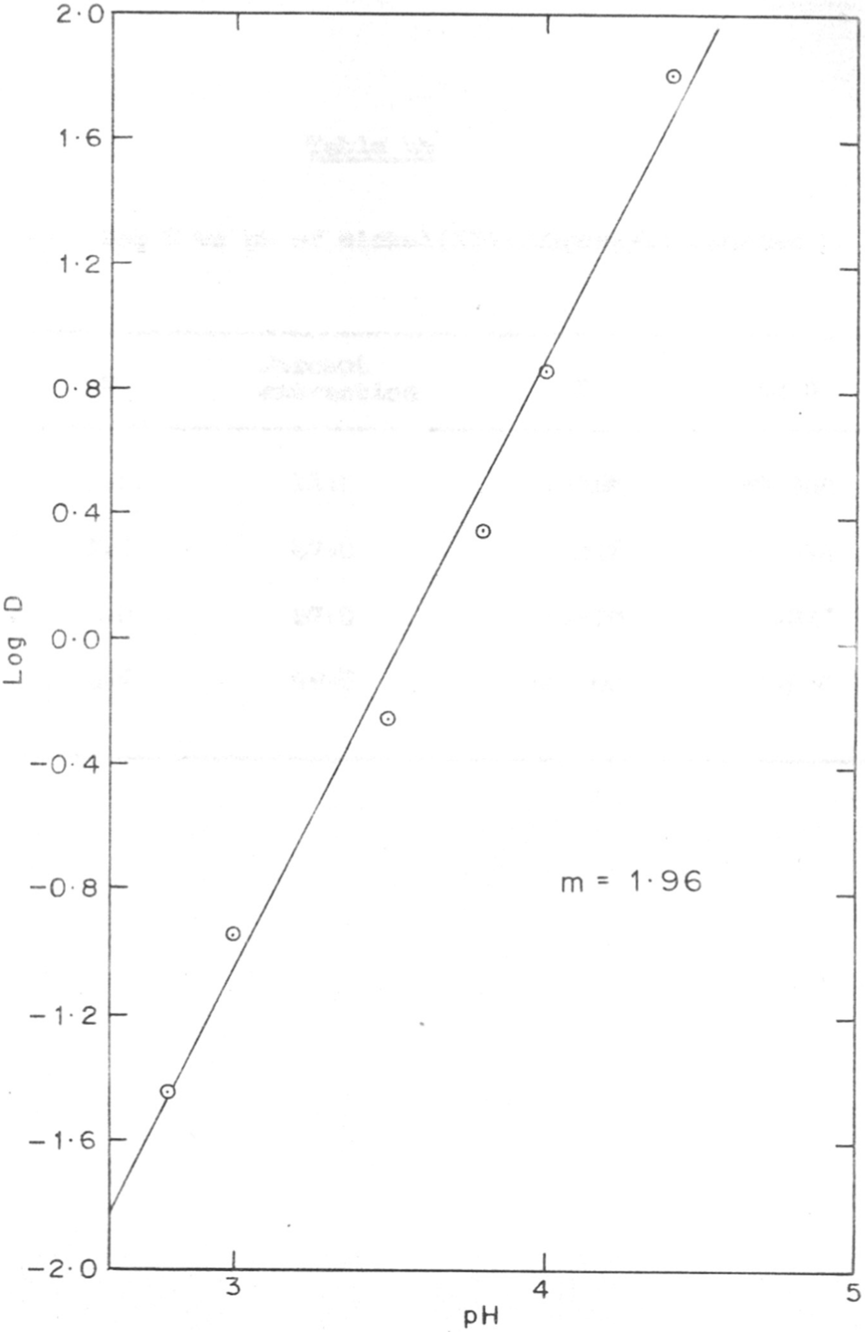


FIG. 43. LOG D vs pH PLOT OF COPPER (II)-REAGENT-II COMPLEX

Table 44

Log D vs pH of nickel(II)-reagent-II complex

pH	Percent extraction	D	Log D
7.0	11.0	0.124	-0.908
7.5	47.0	0.886	-0.052
8.0	87.0	6.690	+0.825
8.5	98.0	49.000	+1.690

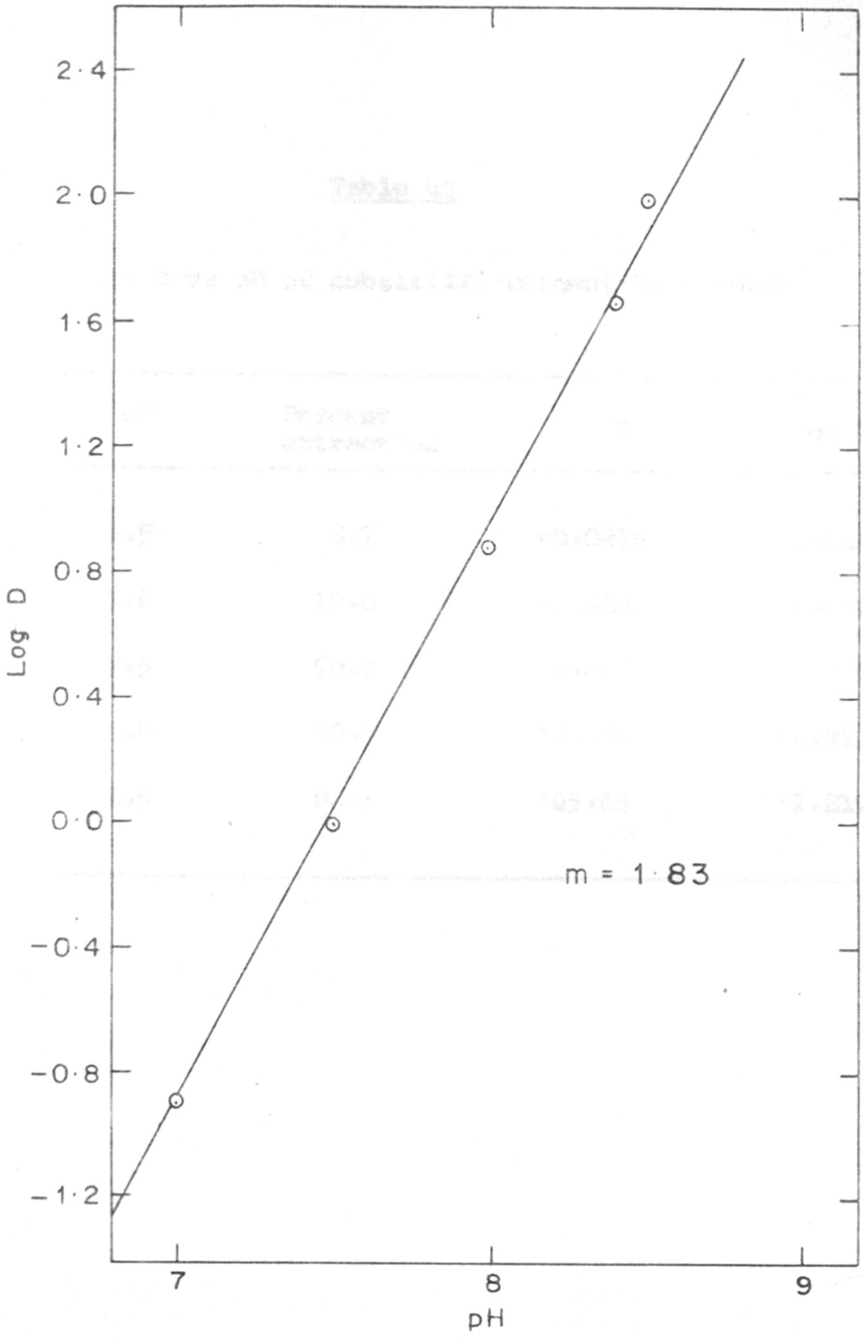


FIG. 44. LOG D vs pH PLOT OF NICKEL (II)-REAGENT-II COMPLEX

Table 45

Log D vs pH of cobalt(II)-reagent-II complex

pH	Percent extraction	D	Log D
6.5	2.1	-0.0215	-1.668
7.0	17.0	-0.688	-0.688
7.5	50.0	1.000	0.000
8.0	89.0	+8.090	+0.910
8.5	98.5	+65.66	+1.817

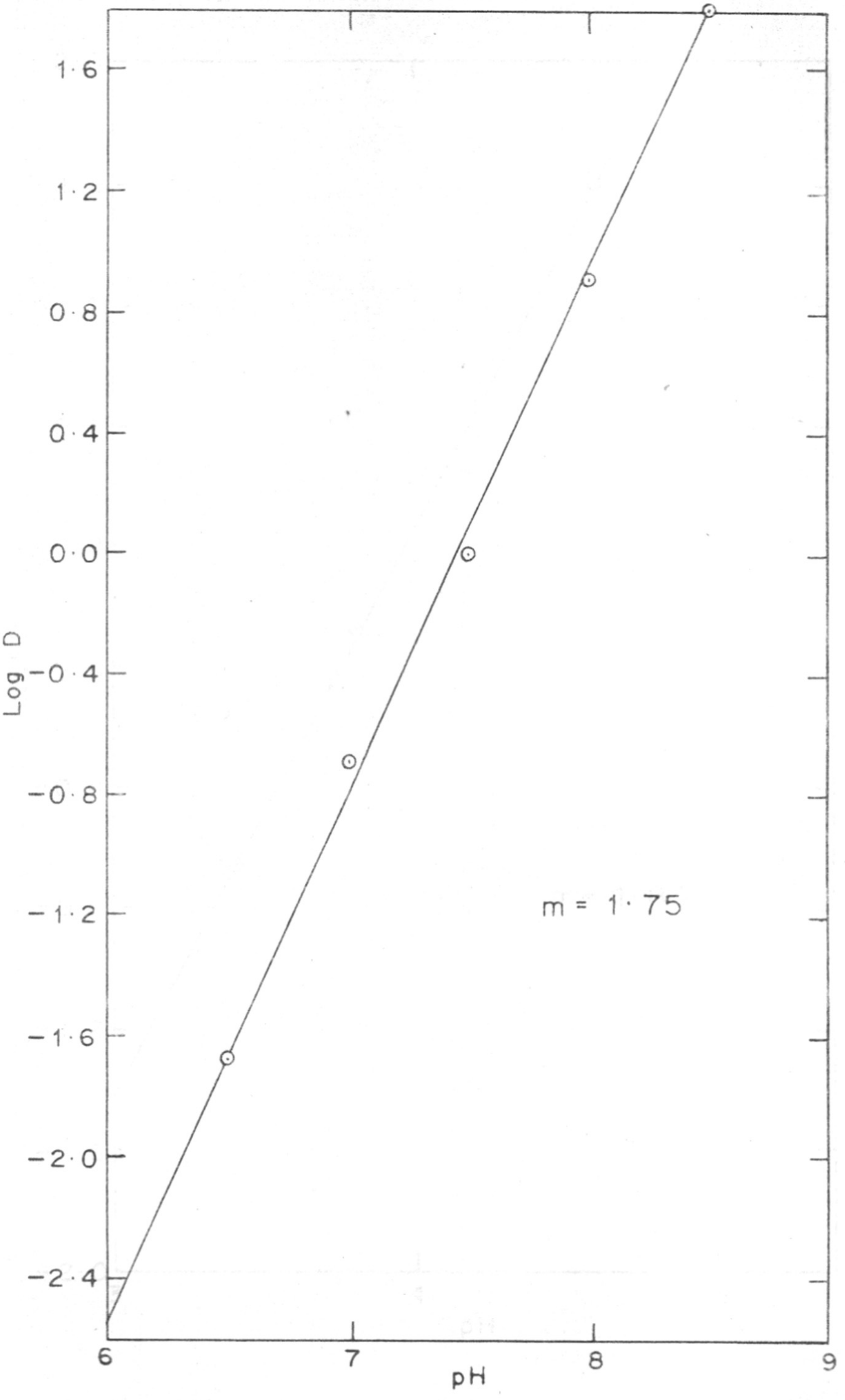


FIG. 45. LOG D vs pH PLOT OF COBALT (II)-REAGENT-II COMPLEX

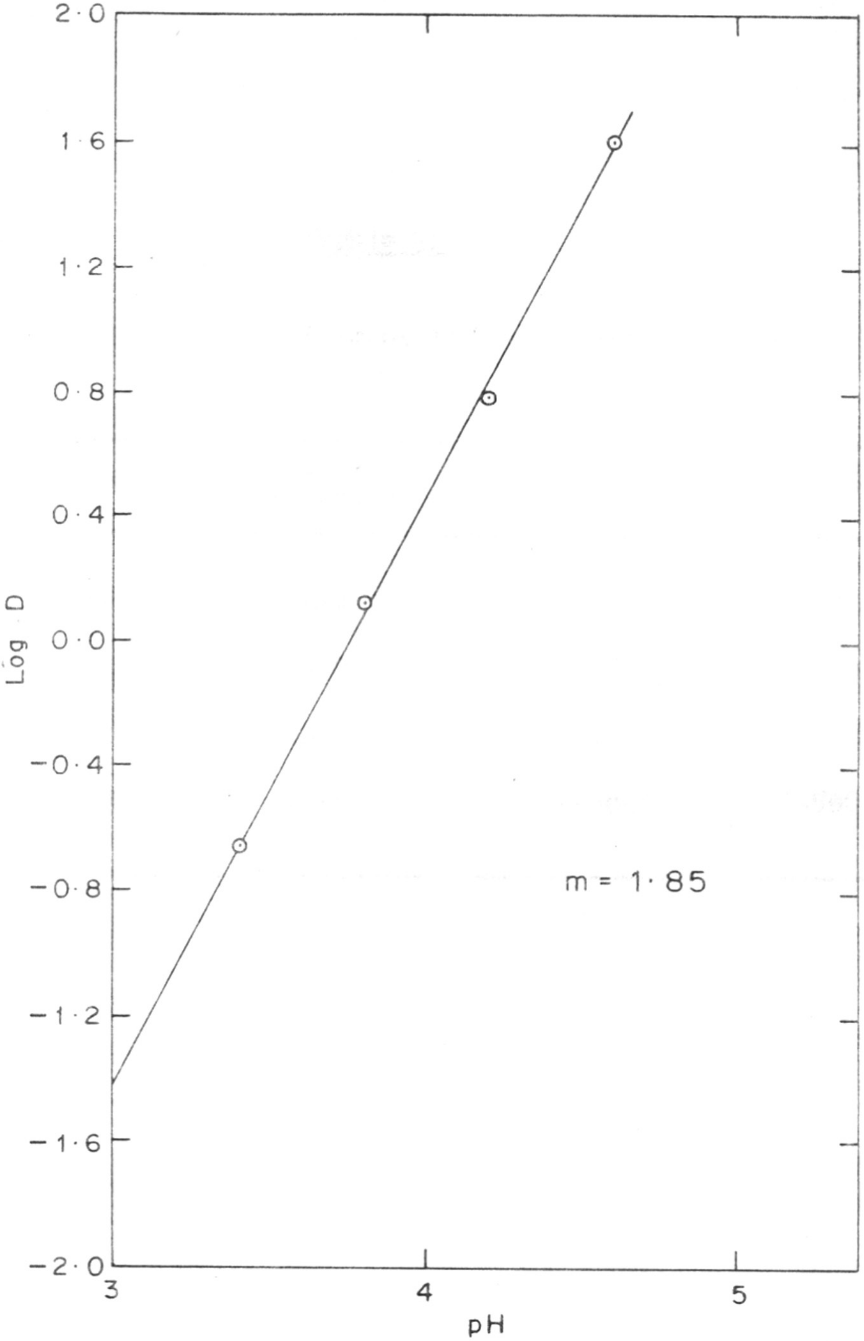


FIG. 46. LOG D vs pH PLOT OF IRON (III)-REAGENT-II COMPLEX

Table 46

Log D vs pH of iron(III)-reagent-II complex

pH	Percent extraction	D	Log D
3.4	18.0	0.220	-0.658
3.8	57.0	1.325	0.122
4.2	86.0	6.140	0.788
4.6	97.5	39.000	1.590

Table 47

Log D vs log L of copper(II)-reagent-II complex (at pH = 3.3)

Molar concentrations of reagent	Log L	Percent extraction	D	Log D
1.0×10^{-2}	-2.000	21.0	0.265	- 0.576
1.5×10^{-2}	-1.824	36.0	0.562	- 0.250
2.0×10^{-2}	-1.699	46.0	0.869	- 0.061
2.5×10^{-2}	-1.602	59.0	1.440	0.158
3.0×10^{-2}	-1.523	66.0	1.940	0.288
3.5×10^{-2}	-1.456	72.0	2.570	0.410
4.0×10^{-2}	-1.398	77.0	3.350	0.525

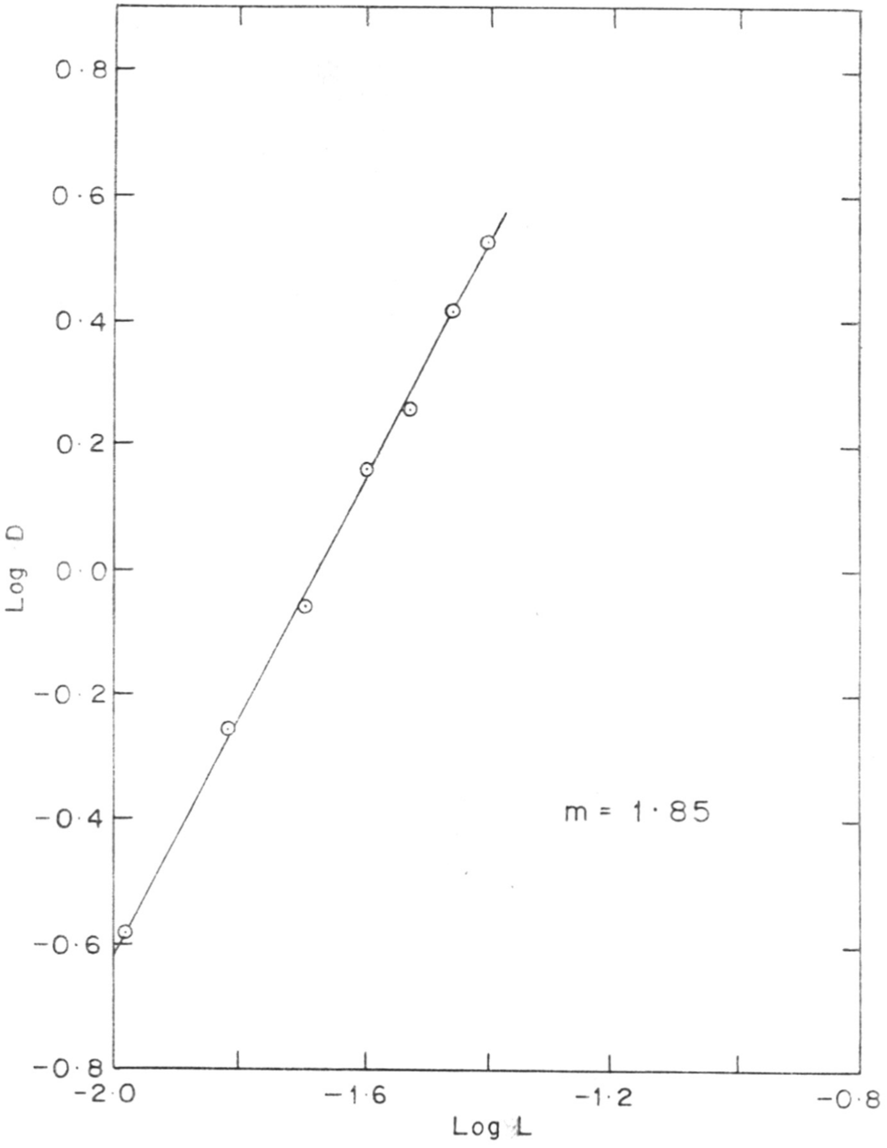


FIG. 47. LOG D vs LOG L PLOT OF COPPER (II)-REAGENT-II COMPLEX

Table 48

Log D vs log L of iron(III)-reagent-II complex (at pH = 3.05)

