STUDIES ON
THE SEPARATION OF HEAVY METALS

(Extraction and Spectrophotometric Determination of Cobalt, Palladium, Nickel, Bismuth, Copper, Platinum and Iron)

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Dedicated to
the living memory of my mother
Smt. Parul Sarkar

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FOREWORD

Recent advances in analytical chemistry are characterised by great progress toward more powerful methods of separation, equalling in significance the development brought about in instrumental methods of determination. Problems of chemical analysis almost always involve two steps : Separation of the desired constituent and measurement of the amount or concentration of this constituent. Much worthy research has been dedicated to the development of more discriminatory methods of estimation, such as spectrophotometric, spectrographic etc. with a view to minimizing the need for separation steps preceding the measurement step. But despite the availability of the modern, more discriminating methods of measurement, successful and effective solutions to many analytical problems depend heavily on separation processes.

Solvent extraction claims a significant position among the separation techniques because of its ease, simplicity, speed and applicability to both tracer and macro amounts of metal ions. The objective of these analytical liquid-liquid extraction procedures lies in the extrapolation to full-scale commercial hydrometallurgical processes from the technical point of view. The methods are highly operative on numerous metallurgical separation systems involving extraction from mini waste and dump leach liquors.

The present thesis is the outcome of a series of investigations carried out to study the separation and spectrophotometric determination of cobalt(II), platinum(IV), palladium(II), copper(II), Bismuth(III), Iron(II), Nickel(II), by using the anlytical reagents such as 4-nitrosoresorcinol, cetyltrimethylammoniumbromide (CTAB), Phenylthiohydantoic acid (PTHA), 2-hydroxy-1-naphthaldoxime, Cacotheline and 2-mercaptobenzoic acid. Auxiliary ligands namely iodide, bromide, pyridine and some of its methyl substituted derivatives and solvents like chloroform, benzene, carbon tetrachloride, ethylacetate were made use of during the investigatory operations.

The main aim of this thesis involves the development of analytical methods for separation and spectrophotometric determination of different heavy metals with the help of various organic reagents. Some of the methods are promising from the stand point of separation of the aforesaid metals from each other. References to the literatures survey have been presented so as to indicate, to some extent, the subject matter of each.

This thesis is divided into seven chapters. A brief chapter-wise summary of the work done is given below:

CHAPTER - I

The first chapter deals with the discussion of basic principles of solvent extraction and separation of metal ions followed by a discussion of spectrophotometry, the analytical basis adopted throughout the course of the work. The chapter ends with a brief outline of the proposed investigation and References.

CHAPTER - II

This chapter describes the use of phenylthiohydantoic acid (PTHA) as an analytical reagent for extraction, separation and spectrophotometric determination of cobalt and palladium. Cobalt forms a complex with PTHA extractable into chloroform. Absorbance of the metal complex shows a linear response over a concentration of 10 ppm of cobalt with molar absorptivity 1.123×10^4 l $mol^{-1} cm^{-1}$ at 480 nm. The system loterates a number of diverse ions. Cobalt has been estimated in synthetic mixtures using the proposed method.

The method has been compared with some other existing methods. The Pd-PTHA complex shows λmax at 370 nm with molar absorptivity 1.303×10^4 l $mol^{-1} cm^{-1}$. The method provides excellent recovery of the metal inpresence of almost all the common ions. The method has been compared with some other existing methods.

CHAPTER - III

In this chapter the use of 2-hydroxy-1-naphthaldoxime as a simple and sensitive reagent for the extraction and spectrophotometric determination of nickel, cobalt and palladium has been described.

Nickel forms a complex with 2-hydroxy-1-naphthaldoxime extractable into carbon tetrachloride. Absorbance of the metal complex shows a linear response over a concentration of 10 ppm of nickel with molar absorptivity 1.202×10^4 l $mol^{-1} cm^{-1}$ at 380 nm.

The system tolerates a number of diversions. Nickel has been estimated in synthetic mixtures using the proposed method. The method has been compared with some other existing methods.

A selective spectrophotometric method for the determination of cobalt with 2-hydroxy-1-naphthaldoxime has been devised. Beer's law is obeyed over 10 ppm of cobalt with molar absorptivity 0.826×10^4 l mol^{-1}cm^{-1} at 400 nm. The method provides excellent recovery of the metal in presence of almost all the common ions tested. The method has been compared with some other existing methods.

Palladium forms a complex with 2-hydroxy-1-naphthaldoxime extractable into chloroform. Beer's law is obeyed over 15 ppm of palladium with molar absorptivity 0.865×10^4 l mol^{-1}cm^{-1} at 400 nm. The method provides excellent recovery of the metal in presence of a large number of diverse ions tested. The method has been compared with some other existing methods.

CHAPTER - IV

This chapter describes the use of cetyltrimethylammonium bromide as an analytical reagent for the extraction and spectrophotometric determination of bismuth and copper.

Bismuth-CTAB complex shows a linear response over a concentration of 25 ppm of bismuth with molar absorptivity 0.822×10^4 l mol^{-1} cm^{-1} at 490 nm. The system tolerates a number of diverse ions. Bismuth has been estimated in synthetic mixtures using the proposed method. The method has been compared with some other existing methods.

For Cu-CTAB complex the Beer's law is obeyed over 10 ppm of copper with molar absorptivity 1.064×10^4 l $mol^{-1}cm^{-1}$ at 360 nm. The method provides excellent recovery of the metal in presence of almost all the common ions tested. The method has been compared with some other existing methods.

CHAPTER - V

This chapter includes the uses of iodide, bromide and pyridine bases as analytical reagents for the extraction and spectrophotometric determination of palladium, platinum and copper.

Palladium forms a complex with potassium iodide and pyridine bases extractable into chloroform. Beer's law is obeyed over 1-10 ppm of palladium with maximum absorbance at 354-365 nm. The method provides excellent recovery of the metal in presence of almost all the common ions tested. The method has been compared with some other existing methods.

Platinum forms complex with KI and pyridine bases extractable into chloroform. Beer's law is obeyed over 5-50 ppm of platinum with

λ_{max} at the region 345-485 nm. The system tolerates a number of diverse ions. Platinum has been estimated in synthetic mixtures using the proposed method. The method has been compared with some other existing methods.

A selective spectrophotometric method for the determination of copper with potassium bromide/potassium iodide and pyridine bases has been devised. Beer's law is obeyed over 5-50 ppm of copper with λ_{max} at 320-360 nm. The method provides excellent recovery of the metal in presence of almost all the common ions tested. The method has been compared with some other existing methods.

CHAPTER - VI

This chapter describes the use of 2-mercaptobenzoic acid as an analytical reagent for spectrophotometric determination of palladium.

The Pd(II)-2-mercaptobenzoic acid complex showed λ_{max} at 420 nm. The system conforms to Beer's law over 10 ppm of palladium with molar absorptivity 1.725×10^4 l $mol^{-1}cm^{-1}$. Palladium has been estimated in synthetic mixtures using the proposed method. By this method, the interferences of most of the diverse ions were overcome and this has been compared with some other existing methods.

CHAPTER - VII

A spectrophotometric method for the determination of iron(II) with Cacotheline has been presented.

The absorbance of the Fe(II)- Cacotheline complex was measured at 530 nm. The system conforms to Beer's law over 2-50 ppm of iron with molar absorptivity 1.49×10^3 l $mol^{-1} cm^{-1}$. The method provides excellent recovery of the metal in presence of almost all the common ions tested. The method has been compared with some other existing methods.

Many obviously inferior reagents and methods are included since the treatment of the subject is intended to be complete. Their inclusion is justified because of two considerations : in future no time need be lost in attempting analytical methods that in the past have been demonstrated as unsatisfactory; and further, an inferior method may, with suitable modifications, be made useful for certain other purposes.

CHAPTER - I

INTRODUCTION

Part I

General Discussion on Solvent-Extraction:

Solvent or liquid-liquid extraction is a technique in which a solute is allowed to distribute itself in a certain ratio between two immiscible solvents, one of which is usually water and the other an organic solvent. It is necessary to clarify the fundamental principles of extractions particularly the various terms used for expressing the effectiveness of a separation.

Partition Coefficient:

An analytical chemist is particularly interested in the aqueous-organic solvent pair since he is concerned with the analysis of the element present in the aqueous phase. If a solute is allowed to dissolve within two immiscible or sparingly miscible solvents, the species is shared between the two layers in such a way that the ratio of concentration of the solute in the two phases at equilibrium at a particular temperature remains constant, provided that the species will have the same molecular weight in both the phases. This ratio is called the distribution or partition coefficient (K_D). Thus for aqueous and organic systems,

$$K_D = \frac{\text{Metal ion Concentration in Organic Phase}}{\text{Metal ion Concentration in Aqueous Phase}} \quad \ldots (1)$$

The law, as stated, is not thermodynamically rigid but is a useful approximation (e.g., it takes no account of the activities of the various species, and for this reason it would be expected to apply in very dilute solution, where the ratio of the activities approaches unity).

When the case is ideal, the species shares itself between the two phases in the ratio of its solubilities. Of course, it also depends upon other factors like acid concentration and extraction of molecular species.

<u>Distribution ratio or Extraction Coefficient (D):</u>

In the solvent extraction technique the primary interest of analysts lies in the fraction of the total solute in one or other phase, quite regardless of its mode of dissociation, association or interaction with other dissolved species. Hence it is required to introduce a reliable quantity to describe the extraction, known as the distribution ratio (D).

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

For a given metal M, present as various species M_1, M_2, M_3 ... M_n and partitioned between an organic phase and an aqueous phase, the extraction can be expressed as

$$D = \frac{[M_1]_{org} + [M_2]_{org} + [M_3]_{org} + \cdots + [M_n]_{org}}{[M_1]_{aq} + [M_2]_{aq} + [M_3]_{aq} + \cdots + [M_n]_{aq}} \quad \ldots (3)$$

In case of polynuclear species, their concentrations are multiplied by the appropriate stoichiometric co-efficient. D and K_D are equal when there is no reaction between the species and other components in either phase.

Percentage extraction:

For analysts, percentage extraction (% E) is more important than the distribution ratio. These two factors are related as follows:

$$\%E = \frac{100\ D}{D + [V_{aq} / V_{org}]} \quad \ldots (4)$$

V_{aq} and V_{org} stand for the volumes of the aqueous and organic phases respectively. On simplification this equation becomes,

$$D = \frac{V_{aq}}{V_{org}} \left[\frac{E}{100-E} \right] \quad \ldots (5)$$

Where E is percentage extraction. When the volume of the organic phase is equal to the volume of aqueous phase

$$D = \frac{E}{100-E} \qquad \ldots (6)$$

When E approaches from 99 to 100%, the distribution ratio varies from 99 to infinity.

Multiple extraction :

The main object of an analyst in the process of extraction is to separate the metal component quantitatively by a single extraction from a mixture of solution. When hundred per cent extraction is not possible by one step single extraction, multiple extraction is applied.

Thus if a fraction L_A of a substance A left after extraction of volume V_{aq} of aqueous phase with n successive portions of organic solvent having each of volume V_o, then

$$L_A = \left[\frac{V_{aq}}{V_{aq} + V_o D} \right]^n \qquad \ldots (7)$$

For rapid and complete extraction, the distribution ratio (D) must be of very high values. In the above system, the partition isotherm is assumed to be linear i.e., $[A_o] / [A_{aq}] = D$

which remains constant for any value of $[A]$. To achieve good results V_o should be low and n should be of high value.

