SOLVENT EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF COBALT(III) AND IRON(III) WITH N-HYDROXY-N,N'-DIPHENYLBENZAMIDINE IN PRESENCE OF AZIDE

A Thesis Presented to the
School of Graduate Studies
Addis Ababa University

In Partial Fulfillment of the
Requirement for the Degree of
Master of Science in Chemistry

BY

GHIRMA MOGES

June 1982

TABLE OF CONTENTS

To My Brothers and Sisters

ACKNOWLEDGEMENTS

I am very grateful to my advisor Dr. B.S.Chandravanshi for identifying the topic of this research, his consistent and stimulating guide, and his unfailing patience during the research. I am most thankful to W/t Hirut Bizuneh, Etse Hiwot Moges, Amsale Tessema and Yilma Tamiru, who did their best in typing the present material. My appreciation also goes to Ato Paulos G.Yohannes, Ato Berhane Tecle, Ato Fikru Tafesse, Dr. G. Haucke, Dr. J. Liebscher and Dr. Ermias Dagne who shared their ideas to me in the ways of finding the success of the project. I am also grateful to the Swedish Agency for Research Cooperation with Developing Countries (SAREC) for the financial assistance made through the Ethiopian Science and Technology Commission, and to the Addis Ababa University which covered part of the expenses. Last, but not least, I am thankful to the Department of Chemistry for giving an opportunity to me to participate in the graduate program.

LIST OF TABLES

LIST OF FIGURES

FIGURE PAGE

ABSTRACT

N-Hydroxy-N,N'-diphenylbenzamidine (HDPBA), a bidentate chelating agent, reacts with cobalt(III) and iron(III) in the presence of azide to give a pinkish red and red-violet coloured mixed ligand complexes, which are quantitatively extractable into chloroform from the aqueous phase at pH 7.4-7.8 and 2-5 respectively, allowing spectrophotometric determinations of the metal ions. The cobalt(III) and iron(III) mixed ligand complexes have wavelengths of maximum absorption at 520 and 520-540 nm with their respective molar absorptivities of 1980 lit. $mole^{-1}$ cm^{-1} and 4895 lit. $mole^{-1}$ cm^{-1}. Beer's Law obeys from 3.6 to 24 ppm for cobalt(III) and from 1.6 to 11.2 ppm for iron(III). The effect of foreign ions and several other experimental variables have been studied. The composition of the cobalt(III) and iron(III) mixed ligand complexes have been determined by spectrophotometric methods and are found to be 1:1:2 (Co: HDPBA:N_3^-) and 1:2:2 (Fe:HDPBA:N_3^-) respectively.

On the basis of the differences in the pH of the reaction media for iron(III) and cobalt(III), a separation procedure for the two metals in a solution has been established followed by spectrophotometric determinations. The method has allowed the separation and determination of varied proportions of iron(III) and cobalt(III) in a solution of the two metal ions. Moreover, the methods have been applied successfully for the separation and determination of cobalt and iron in synthetic samples.

a solution of the two metal ions. Moreover, the methods have been applied successfully for the separation and determination of cobalt and iron in synthetic samples.

1. INTRODUCTION

Analytical Chemistry has been characterized by recent advances of powerful methods of separation and quantitative determinations. The advances made in this field have been a requirement to the development of modern science and technology. Many elements, therefore, which were considered unimportant previously have obtained a high industrial significance at the present moment. For example, the use of germanium and silicon in semiconductor technology; uranium, thorium, the lanthanides and the actindes in nuclear energy programs are to mention some. These developments have necessitated the progress being made in the field of analytical chemistry. Hence, the analytical chemist is forced to include these elements in his analytical schemes which almost always involved the basic problems of the field, separation and quantitative determination. Although rapid advances are being made in the field of new analytical methods based on instrumental techniques, the chemical reaction of a suitable reagent with the substance to be determined still remains the true basis of numerous methods of detection, separation and determination. Organic reagents play a predominant role and find wide application[1-7] in spectrophotometry, titrimetry (as titrants and indicators), spot tests, and last but not least in separation that is, preconcentration methods like precipitation, masking, extraction, and ion-exchange procedures.

Every year, hundreds of papers on the reactions and possible applications of new and previously known organic reagents for inorganic analysis are published. The study of these reagents results in the development of highly sensitive, selective, and rapid methods for the analysis of variety of materials, requiring only simple instrumentation.

The reaction of organic reagents with inorganic ions[3] in solutions can yield products of various properties which can exhibit a change in colour, luminescence, solubility and volatility. The reaction products may be complex compounds or new organic compounds formed due to oxidation-reduction or catalytic actions of inorganic ions. Besides these reaction types, the formation of the products which is insoluble in aqueous solution can be employed for gravimetric determination, separation or precepitation titration of an ion. If the reaction product is less soluble in water than in an organic solvent immiscible with water, it may be extracted into the organic solvent.

In many reactions of organic reagents a conspicious colour or fluorescence is developed, or conversely, a coloured component in solution is decolourized during the reaction, or its fluorescense is quenched. Such reactions can be applied for both qualitative tests and quantitative determinations. Furthermore, these types of reaction are also employed for end-point detection in acid-base, oxidation-reduction or complexmetic titrations.

One of the main applications of organic reagents in the inorganic analysis is the separation and determination of metal ions by solvent extraction and spectrophometry.

1.1 SOLVENT EXTRACTION

Solvent extraction is the partition of one or more components between two liquids of limited miscibility. Such a liquid-liquid partition is caused by the different solubilities of a given substance in the two phases. This method of partition of a given substance from one phase to the other is a rapid and non-instrumental method of separation technique provided the substance is practically soluble only in one of the two phases. It is usually effected in a few minutes using a pear-shaped or cylinderical separatory funnel and is applicable both to trace level impurities and major constitutents.[8-11] Furthermore, inorganic constituents are often separated from an aqueous solution to water-immiscible organic solvents via the formation of inner complexes which may be applied to direct analysis by spectrophotometry, gas chromatography, atomic absorption, radiochemical or other suitable methods.

Solvent extraction, therefore, has so far enjoyed a favored position among the separation techniques because of its ease, simplicity and wide scope.

1.2 CLASSIFICATION OF EXTRACTION SYSTEMS

Extractions are categorized according to different criteria.[12] Some of the common basis of classification are:

a. the type of extraction process or reaction in which the extractable species is formed (physical partition, solvation, formation of chelates or ion pairs etc);

b. the kind of extractable species (simple covalent compounds, chelates, ion-association complexes etc);

c. the type of extracting agent (neutral, acidic or basic);

d. the kinetics of the extraction.

None of these criteria, however, allows an unequivocal classification of all known extraction systems under the given headings.

If the use of organic reagents is considered for extractions applied in inorganic analysis, the most reasonable classification is the one based on the kind of extractable species.

1.3 TYPE OF EXTRACTABLE SPECIES

On the basis of reactions with metal ions, complexing agents (organic and inorganic) used in solvent extraction may be classified[13] as follows.

- i. simple mondentate coordination alone as with $GeCl_4$.
- ii. heteropoly acids; a class of coordination complexes in which the central ion is a complex rather than monoatomic as with phosphomolybdic acid, $H_3PO_3MoO_3$.
- iii. chelation (polydentate coordination) alone as with Al(8-quinolinate)$_3$
- iv. ion association alone as with $Cs^+(C_6H_S)_4B^-$
- v. Simple coordination and ion association as with (Onium), $FeCl_4$. "Onium" stands for cations like $(H_2O)_3H^+$, $RnNH^+_{4-n}$ (where R = alkyl or aralkyl group and n ranges from 1 to 3, and substituted phosphonium

and stibnium ions (R_4P^+ and R_4Sb^+),

vi. chelation and ion association with either positively or negatively charged metal chelates such as Cu(2,9-dimethyl-1,10-phenanthroline)$_2^+$. ClO_4^-.

vii. simple coordination and chelation as in Zn(8-quinolinate, pyridine). This category is of significance for coordinately unsaturated metal chelates, that is, those with monoprotic bidentate ligands in which the coordination number of the metal is greater than twice its valence.

Extraction methods based on the formation of extractable chelates, types iii and vii, are of great importance in analytical chemistry, since they give extremely selective separations. Uncharged metal chelates are usually more soluble in organic solvents than in water with greater efficiency under suitable conditions, pH, concentration and solvent.

1.4 EXTRACTION EQUILIBRIA OF METAL CHELATES[3,14]

The equilibrium processes on the extraction of a metal ion by an organic reagent in the organic solvent from the aqueous phase can be represented by the following schemes:

a. $nHL_{(org)} \rightleftharpoons nHL_{(aq)} \rightleftharpoons nH^+_{(aq)} + nL^-_{(aq)}$

b. $Mn^+_{(aq)} + nL^-_{(aq)} \rightleftharpoons ML_{n(aq)} \rightleftharpoons ML_{n(org)}$

When the two phases are in contact, the equilibrium processes taking place are as follows:

i. distribution of the chelating agent between the two phases given by the distribution constant

$$K_{D,HL} = \frac{[HL]_{(org)}}{[HL]_{(aq)}}$$

ii. the deporotonation of the chelating agent in the aqueous phase is represented by

$$K_{HL} = \frac{[H^+]\,[L^-]}{[HL]}$$

iii. formation of the chelate whose position of equilibrium is determined by the overall stability constant

$$\beta_n = \frac{[ML_n]}{[M^{n+}]\,[L^-]^n}$$

iv. finally the distribution of complex between the two phases, which is represented by distribution constant

$$K_{D,ML_n} = \frac{[ML_n]_{(org)}}{[ML_n]_{(aq)}}$$

The over

The overall extraction process is represented as follows:

$$M^{n+}_{(aq)} + nHL_{(org\ )} \overset{Hex}{=\!=\!=} MLn_{(org} + nH^{+}_{(aq)}$$

where

$$K_{ex} = \frac{[MLn]_{org}\ [H^{+}]_{aq}}{[M^{n+}]_{(aq)}\ [HL]^{n}_{(org)}}$$

The distribution coefficient of the metal ion is defined, assuming no side reactions, by

$$D_M = \frac{[MLn]_{(org)}}{[M^{n+}]_{(aq)}}$$

Hence,

$$D_M = K_{ex}\ \frac{[HL]^{n}_{(org)}}{[H^{+}]_{(aq)}}$$

or $\log D_M = \log K_{ex}\ n \log [HL]_{org} + npH$

In the case of mixed ligand complex formations the equilibrium may be represented as follows:

$$M^{n+m}_{(aq.)} + nHL_{(org)} + mY^{-} \rightleftharpoons MLnYm_{(org)} + nH^{+}_{(aq)}$$

$$K_{ex} = \frac{[MLnYm]_{org}\,[H^+]^n_{(aq)}}{[M^{(m+n)+}]_{(aq)}[HL]^n_{(org)}[Y^-]^m_{(aq)}}$$

Where Y^- is a monodentate ligand. The distribution coefficient of the metal ion is given by

$$D_M = \frac{[MLnYm]_{(org)}}{[M^{(m+n)+}]_{(aq)}}$$

Hence,

$$D_M = \frac{K_{ex}\,[HL]^n_{(org)}\,[Y^-]^m_{(aq)}}{[H^+]^n_{(aq)}}$$

or $\log DM = \log K_{ex} + n \log [HL]_{(org)} + m \log [Y^-]_{(aq)} + npH$

If a certain metal ion has to be transfered into the organic phase, the value of the distribution ratio, D_M for that metal should be as high as possible. Organic ligands, therefore, play an eminent role in extraction separations because they can react with metal ions to give products having the basic requirements for extractability that is, solubility in water immiscible organic solvents due to their marked non-polar nature and electrical neutrality.

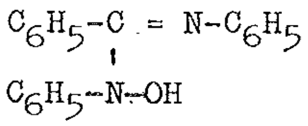
The organic ligands which form water insoluble chelates (inner complexes) with metal ions are those which have acidic functional groups, such as -OH, -SH, -COOH, at one coordination cire and neutral donor groups such as =O, =N-, =S, at another.

In reaction with metal ions, the acidic functional groups lose their protons and replace them by metal-anionic donor atoms bonds. Such reagents can form neutral water insoluble metal chelates or if charged further reactions with monodeutate charged ligands take place forming mixed ligand complexes. The metal chelates so formed in either way are essentially insoluble in an aqueous phase and transfer into an organic phase in a solvent extraction system. Furthermore, the metal chelates extracted into organic solvents are usually intensely coloured or exhibit fluoresence. Hence, the extracted complex is not only used for separation but also for quantitative determination by spectrophotometry or fluorimetry.

One of the important group of organic reagents recently employed in analytical chemistry for solvent extraction and spectrophotometric determination of metal ions are the N-Hydroxy-N,N'-diarylbenzamidines which also form the basis of the present investigation. Hence, the general properties and analytical applications of these compounds are briefly described in the next section.

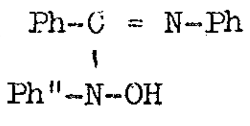
2. N-HYDROXY-N,N'-DIARYLBENZAMIDINES AS ANALYTICAL REAGENTS

N-Hydroxy-N,N'diphenylbenzamidine, I, and its analogues are typical monobasic and bidentate chelating agents. These compounds are represented by the general formula, II, having an analytical functional grouping, III.



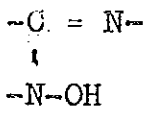
$$\begin{array}{l} C_6H_5-C=N-C_6H_5 \\ \qquad\;\; | \\ C_6H_5-N-OH \end{array}$$

I



$$\begin{array}{l} \;\; Ph-C=N-Ph \\ \qquad\;\; | \\ Ph''-N-OH \end{array}$$

II



$$\begin{array}{l} -C=N- \\ \quad | \\ -N-OH \end{array}$$

III

Where Ph, Ph' and Ph" are phenyl or substituted phenyl groups.

The hydroxyamidines are pale yellow coloured crystalline solids. These compounds are stable toward heat, light and air and can be stored indefinitely. They are insoluble in water but readily soluble in common organic solvents such as alcohol, acetone, chloroform and benzene. Their solutions in organic solvents are light yellow coloured and stable for several days if properly stored.

N-Hydroxy-N,N'-diarylbenzamidines were first synthesized by Ley[15] in 1901 and some of their properties were studied by Ley and Holzweisseg[16]. Their studies were confined to isomerism and reduction of these compounds.

They showed that 1-p-tolyl-2,3-diphenyloxyamidine and 1,2-phenyl-3-p-tolyloxamidine are isomeric and melt at different tempratures. In alcoholic medium, the hydroxyl group of these compounds could be reduced by sulphur dioxide to the corresponding amidine form. They also studied the kinetics of hydrolysis of the hydrochloride salts of hydroxyamidine free bases. However, the analytical potentialities of these compounds remained unexplored until 1974.

N-Hydroxy-N,N'-diphenylbenzamidine (HDPBA) was introduced as an analytical reegent for the first time in 1974 by Satyanarayana and Mishra[17] for the extraction and spectrophotometric determination of vanadium(V). They further extended the analytical application of HDPBA for the determination of other metal ions. Later on Mishra and co-workers have synthesized a large number of substituted hydroxyamidines and extensively studied their analytical potentialities. Several research papers have been published on the applications of hydroxyamidines.[18-33] N-Hydroxy-N,N'-diphenylbenzamidine and its analogues are now widely used as reagents for the detection and determination of several metal ions in gravimetric analysis, solvent extraction and spectrophotometry.