Molar concentrations of reagent	Log L	Percent extraction	D	Log D
1×10^{-2}	-2.000	18.9	0.233	-0.633
1.5×10^{-2}	-1.825	30.5	0.439	-0.357
2×10^{-2}	-1.699	43.0	0.762	-0.118
2.5×10^{-2}	-1.602	56.7	1.310	+0.118
3.0×10^{-2}	-1.523	67.5	2.080	+0.320
3.5×10^{-2}	-1.456	73.0	2.700	+0.430
4.0×10^{-2}	-1.398	78.5	3.620	+0.560

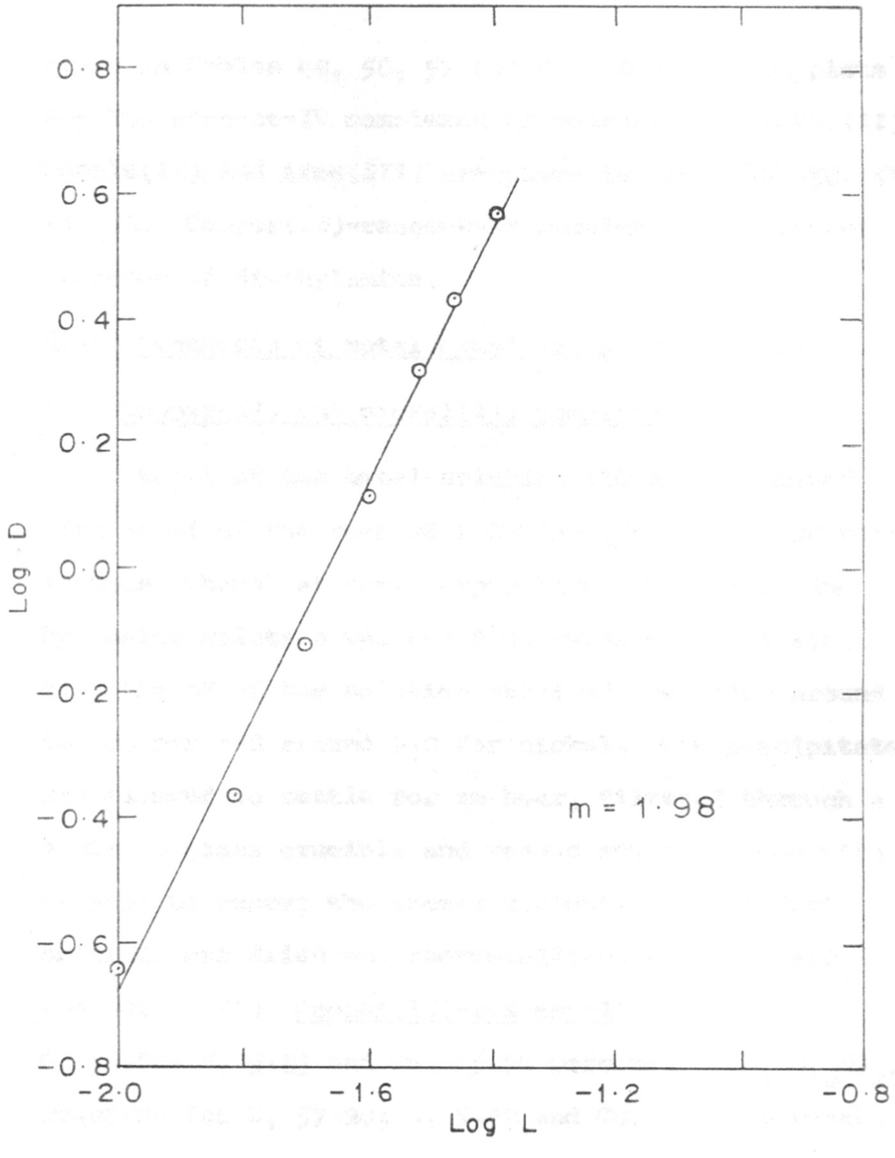


FIG. 48. LOG D vs LOG L PLOT OF IRON (III)-REAGENT-II COMPLEX

given in Tables 49, 50, 51 and 52. Log D vs pH plots for the reagent-IV complexes of copper(II), nickel(II), cobalt(II) and iron(III) are given in Figs. 49, 50, 51 and 52. Copper(II)-reagent-IV complex was extracted in presence of diethylamine.

2.57 Synthesis of metal complexes of reagent-II

(a) Copper(II) and nickel(II) complexes

50 ml of the metal solution (10 mM) was mixed with 50 ml of the reagent solution (50 mM), in 20 percent aqueous ethanol at room temperature. Dilute sodium hydroxide solution was added dropwise with stirring till the pH of the solution attained the value around 6.0 for copper and around 9.0 for nickel. The precipitate was allowed to settle for an hour, filtered through a sintered glass crucible and washed several times with ethanol to remove the excess reagent. The product obtained was dried and recrystallized from benzene.

Analysis: (1) Copper(II)-reagent-II complex

C, 56.70; H, 5.83 and Cu, 15.74 percent; $Cu(C_{10}H_{12}NO_2)_2$; requires for C, 57.20; H, 5.72 and Cu, 15.15 percent.

(2) Nickel(II)-reagent-II complex

C, 57.41; H, 5.87 and Ni, 13.98 percent; $Ni(C_{10}H_{12}NO_2)_2$; requires for C, 57.70; H, 5.78 and Ni, 14.5 percent.

Table 49

Log D vs pH of copper(II)-reagent-IV complex

pH	Percent extraction	D	Log D
2.0	4.0	0.041	-1.38
2.5	27.0	0.37	-0.43
3.0	70.0	2.33	+0.37
3.5	95.0	19.00	+1.28
3.8	98.5	65.66	+1.82

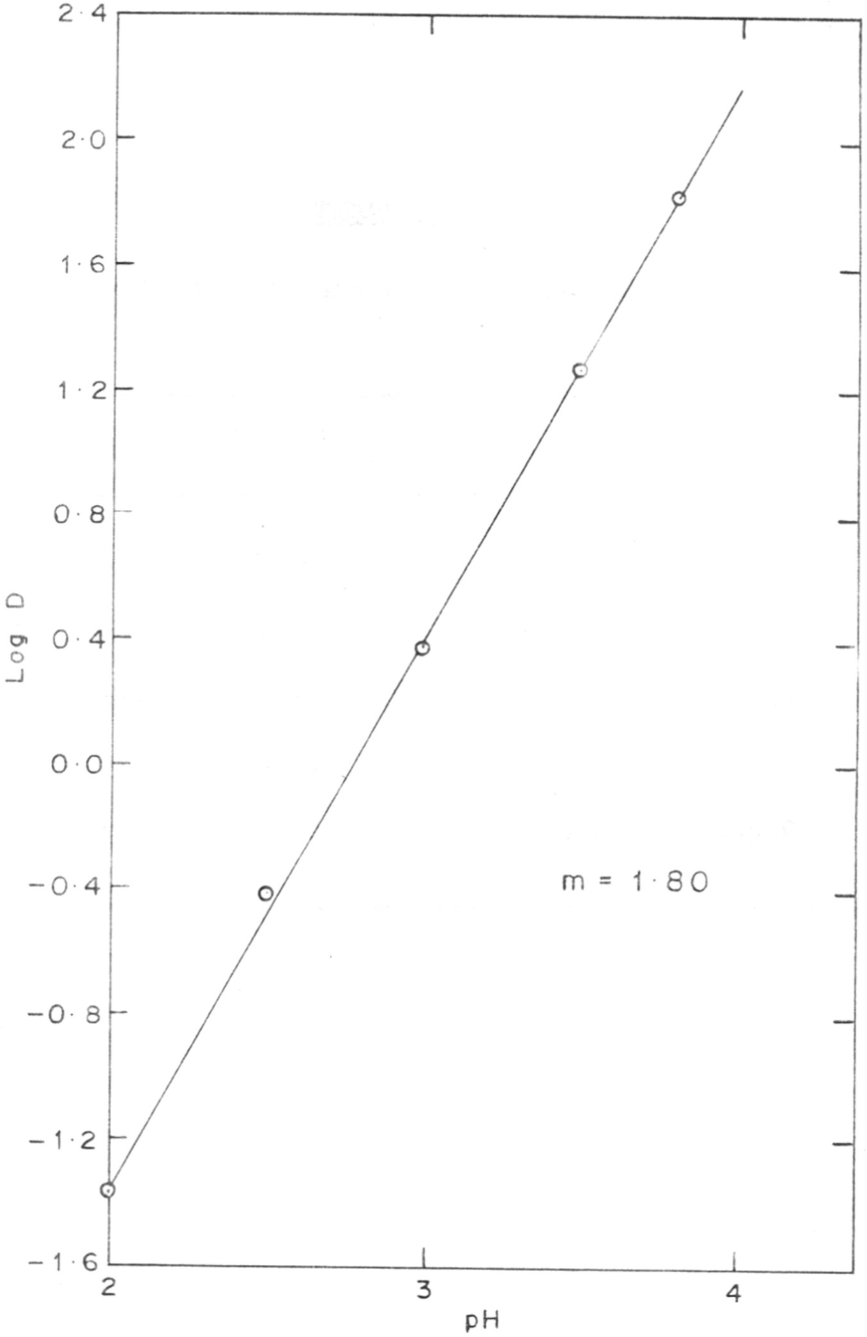


FIG. 49. LOG D vs pH PLOT OF COPPER (II)-
REAGENT–II COMPLEX

Table 50

Log D vs pH of nickel(II)-reagent-IV complex

pH	Percent extraction	D	Log D
5.2	12.0	0.136	-0.865
5.7	51.0	1.040	0.017
6.0	74.0	2.846	0.454
6.3	93.0	13.280	1.123
6.5	97.0	32.330	1.510

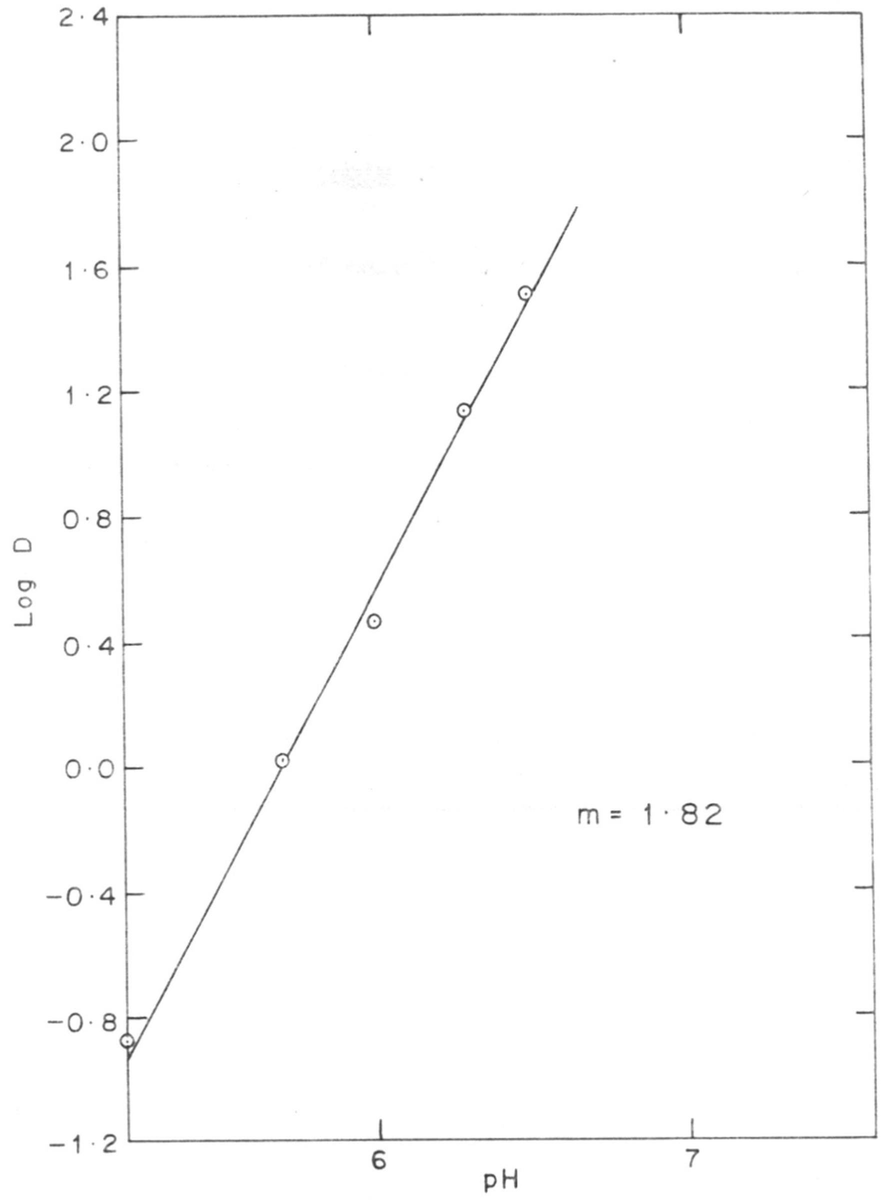


FIG. 50. LOG D vs pH PLOT OF NICKEL (II)-REAGENT-IV COMPLEX

Table 51

Log D vs pH of cobalt(II)-reagent-IV complex

pH	Percent extraction	D	Log D
5.5	5.0	0.0526	-1.28
6.0	25.0	0.333	-0.48
6.5	76.0	3.166	+0.50
7.0	97.0	32.300	+1.51

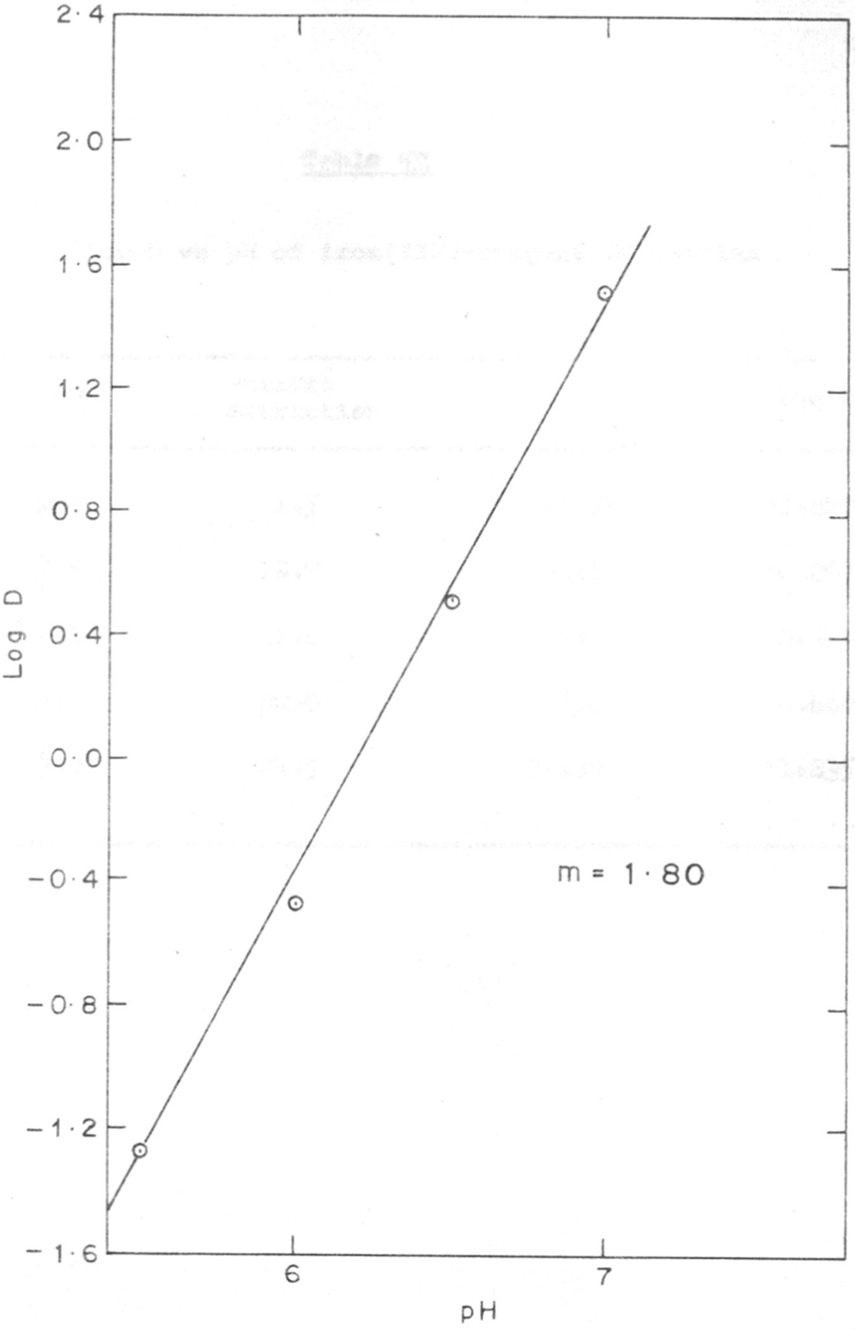


FIG. 51. LOG D vs pH PLOT OF COBALT (II)-REAGENT-IV COMPLEX

Table 52

Log D vs pH of iron(III)-reagent IV complex

pH	Percent extraction	D	Log D
2.1	1.5	0.0152	-1.820
2.5	12.0	0.136	-0.865
2.9	31.0	0.449	-0.347
3.3	82.0	4.550	+0.660
3.7	94.5	17.180	+1.235