Separation Factor :

The term separation factor (β), is required to be introduced when the solution contains two species A and B. The separation factor (β) is related to their individual distribution ratios. It can be shown as,

$$\beta = \frac{[A]_o / [B]_o}{[A]_{aq} / [B]_{aq}} = \frac{[A]_o / [A]_{aq}}{[B]_o / [B]_{aq}} = \frac{D_A}{D_B} \quad \ldots (8)$$

where $[A]_o$, $[B]_o$ are the concentrations of A and B in the organic phase and $[A]_{aq}$, $[B]_{aq}$ are the concentrations of A and B in the aqucues phase.

Complete separation can be achieved when one of the distribution ratios is very small and the other relatively large. If the separation factor is unity, it will be very difficult to separate as the two distribution ratios are equal. In such cases, separation is generally carried out by using counter current extractions.

Classification of Extraction systems :

Various classification of extraction systems have been made but are admittedly arbitrary, since a particular system under certain conditions may be grouped under more then one class. The best compromise might be to classify the systems in terms of the types of chemical compound involved. Such a classification might be:

Uncharged covalent species
Simple molecules e.g., I_2, $HgCl_2$, C_6H_5COOH,
Chelate complexes e.g., aluminium oxinate.

Uncharged electrovalent (ion association complexes)
Halometallic acids, e.g., HF_eCl_4
Amine-anionic complex compounds e.g., $R_3NH^+.FeCl_4^-$
Metal-acid ester complexes e.g., $La(DEHP)_3$
Solvated acids and salts e.g., HNO_3-TBP;
$VO_2(NO_3)_2(TBP)_2$.
Non-solvated salts e.g., $(C_6H_5)_4AS^+.FeCl_4^-$
(DEHP = di-2-ethyl hexyl phosphate;
TBP = tributyl phosphate).

From the view point of theoretical discussion such classifications are meant convenient. For practical purpose, however, it will be more useful to classify according to the type of reagent used, so that the possibilities for separation, etc. can be more easily seen.

Extraction Process :

Thus the main aspects of extraction process are:

(1) Uncharged complex formation.

(2) Distribution of such complex between the two liquid phases.

(3) Interaction of the complex in the organic phase.

Unchargedcomplex formation depends upon several factors.

The complex may be of different types as (i) simple coordination complex, chelate complex or (ii) as ion association complex.

(i) $M^{+n} + nR^{-} \rightleftarrows MR_n$ (co-ordination) ... (9)

Where M^{+n} = n-valent cation and R^{-} = anion of the suitable chelating or coordinating agent.

Examples : Germanium tetrachloride (simple co-ordination complex),

Gallium 8-quinolinate (chelate)

(ii) An ion association complex is formed by co-ordination in either the cation or the anion of the extractable ion pair.

$$M^{n+} + bB \rightleftarrows MB_b^{n+} \text{ (Ion-association)}$$

$$MB_b^{n+} + nX^{-} \rightleftarrows (MB_b^{n+} , nX^{-}) \quad ... (10)$$

Example : $[(C_6H_5)_4P^+, Cl^-]$

$$M^{n+} + (n + a)X^- \rightleftharpoons MX_{n+a}^{a-}$$

$$MX_{n+a}^{a-} + ay^+ \rightleftharpoons (ay^+, \; MX_{n+a}^{a-}) \text{ (Ion-association)}$$

... (11)

Example : $[H^+, FeCl_4^-]$

The stability of a metal coordination complex depends on (a) the acidity of the metal ion (b) basicity of the coordination ligand and (c) special factors related to the configuration of the resultant complex. In the simple co-ordination complex the mono-functional ligands take part and in the chelate complex poly-functional ligands are acting that occupy more than one position in the coordination sphere. The chelate complexes are mostly soluble in organic solvents and hence used in the process of extraction. These chelates are either five or six-membered rings. They may be classified as follows:

(i) Positively charged chelates having requisite number of uncharged basic groups of the ligand e.g., Tris (ethylenediamine)-Iron (II).

(ii) Chelates having are anionic and are uncharged basic group of the ligand i.e., neutral chelates e.g., Nickel dimethyl glyoximate.

(iii) Negatively charged chelates having negatively charged basic group of the ligand e.g. Alizarin derivative of Iron (III).

Ion-association complexes e.g., $[(C_6H_5)_4As^+, ReO_4^-]_2$ are easily extractable in organic solvents like chloroform, benzene etc. The extent of ion-association depends on ionic size of the salt involved and also on other structural factors.

(2) In the second stage of extraction, the chelate complex or ion-association complex is distributed uniformly in the solvent depending upon their solubilities.

(3) The third stage is the interaction of the complex in the organic phase. The chelates are not generally interacting with the solvent. In case of ion-association complexes, polymerisation (when concentration increases) and dissociation (in case of dilute solution) should be considered.

Methods of extraction:

In the analytical laboratory the following three methods of liquid-liquid extractions are in use. They are:

a) Batch extraction
b) Continuous extraction
c) Discontinuous extraction

a) Batch extraction is the simplest method of extraction and is useful when the distribution ratio is large. In this method a given volume of metal salt solution is extracted with a given volume of the organic solvent in a separating funnel by mechanical shaking until equilibrium is attained, and the two layers are then separated. After separation the metal in each phase is estimated.

b) This method of extraction is applied in the case when distribution ratio is small. Here an immiscible solvent flows continuously or both phases are allowed to pass through the solution in counter-current direction.

c) Craig[1] has used this technique for rapid separation and applied in fractionation of organic compounds having similar distribution ratios.

Techniques in extractions :

(i) Organic solvent :

The choice of solvent in the extraction procedure depends on many factors, mainly the solubility of the particular species to be extracted.

(ii) Analysis :

The amount of solute present in both the phases after extraction can be determined in various ways. One important method is back extraction of solute from organic phase with water or acid followed by analysis. Another method consists of direct evaporation of organic solvent when the solvent is volatile and then estimation of the solute. If the solvent is not very volatile, it may be removed by heating with concentrated nitric and perchloric acids followed by estimation. Most recently the estimation of the organic phase may be carried out by radiometric method[2].

(iii) Selectivity :

The selectivity of an extraction system increases by using oxidising or reducing agents. For example, Chromium (III) is not extracted with diphenyl carbazide but chromium (IV) can be extracted from its solution. Sometimes suitable marsing agents such as cyanide, citrate, tartrate, EDTA etc. are also useful to prevent extractions of undesired element.

(iv) Salting-out agent :

Salting-out agents may also play an important role in enhancing the extent of extraction, especially in case of ion-association complexes. The most widely used salting out agents are chlorides and nitrates of ammonium, sodium, magnesium etc. This is probably due to high concentration of the complexing ion supplied by the salting-out agents.

Some Practical Considerations :

Solvent extraction is generally employed in analysis to separate a solute (solutes) of interest from substances which interfere in the ultimate quantitative analysis of the material; sometimes the interfering solutes are extracted selectively. The choice of solvent is governed by the following consideration:

(i) A high distribution ratio for the solute and a low distribution ratio for undesirable impurities.

(ii) Low solubility in the aqueous phase.

(iii) Sufficiently low viscosity and sufficient density differences from the aqueous phase to avoid the formation of emulsion.

(iv) Low toxicity and inflammability.

(v) Ease of recovery of solute from the solvent for subsequent analytical processing. Thus the b.p. of the solvent and the ease of stripping by chemical reagents merits when a choice is possible. Sometimes mixed solvents may be used to improve the above properties. Salting out agents may also improve extractability.

Stripping :

Stripping is the removal of the extracted solute from the organic phase for further preparation for the detailed analysis.

In many colorimetric procedures involving an extraction process the concentration of the desired solute is determined directly in the organic phase by measuring the absorbance of a known volume of the solution of the coloured complex.

Where other methods of analysis are to be employed or where further separation steps are required, the solute must be removed from the organic phase to a more suitable medium. If the organic solvent is volatile the simplest procedure is to add a small volume of water and evaporate the solvent on a water bath; care should be taken to avoid loss of a volatile solute during the evaporation. Sometimes adjustment of the pH of the solution, change in valence state, or the use of competitive water-soluble complexing reagents may be employed to prevent loss of the solute. When the extracting solvent is non-volatile the solute is removed from the solvent by chemical means, e.g., by shaking the solvent with a volume of water containing acids or other reagents, whereby the extractable complex is decomposed. The metal ions are then quantitatively back-extracted into the aqueous phase.

Back-Washing :

Impurities present in the organic phase may sometimes be removed by back-washing. The organic extract when shaken with one or more small portions of a fresh aqueous phase containing the optimum reagent concentration and of correct pH will result in the redistribution of the impurities in favour of the aqueous phase, since their distribution ratios are low; most of the desired elements will remain in the organic layer.

Completion of the analysis :

Having separated a particular element or substance by solvent extraction, the final step involves the quantitative determination of the element or substance of interest. Simple colorimetric or better, spectrophotometric methods may be applied directly to the solvent extract utilising the absorption bands of the complex in the ultraviolet or visible region. A typical example is the determination of nickel as dimethylglyoximate in chloroform by measuring the absorbance of the complex at 366 nm.

With ion-association complexes, improved results can often be obtained by developing a chelate complex after extraction. An example is the extraction of uranyl nitrate from nitric acid into tributyl phosphate and the subsequent addition of dibenzoylmethane to the solvent to form a soluble coloured chelate.

Further techniques which may be applied directly to the solvent extract are flame spectrophotometry and atomic absorption spectrophotometry. An example of the former technique is the determination of copper as the salicylaldoxime complex in chloroform; the organic extract is sprayed directly into an oxyacetylene flame and the spectral emission of copper at 324.7 nm is measured.

Recent Developments :

1. Synergism : The term synergism was first coined by Blake etal[3] in 1958 in their report that when a dialkyl hydrogen phosphate $(RO)_2PO.OH$, is used in conjunction with certain neutral organophosphorous reagents, e.g., TBP, the extracting power of the mixture exceeds the sum of the extracting powers of its components. This phenomenon of greatly enhanced extraction of synergism due to a mixture of extractants has attracted considerable attention in recent years. The review articles by Marcus[4] and De[5] are of interest in this connection.

Synergic systems :

The most intensively studied systems are of the following types : (1) a chelating agent such as HTTA or IPT(-isopropyl-tropolane) and a solvating solvent such as TBP, IBMK (isobutylmethyl ketone), DBSO (dibutyl sulphoxide) and (2) a dialkyl phosphoric acid and a neutral organophosphorous ester(s).

Chelating agent-solvating solvent system :

Considerable work has been done in this area. Irving and Edgington[6] postulated that the conditions for synergic extraction are:

(a) one of the active reagents (HX) should be able to neutralise the charge on the metal ion, preferably by forming a chelate.

(b) the solvent(s) should display any residual coordinated water from the neutral metal complex, rendering it less hydrophilic.

(c) the solvent(s) should not itself be hydrophilic and coordinated less strongly than HX.

(d) the maximum coordination number of the metal and the geometry of the ligands should be favourable.