Hydroxyamidines react with metal ions to form five-membered ring complexes. The metal chelates may

N-Hydroxy-N,N'-diphenylbenzamidine and its analogues have been applied for the grevimetric determination of copper(II)[19] and nickel(II)[20]. They have been used for the spectrophotometric determination of iron(III) and manganese(II)[22] in aqueous solutions. These reagents have also been employed for the solvent extraction and spectrophotometric determination of vanadium(V).[17,30] The use of hydroxyamidines have been extended for the synergic extraction and spectrophotometric determination of vanadium(V)[30,32] in presence of various adduct forming substances like carboxylic acids,[27,28] phenols[29,31] and aldehydes.[23,25]

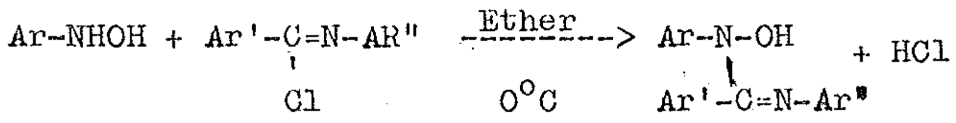
N-Hydroxy-N,N'-diarylbenzamidines have been applied as reagents for the synergic extraction and spectrophotometric determination of iron(III)[24,26], vanadium(V)[23,24,32] and molybdenum(V)[33] by the formation of mixed ligand complexes with thiocyanate. They have also been used for the simultaneous determination of iron(III), vanadium(V) and molybdinum(V).[21]

The formation of mixed ligand complexes of iron(III)[26] and vanadium(V)[23] with hydroxyamidines and azide have also been studied and applied for the extraction and spectrophotometric determination of these metal ions. Studies on the applicability of the N-hydroxy-N,N'-diarylbenzamidines has continued until very recently for the gravimetric, spectrophotometric and extractionphotometric determination of some metal ions.

It is clear from the foregoing literature survey that the use of hydroxyamidines for the determination and separation of cobalt from commonly associated metals such as iron in complex materials have not been reported so far. Hence, N-hydroxy-N,N'-diphenylbenzamidine (HDPBA), the parent compound, has been applied in the present investigation for the determination of cobalt(III) and simultaneous separation and determination of cobalt(III) and iron(III) in the presence of azide by solvent extraction and spectrophotometry in the same solution. The extraction and determination of iron(III) has also been studied in a different condition to improve the sensitivity and selectivity of the reported method. The outcome of the present investigation will further extend the analytical application of the reagent.

2.1 GENERAL METHOD OF SYNTHESIS OF N-HYDROXY-N,N'-DIARYLBENZAMIDINES

Since, N-hydroxy-N,N'-diphenylbenzamidine is not available commercially, it was necessary to synthesize the reagent in the laboratory by the method reported in literature. Although, some of the N-hydroxy-N,N'-diarylbenzamidines were synthesized in 1901, the detailed procedures of the syntheses of these compounds were not described.[15] A general method of syntheses of these compounds was described by Satyanarayana and Mishra[17] in 1974. The method involves the condensation reaction of N-arylhydroxylamine with N-arylbenzimidoylchloride in absolute ether medium at low temperature.



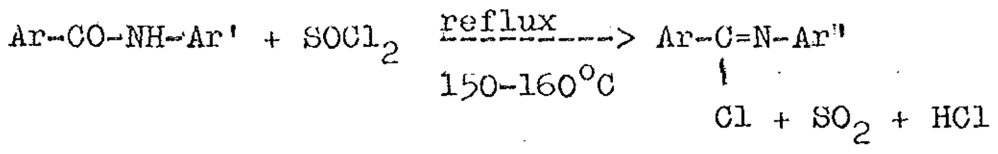
$$\mathrm{Ar{-}NHOH} + \mathrm{Ar'{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}N{-}AR''} \xrightarrow[0^{o}C]{\mathrm{Ether}} \mathrm{\underset{\displaystyle Ar'{-}C{=}N{-}Ar''}{\underset{|}{Ar{-}N{-}OH}}} + \mathrm{HCl}$$

The hydrochloride salts of hydroxyamidines obtained give the corresponding free base on treatment with ammonia. Two to three crystallizations from benzene and petroleum ether or from alcohol gives the pure products. The yield ranges from 40 to 70 percent.

The preparation of a large number of N-hydroxy-N,N'-diarylbenzamidines reported in the litrature have been synthesized by the same method.[18-33] Hence, the synthesis of these compounds require the preparation of the respective N-arylbenzimidoyl chloride and N-arylhydroxylamine.

2.11 METHODS OF PREPARATION OF N-ARYLBENZIMIDOYL CHLORIDES:

A number of methods are reported in the literature[34-36] for the preparation of N-arylbenzimidoyl chlorides. However, the most commonly used method of the synthesis of imidoyl chlorides involves chlorination of benzanilide or substituted anilides of aromatic carboxylic acids with thionyl chloride under reflux.[36] The imidoyl chloride can easily be separated from excess thionyl chloride by fractional distillation under reduced pressure.



$$\text{Ar-CO-NH-Ar}' + SOCl_2 \xrightarrow[150\text{-}160^{\circ}C]{\text{reflux}} \underset{\text{Cl}}{\text{Ar-C}}\text{=N-Ar}'' + SO_2 + HCl$$

Anilides of the corresponding aromatic carboxylic acids can be obtained by addition of slight excess of aromatic acyl chloride to aniline or substituted aromatic amines in aqueous solution of sodium hydroxide with stirring followed by crystallization from boiling benzene.[37]

2.12 METHODS OF PREPARATION OF N-ARYLHYDROXYLAMINES:

Several methods are available for the preparation of N-aryl-hydroxylamines.[38-48] However, the simple and most widely used method[42,43] of preparation is based on the reduction of aromatic nitro compounds with zinc dust and ammonium chloride in aqueous solution at 60-65°C.

$$\text{Ar-}NO_2 \xrightarrow[60\text{-}65^{\circ}C]{Zn/NH_4Cl} \text{Ar-NHOH}$$

The pure products can be obtained by re-crystallization of the crude hydroxylamines from benzene and petroleum ether. N-arylhydroxylamines are highly unstable and therefore, they should be used immediately for further synthesis.

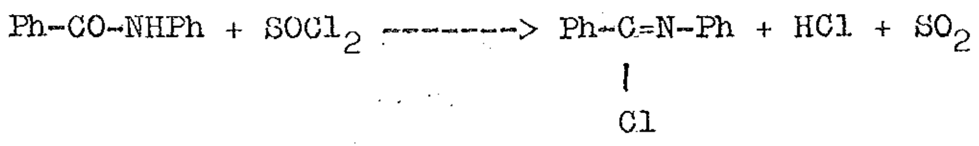
3. EXPERIMENTAL

3.1 SYNTHESIS OF N-HYDROXY-N,N'-DIPHENYLBENZAMIDINE

The preparation of N-hydroxy-N,N'-diphenylbenzamidine required the synthesis of N-phenylbenzimidoyl chloride and N-phenylhydroxylamine. Hence, these compounds were to be prepared for the synthesis of the parent compound(I) according to the literature cited.[17]

3.11 PREPARATION OF N-PHENYLBENZIMIDOYL CHLORIDE: The synthesis of N-phenylbenzimidoyl chloride was made by chlorination of benzanilide using thionyl chloride as a chlorinating agent.[36]

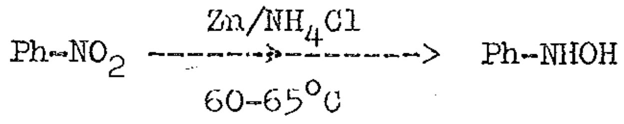
A 20 excess of thionyl chloride was mixed with 33.0g (0.17 mole) of benzanilide and heated for thirty minutes at 110°C, and further heated under reflux at 150-160°C until the reaction mixture turned liquid. The excess thionyl chloride was removed by distillation under partial vacuum. The imidoyl chloride was used as such for the synthesis of the reagent.



$$\mathrm{Ph{-}CO{-}NHPh + SOCl_2 \dashrightarrow Ph{-}\underset{\underset{\displaystyle Cl}{|}}{C}{=}N{-}Ph + HCl + SO_2}$$

Benzanilide which was used for the synthesis of N-phenylbenzimidoyl chloride was prepared by addition of a slight excess of benzoyl chloride to aniline in 10% (w/v) of sodium hydroxide solution with stirring followed by crystallization in boiling benzene.[37]

3.12 PREPARATION OF N-PHENYLHYDROXYLAMINE: N-phenylhydroxylamine was synthesized by the reduction of nitrobenzene with zinc dust and an aqueous solution of ammonium chloride at 60-65°C.[42,43]



$$\text{Ph-NO}_2 \xrightarrow[60\text{-}65^{\circ}\text{C}]{\text{Zn/NH}_4\text{Cl}} \text{Ph-NHOH}$$

50g of nitrobenzene (41.6 ml, 0.41 mole) was mixed with 800 ml of water to which 25g of ammonium chloride was already added. To the mixture was added 60g of zinc dust gradually with stirring in a course of twenty five minutes, so that the temprature of the reaction mixture does not rise beyond 60-65°C due to the exothermicity of the reaction. The product was separated from the zinc oxide produced by suction. 50g of salt was added to the solution to crystallize the N-phenylhydroxylamine. The product was recrystallized from benzene. Yield 55%, melting point 80-81°C (reported value 81°C).

3.13 PREPARATION OF N-HYDROXY-N,N'-DIPHENYLBENZAMIDINE:

N-phenylhydroxylamine (7.525g, 0.07 mole) in absolute ether was added in small portions with stirring to a solution of N-phenylbenzimidoyl chloride (15.0g, 0.069 mole) in 180.0 ml of absolute ether placed on an ice-salt mixture.

First a light brown oilly substance separated which solidified into light yellow crystals on continued stirring. The crystals were filtered and washed with ether. The hydrochloride salt was treated with 32.0 ml of 1.0N ammonia. The precipitated free base was filtered off, recrystallized twice from petroleum ether (60-80°) and benzene (1:2) to give pale yellow crystals. Yield 7.5g, m.p. 161-163°, reported[17] 163°C. The compound was characterized by its melting point and infra red spectrum. The compound is insoluble in water but soluble in chloroform, ethanol, acetone, benzene and acetic acid.

The infra red spectrum of the reagent synthesized indicate (Figure 1) the presence of -OH stretching band at 3080 cm^{-1}. The shift from the normal -OH band, which is lower in the case of the reagent under study, is found to be due to the partial hydrogen bonding of the system OH...N=C. The stretching frequencies assigned to -OH, C-N, C=N are in good correlation with the literature values,[17] 3080, 1425, 1600 cm^{-1} respectively. A sharp band at 3040 cm^{-1} is also observed which is characterstic of aromatic C-H stretching vibrations.

3.2 APPARATUS AND REAGENTS

Apparatus: Beckman (R) Model 24 UV-VIS spectrophotometer equipped with 1 cm matched quartz cells was used. Beckman CHEM MATE pH meter was used for pH measurements.

STANDARD COBALT(II) SOLUTION: A stock solution was prepared by dissolving 4.9412g of analytical grade cobalt(II) nitrate hexahydrate in distilled water followed by dilution to make a litre solution. This solution contains 1mg cobalt per milliliter.

STANDARD IRON(III) SOLUTION: A stock solution was prepared by dissolving 3.5108g of iron(II) ammonium sulphate hexahydrate in 15ml of nitric acid (1:3) followed by dilution with distilled water to make a 500ml of solution. This solution contains 1mg iron(III) per milliliter.

SOLUTION OF FOREIGN IONS: The solutions of foreign ions were prepared from salts following the procedure

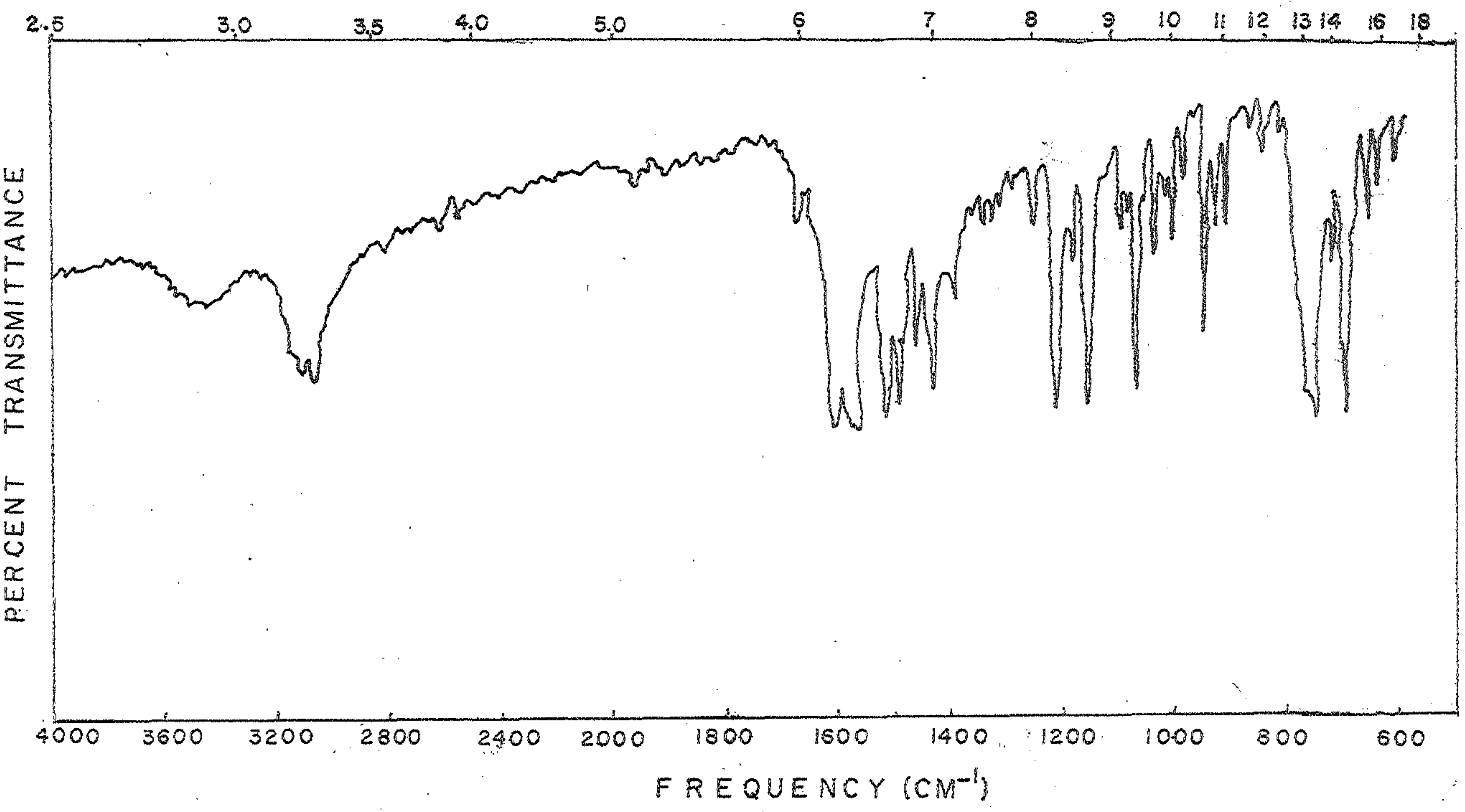


FIG. 1 INFRARED SPECTRUM OF N-HYDROXY-N,N'-DIPHENYLBENZAMIDINE

of West,[49] so that the concentration of the solutions were adjusted to give 10mg per ml of the ion in question.

SOLUTION OF HDPBA: The organic reagent was dissolved in distilled chloroform to give 0.25-0.5% (w/v) solutions.