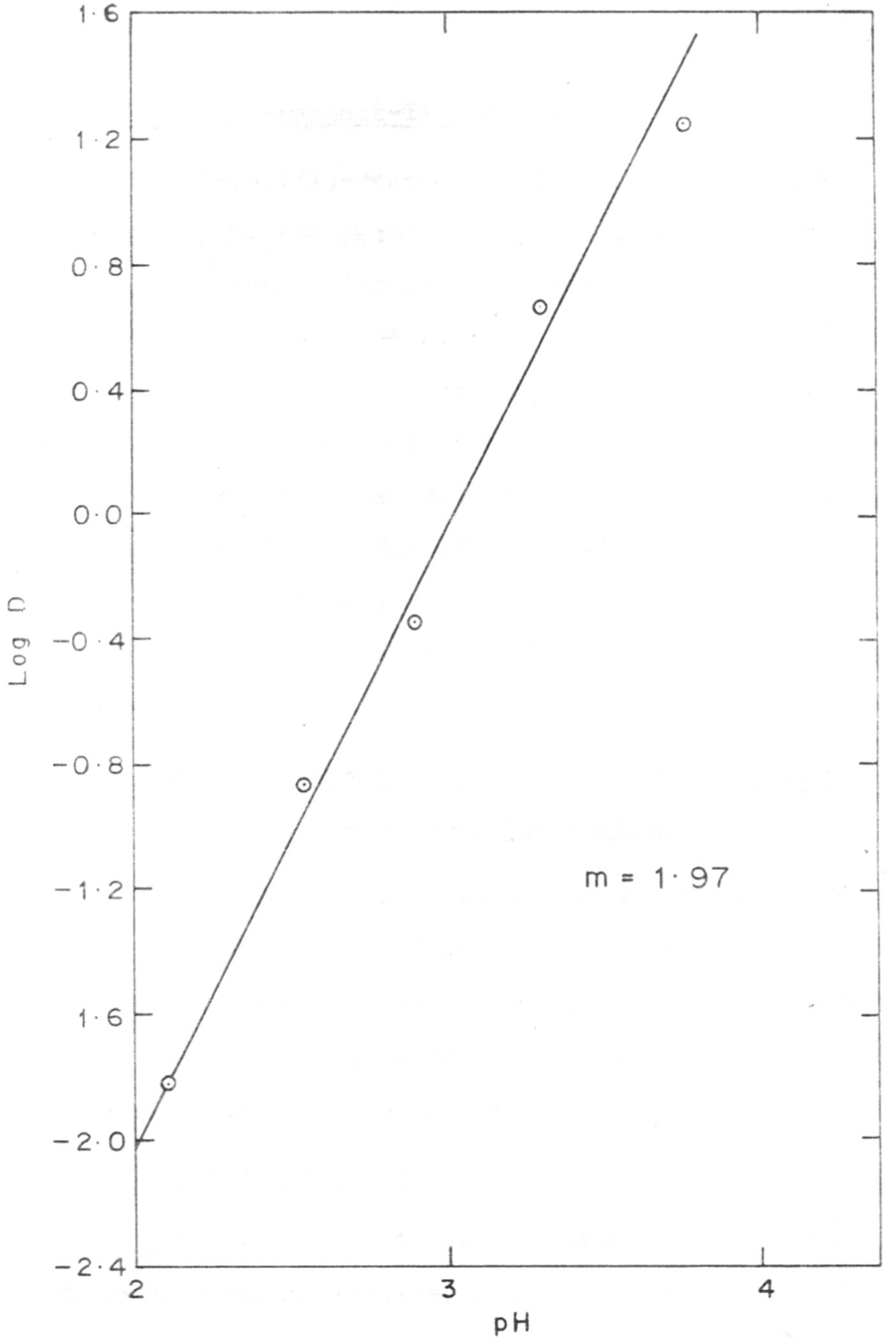


FIG. 52. LOG D vs pH PLOT OF IRON (III)-REAGENT-IV COMPLEX

(b) Iron(III)-reagent-II complex

The iron(III)-reagent-II complex was prepared essentially by the above method, but the precipitate was washed with 1:1 aqueous ethanol since unlike the complexes of copper and nickel, it was soluble in pure ethanol. The washed and dried precipitate was soluble in chloroform. The analysis, however, did not indicate any definite stoichiometry, the best value corresponding almost to $FeL_2(OH)$. The IR spectrum of the compound in carbon tetrachloride is given in Fig. 53 (for comparison the IR spectrum of the copper complex is given in the same figure).

2.58 Behaviour of metal-reagent-II complexes in a silica gel chromatographic column

5 ml of an approximately 0.1% solution of the metal complexes obtained by dissolving the freshly prepared solids in chloroform, were taken on a silica gel column (size 15 cm x 1.5 cm, silica gel type 'Acme') and eluted. The observations are given below.

(i) Copper(II) complex

This was the most easily eluted complex, pure chloroform being sufficient.

(ii) Nickel(II) and cobalt(II) complexes

In these cases the elution with pure chloroform

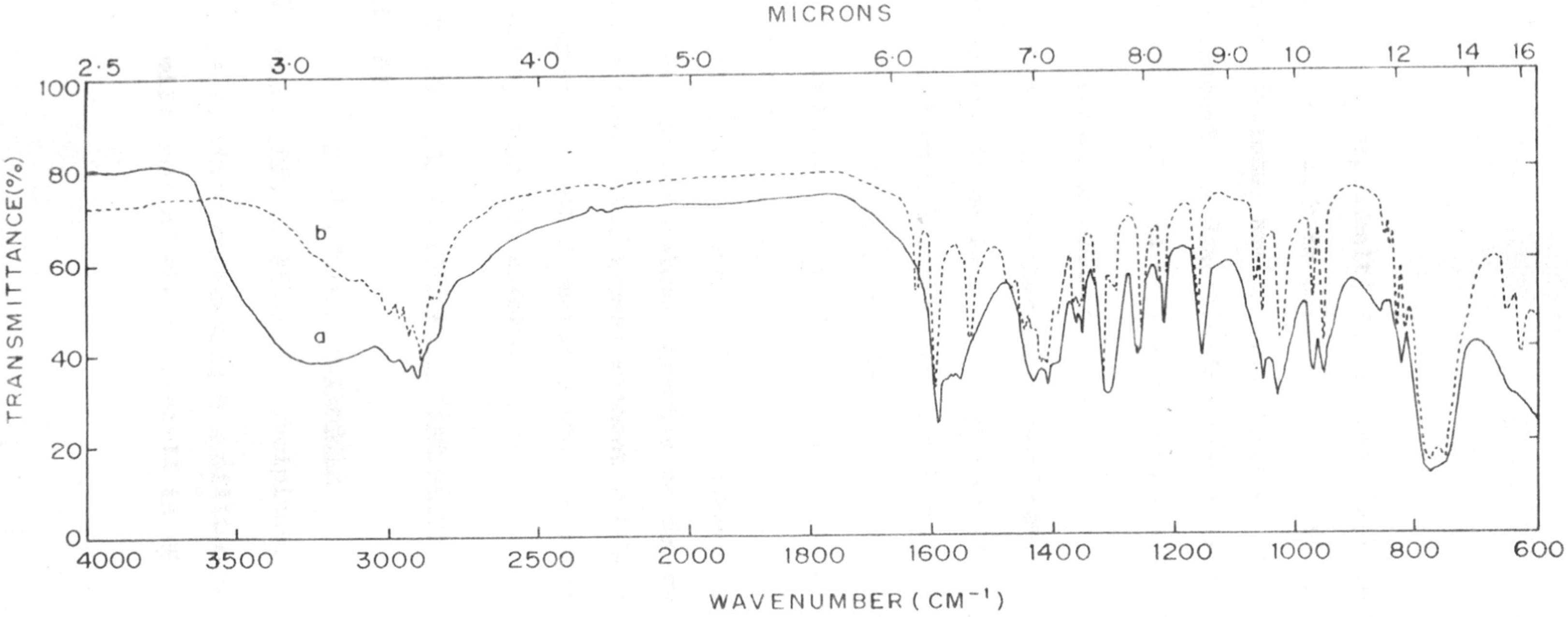


FIG. 53. IR SPECTRA OF (a) IRON (III)-REAGENT-II COMPLEX IN CCl_4
(b) COPPER (II)-REAGENT- II COMPLEX IN CCl_4

was very slow, cobalt(II) eluting slightly better than nickel(II). In both cases, alcohol and acetone gave faster elutions, acetone being better in this respect than alcohol. A fast elution also resulted when a chloroform solution of the reagent was used.

(iii) Iron(III) complex

The solid complex which had been washed with ethanol and dried in a vacuum desiccator was dissolved in chloroform and taken on the column. The complex was found to be strongly adsorbed on the top of the column as a brown band and could not be eluted with pure chloroform, alcohol, acetone, or even by a chloroform solution of the reagent-II. If, however, the complex was taken on the column directly as the chloroform extract containing excess reagent (without first preparing the solid complex) then it could be completely eluted by pure chloroform.

Potentiometric titration studies of metal-reagent-II complexes

2.59 (a) Preliminary experiments

(i) In 25 percent ethanol (precipitation-titration)

A solution containing 0.2 millimole of the metal and 1 millimole of the reagent-II in 25 ml ethanol were taken in a 250 ml beaker. 10 ml of sodium perchlorate solution (1 M) and 65 ml of water were added. The solution was potentiometrically titrated in nitrogen atmosphere with carbonate-free sodium hydroxide solution (0.442 N). At the inflexion point the titration was stopped and the precipitate which had formed was filtered under suction, dissolved in chloroform and then back extracted with 0.1 N hydrochloric acid. The metal in the acid extract was determined by AAS.

Titrations were carried out as given above ~~using~~ for ~~the metals~~, copper(II), nickel(II), cobalt(II) and iron(III). The metal taken for titration and metal found in the precipitate as well as the pH at the inflexion are given in Table 53.

(ii) In 50 percent dioxan

2 ml of the nickel standard solution (10 mM), 20 ml of the o-hydroxyacetophenone oxime solution in dioxan (10 mM) and 1 ml of the standard perchloric acid (0.1002 N) were taken in a 100 ml beaker. 5 ml of dioxan and 5 ml of sodium perchlorate solution (1 M) were added. The solution was diluted to a total volume of 50 ml with deionised water (17 ml) and potentiometrically titrated with carbonate free standard sodium hydroxide solution (0.1044 N) with stirring, in nitrogen atmosphere.

Table 53

Precipitation titration of metal-reagent-II complexes in 25 percent ethanol.

Metal	pH at inflexion	Metal found in precipitate (mg)	Metal taken (mg)
Copper(II)	5.0	12.60	12.71
Nickel(II)	8.0	11.52	11.74
Cobalt(II)	8.4	11.63	11.79
Iron(III)	4.5	11.15	11.17

Titrations were also performed (a) with 1 ml of standard perchloric acid solution alone and (b) with 1 ml perchloric acid plus 20 ml of ligand solutions in dioxan.

Slight precipitation of the complex was observed at the inflexion point. Further studies were carried out only in 75% dioxan.

(b) Final experiments in 75 percent aqueous dioxan

(i) Nickel(II) complexes

4 ml of the nickel(II) standard solution (10^{-2} M), 20 ml of the ligand-II solution in dioxan (10^{-2} M), 2 ml of standard perchloric acid (0.1002 N) and 10 ml of the sodium perchlorate solution (1 M) were taken in a 250 ml beaker. 55 ml of dioxan was added and the solution diluted to 100 ml with deionised water. It was potentiometrically titrated with standard carbonate-free sodium hydroxide solution (0.1044 N) with stirring in a nitrogen atmosphere.

Two more titrations were performed as above, one with 2 ml of the standard perchloric acid solution alone and the other with 2 ml of the standard perchloric acid plus 20 ml of the ligand-II solution in dioxan. The titration curves for acid alone (A), acid + ligand (A+L) and acid, ligand and metal (A+L+M) are given in Fig. 54.

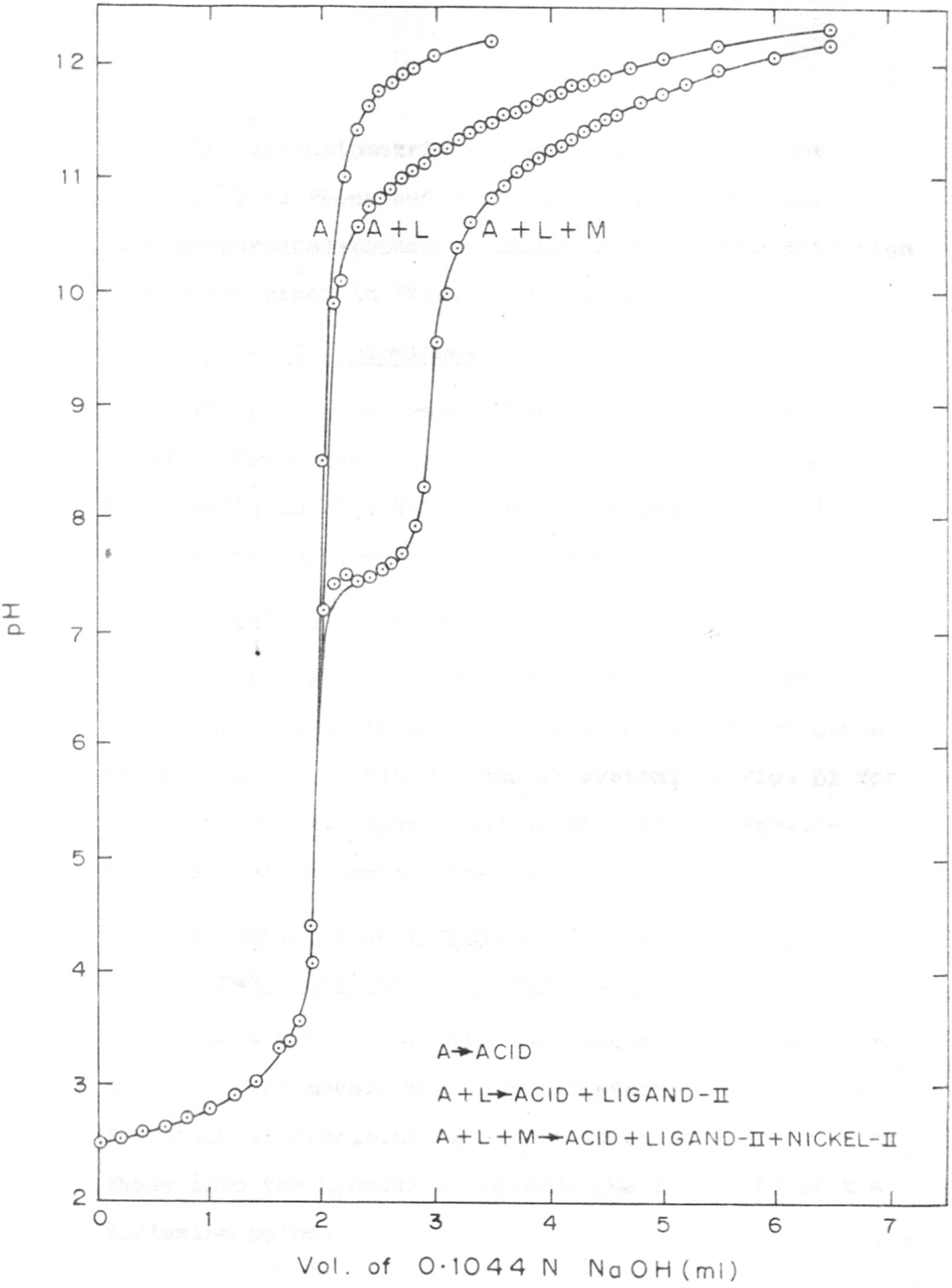


FIG. 54. POTENTIOMETRIC TITRATION CURVES OF NICKEL(II)-LIGAND-II

The potentiometric titration was carried out for nickel as described above using reagent-IV and also o-hydroxyacetophenone oxime (o-HAO). The titration curves are given in Figs. 55 and 56 respectively.

(ii) Copper(II) complexes

The titrations were performed exactly as for nickel. The curves are given in Fig. 57 for copper-reagent-II; in Fig. 58 for copper-reagent-IV and in Fig. 59 for copper-o-hydroxyacetophenone oxime.

(iii) Cobalt(II) complexes

The titrations were done exactly as described for nickel and copper. The titration curves are given in Fig. 60 for cobalt-reagent-II system; in Fig. 61 for cobalt-reagent-IV system and in Fig. 62 for cobalt-o-hydroxyacetophenone oxime system.

(iv) Potentiometric titration of iron(III)- reagent mixed solutions in 75 percent dioxan

These titrations with the reagent:metal ratio used for the other metals were not satisfactory due to the formation of precipitates and an apparent conversion of these into the hydroxide towards the extremity of the inflexion point.