These postulates were valid for the U(VI)-HTTA-TBP and U(VI)-HTTA-TBPO (tributylphosphine oxide) mixtures, synergic enhancement factors of the order of 10^3 and 10^4 respectively were observed. The extracted species were assigned the composition UO_2X_2.TBP and UO_2X_2.(TBPO)$_3$ respectively[7-9], from isopiestic and infrared measurements. The studies were extended to plutonium (VI), americium (III), europium(III) and thorium and the species identified were PuX_3.(TBP)$_2$, AmX_3.(TBP)$_2$, AmX_3.TBPO, $ThX_3(NO_3)$.TBP and $ThX(NO_3)_3$.TBPO.

Healy[10] reported an synergic extraction of uranium (VI), thorium, lanthanides(III), actinides(III) and alkaline earth metals with HTTA-TBP, HTTA-TBPO and HTTA-TPP; TPP is triphenyl phosphate.

Healy[11] further suggested that the reaction for the system uranium (VI)-HTTA-S can be expressed as :

$$UO_2^{2+} + 2HTTA + xS = UO_2(TTA)_2S_x + 2H^+ \qquad \ldots (12)$$

Sekine and Dyrssen[12-17] have reported extensive investigations on solvent extraction of metal ions with mixed ligand. They have described the adduct formation of Cu(II), Zn, Eu(III) and Th with HTTA and TBP or IBMK and with IPT and TBP or IBMK in chloroform and carbon tetrachloride.

Dialkylphosphoric acid (HX)-neutral phosphorous ester(s):

Important cases in this category are : di(2-ethyl-hexyl) phosphoric acid (HDEPH)-TBP, which was the first reported case of synergic extraction[3,18,19]; mono (2-ethylhexyl) phosphoric acid (H_2MEHP)-TBP[20]; dibutyl phosphoric acid (HDBP)-TBP[21] and HDBP-TOPO[22].

Peppard et al[20] investigated the system lanthanide(III), Y(III), Am(III), Cm(III), Th, U(VI)-H_2MEHP-S-diluent, where the synergic agent S was n-decanol, TBP or TOPO and the diluent was toluene, cyclohexene or n-decanol.

Substoichiometric extraction :

Ruzicka and Stary[23,24] first proposed this new technique of substoichiometric extraction and determination of metals, which is applicable to activation analysis and isotope dilution analysis.

In all conventional extraction separation procedures, an excess of the organic reagent is usually used to ensure quantitative separation of the desired metal. In substoichiometric method the organic reagent is added in less than the stoicheiometric amount required for the metal to be determined. By using the same amounts of organic reagent every time, it is possible to isolate always the same amount of the element in question irrespective of the amount of it actually present (subject to the condition that this must be an excess relative to the amount of extractant). This permits highly selective separations. The treatment is essentially that developed by Ruzicka and Stary[23,24].

Liquid Ion-Exchangers:

The use of ligand ion-exchange dates back to 1948 when Smith and Page[25] reported that high molecular weight amines (HMWA) can be used for extraction of acids because their acid salts are insoluble in water but readily soluble in organic solvents such as chloroform, benzene or kerosene :

$$R_3N_{org} + H^+_{aq} + A^-_{aq} \rightleftharpoons R_3NH^+A^-_{org} \text{ (extraction)} \quad \ldots (13)$$

where A^- = anion of simple acid or complex metal acid e.g., $FeCl_4^-$, and $R_3NH^+A^-_{org} + B^-_{aq} \rightleftharpoons R_3NH^+B^-_{org} + A^-_{aq}$ (anion exchange) The amine salt[13] can undergo anion-exchange with an anion (B^-) in the aqueous phase. The order of preference in the organic amine solution is similar to that in anion-exchange resins.

$$ClO_4^- > NO_3^- > Cl^- > HSO_4^- > F^-$$

The earlier work for liquid anion-exchangers (HMWA) has been reviewed by Moore, Green and Prabhu[26-29].

Reversed-phase Partition Chromatography :

In reversed-phase partition chromatography the organic extractant is immobilized on some stationary inert support such as kieselguhr, styrenedivinylbenzene copolymer or simply filter paper. The technique was introduced by Fidelis and Siekierski[30] for the separation of the lighter rare earth on columns of kieselguhr impregnated with TBP, 15 M nitric acid being used as the mobile phase. They extended their work[31] to the heavier rare earths, which are usually difficult to seperate. Fair separations were achieved with 11.5 M , 12.3M and 13 M nitric acid and concentrated hydrochloric acid as the mobile phases.

Combined Ion-Exchange-Solvent Extraction (CIESE) :

Korkisch[32] presented a novel separation technique, viz., combined ion-exchange solvent extraction (CIESE). This is based on simultaneous operation of ion-exchange and solvent extraction.

Ternary Complexes

Betteridge and West[33] described the selective extraction of microgram amounts of dibutylamine silver(I) with an ion-association complex (or ternary complex) with salicylic acid. Dagnall and West[34] described the extraction of a blue ternary complex Ag(I)-1,10-phenanthroline-Bromopyrogallol Red-as the basis of an extremely sensitive spectrophotometric procedure for trace of silver.

Ternary complexes have been reviewed by Babko[35].

Extraction from molten salts

The oldest examples of extractions of solutes from molten salts are the removal of impurities by slag formation in metallurgy, the fire-assay method for separation of gold. None of these is particularly useful in solvent extraction chemistry, although a process akin to slagging was used to remove fission products from rreactor fuel by extraction with magnesium chloride[36,37] according to the reaction (for a tetravalent metal such as a lanthanide).

$$2M_{(m)} + 3MgCl_{2(s)} \rightleftharpoons 2MCl_{3(s)} + 3Mg_{(m)} \quad \ldots (14)$$

where the subscripts (m) and (s) denote the metal and salt phases, respectively.

The use of organic solvents in conjunction with molten salt was reported by Gruen and co-workers[38]. Marcus[39] has given an excellent review of this extraction from molten salts.

Extractive titrations and indicators

Solvent extraction can be used in titrations either simply to provide indication of the end point, or for doing the titration itself. The classic example of end-point detection is the use of carbontetrachloride in the Andrews titration to indicate the complete oxidation of iodine to iodine(I).

Programme of work with iron, cobalt, platinum, copper, palladium, nickel and Bismuth

Numerous methods on spectrophotometric determination of iron, cobalt, platinum, copper, palladium, nickel and Bismuth are available in the literature. Further attempt has been made to apply this technique for the spectrophotometric method of these elements, where the methods are simple.

The basic points of the scheme are:

(i) Review of the literature on spectrophotometric methods of these metals and on their separation from mixtures.

(ii) Choice of appropriate reagents for obtaining suitable complexes and also of solvents.

(iii) Studies on the behaviour of these complexes towards different solvents and an attempt to devise a suitable technique for extraction and separation.

(iv) Actual experiments on extraction and separation.

Throughout the investigation effort has been put to minimise the wastage of chemicals, time and power and to prevent the loss of the precious metals.

Part II

Absorptiometry and Spectrophotometry : Analytical Basis

The colorimetric analysis is based on the variation of the colour of a system with change in concentration of some component. The colour displayed is due to the formation of a coloured compound by the addition of a suitable reagent or it may be inherent in the desired constituent itself. The intensity of the colour may then be compared with that obtained by treating a known amount of the substance in the same manner.

Colorimetry is concerned with the determination of the concentration of a substance by measurement of the relative absorption of light with respect to a known concentration of the substance. In visual colorimetry, natural or artificial white light is normally used as a light source, and determinations are carried out with a simple instrument called a colorimeter or colour comparator. When the eye is replaced by a photoelectric cell (thus largely eliminating the errors due to the personal characteristics of each observer) the instrument is termed a photoelectric colorimeter. This instrument is also known as filter photometer because it is employed with light contained within a comparatively narrow range of wavelengths furnished by passing white light through filters, i.e., materials in the form of plates of coloured glass, gelatin, etc., transmitting only a limited spectral region.

In spectrophotometric analysis a source of radiation is used that extends in to the ultraviolet region of the spectrum. From this, definite wavelengths of radiation are chosen possessing a bandwidth of less than 1 nm. This process necessitates the use of a more complicated and consequently more expensive instrument. The instrument employed for this purpose is a spectrophotometer, and this instrument is really two instruments in one cabinet- a spectrometer and a photometer.

Molecules or atoms which absorb radiation characteristically may be determined or studied by measurement of light absorbed. Light from a suitable source is allowed to pass via an optical system, that isolates a narrow band of wavelengths, through a homogeneous absorbing medium.

The layer is usually planer, liquids and vapours being enclosed in cylindrical or rectangular cells. The intensity of the radiation transmitted by the medium, I is compared with the incident intensity, Io, by allowing each in turn to pass to a suitable detector. Since cells and solvents may absorb radiation, and to compensate also for reflection and similar optical effects from the cell faces, a matched cell containing only the solvent medium is interposed in the beam during the measurement of Io. The detection is often a photoelectric cell (photo cell) sensitive in the required wave length region and forms part of the photometric device which measures the intensity. Since the detector response is related to the radiant energy falling upon it, the instrument normally measures a ratio of the two intensities, I/I_O, termed the transmittance, T. The detection signal may be amplified and presented in various forms, such as percentage transmittance (100T) or 100 I/Io or absorbance, A(-log T).

Two important properties are concerned in absorption measurements, wave length and degree of absorption. The wave length at which absorption occurs are determined by the energy difference, ΔE, between the upper and lower energy states of each possible transition of the molecule (or atom) concerned.

The degree of absorption is expressed by means of an experimentally measured absorptivity per unit quantity of substance. This is termed the extinction co-efficient and is defined by means of Beer-Lambert law. This law is a combination of two absorption laws, which may be stated in a variety of ways.

Lambert's (or Beer's) law deals with optical path length. The law states that the intensity of the emitted monochromatic light decreases exponentially as the thickness of the absorbing medium increases arithmetically or that any layer of given thickness of the medium absorbs the same fraction of the light incident upon it. The law can be expressed as:

$$I = Ioe^{-kl}$$

Where Io = intensity of the incident light falling upon an absorbing medium.

l = thickness of the absorbing medium.

I = intensity of the transmitted light.

k = a constant for the wave length and the absorbing medium.

e = the natural logarithm base.

Rearranging the above equation,

$$\ln Io/I \text{ or } 2.303 \log Io/I = kl$$

$$\text{or} \quad \log Io/I = kl/2.303$$

$$\text{or} \quad \log Io/I = Kl$$

Where K = k/2.303 and is termed the extinction co-efficient or absorbance index. Its value is characteristic at a given temperature for a pure homogeneous liquid or solid, provided it exhibits no directional absorption properties, but not for a gas or solution in which the number of molecules per unit thickness varies with pressure or concentration.

Beer's law deals with concentration. It states that the intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically. The solvent is assumed to be non absorbing, in the simplest case. This can be written in the form,

$$I = Ioe^{-kc}$$

For general use the two laws are combined and using the above mathematical treatment the Beer-Lambert law may be expressed in the form,

$$\text{Log} \quad Io/I = k'Cl$$

$$\text{or } A = k'Cl$$

Where c is the concentration of the absorbing substance as solute, l is the thickness and k', the extinction co-efficient, is a combination of constants. The property log Io/I is linearly related to concentration and path length and is termed the absorbance A; it is also known as the optical density (D).

The Beer-Lambert law is the basis of accurate analytical absorptiometry and spectrophotometry at all wave lengths. Both laws are held to be generally valid, though kortum considered Beer's law to be limiting law, valid only at low concentrations.