AZIDE SOLUTION: A 1.0M azide solution was prepared by dissolving 65g of sodium azide to make a litere solution.

3.3 PROCEDURE FOR EXTRACTION AND DETERMINATION OF COBALT(III)

Transfer an aliquot of cobalt(II) solution containing 0.1 to 0.6mg of the metal into a 100ml separatory funnel. Add 4ml of 30% hydrogen peroxide followed 3ml of 1.0M sodium azide. Adjust the volume of the aqueous phase to 10ml by addition of distilled water. To the solution add a mixture of 4ml of pyridine and 6ml of 0.5% reagent solution, shake the mixture for two minutes and allow the two phases to separate. Dry the organic phase with sufficient anhydrous sodium sulphate after separating the extract from the aqueous phase. Wash the aqueous phase with 2 x 5ml protions of chloroform. Dry the washings after separation. Transfer the chloroform solution into a 25ml volumetric flask. Dilute to volume with chloroform. Measure the absorbance at 520nm against chloroform as blank.

3.4 PROCEDURE FOR EXTRACTION AND DETERMINATION OF IRON(III)

Transfer an aliquot of iron(III) solution containing 0.03 to 0.30mg of the metal into a 50ml beaker add 4ml of 1.0M sodium azide solution followed by 3.0ml of distilled water. Adjust the pH to 4 using 15-16 drops of 2.0M hydrochloric acid. Transfer the solution into a 100ml separatory funnel. Wash the beaker with small amount of water and transfer the washings to the separatory funnel. To the solution add 10ml of 0.25% of HDPBA solution in chloroform followed by shaking of the mixture for two minutes. Allow the two phases to separate. Wash the aqueous phase with 2 x 5ml portions of chloroform followed by drying of the washings. Transfer the chloroform extract and the washings into a 25ml volumetric flask. Dilute to volume with chloroform. Measure the absorbance at 530nm against chloroform as blank.

4. RESULTS AND DISCUSSION

For the sake of convenience, the results and discussion for the extraction and spectrophotometric determination of cobalt(III) and iron(III) are given separately.

4.1 EXTRACTION AND DETERMINATION OF COBALT(III)

4.11 COLOUR REACTION: Cobalt(III) forms a pink-red coloured complex on the reaction with the reagent solution in presence of azide and pyridine, which is readily extractable into chloroform.

4.12 ABSORPTION SPECTRA: A dilute solution of the reagent in chloroform showed negligible absorption in the region 450-700nm. The red coloured cobalt(III)-HDPBA-azide complex showed a maximum absorption at 520nm with molar extinction coefficient of 1980 lit. mole^{-1}cm^{-1}. At high concentration of reagent and azide, well beyond the optimum limits, the wavelength of maximum absorption did not change although a blank solution was necessary for absorbance measurements. The absorption spectra of the reagent and complex are shown

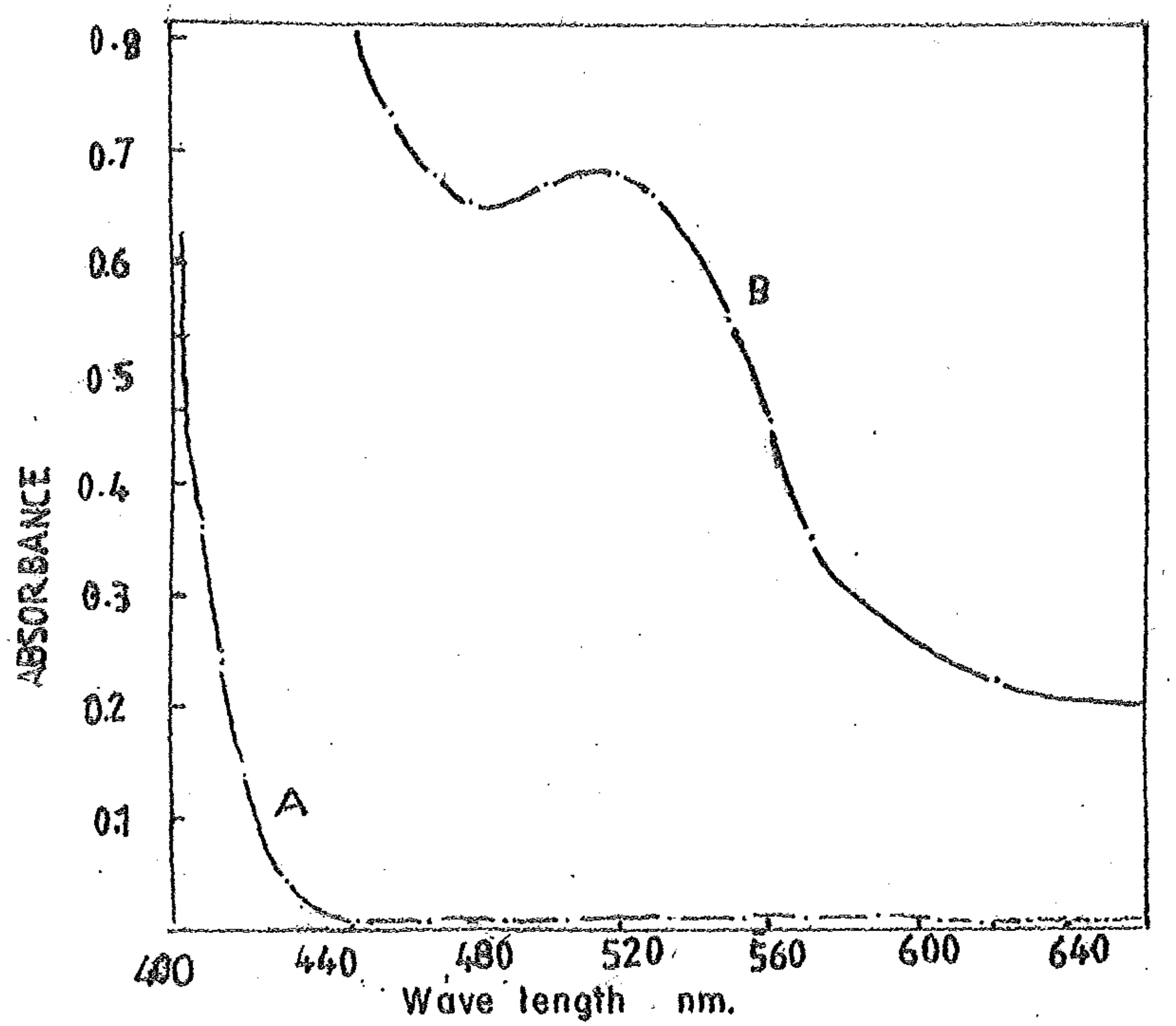


Fig. 2 ABSORPTION SPECTRA OF A HDPBA(1.73X 10^{-4}M)
B. COBALT (III) HDPBA AZIDE COMLEX (3.95 X 10^{-4}M)
IN CHLOROFORM

in Figure 2.

4.13 EFFECT OF VARIABLES: The effect of the experimental variables on the extraction of cobalt(III)-HDPBA-azide complex into chloroform has been investigated. The effect of a particular variable was studied by determining the absorbance following the general procedure described earlier, keeping all experimental parameters constant except the one under study.

Choise of Solvents for Extraction: The cobalt(III) complex can be extracted by chloroform and benzene. Chloroform was found to be the most suitable since the complex is readily extracted into it. It was also preferred because of its low cost, easy to recover, very high solubility of HDPBA in it than in benzene and its higher density than the aqueous phase making an easy separation of the two phases from the separatory funnel.

Effect of Hydrogen Peroxide: The effect of hydrogen peroxide on the formation of cobalt(III) complex from the cobalt(II) solution was studied using different volumes of approximately 30% of hydrogen peroxide and the results indicate a range of 4-5.5%

of hydrogen peroxide **for complete** extraction. Higher amounts of hydrogen peroxide decreases the absorbance of the extract indicating an incomplete extraction of the metal. The results are given in Table 1 and Figure 3.

TABLE 1

EFFECT OF HYDROGEN PEROXIDE ON THE EXTRACTION AND DETERMINATION OF COBALT(III)

Cobalt(III) concentration = 3.06×10^{-4}M

Volume of 30% of H_2O_2 (ml)	Absorbance at 520 nm
0.0	0.349
1.0	0.386
1.75	0.525
2.0	0.570
3.5	0.590
4.0	0.595
4.5	0.596
5.5	0.588
6.0	0.560

Effect of Amount of Pyridine: The extraction of cobalt (III) was studied in the presence of different concentrations of pyridine. The results show an optimum

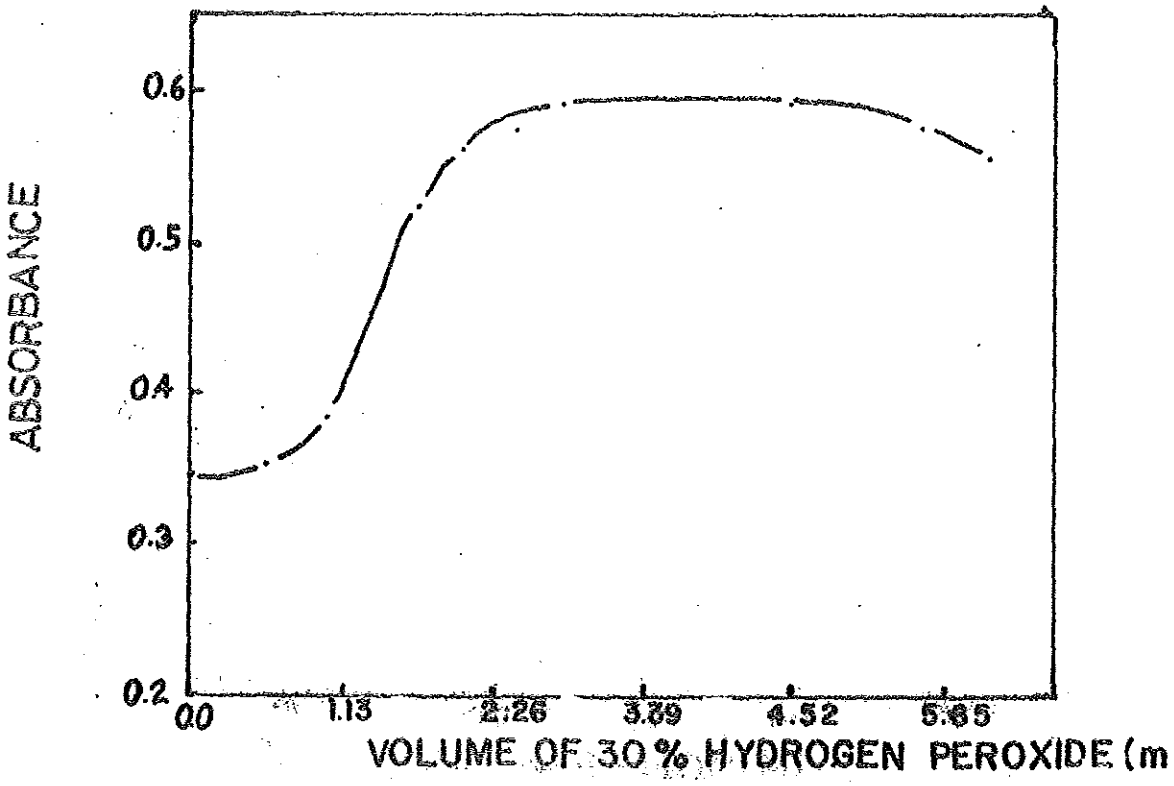


Fig. 3 EFFECT OF HYDROGEN PEROXIDE

range of 0.15 to 0.3M of pyridine with respect to the aqueous phase, corresponding to the pH of 7.4-7.8 for complete extraction (Table 2 and Figure 4).

Other bases were found to be unsuitable for adjusting the pH of the aqueous phase, due to competing complex formation reactions of the metal with bases like ammonia.

TABLE 2

EFFECT OF AMOUNT OF PYRIDINE ON THE EXTRACTION AND DETERMINATION OF COBALT(III)

Cobalt(III) concentration = 3.06×10^{-4}M

Concentration of Pyridine in Aqueous Phase (M)	Absorbance at 520nm
0.000	0.363
0.075	0.531
0.150	0.593
0.225	0.593
0.300	0.594
0.450	0.486
0.500	0.410

Effect of Amounts of Azide: The optimum concentration of azide for the extraction of cobalt(III) as a mixed ligand complex was found to be in the range of 0.20M to

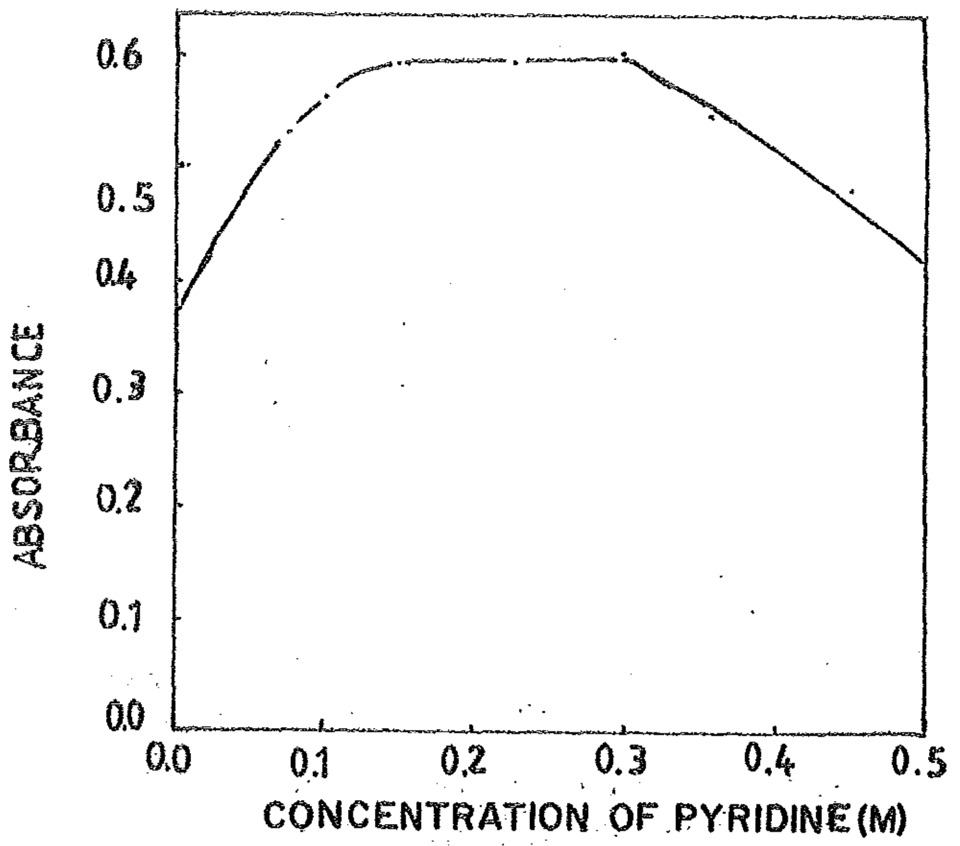


FIG. 4. EFFECT OF CONCENTRATION OF PYRIDINE

0.25M. Higher concentrations above 0.25M upto 0.5M did not have any adverse effect. The results are given in Table 3.