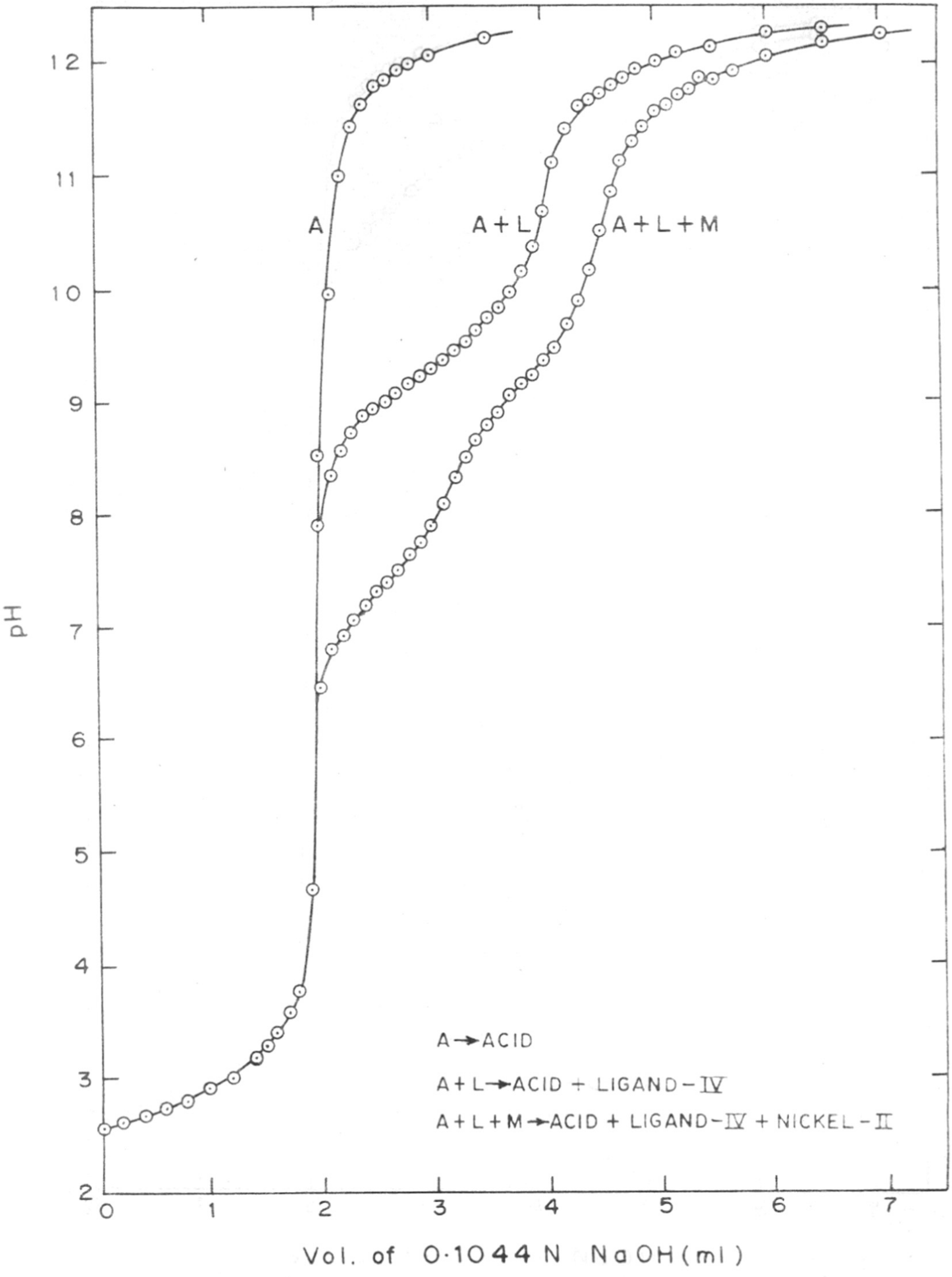


FIG. 55. POTENTIOMETRIC TITRATION CURVES OF NICKEL (II)- LIGAND-IV

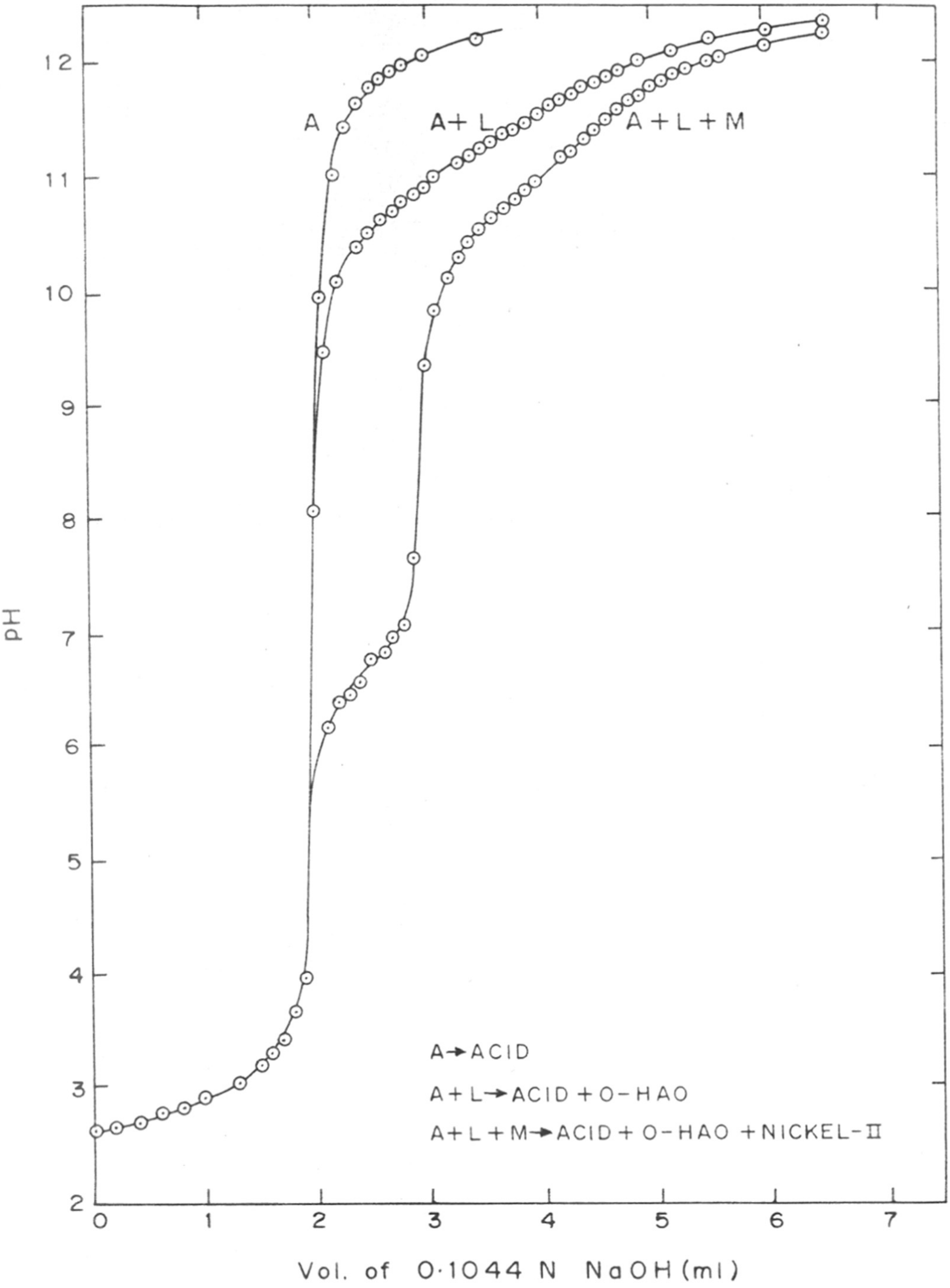


FIG. 56. POTENTIOMETRIC TITRATION CURVES OF NICKEL (II)-O-HAO

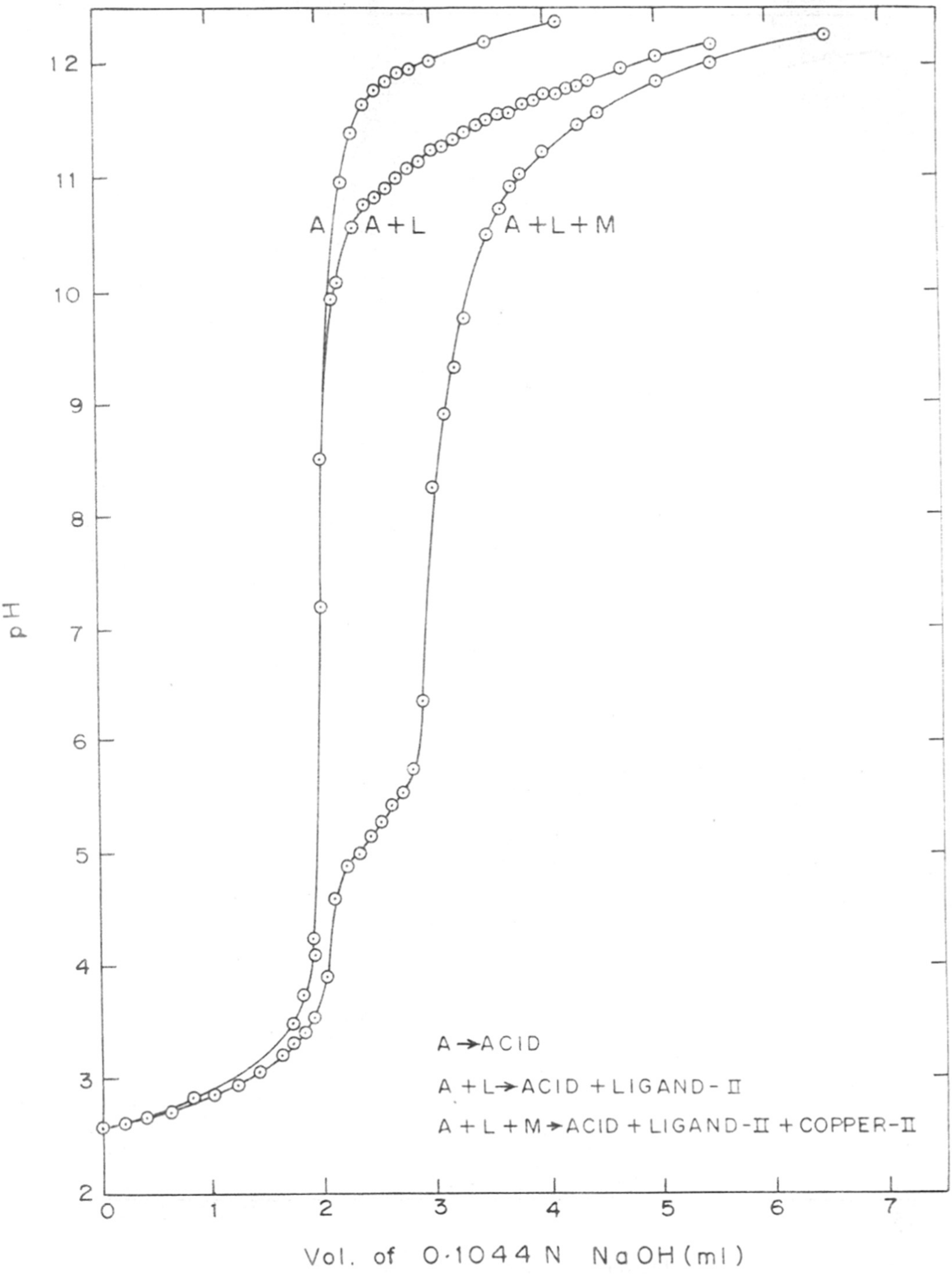


FIG. 57. POTENTIOMETRIC TITRATION CURVES OF COPPER(II)-LIGAND-II

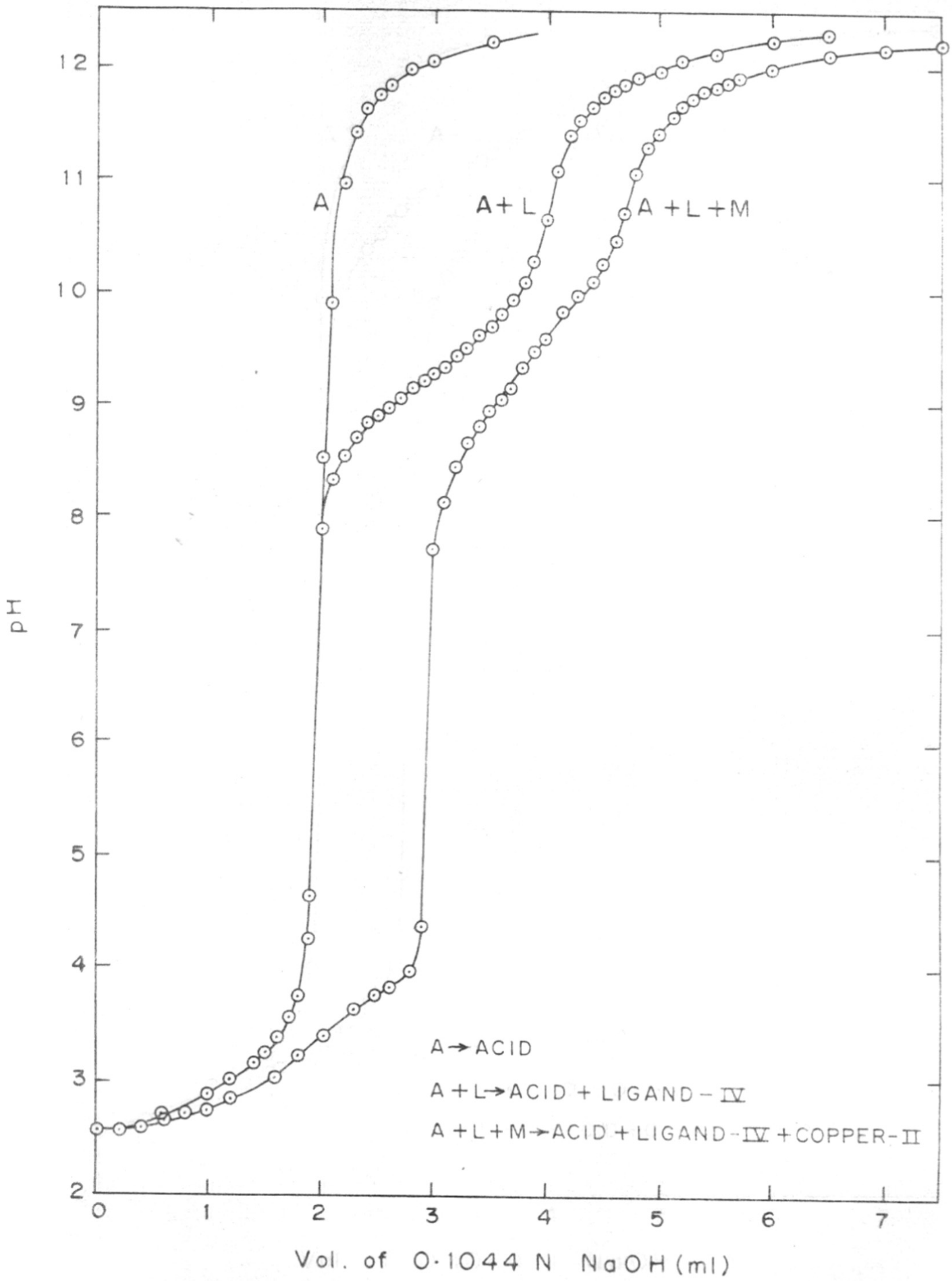


FIG. 58. POTENTIOMETRIC TITRATION CURVES OF COPPER(II)-LIGAND-IV

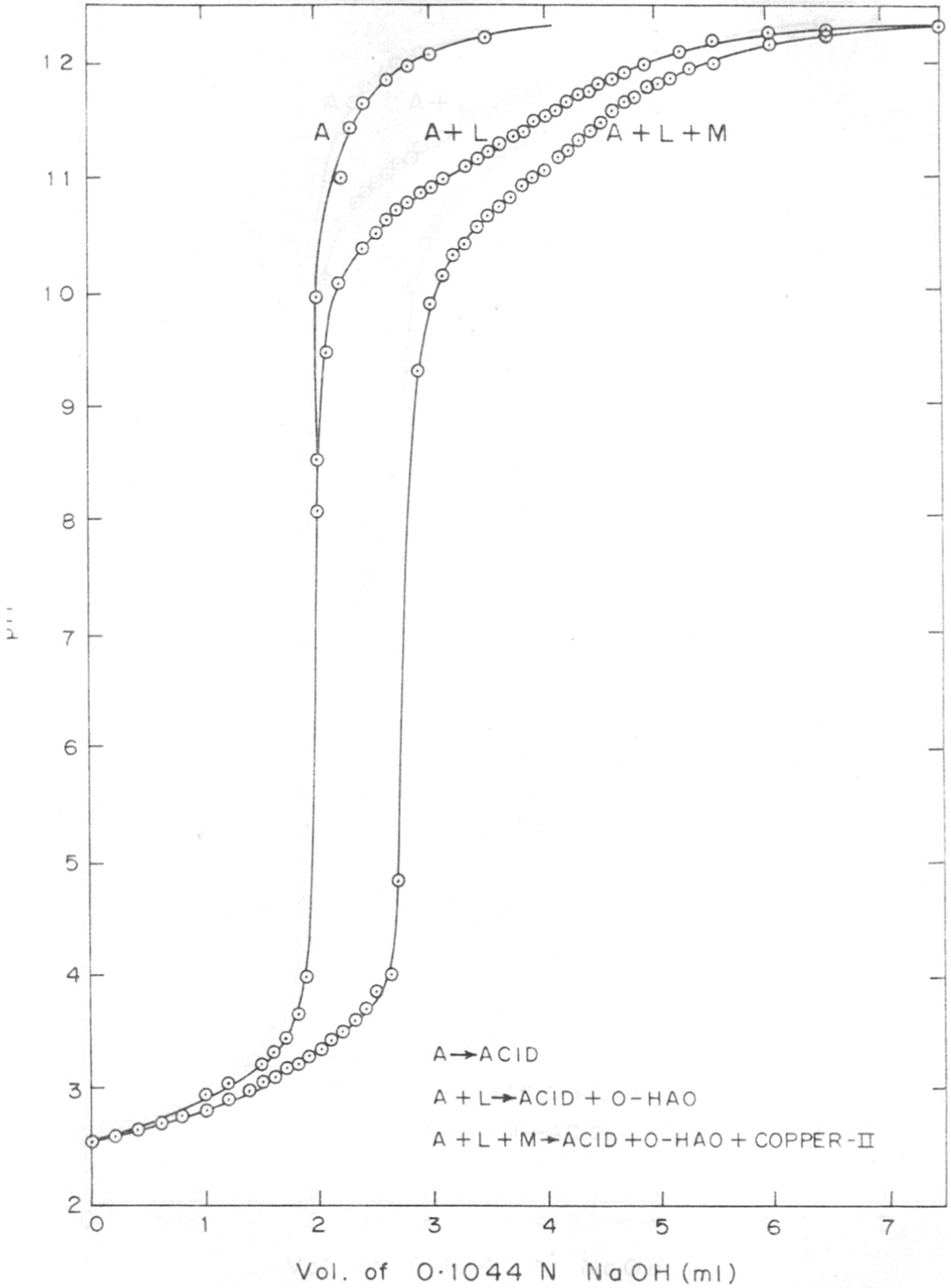


FIG. 59. POTENTIOMETRIC TITRATION CURVES OF COPPER (II)-O-HAO

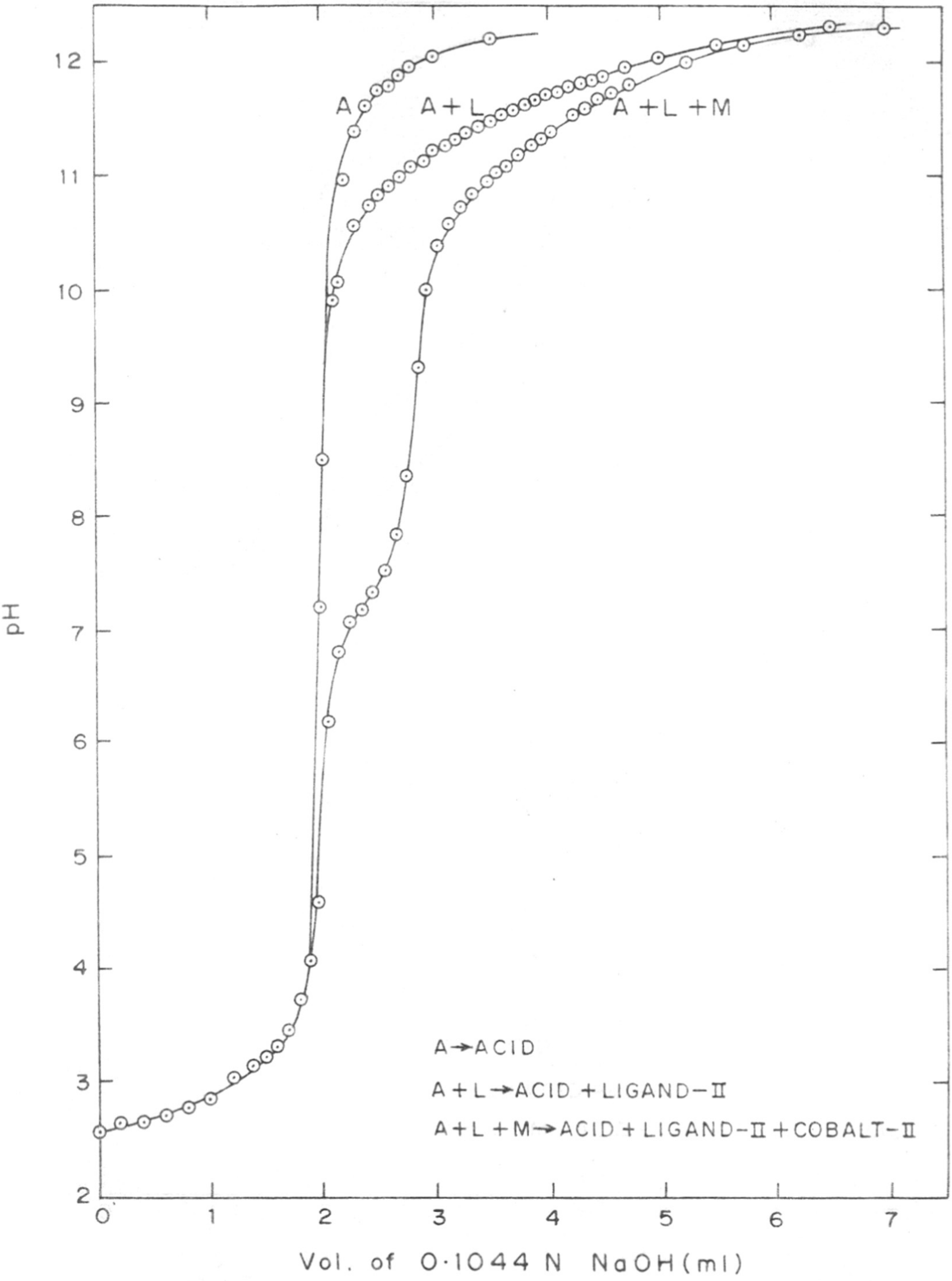


FIG. 60. POTENTIOMETRIC TITRATION CURVES OF COBALT (II) - LIGAND - II

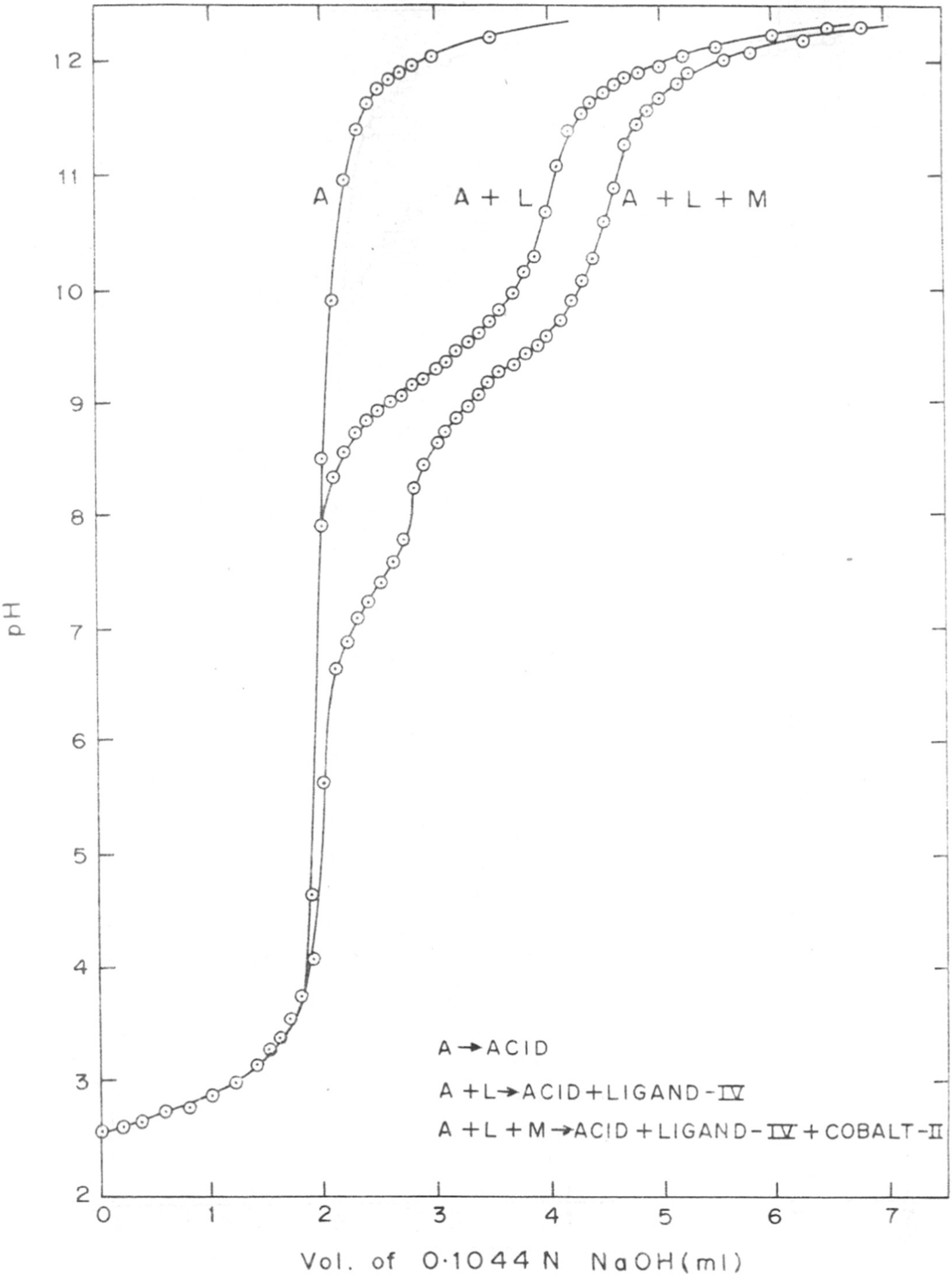


FIG. 61. POTENTIOMETRIC TITRATION CURVES OF COBALT (II) – LIGAND – IV

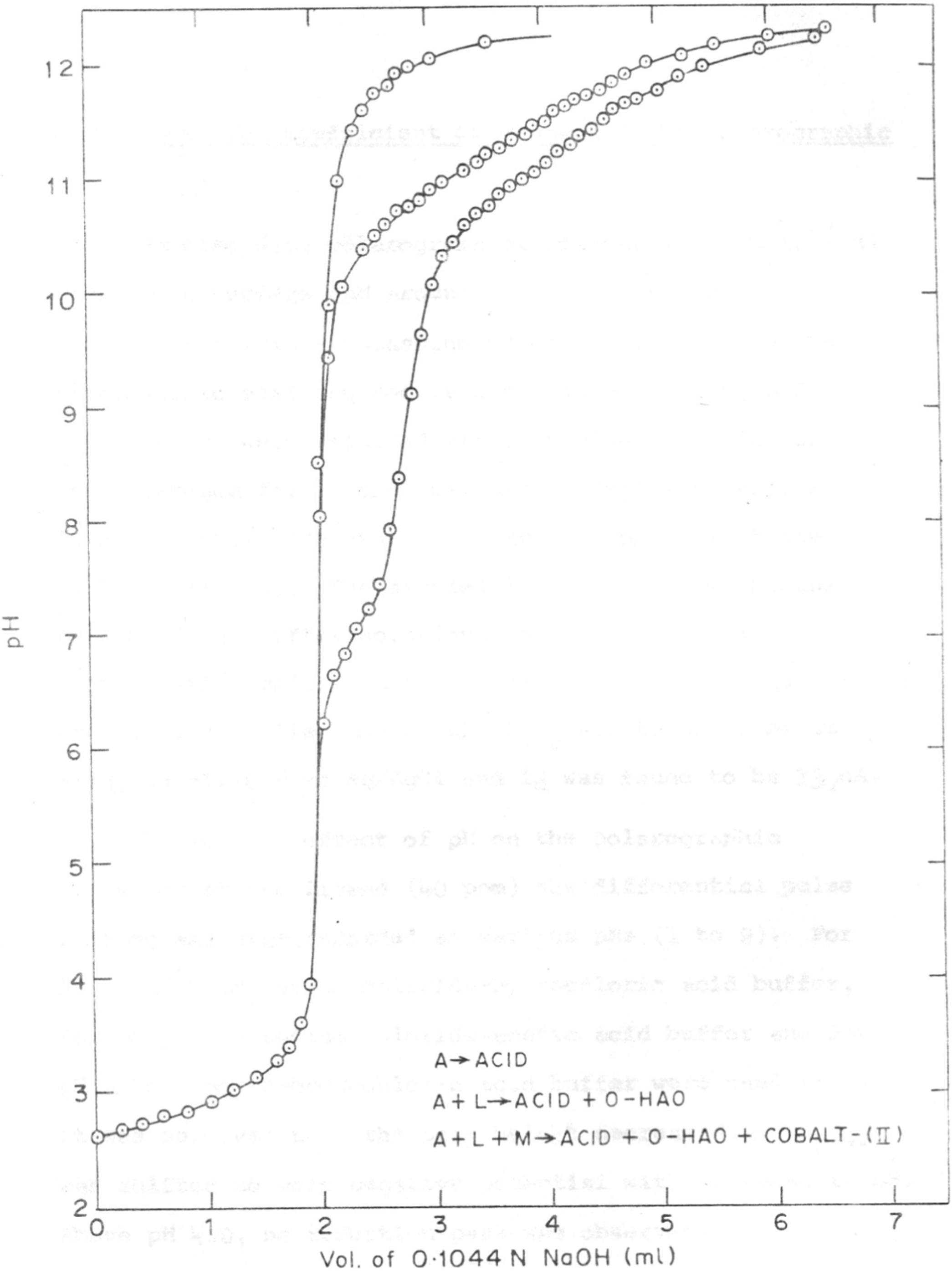


FIG. 62 POTENTIOMETRIC TITRATION CURVES OF COBALT(II)-O-HAO

2.60 Partition coefficient of reagent-II by polarographic method

Sampled d.c. polarograms of reagent-II (2×10^{-3} M) in various buffers (pH around 1.0) viz. universal; hydrochloric acid - potassium chloride; sodium acetate-hydrochloric acid and MacIlvaine, all containing 0.002% triton X-100 were recorded after purging the solution with nitrogen for 10 minutes using PAR-174A polarograph in conjunction with static mercury dropping electrode (SMDE Model 303). The sampled d.c. polarogram obtained in one of the buffer solutions (potassium chloride - hydrochloric acid) is given in Fig. 63. In all the buffers (at pH 1.0) studied above, the $E_{1/2}$ was found to be at -1.25 to -1.30 V vs Ag/AgCl and i_d was found to be 13 μA.