For matched cells (i.e., l constant) the Beer-Lambert law may be written as,

$$C \propto \log \frac{Io}{I}$$

$$\text{or } C \propto \log \frac{1}{T} \quad \left[\text{where } T = \text{transmittance} \right]$$

$$\text{or } C \propto A$$

Hence by plotting A (or $\log \frac{1}{T}$) as originate, against concentration as abscissa, a straight line will be obtained and this will pass through the point C = 0, A = 0 (T = 100%). This calibration line may then be used to determine unknown concentrations of solution of the same material after measurement of absorbances.

Extinction co-efficient or absorptivities :

From Beer's law we have,

$$A = k'Cl$$

The numerical value of k' depends on the units chosen for expressing C and l in the above equation. The intensity units are immaterial and l is always in cm units. If the concentration is expressed in moles per litre, the constant is known as molar or molecular extinction co-efficient (European system) or molar absorptivity (U.S. system) and is written as ϵ, giving the form,

$$A = \epsilon Cl$$

Deviation from Beer's law:

Beer's law will generally hold over a wide range of concentration if the structure of the coloured ion or of the coloured non-electrolyte in the dissolved state does not change with concentration. Small amount of electrolytes, which do not react chemically with the coloured components, do not usually affect the light absorption; large amounts of electrolytes may result in a shift of the maximum absorption and may also change the value of the extinction co-efficient. Discrepancies are usually found when the coloured solute ionises, dissociates or associates in solution, since the nature of the species in solution will vary with the concentration. The law does not hold when the coloured solute forms complexes, the composition of which depends upon the concentration. Also discrepancies may occur when monochromatic light is not used. The behaviour of a substance can always be tested by plotting log Io/I or log T against the concentration : a straight line passing through the origin indicates the conformity to the law.

<u>Some aspects of Colorimetric Determination</u> :

The choice of a colorimetric procedure for the determination of a substance will depend upon such considerations as the following:

1. A colorimetric method will often give more accurate result at low concentrations.

2. The method may frequently be applied under conditions when no satisfactory gravimetric or titrimetric procedure exists.

3. Speed and rapidity, provided the experimental conditions are rigidly controlled to avoid any serious sacrifice of accuracy.

   The criteria for a satisfactory colorimetric analysis are:

   (a) Specificity of the colour reaction

   (b) Proportionality between colour and concentration

(c) Stability of the colour
(d) Reproducibility
(e) Clarity of the solution
(f) High sensitivity.

Proposed Investigation :

Most of the available extraction spectrophotometric methods for the determination of cobalt, palladium, nickel, bismuth, copper, platinum and iron are based on colour-forming reactions with various reagents - mostly organic. In majority of cases, after separation, determinations were carried out by measuring the absorption of the coloured metal complexes in the visible region. Methods based on such colour-forming reactions are always found to be dependent on various factors i.e., the pH of the medium, the reagent concentration, stability and extractability of the coloured complex as also the absorption of the reagent itself.

In the proposed investigation the above mentioned metal ions in micro quantities are made to react with a suitable ligand or ligands to give complexes in the form of coloured precipitates. The precipitates are readily soluble (except cases in Chapter VI and VII where determination procedures are accomplished using aqueous solutions) and extractable in certain immiscible organic solvents. The complexes in organic solvents or in aqueous medium absorb considerably in the visible region and conform to Beer's law for a fairly wide range of metal ion concentration. Further, the solubility and the intensity of the colour systems are found satisfactorily high. Measurement of absorbance of the coloured extract at the wave length recording maximum absorption, has made possible development of new spectrophotometric methods for determination of the metal ions under investigation.

REFERENCES

1. Craig L.C. and Craig D., Technique of organic chemistry. Wissenberger A., Interscience publishers Inc., New York, Vol. 3, Part I, 1953.
2. Sandell E.B., Colorimetric determination of traces of metals, Interscience publishers Inc., New York, 1950.
3. Blake C.A., Bases C.F. Jr., Brown K.B., Culeman C.F. and White J.C., Proc. 2nd intern. Conf. Peaceful Uses At. Energy, Geneva, 1958, 28, 289.
4. Marcus Y., Chem. Rev., 1963, 63, 139.
5. Dey A.K., J. Sci. Ind. Res. (India), 1965, 24, 82.
6. Irving H. and Edington D.N., J. Inorg. Nucl. Chem., 1961, 20, 314, 321.
7. Irving H., and Edington D.N., Proc. Chem. Soc., 1959, 360.
8. Irving H. and Edington D.N., Chem. Ind., London, 1961, 77.
9. Irving and Edington D.N., J. Inorg. Nucl. Chem., 1960, 15, 158.
10. Healy T.V., J. Inorg. Nucl. Chem., 1961, 19, 314, 328.
11. Healy T.V. and Ferraro J.R., J. Inorg. Nucl. Chem., 1962, 24, 1449, 1403.
12. Sekine T. and Dyrssen D.J., J. Inorg. Nucl. Chem., 1964, 24, 1727.
13. Sekine T. and Dyrssen D.J., J. Inorg. Nucl. Chem., 1964, 26, 2013.
14. Sekine T. and Dyrssen D.J., J. Inorg. Nucl. Chem., 1967, 29, 1457.
15. Sekine T. and Dyrssen D.J., J. Inorg. Nucl. Chem., 1967, 29, 1475.

16. Sekine T. and Dyrssen D.J., J. Inorg. Nucl. Chem., 1967, 29, 1481.

17. Sekine T. and Dyrssen D.J., J. Inorg. Nucl. Chem., 1967, 29, 1489.

18. Blake C.A., Horner D.E. and Schmitt J.M., Nucl. Sci. Abstr., 1959, 13, 8345.

19. Sato J., J. Inorg. Nucl. Chem., 1964, 26, 311.

20. Mason G.W., McCarty S. and Pappard D.F., J. Inorg. Nucl. Chem., 1962, 24, 967.

21. Dyrssen D. and Kuca L., Acta Chem. Scand., 1960, 14, 1945.

22. Kennedy J. and Dean A.M., U.K. At. Energy Res. Estab., 1960, 3410.

23. Ruzicka J. and Stary J., Talanta, 1961, 8, 228.

24. Ruzicka and Stary J., Talanta, 1963, 10, 287.

25. Smith E.L. and Page J.E., J. Soc. Chem. Ind., 1948, 67, 48.

26. Moore F.L., U.S. At. Energy Comm. Rept NAS-NS, 1960, 3101.

27. Moore F.L., Anal. Chim. Acta., 1962, 25, 345.

28. Green H., Talanta, 1964, 11, 1561.

29. Prabhu A.R. and Khopkar S.M., J. Sci. Ind. Res. India, 1970.

30. Siekierski S. and Fidelis I.J., J. Chromatog., 1960, 4, 60.

31. Fidelis I. and Siekierski S.J., J. Chromatog., 1961, 5, 161.

32. Korkisch J., Separation Science, 1966, 1, 159.

33. Betteridge D. and West T.W., Anal Chim. Acta, 1962, 26, 101.

34. Dagnall R.M. and West T.S., Talanta, 1964, 11, 1533, 1627.

35. Babko A.K., Talanta, 1968, 15, 721.

36. Wiswall R.H., Egan S.S., Ginell W.S., Miles F.T. and Powell J.R., Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva, 1958, 17, 421.

37. Dwyer O.E., Eshaya A.M. and Hill F.B., Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva, 1958, 17, 428.

38. Green D.M., Friend S., Graf P. and Mcbeth R.L., Proc. 2nd Intern. Conf., Peaceful Uses At. Energy, Geneva, 1958, 28, 112.

39. Marcus Y., Solvent Extraction Chemistry, Eds. Dryssen D., Lilyinzin J.O. and Rydberg J., North Holland, Amsterdam, 1967, p. 555.

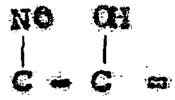
CHAPTER - II

PHENYLTHIOHYDANTOIC ACID AS AN ANALYTICAL REAGENT

The compound, phenylthiohydantoic acid (PTHA) dates back to 1905 when Pozzil-Escot[1] first suggested its use as a qualitative reagent for colbalt. Gutzeit[2] used this compound as a reagent for nickel. Willard and Hall[3] studied the reaction of phenylthiohydantoic acid with solutions of cobalt salts. But the analytical potentiality of the compound has not been discussed so far. In our laboratory it has been noted that PTHA gives coloured complexes with cobalt and palladium. The resulting complexes are extractable into organic solvents under optimum conditions. This properties of the complexes suggested that further studies might lead to the development of methods for separation and spectrophotometric determination of the metals.

Extraction and Spectrophotometric determination of Cobalt with phenylthiohydantoic acid

Introduction

Cobalt forms a variety of mixed complexes with the ligends NH_3, P_y, H_2O, halides, SCN^-, NO_3^-, $CO_3^=$, etc. The most sensitive spectrophotometric methods for the determination of cobalt have been made by the utilization of its colour reaction with the reagents containing  $=\overset{NO}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}=$ group. Cobalt (II) was extracted[4] as the thiocyanate complex at pH 0-4 in presence of citric acid with acetylacetone. The absorbance of the organic extract was measured at 625 nm. If manganese and chromium are present they should be removed by ion-exchange method first. The red complex of cobalt with sodium 4-nitroso-2-hydroxynaphthalene-3,6-disulphonate[5] has been investigated. The complex is stable in acid solution. The metal : ligand ratio was found to be 1:3.

Cobalt from coloured complex with 1-nitroso-2-naphthal[6] at pH 3.5-8.0 which can be extracted into carbontetrachloride. 2-nitroso-1-napthol[7] also gives colour reaction with cobalt. At pH 3-4, in the presence of citrate and hydrogen peroxide the complex was extractable into chloroform and measured at 530 nm.

Lorenzo et al[8] determined cobalt at 550 nm after oxidation to Co^{+3} with alk.H_2O_2 as its 1:2 complex with 1,6-hexanediamine tetra acetic acid at pH 9.5.

Nakashima et al[9] presented a method for the determination of cobalt using 6-amino-2-benzylthio-5-nitroso-4-oxo-3,4-dihydropyrimidine. The yellow complex was extractable into chloforom. The metal : ligand ratio was found to be 1:3. The absorbance was measured at 410 nm.

Rodrignes et al[10] selectively determined Co^{+2} as its complex with chromotropic acid dioxime in ammoniacal solutions spectrophotometrically at 560 nm.

Caseir Laino et al[11] spectrophotometrically determined Cobalt by using ethylene diamine-N-N'-dipropionic acid at the pH 8.0. The absorbance was measured at 535 nm.

Misc. Teruyoshi[12] devised a spectrophotometric technique for the determination of cobalt by using chlorophosphonazo(III) and Zephiramine at pH 9-10.5. The complex was extracted into chloroform and it showed absorbance at 695 nm. The mol. ratio was found to be 1:2:2.

Reddy N. Subba Rani et al[13] developed a method for the spectrophotometric determination of cobalt(II) with salicylaldehyde thiosemicarbazone at pH 5.0. The yellow complex did show absorbance at 400 nm, with molar absorptivity 1.1 x 10^4 l $mol^{-1}cm^{-1}$.