TABLE 3

EFFECT OF AZIDE CONCENTRATION ON THE EXTRACTION AND DETERMINATION OF COBALT(III)

Concentration of cobalt(III) = 3.06 x 10^{-4}M

Concentration of Azide (M)	Absorbance at 520nm
0.000	0.125
0.005	0.358
0.010	0.378
0.020	0.485
0.040	0.514
0.050	0.514
0.060	0.515
0.080	0.517
0.100	0.538
0.150	0.550
0.200	0.594
0.250	0.595
0.500	0.595

Effect of Amount of HDPBA: A 1:6 molar ratio of the cobalt(III)-to-reagent was found to be adequate for the complete extraction of cobalt(III). A large excess of the reagent upto fifty-fold has no influence on the extraction of cobalt(III). However, a blank solution of the reagent was necessary for more than fifteen fold excess of the reagent-to-metal for measurement of absorbance. The results are shown in Table 4.

Order of Addition of Reagents: The best order of addition of reagents was found to be the addition of the HDPBA solution in chloroform and pyridine to the cobalt-(III) and azide solution. Addition of azide or pyridine after the addition of the other reagents require 1-2 hours for the formation of the complex to produce the same result. Addition of hydrogen peroxide after the addition of the azide and HDPBA solution did not have any effect giving the readily extractable coloured complex.

Time of Extraction and Stability of Complex: Following the recommended procedure, the complex was extracted into the choloroform phase within two minutes. The chloroform solution of the complex was found to be stable for at least two hours.

TABLE 4

EFFECT OF AMOUNT OF HDPBA ON THE EXTRACTION AND DETERMINATION OF COBALT(III)

Concentration of cobalt(III) = 1.72×10^{-4}M

Metal: HDPBA (mole ratio)	Absorbance
1:0	0.00
1:1/2	0.15
1:1	0.273
1:2	0.326
1:3	0.328
1:4	0.330
1:5	0.332
1:6	0.337
1:8	0.337
1:10	0.338
1:15	0.338
1:20	0.338
1:40	0.338

Volume of the Aqueous Phase: The volume of the aqueous phase can be varied from one to two times relative to the volume of the organic phase without affecting the mixed ligand complex formation and its subsequent extraction.

4.14 BEER'S LAW: The cobalt(III) mixed ligand complex obeys Beer's law in the concentration range of 3.6 to 24 ppm of cobalt. Varying amounts of cobalt(III) ranging from 0.09 to 0.6mg were extracted following the recommended procedure. A plot of absorbance against cobalt concentration shows linearity in the range mentioned above. The results are shown in Table 5 and Figure 5.

TABLE 5

CALIBRATION CURVE DATA FOR THE DETERMINATION OF COBALT(III)

Cobalt(III) μg/25ml Chloroform	Absorbance at 520nm
90	0.120
100	0.135
200	0.270
300	0.404
400	0.541
500	0.675
600	0.811

4.15 SENSITIVITY: The molar absorptivity of the red complex in chloroform is found to be 1980 lit. mole^{-1} cm^{-1} corresponding to Sandell's[50]

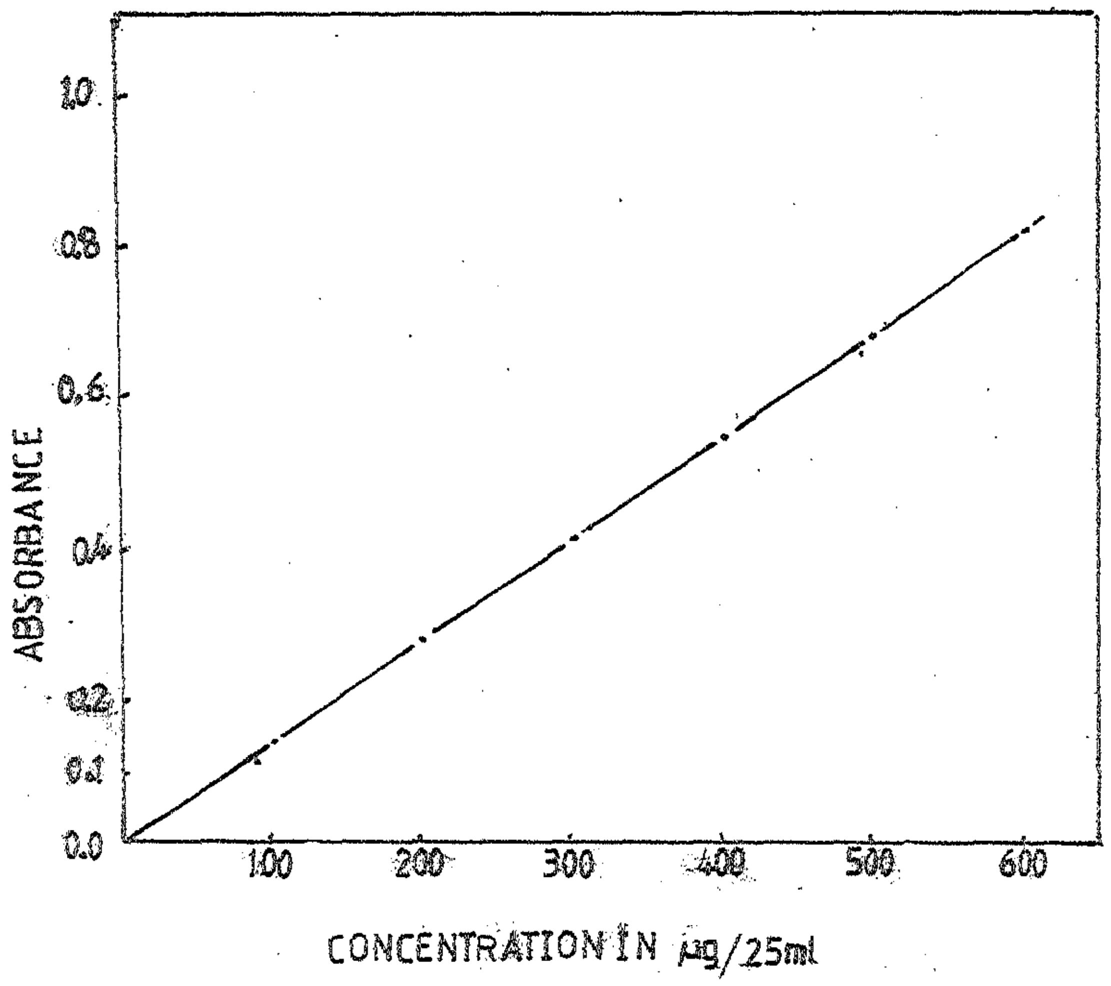


FIG.5 CALIBRATION CURVE FOR COBALT(III)

sensitivity of 0.0297 ug of cobalt per cm^2 at 520nm.

4.16 PRECISION: Ten independent determinations were made on solutions each containing a cobalt(III) concentration of 10 ppm. The measurements give a mean absorbance of 0.542 with a standard deviation of 0.004 corresponding to relative standard deviation of 0.74%. These observations suggest that the method is fairly precise and gives reproducible results.

4.17 EFFECT OF DIVERSE IONS: To study the effect of diverse ions on the coloured system, an aliquot of standard solution containing 200 ug of cobalt-(II) was transferred to a separatory funnel and to this was added a solution containing a known quantity of the diverse ion. The cobalt(II), oxidized by hydrogen peroxide, to cobalt(III) was extracted and determined following the recommended procedure.

Chloride, bromide, nitrate, sulphate, ammonium, alkali metal and alkaline earth metal ions did not interfere. The tolerance limits for the various diverse ions studied are given in Table 6. Iron(II & III), nickel(II), lanthanum-(III), copper(II) are found to have low tolerance limits. Manganese(II) interferes at all levels. Consequently, these ions deserve separation. Masking of iron(III) with fluoride or phosphate was not successful. From the anions, cyanide interferes at all levels. Fluoride, oxalate, thiocyanate have relatively low tolerance limits as indicated in Table 6.

TABLE 6

INFLUENCE OF DIVERSE IONS ON THE DETERMINATION OF COBALT(III)

Cobalt(III) concentration = 200 g/25ml = 8.0 ppm

Ion	Added as	Tolerance limit ppm	Absorbance at 520nm
None	-	-	0.270
Ag^{+}	$AgNO_3$	400	0.273
Al^{+3}	$Al(NO_3)_3$	120	0.268
Cd^{+2}	$Cd(NO_3)_2$	400	0.273
Ce^{+4}	$(NH_4)_2Ce(NO_3)_6$	400	0.260
Cr^{+3}	$Cr(NO_3)_3$	32	0.276
Cu^{+2}	$CuSO_4$	4	0.274
Hg^{+2}	$Hg(NO_3)_2$	800	0.274
La^{+3}	$La(NO_3)_3$	40	0.269
Mo^{+6}	$(NH_4)_2Mo\ O_4$	400	0.274
Ni^{+2}	$Ni(NO_3)_2$	40	0.268
Th^{+4}	$Th(NO_3)_4$	400	0.268
U^{+6}	$UO_2(NO_3)_2$	400	0.273
V^{+5}	NH_4VO_3	200	0.273
W^{+6}	Na_2WO_4	400	0.271
Zn^{+2}	$Zn(NO_3)_2$	400	0.275
Zr^{+4}	$Zr(NO_3)_4$	400	0.268
CH_3COO^{-}	CH_3COONa	800	0.272
AsO_4^{3-}	Na_3AsO_4	800	0.277
$B_4O_7^{2-}$	$Na_2B_4O_7$	800	0.273
Citrate	$C_6H_8O_7$	200	0.265
F^{-}	NaF	40	0.260
PO_4^{3-}	Na_2HPO_4	800	0.277
SbO_4^{3-}	Na_3SbO_4	400	0.274
Tartrate	$C_4H_6O_6$	135	0.267
SCN^{-}	KSCN	40	0.266

4.18 COMPOSITION OF THE COBALT(III) COMPLEX: The cobalt-to-HDPBA ratio in the complex was determined by Job's[51] and mole-ratio methods[52] and the cobalt-to-azide ratio was determined by the simple form of absorptiometric method[53] as described in the following sections.

Job's Method of Continuous Variation: To study the cobalt(III)-to-HDPBA ratio, 4.244 x 10^{-3}M cobalt-(II) in water and 8.5 x 10^{-3}M HDPBA in chloroform were prepared. The mole fractions of cobalt(III) and the reagent were varied with constant molarity (1.7 x 10^{-3}M in a 10 ml aqueous phase) in the presence of 0.5M of azide and extraction was made according to the general procedure. The absorbance was measured and given in Table 7. The absorbance plotted against the mole fraction of the metal indicated that the metal-to-reagent ratio in the complex is 1:1 as shown in Figure 6.

TABLE 7

JOB'S METHOD FOR THE DETERMINATION OF COBALT(III): HDPBA

Concentration of cobalt(III) = 6.8×10^{-4}M
and HDPBA

Concentration of azide = 0.50M
in the aqueous phase

Mole Ratio of Co(III) to HDPBA	Absorbance at 520 nm
10:0	0.180
9:1	0.310
8:2	0.362
7:3	0.454
6:4	0.532
5:5	0.595
4:6	0.522
3:7	0.420
2:8	0.35
1:9	0.202
0:10	0.000

Mole Ratio Method: 4.244×10^{-3}M of cobalt(II) and 1.06×10^{-2}M of HDPBA solutions were prepared in distilled water and chloroform respectively. Extractions were made taking 1 ml of 4.244×10^{-3}M of the cobalt(II) solution and varying the amount of the reagent in the