To see the effect of pH on the polarographic behaviour of the ligand (40 ppm) the differential pulse polarograms were recorded at various pHs (1 to 9). For pH 1 and 2 potassium chloride-hydrochloric acid buffer, for pH 3 to 5 sodium chloride-acetic acid buffer and for pH 8 to 9 borax-hydrochloric acid buffer were used (Fig. 64). It was observed that the peak height decreased and E_{peak} was shifted to more negative potential with increase in pH. Above pH 4.0, no reduction peak was observed.

For calibration of the ligand, concentrations from 10 to 60 ppm were taken in potassium chloride -

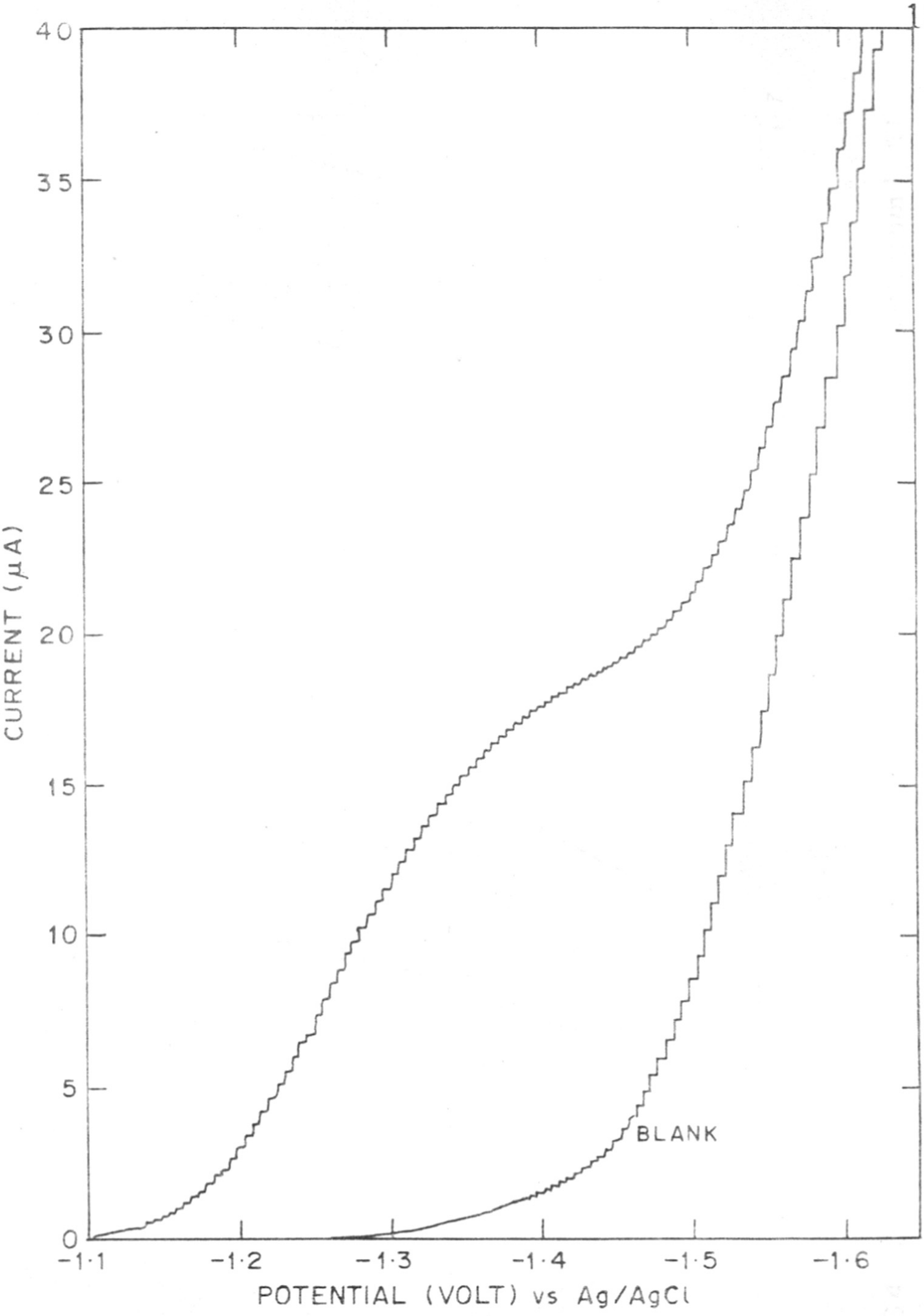


FIG. 63. SAMPLED D.C POLAROGRAM OF REAGENT – II (2×10^{-3} M) IN KCl/HCl BUFFER OF pH 1·0 CONTAINING 0·002 % TRITON X–100

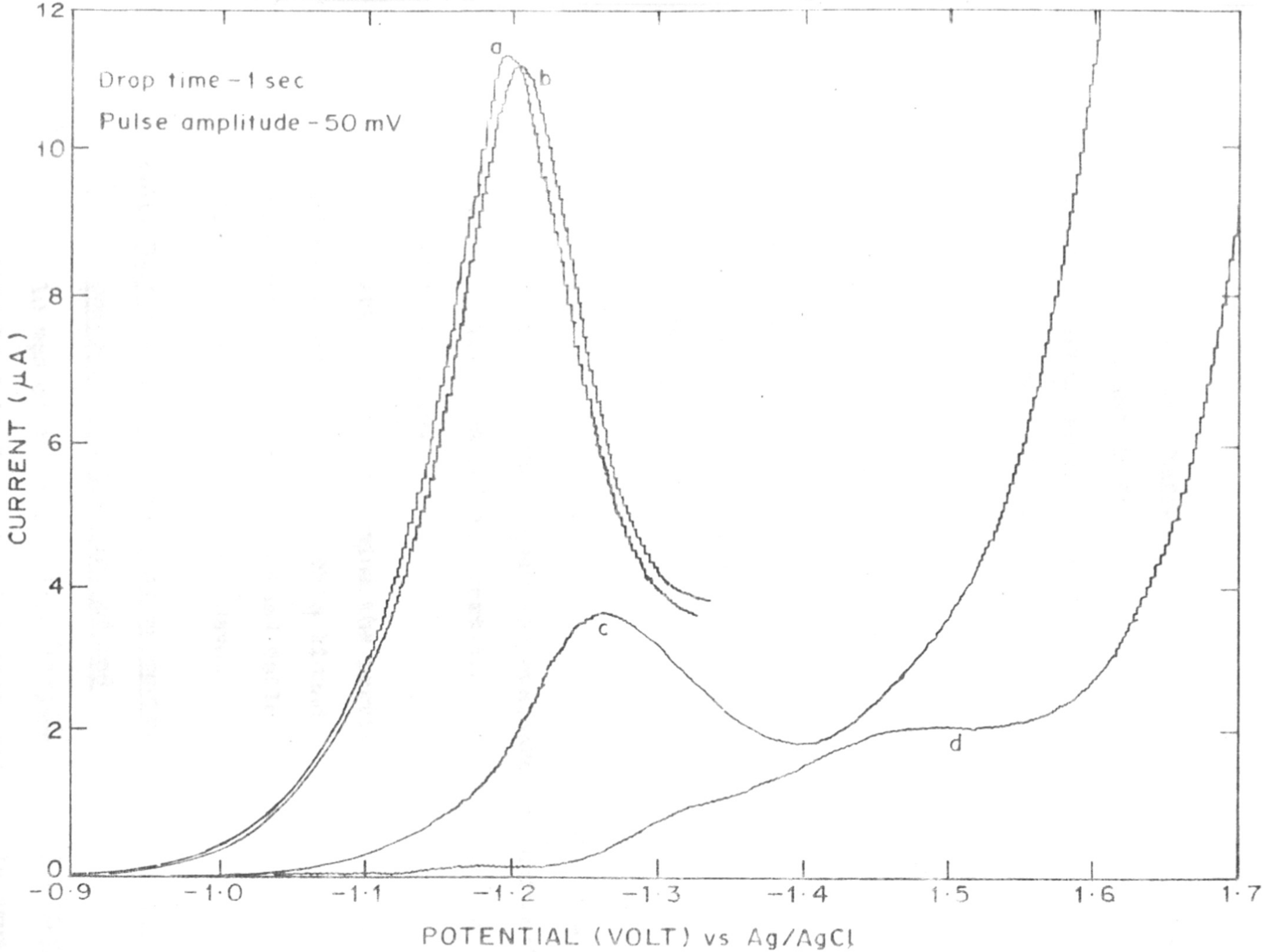


FIG. 64. DIFFERENTIAL PULSE POLAROGRAMS OF REAGENT–II (40 ppm) AT VARIOUS pHs CONTAINING 0·002 % TRITON X–100 (a) pH 1·0, (b) pH 2·0, (c) pH 3·0 AND (d) pH 4·0 Drop time -1 sec. Pulse amplitude -50 mV

hydrochloric acid buffer of pH 1.0 containing 0.002% triton X-100 and differential pulse polarograms were recorded after purging the solutions with nitrogen (Fig. 65). The calibration curve was found to be linear (Fig. 66).