Spectrophotometric determination of cobalt with 1-phenyl-3-thiobenzoylthiocarbamide[14], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol[15], 1,3-cyclohexane dione-dithiosemicarbazone monohydrochloride[16], 1-(2-pyridylazo)-4-benzylresorcinol[17], 5-chloro-7-iodo-8-quinolinol[18], α-methyl-2, 4-dihydroxy benzylidene-2-amino aniline[19], 2'-hydroxy-4-methoxy-5'-methyl chalcone oxime[20], 1-o-methoxy phenyl-3-phenyl-5-(6-methyl-4-hydroxy-2-pyrimidinyl) formazan[21], 2,4-dihydroxy acetophenone thiosemicarbazone[22], 1,5-bis (di-2-pyridylmethylene) thio carbonohydrazide[23], 2-4-dinitrophenylazo-8-quinolinol[24], potassium propyl xanthate[25], Isophthal dihydroxamic acid[26], 2-(3'-sulphobenzoyl) pyridine benzoyl hydrazone[27], 1, 2, 3-indane-tricentrioxime[28], dipicoline dihydroxamic acid[29], 4-formyl-1-phenyl-3-methyl-2-pyrazolin-5-one[30], Isonitrosothiocamphore[31], N-phenylcinnamo hydroxamic acid and thiocyanate[32], 1-(2-quinolylazo)-2, 4,5-trihydroxybenzene[33], 2-[2-(3,5-dibromo pyridyl) azo]-5-diethyl amino benzoic acid[34], 4-(2-thiazolylazo)-1,3 diaminobenzene[35], 2'-hydroxyacetophenone thiosemicarbazone[36], and dithizone[37] have been suggested by various workers.

Zhang Zhengqi et al[38] developed a spectrophotometric method for the determination of cobalt by using 4-(2-5-bromopyridyl) azo)-1,3-dihydroxynaphthalene. The complex was stable in NaOAC-

HOAG buffer solution (pH 5.0). The metal : ligand ratio was found to be 1:2. The absorbance of the complex was measured at 547 nm.

Co^{+2} was determined as its porphyrin complex by Ji Cuirong et al[39] with meso-tetrasulphoporphyrin(I) in pH 4.3. The buffer solution used was AcOH-AcONa. The complex had an absorbance at 426 nm. The metal : ligand ratio was found to be 1:1.

Paria P.K. et al[40] used ninhydrinoxime and pyridine for the spectrophotometric determination of Co(II). The yellowish brown complex was extractable into chloroform. The metal : ligand ratio was determined to be 1:3. The absorbance of the complex was measured at 330 nm.

It has been found that cobalt forms a chocolate brown complex with phenylthiohydantoic acid. This complex is readily extractable into chloroform, which is the basis of our present investigation.

EXPERIMENTAL

Apparatus and Reagents :

A Shimadzu PR-1 model spectrophotometer was used for absorbance measurements. A pair of matched quartz cells of 10 mm optical path length was used for the purpose.

A stock solution of cobalt(II) was prepared from $Co(NO_3)_2 \cdot 6H_2O$ and standardised. A working solution of lower concentration of cobalt was prepared by appropriate dilution with distilled water.

Chloroform and other solutions were distilled before use. Buffer solutions of different pH-values, prepared by standard procedure, were used to adjust the acidity of the aqueous phase. To study the interferences, standard solutions of diverse ions were prepared from their corresponding salts. All other chemicals used were of analytical grade.

Preparation of PTHA[41] :

Monochloroacetic acid (189 gm) and ammonium thiocyanate (152 g) were mixed and to this were added 186 g of aniline and 930 ml of ethyl alcohol. The mixture was heated under reflux on a water bath for six hours, and the mixture was allowed to stand until the undissolved material settled. The clear brownish liquid poured into a large evaporating dish and allowed to cool. The yellow crystals which formed, was filtered and washed with water. The product was purified by recrystallisation from alcohol (m.p. 156–157°C). A 0.2% acetonic solution of the reagent was used to estimate cobalt.

Determination of cobalt :

To an aliquot containing 44.7 μ g of cobalt(II) was added 2 ml of PTHA and adequate amount of buffer (Borax-hydrochloric acid buffer) (pH 8) to make the volume of the aqueous phase to 10 ml and left for 1 minute to ensure complete complexation. Finally, it was equilibrated with chloroform (10 ml) for 30 sec. The separated chocolate brown organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the chloroform extract was read at 490 nm. against a cobalt free reagent blank. Amount of cobalt extracted was deduced from a calibration curve. To study the effects of diverse ions the respective foreign ions were added to the aqueous solution before addition of the reagent.

RESULTS AND DISCUSSION

Absorption Spectrum :

The absorption spectrum of the cobalt complex in chloroform was taken against a blank. The complex exhibits absorption maximum at 490 nm (Fig. 1). The reagent blank did not absorb in this region and the wave length of 490 nm was selected for all analytical measurements. Some other solvents like benzene, ethylacetate and carbon tetrachloride were also tested as extracting solvents. Benzene and ethyl acetate did not extract the complex. The complex in ethyl acetate gave low absorbance compared to chloroform.

Extraction as a function of pH :

The extraction of cobalt in terms of absorbance was investigated in the pH range of 0-12. Extraction of cobalt virtually starts from pH 0.5. The chloroform extracts showed maximum absorbance when the extractions were carried out from aqueous solutions of pH 7.5-8.5. In the pH range, after a single operation, when the extraction process was repeated using the same aqueous phase, the organic extract virtually showed no absorbance. This indicated a complete and quantitative recovery of cobalt in this condition. The results have been shown in Table 1 and Fig. 2.

Reagent concentration and Beer's law:

The optimum reagent concentration was ascertained by extracting cobalt at different concentrations of PTHA. It was noted that 2 ml of 0.1% acetone solution of the reagent was sufficient to extract 44.7 μ g of cobalt in a single operation. The aqueous phase was clear and colourless after extraction and was free from cobalt as tested independently. Higher PTHA concentration (upto 5 ml) had no adverse effects (Table 2). The system conforms to Beer's law over a concentration of 10 ppm of cobalt

(Table 3, Fig. 3). The molar absorptivity of the complex (on the basis of cobalt content) was evaluated to be 1.123×10^4 l $mol^{-1} cm^{-1}$ and Sandell's sensitivity 0.005 μ g/cm^2 at 490 nm.

Stability of colour :

The absorbances of the Co(II)-PTHA complex in chloroform were measured at elapsed intervals of time after the extraction process. The complex is stable for at least 12 hrs as seen from Table 4.

Interferences :

In order to study the effects of diverse ions on the extraction behaviour, 44.7 μg of cobalt was extracted and determined according to the recommended procedure in presence of the respective foreign ions. An ion was considered to interfere if the recovery of cobalt differed by more than ± 3% from the actual amount taken. The results are shown in Table 5.

Determination of cobalt in synthetic mixtures :

In absence of real samples the proposed method was extended to some synthetic mixtures to estimate microgram amounts of cobalt. Average of these determinations was taken in each case (Table 6).

Precision and accuracy :

The proposed method was tested by analysing solutions containing a known amount of cobalt(II). The results in Table 7 show that the method is fairly precise and reproducible requiring only 10-15 min for each run.

Comparison of the Present Method :

The proposed method is very simple and rapid and is comparable well with some other existing methods as seen from Table 8.

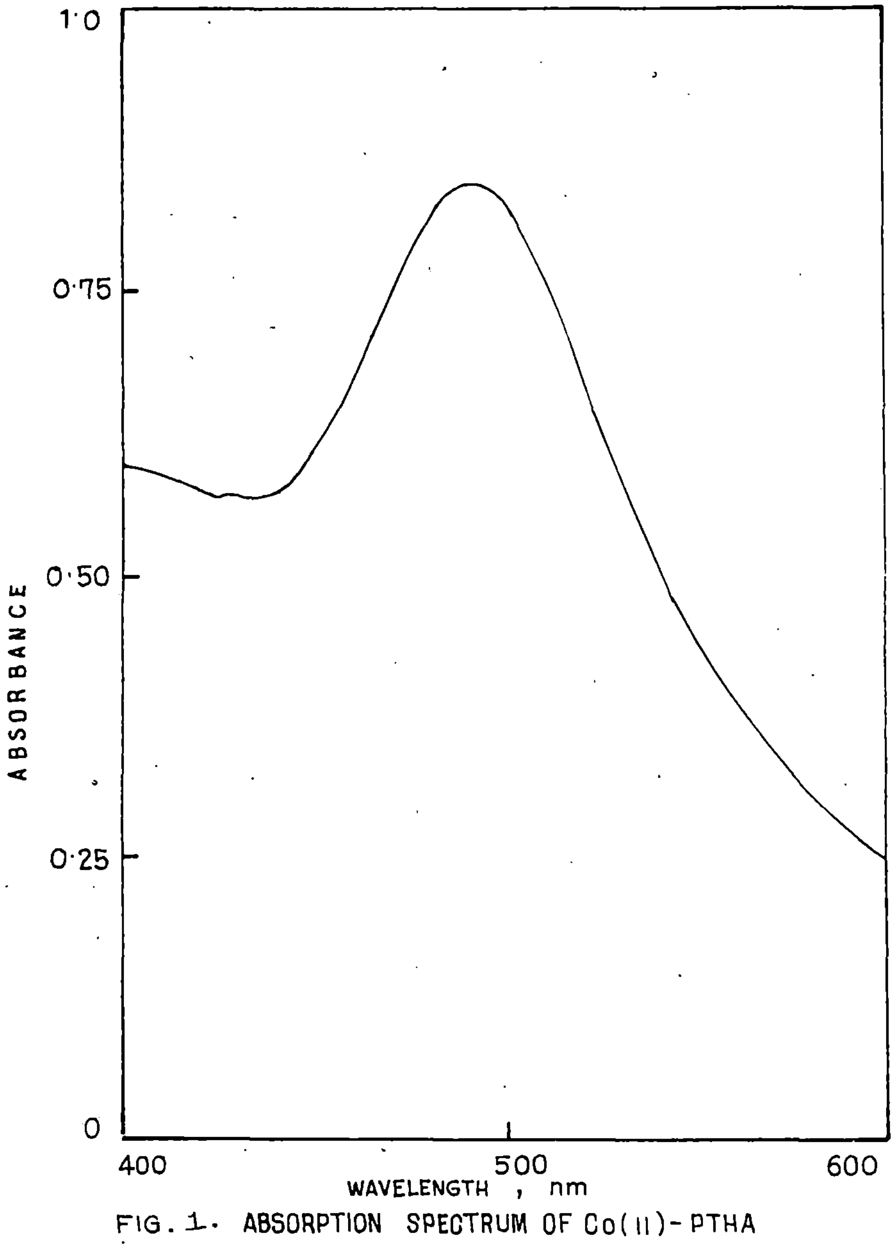


FIG. 1. ABSORPTION SPECTRUM OF Co(II)-PTHA COMPLEX (Co- 4·47 ppm)