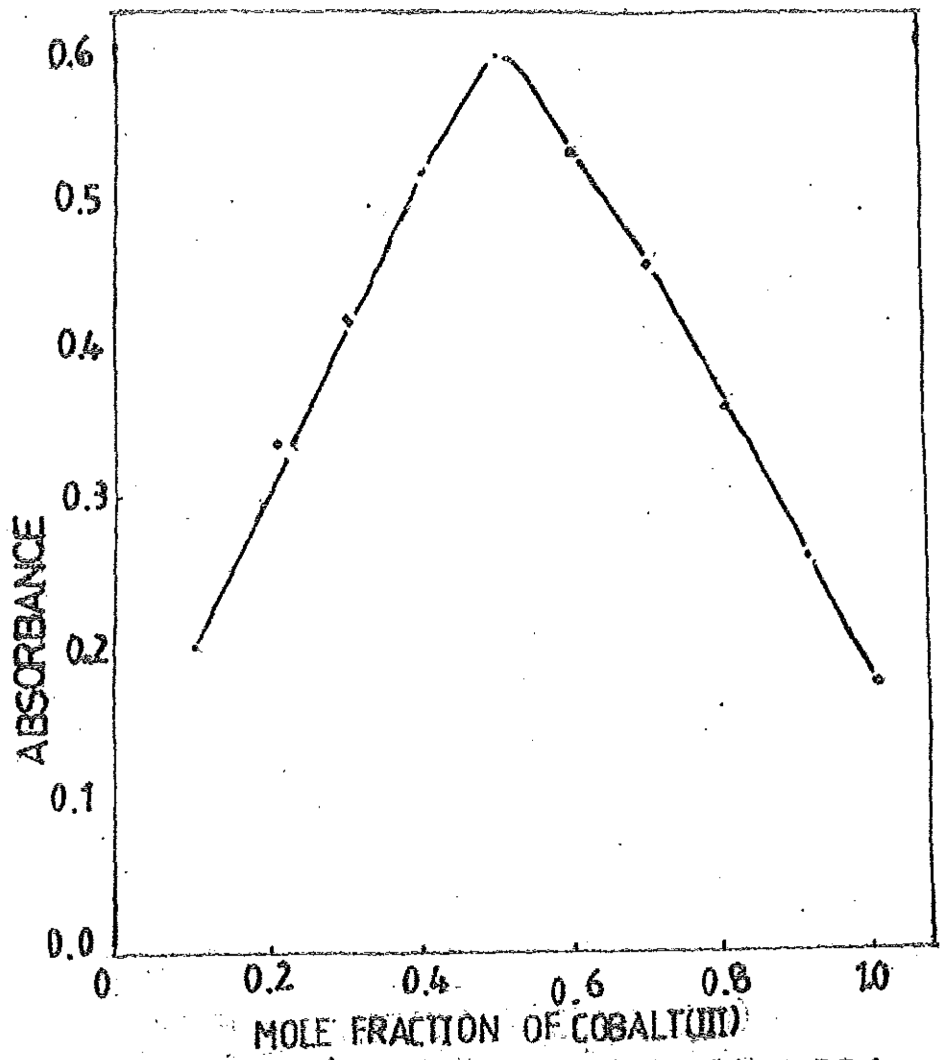


Fig. 6 JOB'S METHOD FOR Co: HDPBA

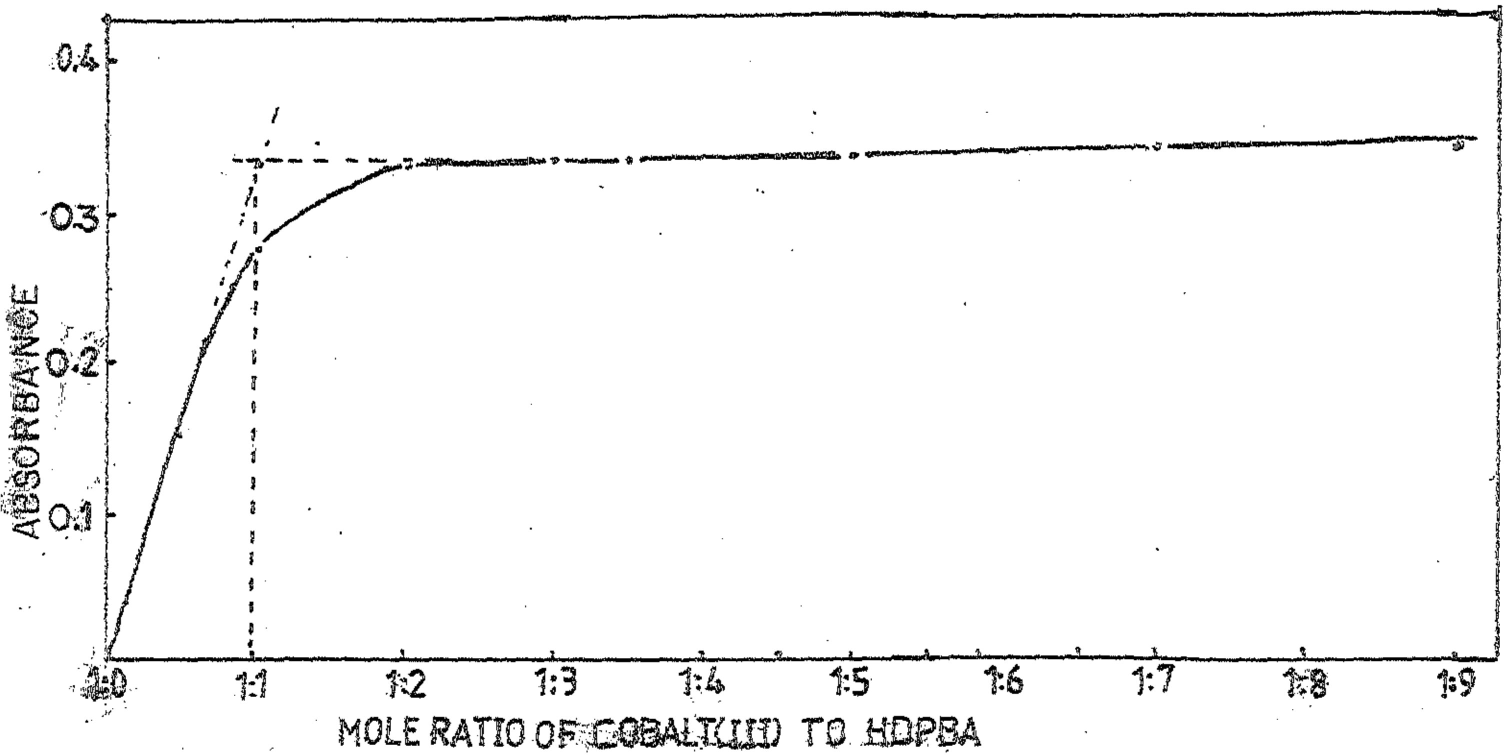


FIG.7 MOLE RATIO METHOD FOR COBALT:HDPBA

ratio of 1:1/2 to 1:40 as depicted in Table 4. The plot of absorbances against the mole ratio of metal-to-reagent is shown in Figure 7. Extrapolations of the tangents of the curve to a point of intersection indicate that cobalt(III)-to-HDPBA in the mixed ligand complex is 1:1.

Absorptiometric Method: To determine the ratio of cobalt to azide in the ternary complex, a series of extractions were made. The concentration of cobalt(III) and HDPBA in excess were kept constant and the concentration of azide was varied. Absorbance measurements were made after each extraction both in the absence and in the presence of azide (Table 8). The absorptiometric plot of $\log \frac{(A - A_{min})}{(A_{max} - A)}$ against $\log [N_3^-]$, (where Amin is absorbance without azide and Amax is the maximum absorbance in presence of azide), shown in Figure 8, indicates slopes of 1.3 and 1.0. These results suggest that the formation of mixed ligand complex takes place in two successive steps and the total number of azide in the mixed ligand complex to be 2.

TABLE 8

ABSORPTIOMETRIC METHOD FOR THE DETERMINATION OF COBALT(III) TO AZIDE RATIO IN THE COMPLEX

Cobalt(III) concentration = 3.06×10^{-4}M

$[N_3^-]$	Log $[N_3^-]$	Absorbance (520 nm)	A-Amin	Amax-A	Log $\frac{(A-Amin)}{(Amax-A)}$
0.000	-	0.125	-		
0.005	-2.3	0.358	0.233	0.237	-0.007
0.010	-2.0	0.378	0.253	0.217	0.0066
0.015	-1.83	0.433	0.308	0.162	0.27
0.0180	-1.75	0.460	0.335	0.135	0.40
0.020	-1.69	0.485	0.360	0.110	0.53
0.040	-1.39	0.514	0.389	0.081	0.68
0.050	-1.30	0.514	0.389	0.081	0.68
0.060	-1.22	0.515	0.390	0.080	0.69
0.080	-1.10	0.517	0.392	0.078	0.70
0.100	-1.0	0.534	0.409	0.061	0.83
0.125	-0.9	0.543	0.419	0.051	0.89
0.150	-824	0.550	0.425	0.044	0.98
0.20	-0.69	0.594	0.469	0.001	2.67
0.25	-	0.595	-	-	-

4.19 EXTRACTION EQUILIBRIUM OF THE COBALT(III) COMPLEX: The extraction of cobalt(III) may be represented, according to the 1:1:2 (Co(III): HDPBA: N_3^-) composition, as follows:

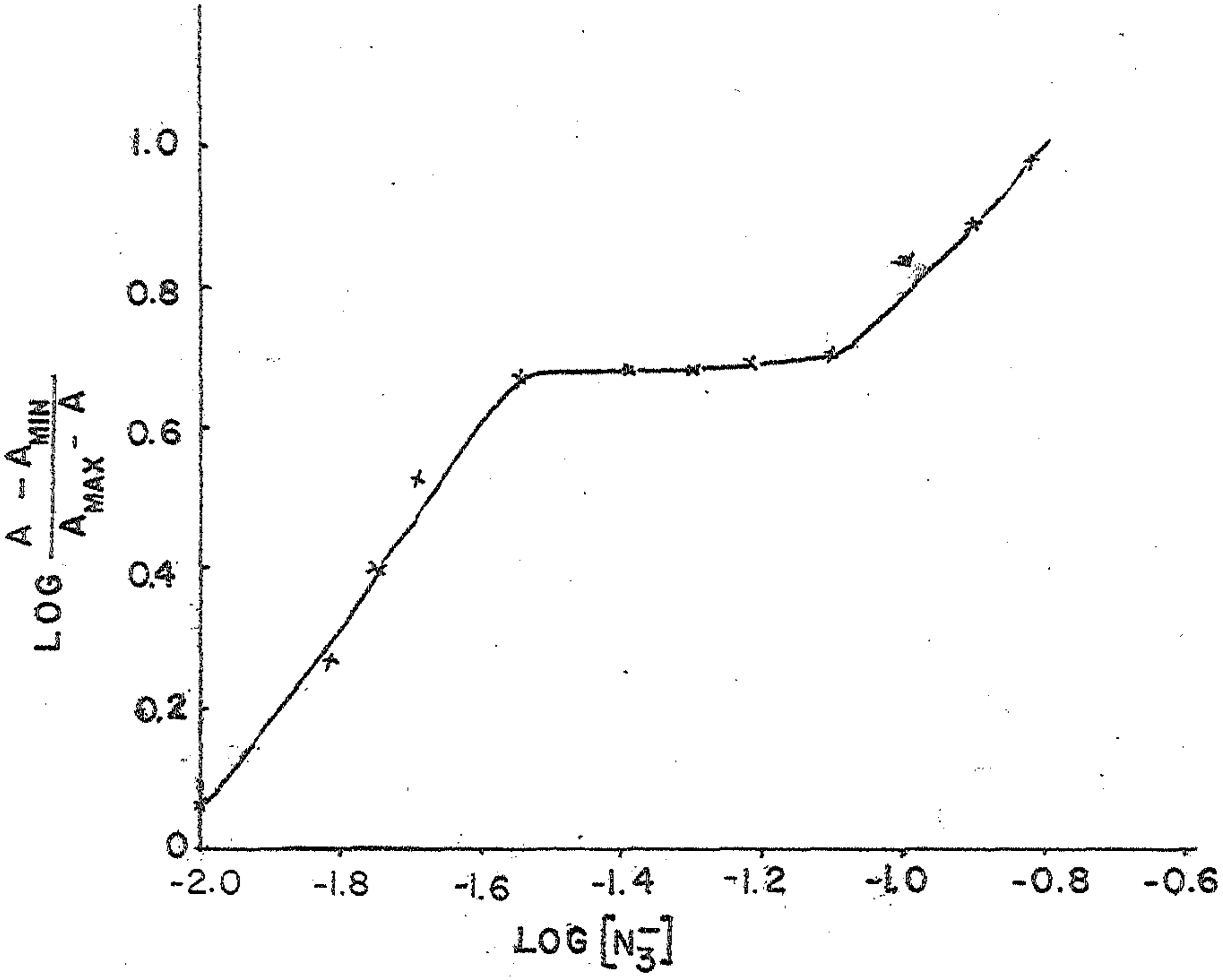


FIG. 8 ABSORPORTIOMETRIC METHOD FOR DETERMINATION OF COBALT(III) TO N_3^- RATIO

$$Co^{3+}_{(aq)} + HL_{(org)} + 2N^{-}_{3(aq)} \rightleftharpoons CoL(N_3)_{2(org)} + H^{+}_{(aq)}$$

Where HL = HDPBA, org = Organic phase and aq = aqueous phase

According to the extraction equilibrium equation given above, the extraction constant for the system may be represented by

$$K_{ex} = \frac{[CoL(N_3)_2]_{(org)}[H^+]_{(aq)}}{[Co^{+3}]_{(aq)}[HL]_{(org)}[N_3^-]^2_{(aq)}}$$

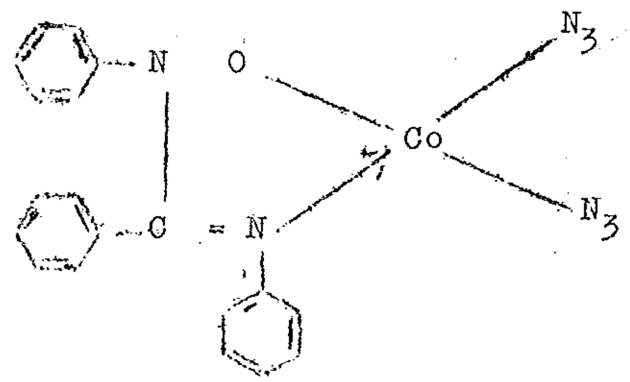
Assuming no side reactions, the distribution ratio of the metal, D_{Co}, may be given by

$$D_{Co} = \frac{[HL]_{(org)}[N_3^-]^2_{(aq)}}{[H^+]_{(aq)}} \cdot K_{ex}$$

or $\text{Log } D_{Co} = \log K_{ex} + \log [HL]_{(org)} + 2 \log [N_3^-]_{(aq)} + pH$

From the equation expressing the distribution ratio, it can be observed that extraction of the cobalt complex is a function of the reagent concentration in the organic phase, and azide concentration and pH of the aqueous phase.

The structure of the complex that may be suggested according to the 1:1:2 (Co: HDPBA: N_3^-) composition would be:



4.2 EXTRACTION AND DETERMINATION OF IRON(III)

4.21 COLOUR REACTION: Iron(III) forms a redish-violet coloured complex on reaction with the reagent solution in presence of azide in acidic medium, at pH 2-5. The mixed ligand complex is readily soluble in chloroform.

4.22 ABSORPTION SPECTRA: A dilute solution 1.73×10^{-4}M of the reagent in chloroform showed negligible absorption in the region 450-700nm. The red-violet coloured iron(III)-HDPBA-azide complex showed a broad maximum absorption at 520-540nm with molar extinction coefficient of 4895 lit. mole^{-1} cm^{-1}. At high concentrations of the reagent and azide, well beyond the optimum limits, there is no shift of the absorption peak. However, a blank solution is necessary for the absorbance measurements when excess of the reagent is used. The absorption spectra are shown in Figure 9.

4.23 EFFECT OF VARIABLES: The effect of the experimental variables on the extraction of the iron(III)-HDPBA-azide complex into chloroform has been investigated. The effect of a particular variable was studied by determining the absorbance following the general procedure described earlier, keeping all experimental parameters constant, except the one under study.

Choice of Solvent for Extraction: The iron(III) complex can be extracted by chloroform and benzene. chloroform was preferred for the simple reason that it has higher density than the aqueous phase allowing easy separation from the separatory funnel in addition to its low cost, easy to recover and high solubility of HDPBA in it than in benzene.

Effect of pH: The complete extraction of the mixed ligand complex was effective in the range of pH 2-5. The desired pH was maintained by 8-18 drops of 2M hydrochloric acid using a pH meter. The absorbance of the complex extracted into chloroform under the desired pH is shown in Table 9. The effect of pH on the extraction of iron is shown in Figure 10. pH lower than 2 and higher than 5 during the extractions showed decrease in the absorbances measured suggesting incomplete extraction of the complex.

TABLE 9

EFFECT OF pH ON THE EXTRACTION AND DETERMINATION OF IRON-(III)

Concentration of iron = 1.073×10^{-4} M

pH	Absorbance (530 nm)
1.0	0.161
1.5	0.446
2.0	0.523
2.5	0.524
3.0	0.524
4.0	0.524
4.58	0.525
5.0	0.525
5.5	0.424
6.0	0.092
6.5	0.036

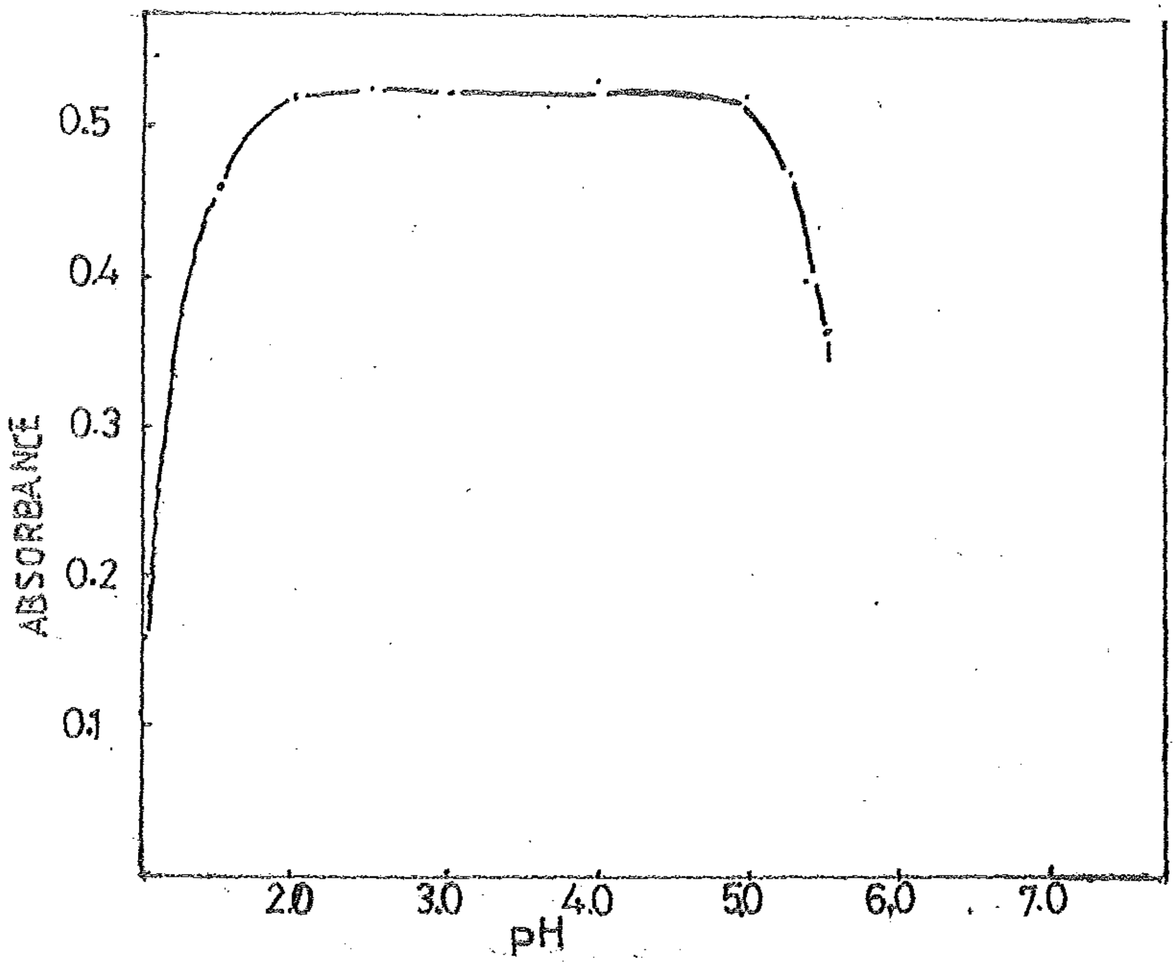


FIG.10 EFFECT OF pH ON THE EXTRACTION IRON (III)
CON. OF IRON (III) = 0.15 mg/25 ml

Effect of Amount of Azide: The optimum concentration range of azide for complete extraction of iron(III) as a mixed ligand complex was found to be 0.25 to 0.50M (Table 10). Higher concentrations above 0.50M did not have any adverse effect. It was also found that the extraction of the metal ion is dependent on the concentration of azide and not on the metal-to-azide molar ratio, the limiting lower concentration of azide being 0.25M.