Using this calibration the partition coefficient of the ligand between chloroform and water was determined as follows. A saturated solution of the ligand in chloroform (218 mg in 5 ml $CHCl_3$) was prepared. This was extracted with water (15 ml) and equilibrated with chloroform (15 ml). The reagent in aqueous layer was taken in potassium chloride - hydrochloric acid buffer of pH 1.0 and this solution was polarogrammed. The concentration of the ligand was evaluated by using the above calibration and its partition coefficient was found to be 12.9.

Attempts to determine the partition coefficient of the copper complex of this ligand by the above mentioned polarographic method failed, as the complex did not give a well-defined wave.

2.61. Distribution co-efficient of copper(II) - reagent II complex by extraction method

10 mgs of the pure copper(II)-reagent II complex was dissolved in 5 ml of chloroform (previously equilibrated

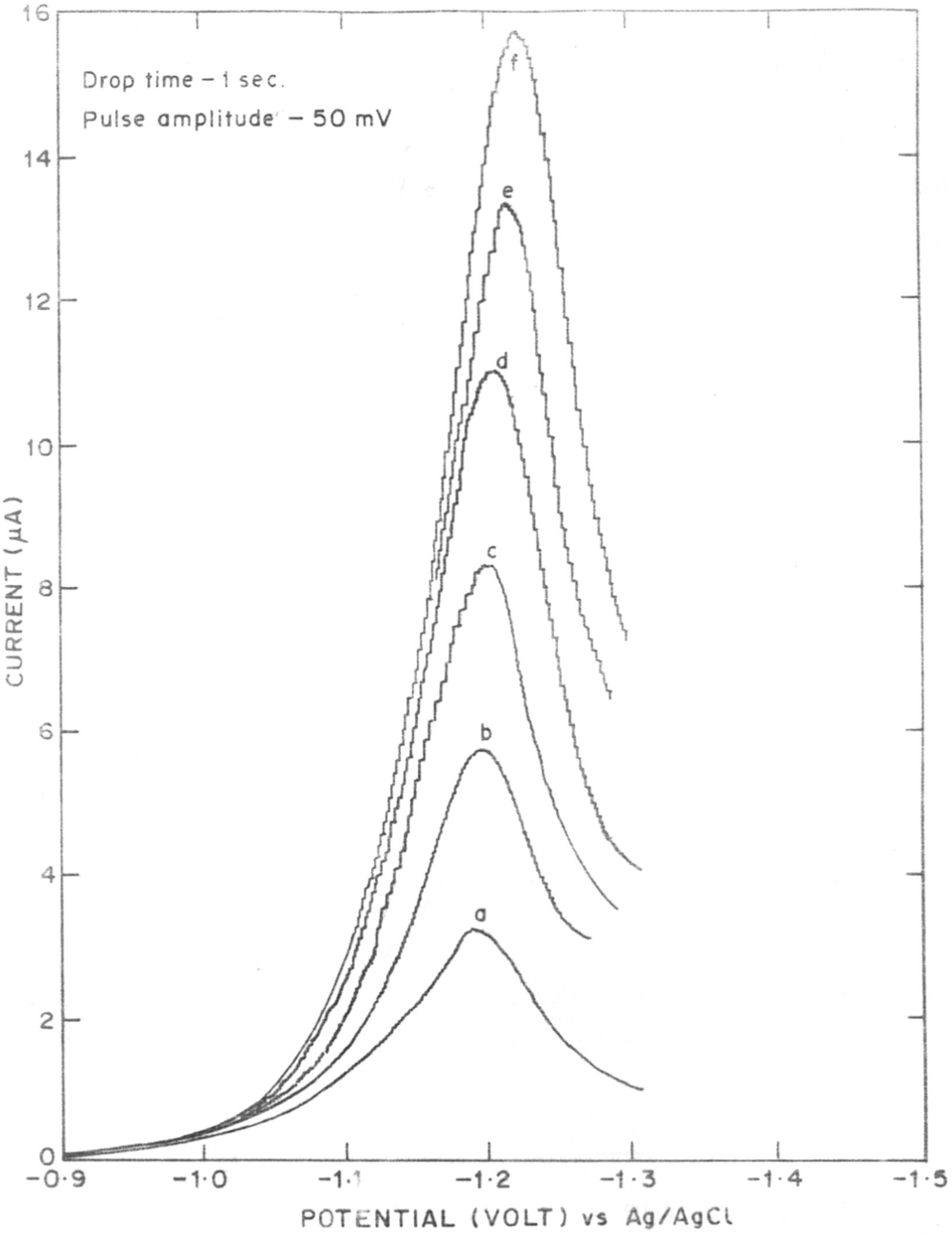


FIG. 65. DIFFERENTIAL PULSE POLAROGRAMS OF REAGENT – II OF VARIOUS CONCENTRATIONS AT pH 1·0 CONTAINING 0·002% TRITON X–100 (a) 10 ppm, (b) 20 ppm, (c) 30 ppm, (d) 40 ppm, (e) 50 ppm AND (f) 60 ppm

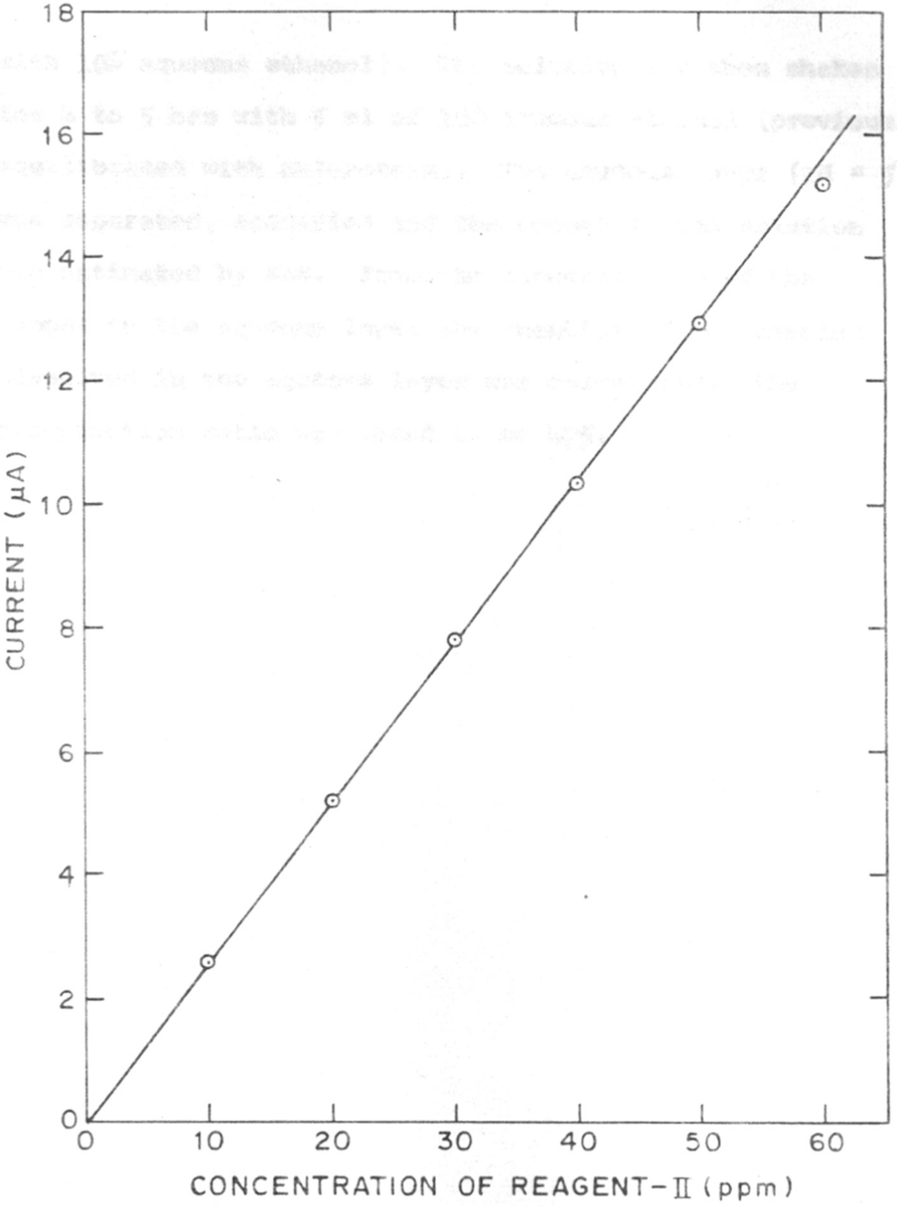


FIG. 66. POLAROGRAPHIC CALIBRATION CURVE OF REAGENT-II AT pH 1·0

with 10% aqueous ethanol). The solution was then shaken for 4 to 5 hrs with 5 ml of 10% aqueous ethanol (previously equilibrated with chloroform). The aqueous layer (pH = 5) was separated, acidified and the copper in the solution was estimated by AAS. From the concentration of the copper in the aqueous layer the quantity of the complex dissolved in the aqueous layer was calculated. The distribution ratio was found to be 475.

CHAPTER III : PRACTICAL APPLICATIONS OF REAGENT-II

3.1 Determination of copper

(a) Silver metal sample

The sample contained traces of copper, silicon and tin.

A known weight (4.50 g) of the silver sample was dissolved in 1:1 nitric acid. The solution was diluted to 100-150 ml and hydrochloric acid added dropwise with stirring to precipitate silver as silver chloride. It was kept warm on the water bath for 1 hr, cooled, filtered and washed with dilute nitric acid. The filtrate was collected and evaporated to a small volume (10-15 ml). The solution was made up to 25 ml.

Into a 10 ml aliquot, 2.5 ml of the ligand solution (10 mM) was added, the pH adjusted to 6.5 and the solution extracted with 25 ml chloroform. A series of aliquots (0.5 ml, 1 ml, 1.5 ml, 2.0 ml) of standard (1 mM) copper solution were similarly treated and extracted. The sample and the standard extracts were dried and the absorbances measured at 336 nm against a reagent blank. The value obtained for percent copper in the sample is given in Table 54.

(b) Silicon-aluminium alloy

The standard sample supplied by the National Metallurgical Laboratory, Jamshedpur was used for the analysis. The certified values for this sample are given below:

Silicon	- 6.15%
Manganese	- 0.195%
Copper	- 0.295%
Iron	- 0.79%
Aluminium	- 92.57%

A known weight of the sample (0.2 g) was dissolved in HCl and fumed with nitric acid and further boiled with 10 ml of HNO_3 after adding 1 g of sodium chlorate and the excess acid removed by evaporation. The residue was boiled for a few minutes with deionised water and the MnO_2 along with SiO_2 was filtered off. The filtrate was made up to 100 ml.

10 ml of the sample solution was taken for determination of copper by extraction-photometry at pH 8.7 (after adding 2.0 g of sodium tartrate). The result obtained is given in Table 54.

(c) Zinc concentrate

The NBS standard zinc concentrate sample was used for the analysis. Certified values for the sample are given below:

Zinc - 47.0%
Lead - 6.0%
Iron - 12.9%
Calcium - 0.08%
Magnesium - 0.16%
Cadmium - 0.14%
Copper - 0.132%
Cobalt - 0.009%
Nickel - 0.006%

A known weight (1.0 g) of the sample was dissolved in hydrochloric acid and evaporated with nitric acid almost to dryness. It was then fumed with 1 ml of conc. sulphuric acid. It was cooled, filtered through No. 40 filter paper and made up to 100 ml.

The copper was determined in a 5 ml aliquot by extraction-photometry at pH 8.5 (using 1.0 g of sodium tartrate). The result obtained is given in Table 54.

(d) 85-a Aluminium alloy

The NBS standard 85-a-aluminium bronze was used for the analysis. Certified values are given below:

Aluminium - 94.28%
Copper - 2.48%
Nickel - 0.41%
Manganese - 0.66%

Iron	-	0.208%
Silicon	-	0.114%
Magnesium	-	1.58%
Titanium	-	0.016%
Chromium	-	0.231%
Zinc	-	0.019%
Lead	-	0.002%

A known weight (0.2 g) of the sample was dissolved in hydrochloric acid. It was fumed with conc. nitric acid and boiled with 10 ml of nitric acid and 1 g of potassium chlorate. It was then evaporated to a small volume, diluted with deionised water, warmed and filtered through No.40 filter paper and made up to 250 ml.

The copper in a 5 ml aliquot was determined by extraction photometry at pH 8.8 (using 2.0 g of sodium tartrate). The result obtained is given in Table 54.

(e) Iron pyrites

A known weight (1.0 g) of the sample was ignited in a platinum crucible to remove the sulphur and the residue treated with hydrofluoric and sulphuric acid to remove the silica. The residue from hydrofluoric acid treatment was fused with potassium pyrosulphate, dissolved in deionised water and made up to 100 ml.

The sample solution was diluted 10 times and 2.5 ml of the solution was taken for determination of copper. The extraction-photometry was carried out as above but using 0.250 g of sodium tartrate at pH 8.5. The result obtained is given in Table 54.

(f) Catalyst spent mass

A catalyst spent mass sample of the following composition was used for the estimation of copper. The percent concentration of the elements as determined by independent analysis are given below:

Copper - 9.97%
Zinc - 1.6
Iron - 2.56
Antimony - 0.49
Carbon - 4.5
Silicon - 80.7

A known weight (0.50 g) of the sample was leached with a mixture of nitric acid and hydrochloric acids. The excess acid was removed by evaporation. The residue was boiled with deionised water and filtered through No. 40 filter paper. The filtrate was made up to 500 ml.

The sample solution was diluted 10 times and the copper in a 5 ml aliquot determined as before but at a pH of 7.5, after adding 10 mg of sodium tartrate. The result obtained is given in Table 54.

(g) Monel   Cu = 31, Ni = 64

A known weight (1.0 g) of monel was dissolved in A.R. nitric acid. The excess nitric acid was evaporated and the residue fumed with 1 ml A.R. perchloric acid. It was then diluted and made up to 100 ml with deionised water.

The sample solution was diluted 100 times and the copper in a 2.5 ml aliquot determined as before but at a pH of 8.6 after adding 0·75 - 1.0 g of sodium tartrate. The result obtained is given in Table 54.

(h) Brass

A standard brass sample of the following composition was used for the determination of copper. The figures given by National Metallurgical Laboratory are

copper - 57.80%
zinc - 39.00%
lead - 2.60%
iron - 0.10%
tin - 0.10%

A known weight (0.1 g) was dissolved in nitric acid and fumed with 1 ml of sulphuric acid. The residue was dissolved in deionised water, filtered through No. 40 filter paper to remove the precipitated lead sulphate and made up to 200 ml.

The sample solution was diluted 10 times and 2.5 ml of the solution was taken for estimation of copper. The extraction-photometry was done as before, but at a pH of 7.5 with the addition of 5 mg of sodium tartrate. The result obtained is given in Table 54.

(i) Aluminium bronze

The NBS standard aluminium bronze was used for this analysis. The certified figures are

copper	- 72.00%
aluminium	- 8.10%
iron	- 6.20%
nickel	- 6.00%
zinc	- 6.20%

A known weight (0.1 g) of the sample was dissolved in nitric acid and fumed with 1 ml of conc. perchloric acid. The residue was dissolved in deionised water and made up to 500 ml.

The sample solution was diluted 10 times and 5 ml of the solution was taken for the estimation of copper. The extraction-photometry was done as before but at a pH of

8.5, after adding 0.5 g of sodium tartrate. The result obtained is given in Table 54.

Analysis of the aqueous layer after extraction of the copper in all the above cases showed that there was no extraction of the other metals like nickel, iron, zinc and aluminium.

3.2 Determination of nickel

(a) Thin film coating

The thin film was present as a coating on ceramic cylindrical shaped base. 1.0 g of the sample was extracted with a mixture of hydrochloric acid and nitric acid. The excess acid was evaporated and the residue dissolved in deionised water. The solution was filtered through No. 40 filter paper and made up to 25 ml.

5 ml of the sample solution was taken for extraction. The nickel in the solution was complexed with reagent-II at pH 9.0 in presence of 10.0 - 25.0 mg of hydroxylamine hydrochloride and extracted with 25 ml of chloroform as usual. The extract was dried and the absorbance measured at 360 nm against a reagent blank. The result obtained is given in Table 55.

(b) Cadmium-nickel solid solution

The sample contained 1.0 percent nickel and 99.0 percent cadmium.

The sample (0.1 g) was dissolved in a mixture of hydrochloric acid and nitric acid. The excess acid was evaporated off and the residue dissolved in deionised water and made up to 100 ml.

5 ml of the sample solution was extracted using reagent-II at pH 9.0 exactly as in the case of sample 'a' without using any masking agent (Table 55).

(c) <u>Stainless steel</u> (NML standard sample 20.1)

The standard sample supplied by N.M.L. Jamshedpur was used for the analysis. The certified figures are given below:

Carbon - 0.38%
Silicon - 0.042%
Manganese - 0.250%
Sulphur - 0.082%
Chromium - 11.62%
Nickel - 6.66%
Copper - 0.119%
Iron - 80.62%

A known weight (1.0 g) of the sample was dissolved in a mixture of hydrochloric and nitric acids and the excess acid was evaporated off. The residue was dissolved in deionised water and made up to 250 ml.

The solution was diluted 20 times, 5 ml of the solution was treated with nitric acid and perchloric acid and evaporated to dryness. 2-3 ml of hydrochloric acid was added again and evaporated to small volume. The sample was diluted to 5-10 ml with deionised water and subjected to ether extraction to remove iron. The aqueous layer from the ether extract was taken in a 25 ml beaker and the excess acid was evaporated. It was diluted to 5-10 ml, and treated with 0.250 g of hydroxylamine hydrochloride, 0.1 g of sodium thiosulphate and 2.5 ml of reagent-II solution. The pH of the solution was adjusted to 9.0 with diethylamine, the nickel complex extracted with chloroform and the absorbance measured. The result is given in Table 55.

3.3 Simultaneous determination of copper and nickel

(a) 34-a-Steel acid open-hearth standard sample

The NBS standard 34-a-steel acid open-hearth was used for this analysis. The certified figures are

carbon - 0.976%
nickel - 0.232%
molybdenum - 0.003%
sulphur - 0.026%

manganese - 0.0501%
chromium - 0.275%
arsenic - 0.009%
silicon - 0.276%
phosphorous - 0.028%
vanadium - 0.007%
copper - 0.222%

A known weight (0.5 g) was dissolved in HCl and fumed with nitric acid and further boiled with 10 ml of HNO_3 and 1 g of sodium chlorate and the excess acid was removed by evaporation. The residue was boiled with deionised water and filtered. The filtrate was made up to 250 ml.

5 ml of the sample solution was extracted with about 20 ml ether to remove most of the iron. The excess acid in the solution was removed by evaporation and the residue dissolved in deionised water. The aqueous solution containing copper, nickel, chromium and some iron was treated according to the procedure given in Section 2.36 for simultaneous determination of copper and nickel (Table 56).