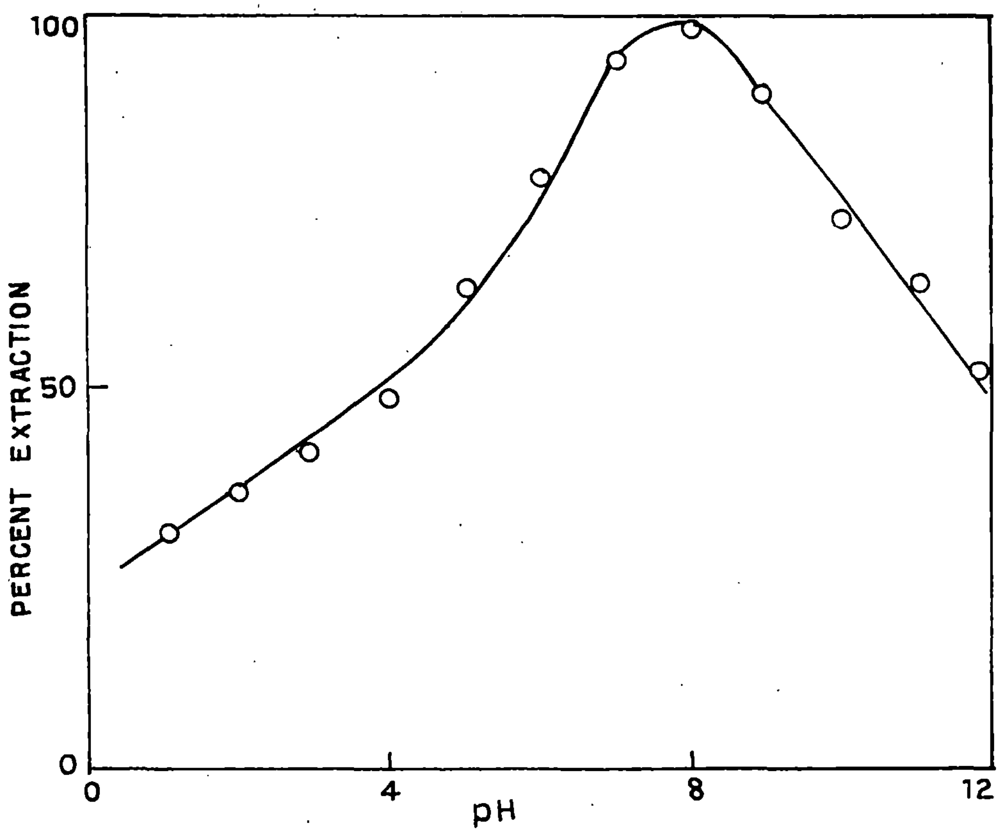


FIG. 2. EXTRACTION CURVE OF Co(II)-PTHA COMPLEX

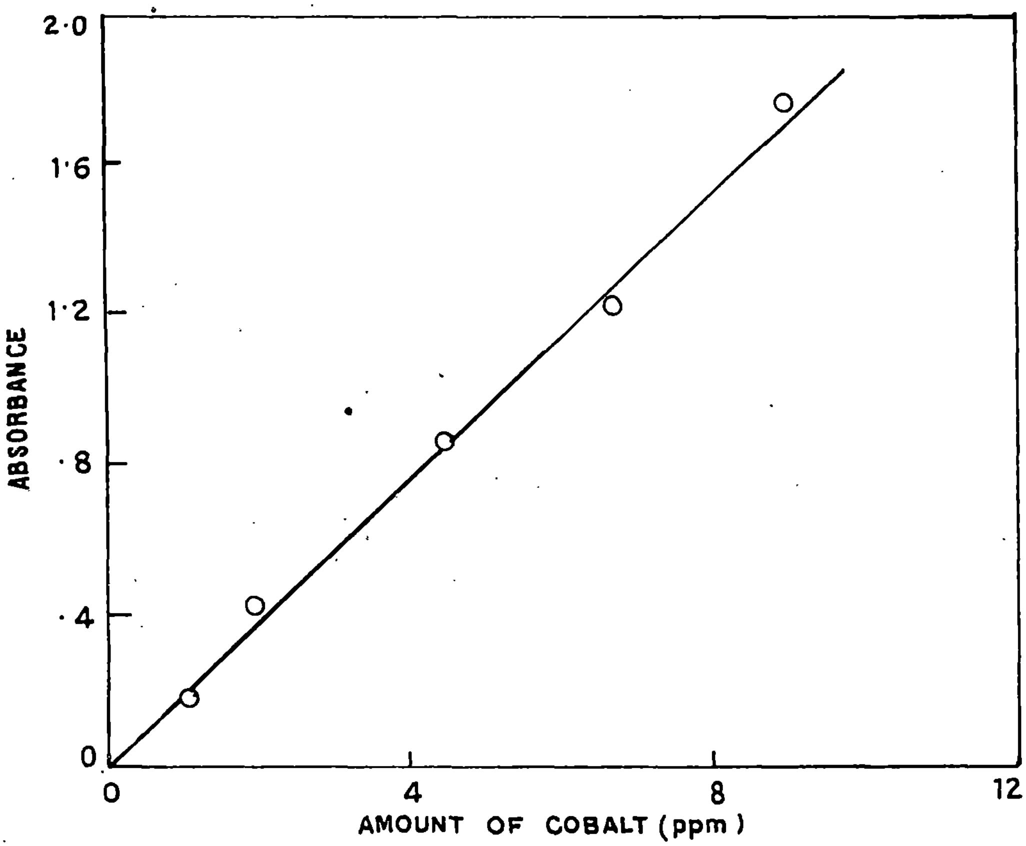


FIG. 3. CALIBRATION CURVE FOR COBALT (CO - PTHA SYSTEM)

Table 1. Variation of absorbance of the chloroform extract containing the Co(II)-PTHA complex. (The aquecus phase (10 ml) contains 44.7 μ g of cobalt and 2 ml of 0.1% acetonic solution of PTHA).

pH	Absorbance at 490 nm	pH	Absorbance at 490 nm
1	0.260	7	0.642
2	0.315	8	0.840
3	0.362	9	0.685
4	0.410	10	0.610
5	0.502	11	0.542
6	0.560	12	0.440

Table 2. Effect of phenylthiohydantoic acid concentration. The aqueous phase (10 ml) (pH 8) contains 44.7 μ g of cobalt. 0.1% Acetonic solution of PTHA was used

Reagent added in ml	Absorbance at 490 nm	Reagent added in ml	Absorbance at 490 nm
0.05	-	1.75	0.840
0.10	-	2.0	0.840
0.25	0.06	2.25	0.842
0.50	0.182	2.5	0.835
0.75	0.315	2.75	0.840
1.0	0.450	3.0	0.835
1.25	0.502	4.0	0.835
1.5	0.788	5.0	0.830

Table 3. Beer's law data

Concentration of cobalt (ppm)	Absorbance at 490 nm
1.12	0.180
2.23	0.400
4.47	0.845
6.70	1.220
8.94	1.760

Table 4. Variation of absorbance with time

Time in hr. measured after extraction	Absorbance at 490 nm
0.25	0.840
0.50	0.840
1	0.842
2	0.838
4	0.840
8	0.840
12	0.840

Table 5. Effect of diverse ions on the determination of 44.7 μg of cobalt. Average of three determination was taken.

Ion added	Amount tolerated	Ion added	Amount tolerated (μg)
Tartrate	4000	Calcium	4000
Arsenate	4000	Barium	4000
Nitrate	4000	Strontium	4000
Thiocyanate	4000	Cadmium	4000
Thiosulphate	4000	Uranium	1000
Ascorbate	4000	Iron[+]	3000
Phosphate	2000	Zr(IV)	200
Borate	2000	Zn(II)	200
Bromide	2000	Pd(II)	4000
Iodide	2000	Pt(IV)	4000
Fluoride	2000	Au(III)	4000
Phthalate	2000	Bi(III)	4000
Citrate	2000	Cu(II)[*]	1000
Oxalate	2000	Pb(II)[**]	4000
Mg(II)	4000	Ag(I)	1000
Sn(II)	200	Th(IV)	200
V(V)	200	Cr(III)	200
Hg(II)	20	Mo(VI)	4000
EDTA	nil		

[+] In presence of F

[*] in presence of ascorbate

[**] absorbance measured after two hours of extraction

Table 6. Determination of cobalt in synthetic mixtures

Composition with amounts in g	Cobalt found
1. Co(44.7) + Cu(100) + Fe(100)*	45.5
2. Co(44.7) + Pd(100) + Pt(100) + Rh(100)	44.0
3. Co(44.7) + Ag(100) + Pb(100)	44.5
4. Co(44.7) + Bi(100) + Fe(100)*	43.5
5. Co (44.7) + Mo(100) + V(100)	45.0

*in presence of citrate, ascorbate and F

Table 7. Reproducibility of cobalt recovery

Cobalt taken µg		Cobalt found µg	Mean µg	Std. Dev. %
1.	11.18	10.5, 9.5, 9.0 11.0, 10.0, 12.0	10.33	1.08
2.	22.35	21.0, 23.0, 22.5 21.0, 22.0, 23.5	22.16	1.03
3.	44.70	45.5, 43.5, 44.0 46.0, 43.0, 44.5	44.42	1.15
4.	67.0	65.5, 66.0, 67.5 66.0, 64.5, 66.0	65.92	0.97

Table 8. Comparison of the Present Method

Ref.	Reagent	pH	max	Molar absorptivity	Interference
42.	Cetyltrimethyl ammonium bromide	4M HCl to pH 8	625	1.9×10^3	Cu, Zn, Hg, Cd* EDTA*
40.	Ninhydrin oxime	3-6	330	1.97×10^4	Rh(III) and NO_2^-
43.	2,2'-dipyridyl ketone-2-picolyl-imine	8.5-11.1	580	4.42×10^4	Ni*(II), Cu*(II)
44.	Isonitroso thiocamphor	1M HCl to 1M NaOH	240 295 325	1.7×10^4	Pd*, Cu*, EDTA*
45.	Thioglycolic acid anilide	5.6-9.8	485	1.128×10^4	Be*(II), Fe*(III), Al*(III), Bi*(III), Th*(IV), Pb*(II), Cd*(II), Cr*(III), U*(VI), Cu*(II), Hg*(II), Sn*(II), EDTA*
	Present method	7.5-8.5	490	1.123×10^3	Ni, EDTA, Cu*, Pb* and Fe*

*masking agents used.

Extraction and Spectrophotometric Determination of Palladium(II) with Phenylthiohydantoic Acid

Introduction

Literature shows that palladium has an affinity to form complexes with the ligands containing N,S,P, As, Se. The most widely used reagents are, p-nitroso aniline derivatives[46], in the detection and estimation of the metal.

Palladium(II) forms complex with sodiumdiethylthiocarbamate[47] at pH 11. The complex is extractable into carbon tetrachloride and absorbs maximum at 305 nm. Benzoylmethyl glyoxime[48] is also a good reagent for palladium(II).

Another important reagent for the determination of palladium is 2-nitroso-1-naphthol[49]. Palladium was extracted at pH 1.5-3.5 into toluene in presence of EDTA and measured at 370 or 550 nm. 1-(2-pyridylazo)-2-naphthol[50] forms a green chelate with palladium(II) which can be extracted into chloroform at pH 2-5. The absorbance was measured at 678 nm.

Gowda H. Sanke et al[51] presented a photometric method for the determination of Pd(II) by using triflupromazine hydrochloride. The red coloured complex is formed in the pH 1.4-2.7. The metal : ligand ratio is 1:1. The absorbance of the complex was measured at 480 nm.

Gowda H. Sanke et al[52] developed a method for the spectrophotometric determination of palladium by using prochlorperazine maleate. The red coloured 1:2 (metal : ligand) complex that formed in the pH range 0.1 to 3.0 had an absorbance at 480 nm.

Po. Weihung Ma et al[53] determined palladium spectrophotometrically by using 4-[(5-chloro-2 pyridyl)azo]-1,3-diamino benzene. The complex has a purple red colour and extractable into n-pentanol. It is stable in the strong acid medium. The complex showed absorbance at 594 nm.