TABLE 10

EFFECT OF AZIDE CONCENTRATION
ON THE EXTRACTION AND DETERMINATION OF IRON(III)

Concentration of iron = 1.073×10^{-4}M

Concentration of Azide (M)	Absorbance at 530 nm
0.00	0.054
0.02	0.085
0.03	0.120
0.04	0.143
0.05	0.170
0.06	0.220
0.08	0.340
0.10	0.360
0.15	0.470
0.20	0.480
0.25	0.520
0.30	0.525
0.40	0.526
0.50	0.525

Effect of Amount of HDPBA: A 1:5 molar ratio of the iron(III) to reagent was found adequate for the complete extraction of iron(III) as a mixed ligand complex (Table 11). A large excess of the reagent upto fifty-fold has no influence. However, a blank solution of the reagent was necessary for more than fiften-fold excess of the reagent-to-metal for measuring the absorbance at 530 nm. The results are indicated in the table which is also used for studying composition by mole ratio method.

TABLE 11

EFFECT OF THE AMOUNT OF HDPBA ON THE EXTRACTION AND DETERMINATION OF IRON(III)

Concentration of iron(III) = 8.6 x 10^{-5}M

Iron: HDPBA (mole ratio)	Absorbance at 530 nm
1:0	0.00
1:1	0.175
1:2	0.286
1:2.4	0.330
1:3	0.362
1:4	0.406
1:5	0.420
1:6	0.421
1:8	0.420
1:10	0.421
1:20	0.420
1:40	0.421

Order of Addition of Reagents: The best order of addition of reagents was found to be adding the chloroform solution of HDPBA to the iron-azide solution whose pH is adjusted to the desired value. The complex does not form readily if the azide solution is added to the iron-HDPBA mixture. Moreover, adjustment of a desired pH is obviously difficult in the latter case.

Time of Extraction and Stability of Complex: Following the recommended procedure, the complex was extracted into chloroform phase within one minute. The complex in chloroform was found to be stable for at least 48 hours.

Volume of Aqueous Phase: The volume of the aqueous phase does not have any effect on the formation and extraction of the complex provided the pH and the azide concentration are within the optimum range. A five fold increase in the aqueous volume relative to the volume of the organic phase did not have any effect on the extraction.

4.24 BEER'S LAW MOLAR ABSORPTIVITY AND SENSITIVITY:

The coloured system obeys Beer's law from 1.6 to 11.2 ppm of iron(III) as shown in Table 12 and Figure 11. The molar absorptivity of the mixed ligand complex in chloroform is found to be 4895 lit. mole^{-1} cm^{-1} with Sandell's[50] sensitivity of 0.0114 μg of iron per cm^2.

TABLE 12

CALIBERATION CURVE FOR THE
DETERMINATION OF IRON(III)

Concentration of Iron μg/25 ml in chloroform	Absorbance at 530 nm
40.0	0.140
50.0	0.174
100.0	0.350
120.0	0.420
150.0	0.524
200.0	0.700
250.0	0.874
280.0	0.978

4.25 PRECISION: Ten independent determinations were made on solutions of iron(III) each containing 6 ppm. Absorbance measurement for each extraction gave a mean of 0.525 with a standard deviation of 0.00164 which corresponds to relative standard deviation of 0.3%. These results suggest that the method is fairly precise and gives reproducible results for the determination of iron(III).

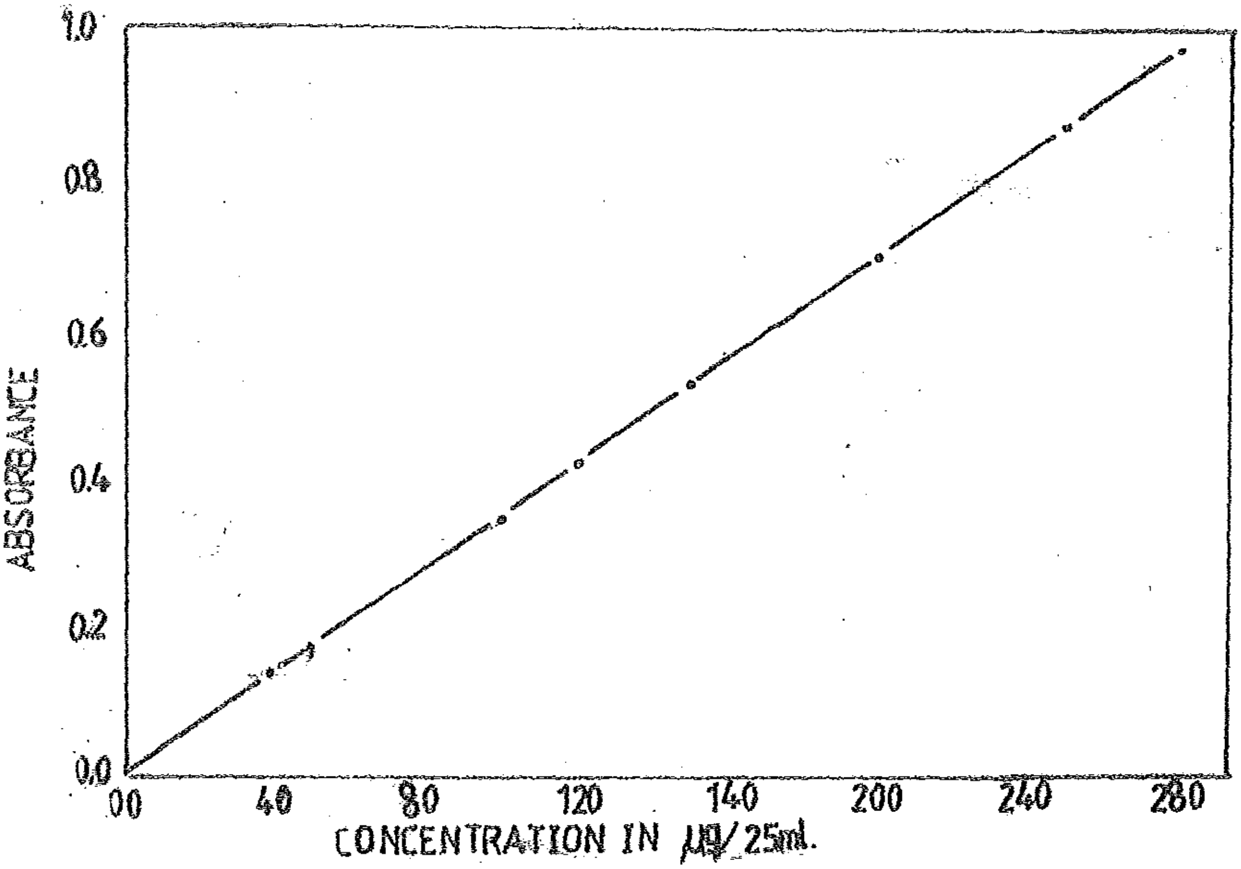


Fig.II CALIBRATION CURVE FOR THE DETERMINATION OF IRON (III)

4.26 **INFLUENCE OF DIVERSE IONS:** To study the effect of diverse ions on the coloured system, an aliquot of standard solution containing 0.15mg of iron(III) was transferred to a 50ml beaker followed by addition of a solution containing a known quantity of the diverse ion. Determination of iron(III) was made after each extraction according to the general procedure described earlier.

Chloride, bromide, nitrate sulphate, ammonium, alkali metal and alkaline earth metal ions did not interfere. The tolerance limits for various ions were studied (Table 13). Vanadium(V) interferes at all levels while tungsten(VI), molybdenum(VI) and uranium(VI) were found to have low tolerance limits. From the anions, cyanide and thiocyanate were found to have low tolerance limits.

TABLE 13

EFFECT OF DIVERSE IONS ON THE DETERMINATION OF IRON(III)

Concentration of iron(III) = 6 ppm

Ion	Added as	Amount added ppm	Absorbance at 530 nm
Al^{+3}	$Al(NO_3)_3$	400	0.520
Cd^{+2}	$Cd(NO_3)_2$	800	0.523
Cr^{+3}	$Cr(NO_3)_3$	800	0.529
Co^{+2}	$Co(NO_3)_2$	400	0.529
Cu^{+2}	$Cu(NO_3)_2$	200	0.530
Hg^{2+}	$Hg(NO_3)_2$	200	0.522
La^{+3}	$La(NO_3)_2$	400	0.520
Mn^{+2}	$MnCl_2$	600	0.524
Mo^{+6}	$(NH_4)_2MoO_4$	50	0.520
Ni^{+2}	$Ni(NO_3)_2$	400	0.527
U^{+6}	$UO_2(NO_3)_2$	50	0.521
W^{+6}	$Na_2(WO_4)$	50	0.520
Zn^{+2}	$Zn(NO_3)_2$	800	0.524
Zr^{+4}	$ZrCl_4$	800	0.527
AsO_4^{3-}	Na_3AsO_4	400	0.524
$B_4O_7^{-2}$	$Na_2B_4O_7$	400	0.526
CN^-	NaCN	40	0.528
PO_4^{-3}	$(NH_4)_2HPO_4$	400	0.526
SCN^-	KSCN	40	0.530
Citrate	$C_6H_8O_7$	100	0.521
Tartrate	$C_4H_6O_6$	100	0.519

4.27 COMPOSITION OF THE IRON(III) COMPLEX: The composition of the mixed ligand complex was determined by different methods. The ratio of the iron(III)-to-HDPBA in the ternary complex was determined by Job's method of continuous variation[51] and mole-ratio method[52]. In the case of the metal-to-azide ratio a plot of log D against log $[N_3^-]$[54] was made and the slope of the curve gave the approximate number of azide ions in the ternary complex.

Method of Continuous Variation: 5.3610^{-3}M solutions of iron(III) and HDPBA were prepared in distilled water and chloroform respectively. In the extractions, the mole fractions of iron(III) and HDPBA were varied with total constant molarity of 5.36×10^{-4}M with respect to the aqueous phase in the presence of 0.5M sodium azide, the results of which are shown in Table 14. The absorbance measured is plotted against the mole fraction of the metal. The result suggests that the metal-to-HDPBA is 1:2 as shown in Figure 12.

Mole Ratio Method: 2.68×10^{-3}M of iron(III) and 1.072×10^{-2}M HDPBA solutions were prepared and extractions were made according to the recommended procedure, taking 1.0ml of the 2.6×10^{-3}M iron(III) solution and varying the amounts of HDPBA from 1:1 to 1:40 molar ratio of iron(III)-to-HDPBA. The results are shown in Table 11 on page 45. A plot of the absorbance against the metal-to-ligand ratio is shown in Figure 13. Extrapolation of the tangents of the curve to a point of intersection indicate that the metal-to-reagent ratio is 1:2 which is also supported by Job's method of continuous variation.

TABLE 14

METHOD OF CONTINUOUS VARIATION FOR THE DETERMINATION OF IRON(III) TO HDPBA RATIO

Concentration of reactants = 5.36×10^{-4}M

Iron(III)-HDPBA Ratio	Absorbance at 520 nm
10:0	0.044
9:1	0.094
8:2	0.178
7:3	0.252
6:4	0.422
5:5	0.480
4:6	0.520
3:5:6,5	0.512
3:7	0.52
2.5:7.5	0.504
2:8	0.460
1:9	0.244
0:10	0.005