(b) Monel

A known weight (0.1 g) of the metal was dissolved in nitric acid and the excess acid was evaporated. The residue was fumed with perchloric acid and made up to 500 ml with deionised water.

The solution was diluted 10 times and 4 ml of the solution was taken for simultaneous extraction of copper and nickel. Hydroxylamine hydrochloride (25-50 mg) was used to mask the small amount of iron present in the solution. The copper and nickel in the sample was determined by extraction-photometry as given above (Table 56).

Table 54

Determination of copper in some samples using reagent-II.

No.	Sample	Copper reported (%)	Copper found by extraction-photometry (%)
a	Silver	0.0055	0.0054
b*	6% Si-Al, alloy	0.295	0.292
c*	Zinc concentrate	0.132	0.129
d*	85-a-Aluminium alloy	2.48	2.45
e	Iron pyrites	2.73	2.69
f	Catalyst spent mass	9.97	10.10
g	Monel	32.83	32.90
h*	Brass	57.80	57.70
i*	Aluminium bronze	72.00	71.82

* Standard samples

Table 55

Estimation of nickel in samples using reagent-II

No.	Sample	Value reported or found by independent method	Nickel found by extraction-photometry
1	Thin film	50.9 μg	50.2 μg
2	Ni/Cd-solid solution	1.0%	0.99%
3	Stainless steel 20.1	6.66%	6.51%

Table 56

Simultaneous extraction-photometric determination of copper and nickel in samples using reagent-II

Sample	Percent copper		Percent nickel	
	Reported	Found	Reported	Found
34-a-steel acid open-hearth	0.222	0.226	0.232	0.229
Monel	32.83	32.63	64.77	64.08

CHAPTER IV : RESULTS AND DISCUSSION

Reagent I, viz. 2,4-dimethyl-6-hydroxyacetophenone, was used in this work mainly for preparing its oxime, i.e. reagent-II. Since complexes of metals with a reagent similar to reagent-I have been reported,[86-92] it was thought worthwhile to investigate its use for chelating extraction. The I.R. spectrum of the reagent (Fig. 1) shows the C=O absorption band at 1600 cm^{-1}, the shift from the normal ketonic band at 1670 cm^{-1} being due to the conjugated chelate system.[93] The OH absorption band is also greatly shifted and merged with the nujol absorption bands,[94] due to hydrogen bonding in the chelate system. The nmr spectrum (Fig. 2) shows the expected features. The chelated structure of the compound would suggest a fair degree of stability for complexes with transition metals.

The I.R. spectrum of reagent-II (Fig. 3) shows two bands, one at 3430 cm^{-1} due to the oximino -OH group and the other at 3325 cm^{-1} due to the H-bonding of the phenolic -OH to the N of the oximino group. The strong peaks at 1620 cm^{-1} and 1575 cm^{-1} are due to the C=N vibration coupled with the C=C aromatic stretching vibrations.

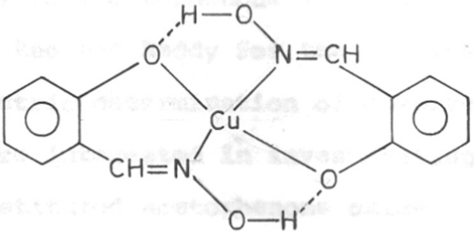
Figures 4 and 5 show the potentiometric titration curves of reagents I and II in 25% ethanol. The titrations were carried out in order to find the ionization constants (K_1) of these reagents. As mentioned in

Chapter I, the proton stability constants ($\frac{1}{K_1}$) would give an idea of the stabilities of transition metal complexes. In Figs. 4 and 5, the inflexions in the pH vs V curves are not easily descernible; but the peaks in the differential curves are sharp and occur at the theoretical volumes of added alkali. The 'end point error' is hence negligible and we may take pK_1 as the pH at the half-neutralization point; the value is the same as that obtained by substitution in known relations[95,96] for potentiometric titration curves. We get pK_1 for ligands I and II as 10.15 and 9.95 respectively.

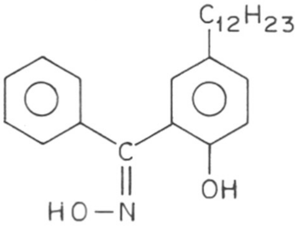
Reagent I by itself is not useful for extraction of metals. The hydroxy complexes are obviously more stable than the chelates. The extraction is better in the presence of ammonia, except in the case of iron(III) and manganese(II) which precipitate as hydroxides on addition of excess ammonia. Since ammonia by itself does not lead to extraction of copper, nickel and cobalt by an inert solvent, the efficacy of the ligand I - ammonia combination can be ascribed to some intermediate compound. The formation of ketimines from ammonia and ketones has been reported.[97,98] We have observed a marked reduction of the polarographic waveheight of ammoniacal nickel(II) solutions a few hours after the addition of reagent I.

Table 2 shows that for the extraction of copper, diethylamine is more effective than ammonia. 'Triple extraction' as mentioned in the Table means extraction with three successive lots of (reagent I + diethylamine) dissolved in chloroform. Table 3 shows that the reagent I - diethylamine - tartrate combination is useful for the separation of copper(II) from nickel(II), provided too much excess of tartrate is avoided. The overall conclusion from the studies with reagent I is that it forms only weak chelates with metals but a fair degree of extraction is achieved in the presence of ammonia or an amine. Although no satisfactory method could be devised for simple separations or extraction-photometric determinations, the observations led to the use of diethylamine in extractions with reagents II and IV to be described later in this thesis.

Salicylaldoxime has been known for a long time as a reagent for precipitation of several metals, particularly copper.[99,100] The chelate of copper(II) has the planar structure



The complex, being uncharged, would be soluble in organic solvents. Salicylaldoxime has accordingly been used for the solvent extraction of metals such as copper and nickel.[101,102,103] Kinetics of the reaction between copper(II) and salicylaldoxime in the two phase system has recently been studied.[104] o-Hydroxyketoximes have also come into prominence, especially for possible commercial applications, as has been mentioned in Chapter I. Most of these are compounds with long side-chains, e.g.



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The study of o-hydroxyaryl ketoximes for their analytical applications has been confined chiefly to unsubstituted o-hydroxyacetophenone (o-HAO),[105-109] which was used by Rao and Reddy for the simultaneous extraction-photometric determination of copper and nickel.[105] We were interested in investigating the likely use of substituted acetophenone oximes and for this purpose first selected reagent II (2,4-dimethyl-6-hydroxyacetophenone oxime or DMHAO for short). The reagent is useful in extracting several metals as is seen from Table 6. Zinc(II), chromium(III) and iron(II) are not extracted. Polarographic studies carried out in this laboratory (not reported here) show that the zinc wave is not at all affected by the presence of ligand II. This shows that zinc is not complexed by the reagent. Table 7 shows λ_{max} and molar absorbances of some of the complexes of interest. The absorbances of the complexes of copper and nickel with this ligand are higher than those of the corresponding complexes with o-hydroxyacetophenone oxime (o-HAO). The ϵ_M values for copper(II) and nickel(II) complexes are $(7.3 \pm 0.1) \times 10^3$ l mole^{-1} cm^{-1} and $(6.2 \pm 0.1) \times 10^3$ l mole^{-1} cm^{-1} with DMHAO and $(3.2 \pm 0.1) \times 10^3$ l mole^{-1} cm^{-1} and $(4.1 \pm 0.1) \times 10^3$ l mole^{-1} cm^{-1} with o-HAO respectively. The variation of percent extraction with pH (Tables 8-11 and Figs. 11-14) follow the usual pattern of the shift of complex equilibria in aqueous solution with pH, when the anion of a weak acid is used as the ligand. This leads to a certain pH range in which maximum concentration of the complex is attained. Beyond this range, the metal hydroxide tends to get precipitated and the complexes with ligands other than OH^- break up. Figures 15 to 18 give the Beer's law plots for the extracted complexes of copper(II), nickel(II), cobalt(II) and iron(III) and show that reagent II is suitable for the extraction-photometry of these individual metals.

Section 2.14 shows that for most of the metals extracted, the 'inert' solvent used exerted no specific effect. This would mean that these complexes are 'coordinatively saturated' as mentioned in Chapter I of this thesis.[64,65] Since the extraction of iron(III) is markedly enhanced by the use of n-butanol, it would be tempting to assume that the iron(III) is coordinatively 'unsaturated' and is extracted as ion pairs such as $[FeL_2]^+ (ClO_4)^-$ or $[FeL]^{2+} (ClO_4)_2^{2-}$ where L^- is the ligand anion. The situation would be the same as in the extraction of the perchlorates of cobalt, nickel etc. by higher alcohols as mentioned in Chapter I. This point will be considered again in a later part of this Discussion.

Sections 2.15 to 2.19 deals with a few separations using reagent II and some of the well-known masking agents. Section 2.15 and Table 12 show that thiosulphate has only a limited masking action on copper(II). Although log K for the thiosulphate complex of copper(II) is 12.3, it is not strong enough to mask the copper(II) effectively.[110] Section 2.16 and Table 13 show that oxalate can effectively mask nickel(II) and allow copper(II) to be extracted only if the pH is below 7.2. The log K values for the neutral oxalate complexes of copper(II) and nickel(II) are 4.5 and 7.2 respectively.[111] Since the log of the stability constants of the copper and nickel complexes of reagent II are 17.7 and 16.8 respectively (as will be seen from the experiments in Section 2.59) and since 100% of the copper is extracted above pH 4.5 and no nickel is extracted below pH 6.5, it is possible to extract most of the copper at around pH 7.0 in the presence of oxalate. Repeated extractions at slightly lower pH can serve to separate all the copper, but this was not pursued as tartrate was found to be a better masking agent as is seen from Section 2.17 and Table 14. Complete separation can be achieved with reagent II + tartrate at about pH 8.0. The values of log K for the (neutral) tartrate complexes of copper(II) and nickel(II) are 3.2[112] and 9.90[113] respectively and this, coupled with the use of pH's below 8.0 explains the masking action of tartrate on nickel(II). The separation of copper(II) from iron(III) is still easier as seen from Table 15, a complete separation being effected in a pH range 7.5 to 10.0. The log K values of the tartrate complex of copper(II) and iron(III) are 3.2 and 18.06[113] respectively. Tables 17 and 18 give general lists of interferences in the extraction-photometric determination of copper(II) and nickel(II) respectively. The separation of nickel(II) from iron(III) is not possible even with the use of tartrate as masking agent; but since iron(II) is not extracted, the nickel(II) can be easily separated if hydroxylamine is added to reduce the iron(III) first (cf. Section 2.22 and Table 19).

Section 2.24 and Table 21 show that the reagent is suitable for the simultaneous extraction-photometric determination of copper(II) and nickel(II) with relative errors ranging from 0.2 to 2.1% for copper and 0.2 to 1.7% for nickel. Hydroxylamine is effective in suppressing the interference of iron as seen from experiments Nos.7, 8 and 9 in Table 21. The interference of various ions in the simultaneous determination of copper and nickel is given in Table 22.

Tables 23 and 24 show the results of attempts to separate copper(II) from cobalt(II). Thiosulphate and tartrate are both ineffective in selective masking of copper and cobalt respectively; log K for the cobalt-tartrate complex is only 2.1.[112]

It was earlier mentioned that addition of diethylamine had a beneficial effect on extractions with reagent I. This prompted similar trials with reagent II. The results are given in Tables 25-A and 25-B. It is seen from Table 25-A that diethylamine scarcely affects the λ_{max}, but leads to a marked increase in the molar absorbances. The largest increase is for nickel(II) (from 6200 to 9200) and the smallest increase is for copper(II) (from 7300 to 7700). Such enhancement in ϵ_M without change in λ_{max} is not easily explained.

Sections 2.31 to 2.34 deal with the use of diethylamine in separations. The separation of copper from nickel using tartrate as a masking agent is easier with addition of diethylamine than without such addition. (Compare Table 26 with Table 14). When diethylamine is added, much less tartrate is needed, the pH of extraction can be as low as 4.6 and the pH range may be from 4.6 to 6.5. The beneficial effect of diethylamine is even more striking in the copper/cobalt separation. Comparing Table 27 with Table 24, it is seen that only with the addition of diethylamine is it possible to use reagent II for this separation.

It has already been noted that chromium(III) is not extracted by reagent II/chloroform, and it might be considered a simple matter to separate nickel(II) from chromium(III) or copper(II) from chromium(III). As regards the nickel/chromium pair, Table 20 shows that although no chromium is extracted, the extraction of nickel is appreciably suppressed. This is an example of 'suppression of extraction'[80,81] mentioned in Chapter I of this thesis. It could be due to the nickel complex being absorbed on the micelles of $Cr(OH)_3$ or a hydroxy-Cr-ligand complex. Such an effect is also noticed in the extraction of copper(II) in presence of chromium(III) as seen from Table 28. One way of overcoming this difficulty is to add diethylamine, as shown in Table 29. Instead of diethylamine, aniline can also be used, but it is less effective. Another method is to add sufficient iron(III) to the mixed solution of copper(II) and nickel(II), and extract using reagent-II without any tartrate or diethylamine. The extractions of copper(II) and nickel(II) are then complete, but that of iron(III) is only partial, as mentioned in Section 2.35. The suppressive effect of chromium(III) appears to be selective towards iron(III). As mentioned in Section 2.36, this effect can be used for the simultaneous determination of copper(II) and nickel(II) in the presence of iron(III) and chromium(III).

Section 2.37 describes the preparation of the hitherto unreported compound 3,5-dibromo-2,4-dimethyl-6-hydroxyacetophenone. The I.R. spectrum of this compound in nujol (Fig. 25) shows a broad band around 3300 cm^{-1} due to H-bonding of the phenolic -OH to O of the ketonic group. The strong peak at 1670 cm^{-1} is due to -C=O and at 1570 cm^{-1} is due to -C=C stretching vibrations.

The NMR spectrum in CCl_4 (Fig. 26) shows the following proton chemical shifts (in δ):
$C_{(2)}$-CH_3: 2.43; $C_{(4)}$-CH_3: 2.47; -$COCH_3$: 2.64 and -OH: 8.4.

Section 2.38 describes the preparation of reagent IV, i.e. the oxime of reagent III. The I.R. spectrum of this reagent in nujol (Fig. 27) shows three bands in -OH stretching region viz. at 3500 cm^{-1} due to the oximino -OH group; at 3480 cm^{-1} and at 3300 cm^{-1} due to hydrogen bondings of phenolic -OH to Br and to the N of the oximine group respectively. The peaks at 1620 cm^{-1} and at 1575 cm^{-1} are due to C=N and C=C stretching vibrations.

Figures 28 and 29 give the potentiometric titration curves of reagents III and IV in 50% ethanol. The compounds are not sufficiently soluble in 25% ethanol. Unlike the titration curves of reagents I and II, the curves 28 and 29 clearly show prominent inflexions at the expected equivalent points. The ionization constants are $10^{-7.50}$ and $10^{-8.30}$ respectively; these values show the compounds to be stronger acids than reagents I and II. This would mean that the proton stability constants have been lowered by substitution by Br in the nucleus. The reagents may therefore be expected to be somewhat weaker chelating agents for metals.[114]

Sections 2.40, 2.41 and 2.42 deal with experiments on the use of reagent III (with and without added ammonia, diethylamine or aniline). These were carried out on the pattern of the work with reagent I and led to essentially the same results; but as the blank absorbances are relatively high, reagent III has no potential for applications. The experiments are recorded merely for completeness of presentation.

Regarding the use of reagent IV the following questions are to be answered, viz. how are the molar absorbance, the λ_{max} and the peak resolution of the several complexes affected by

(a) use of reagent IV in place of reagent II (without diethylamine);

(b) the use of diethylamine along with reagent IV; and

(c) the use of reagent IV in place of reagent II if diethylamine also has to be used?

Comparison of Tables 7 and 33 provide an answer to (a) and shows that the substitution of two bromine atoms in the aromatic nucleus leads to an increase in the molar absorbances of the complexes of all the metals; the largest increase of over 100% being for iron(III), followed by nickel(II). Comparison of Tables 7 and 30 as well as of the Figs. 10 and 30 show that use of reagent IV results in an increase of λ_{max} in all cases, though the increase is very slight for iron(III) and manganese(II). There is no appreciable increase in the resolution of the peaks; there is, in fact, a slight decrease of 2 nm in the resolution of the copper(II)/nickel(II) peaks.

As mentioned in the text, the copper complex of reagent IV has to be extracted with addition of diethylamine. Otherwise there is no extraction into chloroform, and the benzene extracts quickly become turbid and deposit the solid complex. However, there is no quantitative relation between the percent extraction of copper (as a stable complex) and the proportion of diethylamine used. We cannot therefore assume a strong coordination of the diethylamine molecules to the copper.

If a metal M is extracted both as the complex MA_x (A being the anion of a reagent HA) and as the complex MA_xB_y (B being a solvent or other neutral species which brings about a synergistic extraction of M) then the overall distribution coefficient would be given by

$$D = \frac{K' \, [HA]_o^x \, [B]_o^y}{[H^+]^x}$$

where K' is a composite extraction constant. The effect of diethylamine however satisfies the usual definition of the synergic effect.[115]

The figures in Table 38 give an answer to question (b) and show that unlike the case with reagent II (Table 25-A), use of diethylamine does not lead to a uniform increase in the molar absorbances of the complexes of all the metals investigated; for cobalt and iron, there is actually a decrease in molar absorbance when using diethylamine. However, it has been observed that, as in the case of reagent II (Table 25-B) there is an increase in percent extraction of all the metals, particularly at lower pH's when using diethylamine along with reagent IV.

Finally, the answer to question (c) would be - by comparing the last columns in Tables 25-A and 38, that if diethylamine is to be used, there is no advantage in using reagent IV instead of reagent II for the determination of copper, nickel or cobalt. The iron(III) complex of reagent IV has not only a higher molar absorbance than that of reagent II (10000 as compared to 6600), it is also extracted much better at lower pH's as can be seen from Tables 11 and 37 (Figs. 14 and 38). However, the extract of the iron(III) -ligand IV complex does not obey Beer's law (Fig. 34), probably owing to a high blank (Fig. 30). The effect of diethylamine on the extractability of the copper complex could be made use of in a number of ways. Section 2.49 and Table 40 show that nickel(II) can be separated from coppper(II) using reagent IV and sodium thiosulphate as a masking agent for copper, without adding diethylamine. This method, however, fails to separate cobalt(II) from copper(II) as seen from Table 42. Table 41 shows that copper can be separated from nickel using reagent IV, oxalate and diethylamine and in this respect reagent IV is more useful than reagent II. The rest of the work with reagent IV was modelled on reagent II and need not be discussed here.