Procedures based on the formation of palladium(II) complexes with thiocaprolactum[54], 2-pyridine carboxaldehyde-2-pyridyl hydrazone[55], N-phenyl-N'-(α-pyridyl) thiourea[56], meso-tetrakis (4-sulfophenyl) porphyrin[57], 3-bromo-2-hydroxy-5-methyl acetophenone hydrazone[58], N,N-dimethyl-N-(4-phenyl-2-thiazolyl) thiourea[59], 2-furaldehyde-2-pyridyl-hydrazone[60], 1-pyrrolidine carbodithioate[61], 3,5-dichloro-2-hydroxy-acetophenoneoxime[62], 2-methyl-1,4-napthoquinone thiosemicarbazone[63], 2-thiopyrogallol and β-mercaptoresorcinol[64], Eriochrome Azurol B and Cetyltrimethyl ammonium bromide[65], 2-(2',4'-dihydroxy-3'-nitrophenyl)azo-3-cyano-4-methyl-5-ethoxy carbonyl thiophene[66], phenanthroquinone monoxime[67], 1-(2'-amino-4'-methyl-phenyl)-4,4,6-trimethyl 1, H, 4H-pyrimidine-2-thiol[68], 3-Acetoxy-7-methyl phenothiazine[69], benzyl dimethylphenylammonium chloride[70], 5-(3,5-dibromo-2-pyridylazo)-2,4-diamino toluene ethanol[71], arylazo-2-hydroxynaphthalene-3,6-disulphonic acid[72], thiolactams and Rose Bengal[73], 2-(2-benzothiazolylazo)-5-dimethylamino benzoic acid[74], 2-(3,5, dibromo-2-pyridyl azo)-5-dimethylaminoaniline[75], isonitroso-thiocamphor[76], tin(II) chloride and Rhodamine 6G[77], 2-allyl thiourea and thiocyanate[78], 5-chloro-2,4-dihydroxy propiophenone-oxime[79] have been suggested by various workers.

H. Shoukun et al[80] have developed a spectrophotometric method for the determination of palladium by using p-aminophenyl fluorone and cetyltrimethyl ammonium bromide. The complex is stable in the pH range 6.9-7.8 with an absorbance at 583 nm. The metal : ligand ratio was 1:3.

Zhang Guang et al[81] devised a technique for the spectrophotometric determination of palladium with 4-(2-thiazolylazo)-1,3-diamino benzene). The purple complex was stable in perchloric acid medium. The metal : ligand ratio was found to be 1:1. It showed absorbance at 584 nm.

The extraction of palladium(II), a red complex with 4-(2-thiazolylazo) resorcinol by tetraphenyl phosphonium chloride in chloroform was studied by Siroki M. et al[82]. Quantitative extraction was achieved in the pH range between 2 and 10. The absorbance of the complex was measured at 525 nm.

In the present investigation phenylthiohydantoic acid has been used for the extraction, separation and spectrophotometric determination of palladium.

EXPERIMENTAL

Apparatus and Reagents :

Absorption measurements were carried out with a Shimadzu PR-1 model spectrophotometer equipped with a pair of matched quartz cells of 10 mm optical path length.

$PdCl_2$ (Johnson and Matthey) (1 gm) was dissolved in HCl (1 ml) and diluted to 250 ml with distilled water. This was standardised with dimethylglyoxime. A working solution of palladium(II) (60 ppm) was prepared by appropriate dilution.

Pyridine, chloroform and other solvents were distilled before use. Buffer solution (pH 4) prepared by standard method, was used to adjust the acidity of the aqueous phase. To study the interferences, standard solutions of diverse ions were prepared from this corresponding salts. All other chemicals used were of analytical grade.

Phenylthiohydantoic acid (PTHA) was prepared by the method as described earlier.

Determination of palladium :

To an aliquot containing 60 μg of palladium was added 1.5 ml of PTHA (0.1%) and 0.2 ml of pyridine followed by adequate amount of buffer (pH 4) (potassium hydrogenphthalate-hydrochloric acid buffer) to make the volume of the acqueous phase upto 10 ml and left for 1 min to ensure complete complexation. The solution was then equilibrated with chloroform (10 ml) for 30 sec. The separated organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. The absorption of the chloroform extract was measured at 370 nm against a blank and the amount of palladium deduced from a calibration curve. To study the effects of diverse ions the desired foreign ion was added to the system before addition of the reagents.

RESULTS AND DISCUSSION

From a slightly acidic solution palladium(II) gives a brown complex with phenylthiohydantoic acid. The complex is extractable into chloroform. Addition of traces of pyridine, prior to the extraction, enhances the absorbance of the resulting complex. Use of α-picoline/β-picoline/γ-picoline or 2,4,6-collidine shows similar behaviour.

Absorption Spectra:

The absorption spectrum of the palladium(II) complex in chloroform showed maximum absorbance at 370 nm with a shoulder around 310 nm, Fig. 1. The reagent blank itself showed insignificant absorbance beyond 310 nm. Hence wave length of 370 nm was selected for all analytical measurements. Some other solvents like ethyl acetate, benzene or carbon tetrachloride were also tested as extracting solvents. But the palladium complex in chloroform gave maximum absorbance.

Extraction as a function of pH :

The extraction of palladium in terms of absorbance was investigated in the pH range 0-12. Extraction starts from pH 1, the organic extract showed steady maximum absorbance when palladium was extracted from aqueous solution of pH 3-7. The aqueous phases were clear and colourless in each case. This indicated complete and quantitative extraction of palladium. Extraction however decreases beyond pH 8 or at higher acidities. The absorbance of the chloroform extract as a function of pH is shown in Table 1 and Fig. 2.

Reagent Concentration and Beer's law :

The optimum reagent concentration was ascertained by extracting palladium at different concentrations of PTHA keeping other variables constant. It was found that 1.5 ml of 0.1% acetonic solution of PTHA along within 0.2 ml of pyridine was sufficient to extract 60 μg of palladium in a single operation. Higher reagent concentration (upto 4 ml) had no adverse effects on extraction. Results have been shown in Table 2.

The absorbance of the organic extract showed a linear response over a concentration of 12 ppm of palladium (Table 3, Fig. 3). The molar absorptivity of the complex (based on palladium content) was found to be 1.307×10^4 l $mol^{-1}cm^{-1}$ and Sandell's sensitivity $0.008 \mu g/cm^2$ at 370 nm.

Stability of Colour :

The absorbance of the Pd(II)-PTHA complex in chloroform was measured at elapsed intervals of time of the operation. The absorbance remains unchanged at least for 12 hrs. The complex is thus sufficiently stable as shown in Table 4.

Interference :

To study the effects of diverse ions, palladium was extracted in presence of the respective foreign ions and spectrophotometrically determined as above. Deviation of not more than ± 3% from recovery of palladium was taken as the tolerance limit for the diverse ions, tested. In the estimation of 60 μg of palladium, the following ions did not interfere when present in amounts (μg) shown in Table 5.

Determination of palladium in synthetic mixtures :

In absence of real samples the proposed method was extended to some synthetic mixtures to estimate microgram amounts of palladium. Average of three determinations was taken in each case (Table 6).

Precision and accuracy:

The proposed method was tested by analysing solutions containing a known amount of palladium(II). The results in Table 6 indicate the method to be fairly precise and reproducible requiring only 10-15 min for each run (Table 7).

Comparison of the Present Method:

The present method for the spectrophotometric determination of palladium is very simple and rapid and comparable to some other existing methods. The sensitivity of the method may not be as high as the other ones (Table 8), but it provides excellent recovery of palladium in micro quantities in presence of almost all the common ions tested.

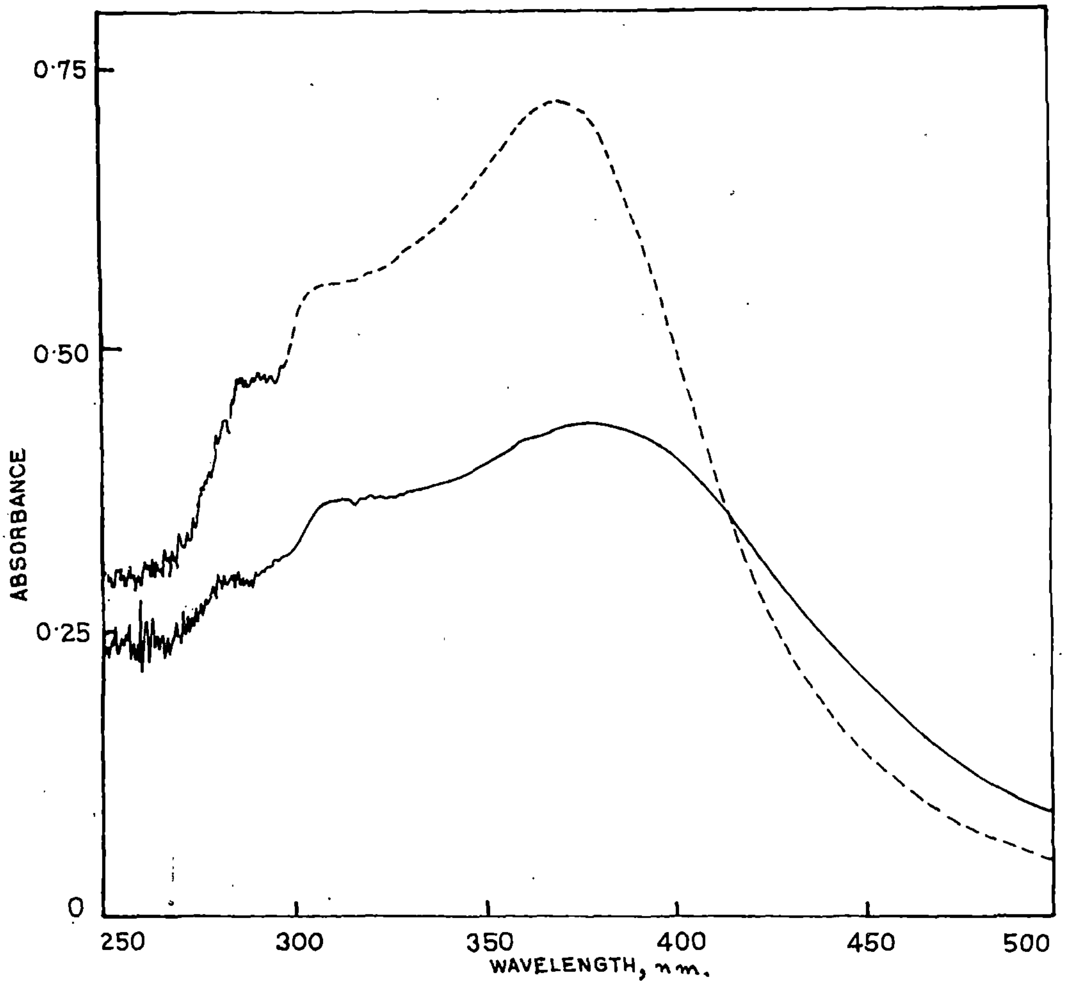


FIG : 1, ABSORPTION SPECTRUM OF Pd(II) - PTHA COMPLEX (6ppm Pd)
A- In presence of pyridine, B- In absence of pyridine .