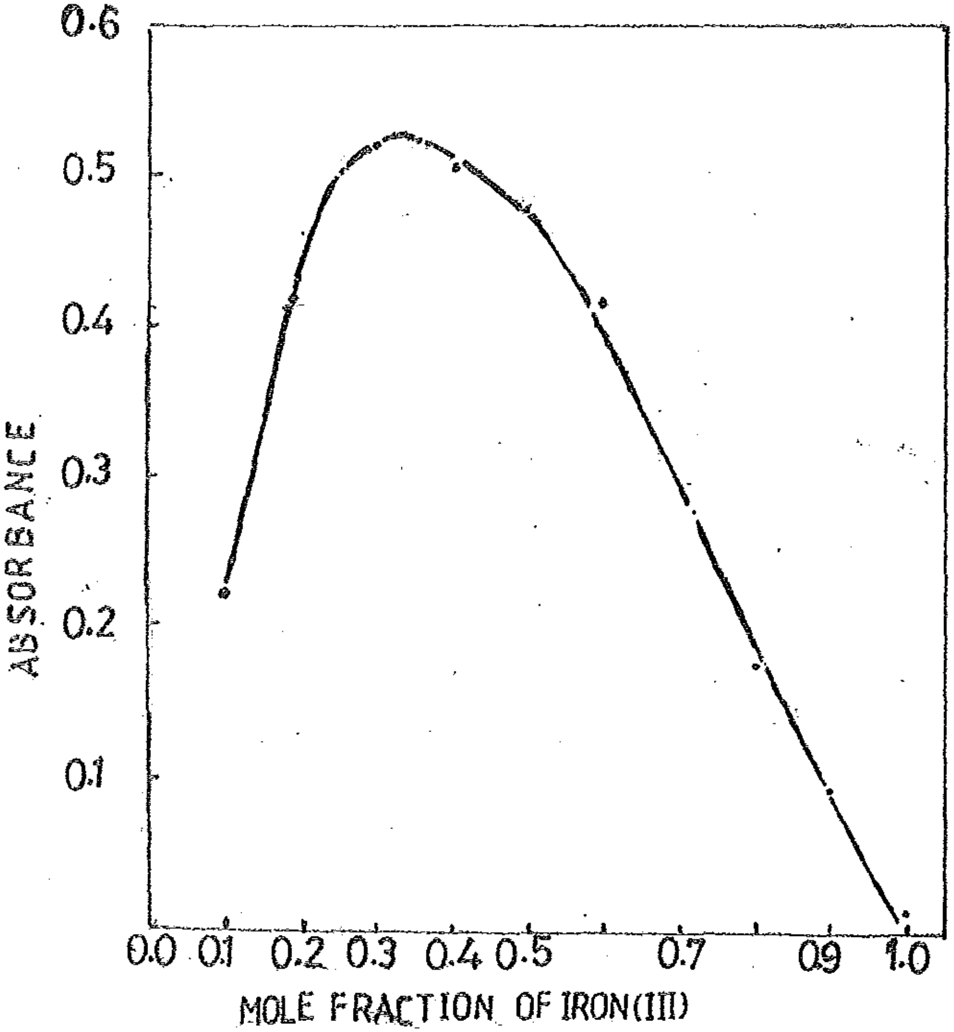


Fig. 12 JOB'S METHOD FOR IRON (III): HDPBA

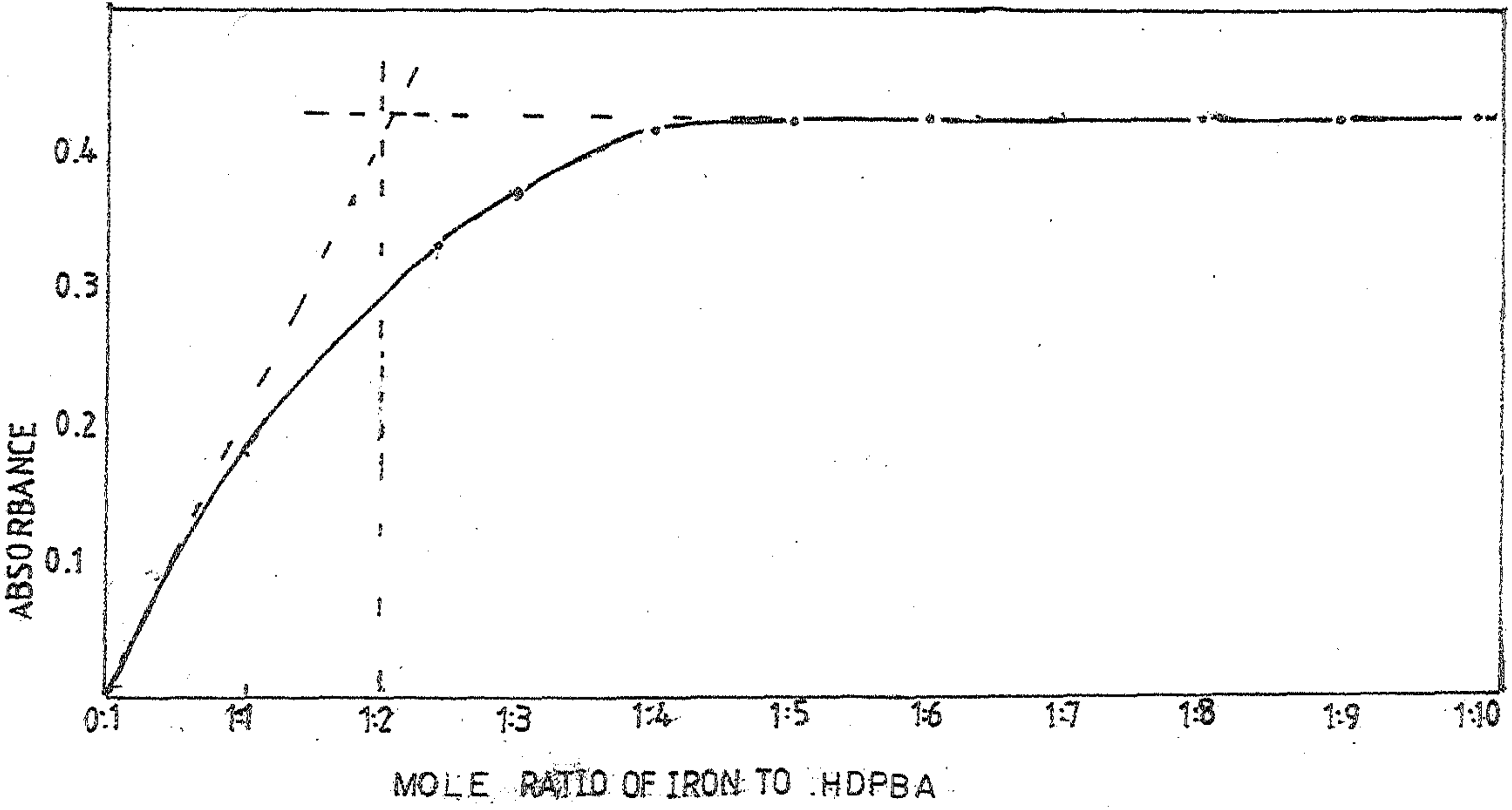


FIG.13 MOLE RATIO METHOD FOR IRON(III) : HDPBA

Extraction Method: To determine the ratio of iron(III) to azide in the ternary complex, a constant excess of HDPBA and constant amount of iron(III) were taken and the concentration of azide was varied. The absorbance was measured after each extraction following the general procedure for iron(III). The results are shown in Table 15 along with the calculated distirbution ratio, D_{Fe}, for each azide concentration.

TABLE 15

DATA FOR DETERMINATION OF IRON(III): AZIDE BY EXTRACTION METHOD

Concentration of iron = 1.073×10^{-4}M

Concentration of azide (M)	Log $[N_3^-]$	Absorbance (530nm)	Log D_{Fe}
0.05	-1.30	0.180	-0.288
0.06	-1.22	0.223	-0.132
0.075	-1.13	0.33	+0.152
0.08	-1.20	0.345	+0.198
0.10	-1.0	0.365	+0.350
0.15	-0.82	0.469	+0.920
0.2	-0.7	0.487	+1.100

A plot of log D_{Fe} against log $[N_3^-]$ shown in Figure 14 gives a slope of 2.2 which suggests the number of azide ions in the mixed ligand complex to be 2.

The composition of the complex is, therefore 1:2:2 (Fe: HDPBA: N_3^-).

4.28 EXTRACTION EQUILIBRIUM OF THE IRON(III) COMPLEX:

According to the composition 1:2:2 (FE: HDPBA: N_3^-) the extraction equilibrium may be represented by the following equation:

$$Fe^{+3}_{(aq)} + 2HL_{(org)} + 2N^-_{3(aq)} \rightleftharpoons Fe\ L_2(N_3)_{2(org)} + H^+_{(aq)}$$

where HL = HDPBA, org = organic phase and aq = aqueous phase. The extraction constant, Kex, may be represented by

$$K_{ex} = \frac{[FeL_2(N_3)_2)]_{(org}\,[H^+]_{(aq)}}{[Fe^{3+}]_{(aq)}[HL]^2_{(org)}[N_3^-]^2_{(aq)}}$$

Assuming no side reactions, the distribution ratio, D_{Fe}, can be expressed a

$$D_{Fe} = K_{ex}\frac{[HL]^2_{(org)}[N_3^-]^2_{(aq)}}{[H^+]_{(aq)}}$$

or

$$\log D_{Fe} = \log Kex + 2\log [HL]_{org} + 2\log [N_3^-]_{(aq)} + pH.$$

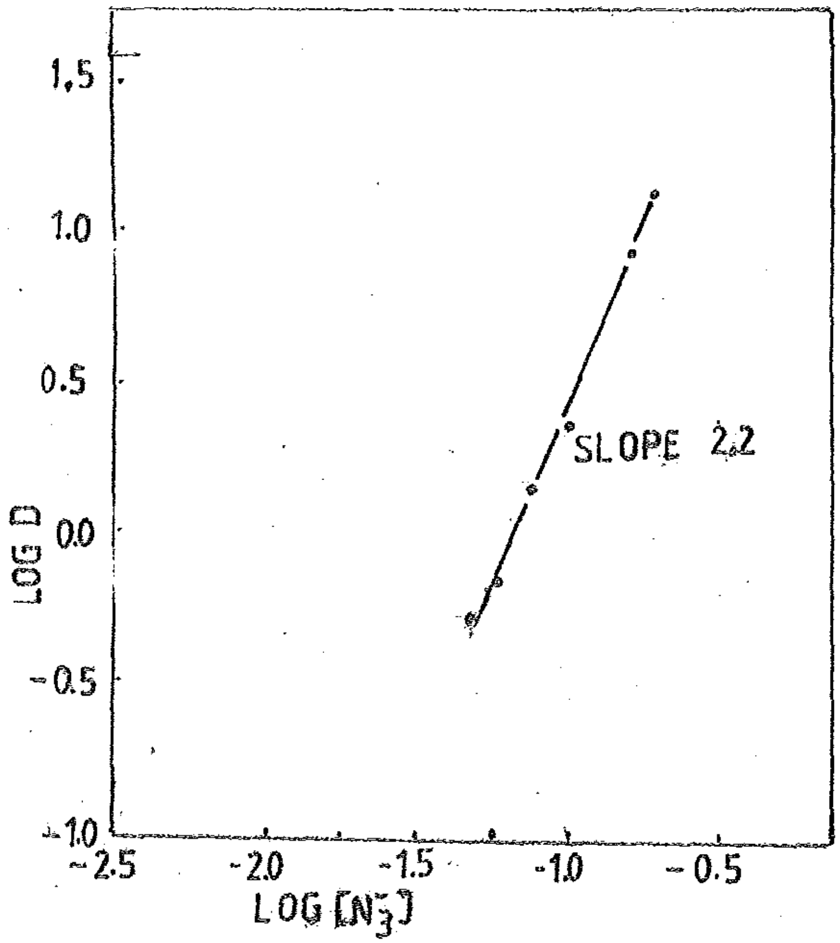
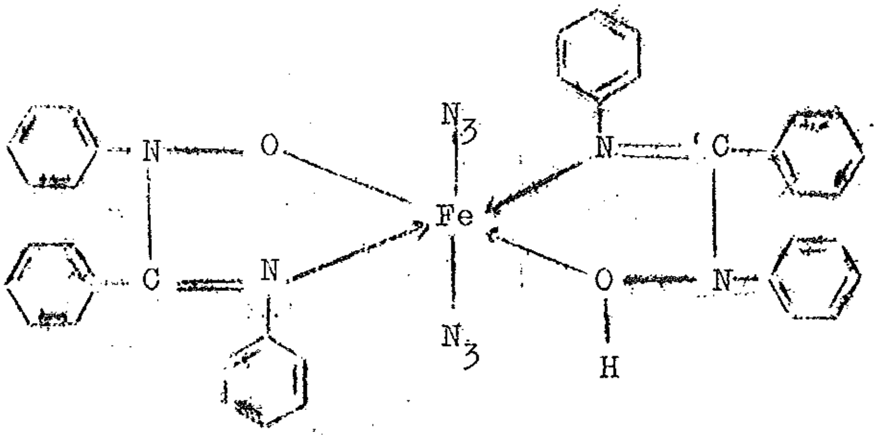


FIG.14 EXTRACTION METHOD FOR IRON(III)

AZIDE RATIO

From the equation expressing the distribution ratio it can be concluded that extraction of the metal is a function of reagent concentration in the organic phase and the azide concentration and pH of the aqueous phase.

The composition of the complex being 1:2:2 (Fe: HDPBA: N_3^-) and extractability as neutral complex into chloroform, it may be suggested that only one HDPBA molecule is deprotonated, hence the formula of the complex would be $[Fe\ (L)\ (HL)\ (N_3)_2]$ which may possibily have the following structure.



The complex may thus have the name diazido-bis (N-hydroxy-N,N'-diphenylbenzamidine) ferrate(III).

4.3 SEPARATION AND DETERMINATION OF IRON(III) AND COBALT FROM EACH OTHER

By virtue of the difference in the pH of reactions of iron(III) and cobalt(III), an effective separation of the two metals from a mixture was made, followed by spectrophotometric determinations at their respective wave lengths of maximum absorption.

The procedure is essentially the same for the separations. Iron(III) was extracted at pH 5 following the recommended procedure from a mixture of the two metals. The remaining aqueous phase containing cobalt(II) was extracted by HDPBA in chloroform-pyridine solution after oxidation to cobalt(III) with hydrogen peroxide. The volume of the aqueous phase for the extraction of cobalt(III) should not exceed 15ml.

The method enables the separation of widely varied amounts of the two metals. The results shown in Table 16 indicate sample containing 10:1 to 1;5 (Fe:Co) by weight could be separated and determined accurately using the method.

TABLE 16

SEPARATION AND DETERMINATION OF IRON AND COBALT FROM EACH OTHER

Iron Content (mg)	Iron Found[a] (mg)	Cobalt Content (mg)	Cobalt Found[a] (mg)
0.10	0.101	0.50	0.496
0.15	0.152	0.50	0.494
0.20	0.203	0.40	0.397
0.25	0.252	0.30	0.297
0.40	0.405	0.30	0.302
0.60	0.607	0.30	0.302
0.80	0.805	0.20	0.197
1.0	1.007	0.10	0.099

[a] Average of three determinations.

The results in the table above indicate the relative error is generally less than 1% for the determination of each metal and may be applied to samples containing iron and cobalt in the range 10;1 to 5 (Fe:Co) by weight. The method may be suggested for the analysis of materials which do not have constituents that interfere with the determination of both iron and cobalt in the present methods. Therefore samples containing vanadium, manganese and copper required prior separation or masking of these

4.4 APPLICATIONS OF THE METHODS

The applicability of new methods of analysis require the tests of validity by determining the constituents in question in standard samples. Due to unavailability of standard samples, however, the present method for cobalt(III) and iron(III) were tested for their validity by determining the contents of synthetetic samples, that correspond to the composition of the minerals-erythrite,[55] 2 $[(Co_3(AsO_4)_2 \cdot 8H_2O]$, scorodite,[56] $Fe(AsO_4)2H_2O$, and daubereelite,[57] $FeS. Cr_2S_3$.

4.41 Determination of Cobalt in Synthetic Erythrite Sample:

A synthetic erythrite sample was prepared by mixing 0.873g (0.003 mole) of cobalt(II) nitrate hexahydrate and 0.848g (0.002 mole) of sodium arsenate, $Na_3AsO_4 12H_2O$. The mixture was dissolved in dilute hydrochloric acid and diluted with distilled water to 100ml.

The cobalt content of an aliquot of the solution of the synthetic erythrite sample was extracted and determined following the general procedure for cobalt(III) described earlier. The results are shown in Table 17.

TABLE 17

DETERMINATION OF COBALT IN THE SYNTHETIC ERYTHRITE SAMPLE

Measurement	Cobalt Content (g)	Cobalt Found (g)
1	0.1767	0.1759
2	0.1767	0.1741
3	0.1767	0.1759
4	0.1767	0.1756
5	0.1767	0.1741
Mean	0.1767	0.1751

The results in the table indicate that the method for the synthetic sample, erythrite, is precise and accurate corresponding to a standard deviation of 0.002 and relative error of 0.9%. The results obtained indicate that method can be applied for the determination of cobalt in diverse samples.

4.42 Determination of Iron in Synthetic Scorodite and Daubereelite Samples: The method for iron(III) was tested by determining the amount of iron in the synthetic mixtures which correspond to the minerals scorodite and daubereelite.

i. To prepare a synthetic mixture in the composition of scorodite, 0.4033g (0.001 mole) of iron(III) nitrate nona-hydrate $Fe(NO_3)_3 \cdot 9H_2O$, was mixed with 0.424g (0.001 mole) of sodium arsenate, $Na_3AsO_4 \cdot 12H_2O$, and the mixture was dissolved in distilled water, followed by addition of 5ml of nitric acid (1:3). The solution was finally diluted with distilled water to 100ml after boiling off and cooling.

ii. A mixture of 0.784g (0.002 mole) of ammonium iron(II) sulphate, 1.600g (0.004 mole) of chromium(III) nitrate nona-hydrate and 0.624g (0.008 mole) of sodium sulphide, in the ratio of 1:2:4 [Fe(II):Cr(III):S(II)] that correspond to the composition of daubereelite, was decomposed by 10ml of nitric acid (1:3) followed by addition of about 50ml distilled water. The solution was boiled off to remove the oxides of nitrogen and diluted with distilled water to 100ml after cooling.