Sections 2.54 to 2.59 deal with investigations on the compositions and stabilities of the extractable complexes of copper(II), nickel(II), cobalt(II) and iron(III). As mentioned in Chapter I, the slope of the log D vs pH straight line plot would give the number n of ligands attached to one atom of the metal. As shown in Figs. 43 to 46, the slopes of all the straight line plots for the metal - reagent II complexes are very nearly 2.0. While this is acceptable for the divalent metals, copper, nickel and cobalt, it looks prima facie improbable for iron(III). As is evident from equation (5) given in Chapter I, the plot of log D vs log $[HL]_o$ at a definite pH should also be a straight line with a slope equal to n. In practice, it has been shown that if a fairly large excess of reagent is used, one can plot log D vs log L where L is the total ligand concentration. Figure 47 bears this out for the copper - ligand-II complex. Figure 48 confirms that the iron(III) complex also has a 1:2 stoichiometry. The same stoichiometry is obtained for all the complexes of reagent IV. Any doubt regarding the stoichiometries of the complexes of copper and nickel is removed by the preparations described in Section 2.57. The preparation of a 'pure' complex of iron(III) with reagent II was not successful, but a composition approximating to $FeL_2(OH)$ was obtained for the washed and dried solid. Figure 53 shows the IR solution spectra of the iron(III) and copper(II) complexes. The broad

OH band in the region is similar to those found in metal hydroxides, especially hydrated iron oxides.[116,117] The precipitated complex was soluble in pure ethanol; hence 1:1 aqueous ethanol was used for washing to remove the excess ligand. It may be reasonably inferred that at least part of the (OH) was introduced during the washing process. The precipitated complex can therefore be assumed to have a composition corresponding to $FeL_2(OH)_x(OEt)_{1-x}$, $x < 1.0$. Here we have also to consider whether the complexes which are extracted into chloroform (or precipitated in the preparative procedure) are coordinatively saturated. Nickel(II) being a d^8 ion is known to form square planar complexes. Similarly copper(II), a d^9 ion, forms severely distorted (tetragonal John-Teller distortion) octahedral complexes. Both these ions would be coordinatively saturated with two bidentate ligand moieties, although the copper(II) complex will be loosely coordinated to two extra donor atoms, which may be the O's from the solvent molecules (H_2O or EtOH) or may be the N's from the free reagent molecules (HL). In the case of cobalt(II), it may form either a tetrahedral or an octahedral complex. We might suppose for instance that initially it forms a tetrahedral complex, but on extraction into the organic layer containing excess reagent it might either retain the tetrahedral coordination or change into an octahedral coordination with two extra reagent molecules. The case of the iron(III) complex is different from the others; the 1:2 stoichiometry means that either (a) the iron is extracted as an ion pair $(FeL_2)^+X^-$ as mentioned earlier in this Discussion or (b) it is extracted as $FeL_2(OH)_x(OEt)_{1-x}$, $x < 1.0$. In either case the species will be coordinatively unsaturated unless a sufficient number of solvent molecules are coordinated to the iron. For instance, the ion-pair may be $[FeL_2(EtOH)_2]^+ClO_4^-$. The neutral species may be $FeL_2(OH)_x(OEt)_{(1-x)}EtOH$ or $FeL_2(OH)_x(OEt)..HL$, the coordination to HL being rather loose, so that the observed quantitative dependence of log D on log L shows a 1:2 rather than a 1:3 complex. Of these, the ion-pair type of species seems to be less probable since the extractant is the inert solvent chloroform. It is also difficult to understand how an ion-pair complex such as $[FeL_2(EtOH)_2]^+ClO_4^-$ would precipitate out of a 10% ethanolic medium and change to a species with Fe-OH bonding as seen in IR (Fig. 53) on washing with 50% ethanol. The large solubilizing effect of n-butanol (when used as extractant in place of chloroform, as noted earlier in connection with Section 2.14) may be attributed to the replacement of -OH in $FeL_2(OH)_x(OEt)_{1-x}\cdot EtOH$ by $-OC_4H_9$ rather than by coordination of two C_4H_9OH molecules to Fe in the ion-pair. The solubility in chloroform of a complex containing a small proportion of metal-bonded (OH) groups need not be surprising. It has been reported[118] that while the complex $VO(L')(OH)_2$ (L' = 2-mercaptopyridine N-oxide) is not extractable with chloroform, it can easily be converted, by treatment of the solution with an alcohol to the complex $VO(L')(OR)(OH)$, which is extractable. The differences in the compositions of the complexes of copper(II) and nickel(II) on the one hand and of iron(III) on the other are also seen in their different behaviours towards chromatographic elution on a silica gel column. These experiments were initially designed to remove the excess free ligand from the precipitated complexes. The strong irreversible adsorption of the iron complex points to the presence of Fe-OH groups.

The precipitation-titration experiments mentioned in Section 2.59(a) were carried out in order to establish that, at the inflexion point of a pH titration, the metals concerned did indeed form complexes (with reagent II) which were soluble in chloroform and which contained the stoichiometric proportions of metal in each case. This was considered an essential preliminary to the actual potentiometric titrations in 75% dioxan . Titrations in 25% - 75% dioxan had been previously reported for the complexes of salicylaldoxime and o-hydroxyacetophenone.[119-122] Section 2.59(a)(ii) shows that 50% dioxan was not quite satisfactory. The method of calculation[123] is given below.

The first quantity calculated is n_A, given by

$$n_A = 1 - \frac{(v_2 - v_1)(N + E^o)}{(V^o + v_1) \times T_L^o}$$

v_1 = titration value for A (strong acid) alone

v_2 = titration value for A+L (ligand)

N = normality of NaOH

E^o = initial acid concentration

v^o = initial total volume

T_L^o = total ligand concentration taken

Next, $\bar{n}$ is calculated from

$$\bar{n} = \frac{(v_3 - v_2)\,[N + E^o + T_L^o\,(1 - n_A)]}{(V^o + v_2) . T_M^o . \bar{n}_A}$$

where v_3 = titration value for A+L+M (metal)

T_M^o = total metal concentration taken

and $\bar{n}$ is the 'ligand number' i.e.

$$\bar{n} = \frac{\text{concentration of ligand anions combined with the metal}}{\text{total concentration of the metal}}$$

and the other symbols are as given for calculation of n_A.

Now L or $[L^-]$, the concentration of the free ligand anion is calculated at a given pH by

$$L = \frac{K_i\,(T_L^o - \bar{n}\,T_M^o)}{K_i + [H]}$$

where K_i = ionization constant of the reagent

$[H]$ = hydrogen ion concentration at the given pH.

The equilibrium constants K_1 and K_2 are calculated from the relation

$$K_1 L\,(1-\bar{n}) + K_1 K_2 L^2\,(2-\bar{n}) = \bar{n}.$$

For a divalent cation M^{2+}, K_1 and K_2 are given by

$$K_1 = \frac{[ML]^+}{[M^{++}][L^-]} \; ; \qquad K_2 = \frac{[ML_2]}{[ML^+]\;[L^-]}$$

Since we are interested mainly in the 1:2 complex only, the value of the formation constant

$$K_f = K_1K_2 = \frac{[ML_2]}{[M^{++}][L^-]^2}$$

is more important. The results of the calculations given in Table 57 show that for the ML_2 complexes of nickel(II) and cobalt(II) the stabilities are in the order: o-HAO ~ DMHAO > DBDMHAO which is also the order of the proton stability constants. Interestingly the stabilities of the copper(II) complexes are in the order: o-HAO > DMHAO ≈ DBDMHAO. Considering the published values for the stability constants of the copper complexes of salicylaldoxime and its methyl derivatives,[116,117,118] we see that the order of stabilities of copper(II) complexes are: salicylaldoxime > 5-methyl salicylaldoxime ≈ 5-chloro-salicylaldoxime ≈ 5-nitrosalicylaldoxime ≈ o-HAO > DMHAO ≈ DBDMHAO.

Complex stability is not the sole criterion for the utility of a reagent in solvent extraction or extraction-photometry. The partition coefficient of the complex, its spectral properties, amenability to Beer's law, partition coefficient of the reagent itself, all come into play. Section 2.60 describes the

Table 57

Stability constants of the complexes of copper(II), nickel(II), cobalt(II) and hydrogen with substituted o-hydroxyacetophenone oximes determined in 75% dioxan

Ligand[+]	Log K values of complexes of			
	copper(II)	nickel(II)	cobalt(II)	Hydrogen
DMHAO	17.70	16.75	14.70	11.20
DBDMHAO	17.25	11.70	11.0	9.25
o-HAO	20.05 21.38*	14.70 14.80*	14.70	10.80

* Values reported by previous workers[119]

\+ DMHAO = 2,4-dimethyl-6-hydroxyacetophenone oxime

DBDMHAO = 3,5-dibromo-2,4-dimethyl-6-hydroxyacetophenone oxime

o-HAO = orthohydroxyacetophenone oxime.

determination of the partition coefficient K_{DR} of the reagent II by a differential pulse polarographic method. This value of K_{DR}, along with results obtained from the studies on log D vs pH and the values for K_1 and K_f ($= K_1K_2$) obtained from the potentiometric titration experiments, can be used to calculate the partition coefficient of the metal complex. The simple extraction procedure given in Section 2.61 can then be used to calculate the proportion of the copper complex which exists (in the absence of added excess reagent) in the aqueous layer at a given pH. These calculations are given below.

The total reagent added in the experiments on the variation of log D with pH (Section 2.11) was 125 micromoles, and the total copper added was 1 micromole. At pH = 3, the percent extraction of copper is 10.2. Thus 0.2 micromole~~cule~~ of the reagent would have combined with the copper and the total uncombined reagent = 124.8 micromole. From the partition coefficient of HL (= 12.9) and the known volumes of the organic and aqueous layers (10 ml and 15 ml respectively) we calculate $[HL]_o = 1.11 \times 10^{-2}$ and $\log [HL]_o = -1.952$. Substituting in $\log D = \log K^* + n \log [HL]_o + n\,pH$ we get $\log K^* = -3.04$ at pH = 3.0. Similarly we get $\text{Log } K^* = -3.22$ at pH = 4.0

An average value of -3.13 may be assumed for log K^*. As given in Chapter I,

$$K^* = \frac{K_f\, K_{DX}\, K_i^n}{K_{DR}^n}$$

Therefore, $\text{Log } K^* = \text{Log } K_f + \text{Log } K_{DX} + n \text{ Log } K_i - n \text{ Log } K_{DR}$.

The experimental values for Log K^*, Log K_f, Log K_i and Log K_{DR} are now substituted, taking care to choose the K_f and K_i values from the same set of experiments (i.e. potentiometric titrations in 75% dioxan) since K_f has been calculated assuming this particular value of K_i (see Table 57).

$$\begin{aligned} \text{Log } K^* &= -3.13 \\ \text{Log } K_f &= 17.70 \\ \text{Log } K_i &= -11.20 \\ \text{and} \quad \text{Log } K_{DR} &= 1.11. \\ \text{we get} \quad \text{Log } K_{DX} &= 3.8 \\ \text{or} \quad K_{DX} &= 6310 \end{aligned}$$

The experimental value (475) obtained from the simple extraction procedure (Section 2.61) is the ratio of

$$\frac{\text{total copper in organic layer } (T_o)}{\text{total copper in aq. layer } (T_a).}$$

While the numerator gives the correct concentration

$[CuL_2]_o$ of the copper complex in the organic layer, the denominator is higher than the concentration $[CuL_2]_a$ of the undissociated complex in the aqueous layer since

$$T_a = [CuL_2]_a + [CuL^+]_a + [Cu^{2+}]_a$$

whereas $$T_o = [CuL_2]_o$$

We conclude that only $\frac{475}{6310}$ i.e. about 7.5% of the total copper in the aqueous layer is present as the undissociated complex.

The main points of this Chapter on discussion are summarised below:

(1) Reagent II, viz. 2,4-dimethyl-6-hydroxyacetophenone oxime (DMHAO) is better than unsubstituted o-hydroxyacetophenone oxime (o-HAO).

(2) Reagent IV, viz. 3,5-dibromo-2,4-dimethyl-6-hydroxyacetophenone oxime (DBDMHAO) is better than reagent II only for the separation of nickel(II) from copper(II) and copper(II) from cobalt(II).

(3) Use of suitable masking agents and experimental conditions (especially the optimum pH) can lead to the successful extraction-photometric determination (using reagent II) of nickel(II) or copper(II) or both simultaneously, in the presence of iron(III) and chromium(III).

(4) The complexes of reagents II and IV of all the four metals investigated except reagent IV complex of iron(III) obey Beer's law.

(5) Zinc(II), iron(II) and chromium(III) are not extracted. Chromium(III) suppresses the extraction of copper(II), nickel(II) and iron(III).

(6) Addition of diethylamine (DEA) enhances the extraction of metals with reagents II and IV. For the extraction of copper(II) with reagent IV, addition of DEA is essential.

Use of proper experimental conditions can lead to the effective separation of copper from nickel and/or iron by the use of reagent II alone. But for a separation of copper from cobalt, addition of DEA is essential. DEA also minimises the suppressive effect of chromium(III).

If DEA is used, reagent II gives still higher molar absorbances, and the advantages vis-a-vis unsubstituted o-hydroxyacetophenone are more marked. DEA does not enter into the composition of the complex. The synergistic effect appears to be due more to a solubilizing action of DEA on the complexes.

~~Use of proper experimental conditions can lead to effective separation of copper from nickel and/or~~

~~iron by use of reagent II alone. But for a separation of copper(II) from cobalt(II), addition of DEA is essential. DEA also minimises the suppressive effect of chromium(III).~~

(7) All the complexes have 1:2 stoichiometries. Such a stoichiometry is natural for the divalent ions, but not for iron(III). The iron complex may have the composition $FeL_2(OH)_x(OEt)_{1-x}.EtOH$ or $FeL_2(OH)_x(OEt)_{1-x}...HL$.

(8) Values obtained for the stability constants of the complexes of copper(II), nickel(II) and cobalt(II) show an order of stabilities Cu > Ni > Co instead of the Irving-Williams series Ni > Cu > Co for all the three reagents, DMHAO, DBDMHAO and o-HAO. Taking individual metals, the stabilities of the nickel and cobalt complexes are in the order of o-HAO ≈ DMHAO > DBDMHAO whereas for copper the order is o-HAO > DMHAO ≈ DBDHAO.

Chapter III gives some of the practical applications of reagent II in the extraction-photometric determination of copper or nickel or both simultaneously in a number of actual samples using reagent II. The use of reagent IV is quite similar and this reagent has therefore not been used. When chromium(III) is present, the determinations can be made by three methods: (i) by oxidizing the chromium(III) to chromium(VI) and evaporating off the CrO_2Cl_2 with hydrochloric acid; (ii) by extracting with ligand IV in the presence of diethylamine and (iii) by extracting with ligand II after adding excess iron(III), so that the chromium(III) selectively suppresses the extraction of iron(III) and all the copper(II) or nickel(II) can be extracted. Methods (ii) and (iii) were developed in the course of the present work and are superior to method (i).

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SUMMARY

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This thesis describes the results of investigations carried out on the solvent extraction of the chelates of some transition metals with the oximes of substituted o-hydroxyacetophenone. Previous work reported in the literature relates to the analytical uses of salicylaldoxime and o-hydroxyacetophenone oxime. The present work deals not only with the analytical uses of substituted o-hydroxyacetophenone oximes, but also with the compositions and stabilities of the concerned chelates.

Chapter I is a general introduction which briefly highlights the importance of solvent extraction in the field of analytical and industrial chemistry and the salient points of the relevant theory, with a critical review of the literature.

Chapter II describes the present studies on the solvent extraction of some transition metal chelates (particularly those of copper, nickel, iron and cobalt) using 2,4-dimethyl 6-hydroxyacetophenone, 3,5-dibromo-2,4-dimethyl-6-hydroxyacetophenone and the two respective oximes. The ketones were studied because of reports in the literature about the metal chelates of similar o-hydroxyaryl ketones. 2,4-Dimethyl-6-hydroxyacetophenone

(termed reagent I or ligand I) did not prove to be a good extraction reagent, except for copper(II) for which it had to be used at a pH of 8.5 - 9.0 along with added aniline. Ammonia or diethylamine also gave this type of synergic extraction, but these extracts gave high absorbance values for the blank. 3,5-Dibromo-2,4-dimethyl-6-hydroxyacetophenone (reagent III or ligand III) showed a behaviour similar to that of reagent I, a fair degree of extraction being possible with the addition of ammonia. It was clear that both ligand I and ligand III formed rather weak chelates with metals. But the synergic effect of diethylamine - particularly in extractions with reagent I - suggested the use of the amine along with the oximes of reagents I and III, which are termed reagents II and IV respectively in this thesis.

Reagent II (or ligand II) formed extractable complexes with a number of metals. The molar absorptivities of the extracts of copper(II) and nickel(II) were substantially higher than those of unsubstituted o-hydroxyacetophenone oxime. The extracts in chloroform obeyed Beer's law. Copper(II) could be determined by extraction-photometry in the presence of iron(III) and nickel(II) by using tartrate as a masking agent. Oxalate was ineffective in masking nickel(II) in presence of copper(II) and thiosulphate was ineffective in masking copper(II). Reagent II could, however, be used for the simultaneous extraction-photometry of copper(II) and nickel(II). When iron(III) was present, it was necessary to use hydroxylamine to reduce the iron to iron(II) Chromium(III) by itself was not extracted by reagent II; but it had the peculiar ability to suppress the extractions of copper, nickel and iron. The synergic effect of diethylamine (or aniline) first noted when using ligand I, was used to advantage in the separation of copper(II) from chromium(III) and cobalt(II). The optical properties of the extracts of the metals with the reagent II-diethylamine combination were studied. The addition of diethylamine led to higher molar absorptivities and better extractions. The behaviour of ligand-IV was generally similar to that of ligand-II. One important difference was that the copper(II) chelate of ligand-IV could not be satisfactorily extracted unless diethylamine or aniline were added. This made it possible to separate nickel(II) from copper(II) by extraction with ligand IV (without diethylamine) after adding thiosulphate as a masking agent. On the other hand, copper(II) could be separated from chromium(III) by using ligand-IV along with diethylamine.

Chapter II also describes the work on the compositions and stabilities of the chelates of the metals with ligands II and IV. The stoichiometries were 1:2 (metal:ligand) in all cases, as deduced from the slopes of the Log D vs pH plots. The solid complexes of copper(II) and nickel(II) were analyzed and shown to be 1:2 complexes. In order to explain the 1:2 stoichiometry of the iron(III) complex, the behaviour of the complexes of copper, nickel, cobalt and iron in silica gel column chromatography was studied.

The potentiometric titration studies in 75% aqueous dioxan of the complexes of copper(II), nickel(II) and cobalt(II) with ligands II and IV and also with o-hydroxyacetophenone oxime (for comparison) are next given. From these studies, the stability constants of the concerned complexes were determined. Chapter II also outlines a polarographic procedure for determining the partition coefficient of reagent-II. The distribution coefficient of the copper(II)- ligand II complex was determined by a simple extraction procedure.

Chapter III is a short chapter giving some examples of the practical application of reagent II in the analysis of actual samples including samples certified by NBS (USA) and NML (India).

Chapter IV gives a discussion of the experimental results obtained in Chapters II and III. Particular attention is paid to a discussion of the synergic effect of diethylamine, the composition of the complexes (in particular of the iron(III) complex), the relative stability constants, the suppressive effect of chromium(III) and the effect of common masking agents on the extractions.

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