An aliquot of each synthetic mineral sample solution was transferred to a separatory funnel and iron(III) was extracted and determined following the general procedure for iron(III). The results are given in Table 18.

TABLE 18

DETERMINATION OF IRON(III) IN SYNTHETIC SAMPLES OF SCORODITE AND DAUBEREELITE

Sample	Iron Content (g)	Iron Found (g)	Standard deviation
Scorodite	0.0558	0.0549	0.006
Daubereelite	0.1116	0.1097	0.008

[a] Average of five determinations.

The results in the table indicate that the method for determination of iron in the synthetic samples of scorodite and daubereelite is fairly precise. The method can, therefore, be applicable for diverse samples.

The results obtained by the application of the present methods for the separation and determination of iron and cobalt in the synthetic samples have been subjected to the statistical treatments. It has been found that mean values and actual values do not have significant difference at 95% and above probability levels.

4.5 COMPARISON WITH OTHER METHODS FOR COBALT

Among the several reagents recommended for the spectrophotometric determination of cobalt, ammonium thiocyanate,[58-59] tetraphenylarsonium salt and thiocyanate,[60] nitroso-R salt,[61] 2-nitroso-1-naphthol,[62,64] 1-nitroso-2-naphthol,[65] 2-nitroso-1-naphthol-4-shlphonic acid[66] and o-nitrosoresorcinol[67] are in general use.

The comparative study of the proposed method for cobalt, in regard to selectivity and sensitivity, with other well known spectrophotometric methods are summarized in Table 19 and 20

The selectivity of the present method for cobalt is comparable to most of the other methods while the sensitivity of the present method is relatively low in comparison to most of the methods.

TABLE 19

SENSITIVITIES OF THE METHODS FOR COBALT

Reagent	Colour of Complex	λ_{Max} nm	Sensitivity µg Co cm^{-2}	Reference
Ammonium thiocyanate	Blue	620	0.055	58-59
Tetraphenylarsonium with thiocyanate	Blue	620	0.034	60
(1-2-Pyridylazo)-2-naphthol (PAN)	Red-violet	590	0.0022	68
o-Nitrosoresorcinol	Yellow-green	430	0.0025	67
2-Nitroso-1-Naphtol-4-Sulphonic acid	Pink	525	0.0042	66
1-Nitroso-2-naphthol	Red-violet	550	0.0075	65
2-Nitroso-1-naphthol	Red-violet	530	0.0042	62-64
N-Hydroxy-N,N'-diphenylbenzamidine in presence of azide	Pinkish-red	520	0.028	-

TABLE 20

SELECTIVITIES OF THE METHODS FOR COBALT

Reagent	pH	Interference	Reference
Ammonium thiocyanate	4-5	Ni(II),Fe(III),V(V), Cu(II),Cr(III),Cr(VI)	58, 59
Tetraphenylarsonium chloride with thiocyanate	5.5	Fe(III),Mo(VI),U(VI) Cu(II),V(V)	60
1-(2-pyridylazo)-2-naphthol (PAN)	3.6	Cu(II),Ni(II)	68
2-Nitroso-1-naphtol-4-sulphonic acid	2.5-5	Cu(II),Fe(II),Ni(II)	66
1-Nitroso-2-naphthol	4.5-5	Cu(II),Fe(II),Mn(II)	65
2-Nitroso-1napthol	2-2.5	Cu(II),Fe(II)	62, 64
Nitroso-R salt	5.0-6.0	Cu(II),Ce(IV) Fe(III), Ni(II)	61
N-Hydroxy-N,N'-diphenylbenzamidine with azide	7.4-7.8	Mn(II),Cu(II), Fe(III)	-

4.6 COMPARISON WITH OTHER METHODS FOR IRON

There are several reagents in general use for the spectrophotometric determination of iron. These include thiocyanate,[69-71] tributyl ammonium salt with thiocyanate,[72] 1,10-phenanthroline and its derivatives,[73-75] 2,2-bibyridine,[76] 2,2', 2"-terpyridine,[72] ferron,[77] nitroso-R salt,[78] mercapto-acetic acid[79] and salicylic acid.[80]

The sensitivity and selectivity of the present method has been compared with other well known methods. Table 21 and 22 clearly indicates that the present method is comparable to most of the commonly used methods in regard to both selectivity and sensitivity.

TABLE 21

SENSITIVITIES OF THE METHODS FOR IRON

Reagent	Colour of Complex	λ_{Max} nm	Sensitivity µg Fe cm^{2}	Reference
Ammonim thiocyanate	Red	480	0.008	69-71
Tributyl ammonium salt with thiocyanate	Red	480	0.0025	72
1,10-Phenanthroone	Orange-red	508	0.005	73-75
4,7-Biphenyl-1,10-phenanthroline	Red-violet	533	0.0025	75
2,2'-Bipyridine	Pink	522	0.007	76
2,2',2"-Terpyridine	Violet	552	0.005	72
Ferron	Blue	610	0.015	77
Nitroso-R salt	-	720	0.0023	78
Mercaptoacetic acid	Red-violet	540	0.014	79
Salicylic acid		520	0.030	80
N-Hydroxy-N,N'-diphenylbenzamidine with azide	Red-violet	520-540	0.012	-

TABLE 22

SELECTIVITIES OF THE METHODS FOR IRON

Reagent	pH or Acidity	Interference	Reference
Ammonium Thiocyanate	0.05-2M HCL	Ag(I),Hg(I),V(IV), Mo(VI),Cd(II),F^-, PO_4^{3-}, AsO_4^{3-}	69-71
1,10-Phenanthroline	2-9	Cu(II),Hg(I),Ni(II), Cd(II),Co(II),PO_4^{3-}	73-75
4,7-Biphenyl-1,10-phenanthroline	4.6	Hg(I),Ni(II),Cd(II), Co(II)	75
2,2'-Bipyridine	3-9	Co(II),Cu(II)	76
Mercapto-acetic acid	7-12	Co(II),Ni(II),V(V) Pb(II),Bi(III),Hg(I)	79
Salicylic acid	2.5-2.7	Mn(II),Cu(II)	80
N-Hydroxy-N,N'-diphenylbenzamidine with azide	2-5	V(V)	

5. CONCLUSION

Simple, rapid and highly selective methods for the extraction and spectrophotometric determination of cobalt and iron have been described. The sensitivity of the present method for iron is comparable to most of the other well known methods, while the method for cobalt is less sensitive than most of the common methods. The methods can be applied for the determination of cobalt and iron in diverse samples, accurately and precisely. Separation and determination of iron and cobalt from each other can be made in a wide range of proportions within less than 1% error.

6. REFERENCES

1. J.F.Flagg, "Organic Reagents Used in Gravimetric and Volumetric Analysis", Interscience Publishers, Inc., New York, (1947).
2. F.J.Welcher, "Organic Analytical Reagents", Vol.I-IV, D.Van Nostrand Co., New York, (1947-48)
3. Z.Holzbecher, L.Divis, M.Kral, L.Sucha and F.Vlacil, "Handbook of Organic Reagents in Inorganic Analysis", Ellis Harwood, Sussex (1976).
4. I.M.Kolthoff, P.J.Elving and E.B.Sandell, "Treatise on Analytical Chemistry", Part I, Vol.II, Interscience Publishers Inc., New York(1961).
5. A.I.Vusev and N.C.Polianshi, "The Use of Organic Reagents in Inorganic Analysis", Pergamon Press, Oxford (1960).
6. H.A.Flaschka and A.J.Varnard, Jr., "Chelates in Analytical Chemistry", Marcell Dekker Inc., New York, Vol I(1967); Vol.II(1969); Vol.III(1972).
7. F.K.Snell, C.T.Snell and C.A.Snell, "Colourimetric Methods of Analysis", Vol.II, D.Van Vostrand Co., Inc., New York (1949).
8. G.H.Morrison and H.Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley and Sons, Inc., New York (1957).
9. G.H.Morrison and H.Freiser, Anal. Chem, 1960; 32 37R; 1962, 34, 64R; 1964, 36, 93R; 1968, 40 522R; 1966, 38, 131R.

10. J.Stary, "The Solvent Extraction of Metal Chelates", Pergamon Press, London (1964).
11. D.Dyressen, J.O.Liljenzin and J.Rydberg, "Solvent Extraction Chemistry", North-Holand, Publishing Company Ltd., Amsterdam (1967).
12. Reference 3, pp 189.
13. H.H.Bauer, G.D.Christian, J.E.O'Reilly, "Instrumental Analysis", Allyn and Bacon, Boston (1978), p 609
14. J.Inczedy, "Analytical Application of Complex Equilibria", Ellis Horwood, Sussex pp 259-270 (1976).
15. H.Ley, Chem.Ber., 1901, 34, 2620.
16. H.Ley and E.Holzweissing, Chem Ber., 1903, 36 19
17. K.Satyanarayana and R.K.Mischra, Anal.Chem, 1974 46, 1609.
18. K.Satyanarayana and R.K.Mishra, J.Indian Chem.Soc., 1976, 53, 63, 469, 928.
19. K.S.Patel and R.K.Mishra, J.Indian Chem.Soc.,1978, 55,462.
20. K.Sayanarayana and R.K.Mishra, Ind.J.Chem. 1975, 13 295.
21. R.S.Kharsan, K.S.Patel and R.K.Mishra, Michrochimica Acta, 1979, 353.
22. K.S.Patel and R.K.Mishra, J.Indian Chem.Soc.,1978, 55, 773
23. R.S.Kharsan, K.S.Patel and R.K.Mishra , Talanta, 1979, 26, 254, 50.

24. K.S.Patel, R.S.Kharsan, K.K.Deb and R.K.Mishra J.Indian Chem.Soc. 1979, 56, 263

25. R.S.Kharsan, K.S.Patel and R.K.Mishara Fresenius Z.Anal.Chem., 1979, 297, 159

26. K.S.Patel, K.K.Deb and R.K.Mishra, Bulletin Chem. Soc.Japan, 1979, 52, 595

27. K.S.Patel, R.S.Kharsen and R.K.Mishra, Proc.Indian A Acad. Sci., 1979, 88A(4), 297

28. K.S.Patel, K.K.Deb and R.K.Mishra, Separation Science and Technology, 1979, 14(4),333

29. K.S.Patel, K.K.Deb and R.K.Mishra Annali di Chimica, 1978, 68, 803.

30. K.S.Patel, K.K.Deb and R.K.Mishra, Separation Science and Technology, 1979, 14(9), 815

31. R.S.Khasan, K.S.Patel and R.K.Mishra, Journal of the Less Common Metals, 1979, 64, 155

32. K.S.Patel and R.K.Mishra, Bull.Chem.Soc.Japan, 1979 52, 592

33. R.S.Kharsan, K.S.Patel and R.K.Mishra, Fresenius Z.Anal.Chem., 1979, 295, 415.

34. I.Vgi, R.Beck and U.Fetzer., Ber., 1962, 95, 126

35. E.Beckmann, Ann. 252, 1.

36. O.Wallach, Ber.dt.Chem.Ges., 1876, 9, 1212

37. J.L.Norula, "Advanced Practical Organic Chemistry", Sultan Chand and Sons, New Delhi (1970) p318.

39. H.Zinin, J.Prakt.Chem., 1842, 27 140; C.A., 1908, 2, 2701.

40. R.Willstater and H.Kubli, Ber., 1936, 41, 198.

41. A.Lapworth and R.D.Howarth, J.Chem.Soc. 1921,770

42. C.S.Marvel and O.Kamm, J.Am.Chem.Soc., 1919 41, 276

43. H.Gillman and A.H.Blatt, "Organic Synthesis", Vol.I, 2nd Ed., John Wiley and Sons Inc., New York (1941) p445.

44. G.E.Utzinber and F.A.Regnass, Helv.Chim.Acta, 1954, 37, 1885.

45. Peirson, Bull.Chem.Soc., 1899, 21(111)780

46. E.Boyland, D.Manson and R.Nery, J.Chem.Soc., 1962, 114, 606.

47. E.Muller, D.Fries and H.Metzer, Chem.Ber, 1955, 88, 1891.

48. M.J.Murray and W.E.Water, J.Am.Chem.Soc., 1938, 60, 2818.

49, P.W.West, J.Chem.Educ., 1941, 18, 528

50. E.B.Sandell, "Colorimetric Determination of Metals", 3rd Ed., Interscience Publishers, Inc., New York, (1958) pp80-81.

51. J.Job, Compt.rend, 1928, 180, 928; W.C.Vesburgh and Cooper, J.Am.Chem.Soc, 1941, 63, 437

52. J.H.Yoe and A.L.Jones, Ind.Eng.Chem.Anal, Ed., 1944, 16 111.

53. S.P.Bag, A.B.Chatterjee, A.K.Chakrabarti and P.R. Chakrabarty, Ind.J.Chem., 1980, 19A, 1200

54. Reference 14, pp 260 - 261.

55. I.Vanders and P.F.Kers, "Mineral Recognition", John Wiley & Sons, Inc., New York, (1967) p 248.

56. M.Kuzin and N.Egorov, "Field Manual of Minerals", Mir Publishers, Moscow (1976) p.16.

57. Ref.56, p.183

58. N.Uri, Analyst, 1947, 72, 478

59. E.S.Tomula, Z.Anal.Chem., 1931, 83, 6

60. Ref.3, p.568

61. K.J.McNaught, Analyst, 1942, 67, 97

62. H.R.Marston and D.W.Dewey, Austrialian J.Exptl.Biol. Med.Sci., 1940, 18, 343

63. A.Claissen and A.Daamen, Anal.Chim.Acta, 1955, 12, 547.

64. H.Baron, Z.Anal.Chem. 1953, 140, 173

65. W.E.Nichol, Can.J.Chem., 1953, 13, 145

66. Ref. 3, p.567, Ref 51 p.414

67. G.H.Ellis and J.F.Thompson, Ind.Eng.Chem.Anal.Ed. 1945, 17, 254

68. Ref. 3, p.567

69. J.T.Woods and M.G.Mellon, Ind.Eng.Chem.Anal Ed., 1941, 13, 551.

70. T.C.J.Ovenston and C.A.Parker, Anal.Chem.Acta, 1949 3, 277.

71. W.Hacker, A.Zimmermann, and H.Rechmann, Z.Anal.Chem. 1949, 129, 104

72. Ref. 51, p.525.

73. W.B.Fortune and M.G.Mellon, Ind.Eng.Chem.Anal.Edl, 1938, 10, 60

74. I.M.Kolthoff, T.S.Lee, and D.L.Luessig, Anal.Chem. 1948, 20, 985

75. A.A.Schilt, G.F.Smith, and A.Heimuch, Anal.Chem, 1956, 28, 806

76. M.L.Moss and M.G.Mellon, Ind.Eng.Chem., Anal.Ed., 1942 14, 862

77. J.H.Yoe, J.Am.Chem.Soc.1932, 54, 4139

78. G.P.Sideris, Ind.Eng.Chem.Anal.Ed., 1942, 14, 756

79. H.W.Swank and M.G.Mellon Ind.Eng.Chem., Anal.Ed., 1938, 10, 7.

80. R.O.Scott, Analyst, 1941, 66, 142