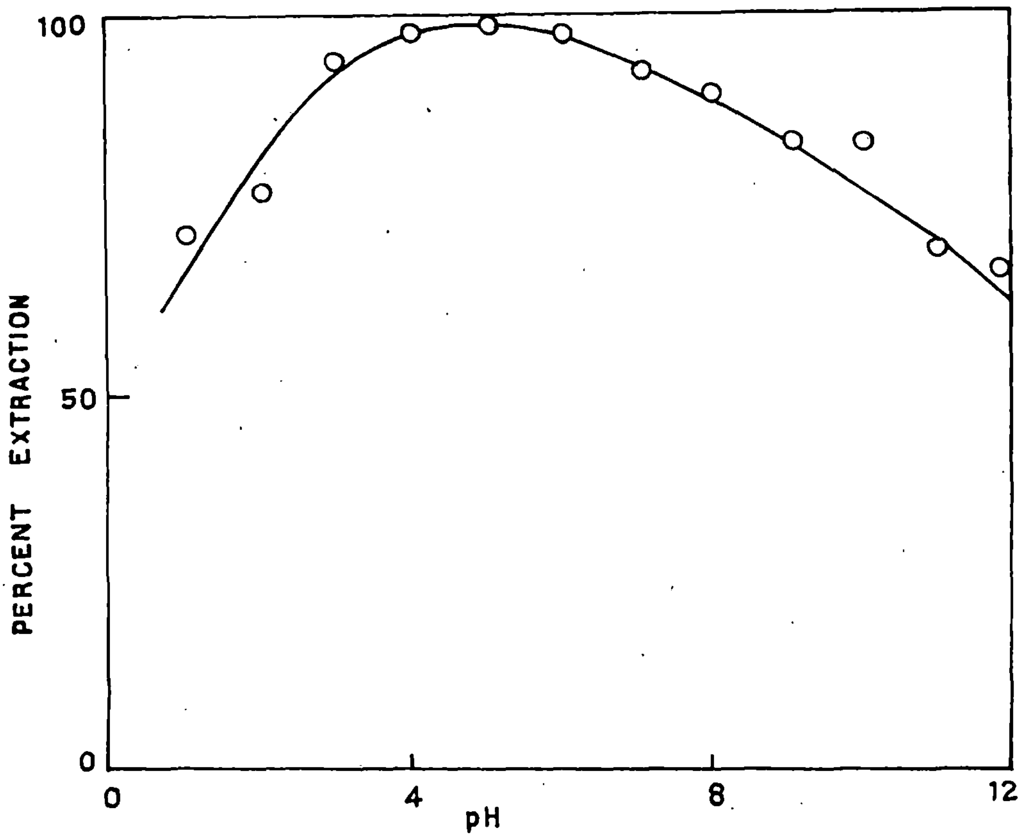


FIG. 2. EXTRACTION CURVE OF Pd (II)- PTHA COMPLEX

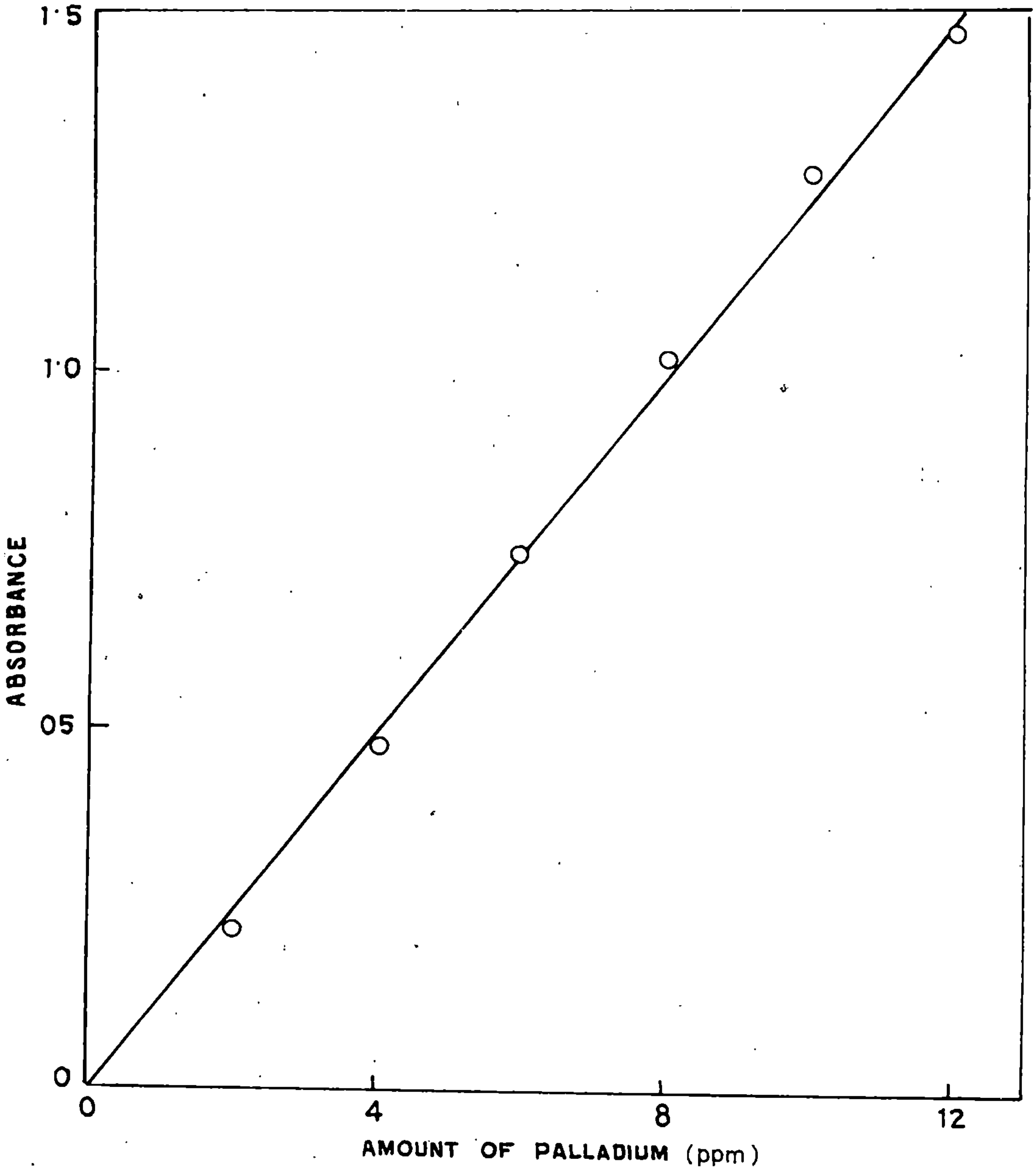


FIG.3. CALIBRATION CURVE FOR PALLADIUM (Pd-PTHA SYSTEM)

Table 1. Variation of absorbance of the $CHCl_3$ extract with pH (The aqueous phase (10 ml) contains $60\,\mu g$ of Pd, 1.5 ml of 0.1% PTHA and 0.2 ml pyridine)

pH	Absorbance at 370 nm	pH	Absorbance at 370 nm
1	0.542	7	0.705
2	0.562	8	0.682
3	0.704	9	0.630
4	0.732	10	0.632
5	0.754	11	0.552
6	0.732	12	0.520

Table 2. Effect of PTHA. The aqueous phase (10 ml) (pH 4) contains $60\,\mu g$ of Pd and 0.2 ml of pyridine. 0.1% Acetonic solution of the reagent was used.

Reagent added in ml	Absorbance at 370 nm	Reagent added in ml.	Absorbance at 370 nm
0.05	-	1.50	0.750
0.10	0.110	1.75	0.748
0.15	0.150	2.0	0.750
0.20	0.250	2.25	0.745
0.30	0.382	2.5	0.740
0.50	0.475	3.0	0.740
0.75	0.565	4.0	0.740
1.00	0.695	5.0	0.725
1.25	0.740		

Table 3. Beer's law data

Concentration of palladium (p.p.m)	Absorbance at 370 nm
2	0.222
4	0.474
6	0.750
8	1.020
10	1.280
12	1.472

Table 4. Variation of absorbance with time

Time in hour measured after extraction	Absorbance at 370 nm
0.25	0.750
0.50	0.750
1	0.748
2	0.750
4	0.750
8	0.744
12	0.745

Table 5. Effect of diverse ions on the determination of 60 μg of palladium. Average of three determinations was taken

Ion added	Amount tolerated (μg)	Ion added	Amount tolerated (μg)
Nitrate	4000	Gold	4000
Borate	4000	Iron	4000
Oxalate	4000	Calcium	4000
Thiocyanate	4000	Barium	4000
Phthalate	2000	Strontium	4000
EDTA	2000	Zinc	4000
Bromide	2000	Uranium	4000
Iodide	2000	Cobalt	4000
Ascorbate	2000	Cadmium	4000
Citrate	2000	Nickel	4000
Tartrate	2000	Chromium	4000
Fluoride	2000	Vanadium	4000
Arsenate	2000	Bismuth	4000
Phosphate	2000	Lead	2000
Thiosulphate	2000	Silver	500
Rhodium	2000	Platinum	600
Molybdenum	600	Mercury	400
Thorium	600	Copper	400

Table 6. Analysis of Synthetic mixtures

Composition with amount in μg	Palladium found in μg
1. Pd(6) + Pt(200) + Rh(200)	61.5
2. Pd(60) + Fe(200) + Cu(100)	60.5
3. Pd(60) + Ni(200) + Co(200)	62.0
4. Pd(60) + Zn(200) + Cd(200)	60.0
5. Pd(60) + Mo(100) + V(200)	60.5
6. Pd(60) + Hg(100) + Cr(200)	58.5

Table 7. Reproducibility of palladium recovery

	Palladium taken (μg)	Palladium found (μg)	Mean (μg)	Std. Dev. (%)
1	15	13.0, 14.5, 17.5 16.0, 15.5, 13.0	14.92	1.77
2	30	30.5, 32.0, 31.5 29.0, 30.0, 31.0	30.66	1.07
3	60	60.0, 60.5, 62.0 61.5, 60.0, 61.0	60.83	0.82
4	90	91.5, 90.0, 92.5 92.0, 91.0, 90.0	91.16	1.03

Table 8. Comparison of the present method

Ref.	Reagent	pH	λ_{max}	Molar absorptivity	Interference
74	2-(2-benzothiazolylazo)-5-(dimethylamino)benzoic acid	2-6	695	4.96×10^4	Ag*(I), Co*(II) Ni*(II), Os*(VIII), Pt*(IV) and V*(V).
76	Isonitrosothio-camphor	pH 2.0 to 5M HCl	450	3.90×10^3	Cu*, Hg, Co*, Pt* and S_2O_3
71	5-(3-5 dibromo-2-pyridylazo)-2,4-diaminotoluene	0.1-0.6M HCl	600	1.05×10^5	- (common cations and anions do not interfere)
67	Pehnanthraquinone monoxime	2.0-5.4	430	2.072×10^4	- (common ions do not interfere)
83	Prochlorperazine maleate	0.1-3.0	480	4.63×10^3	-
	Present method	3-7	370	13070	Co*

* masking agents used.

REFERENCES

1. Pozzil-Escot E., An Chin and Chim appl., 10 (1905), 147.

2. Gutzeit G., Helv. Chim Acta, 12 (1929), 713, 821.

3. Willard H.H. and Hall D., J. Am. Chim. Soc., 44, (1922), 2219, 2226.

4. Hibbits J.O., Rosenberg A.F. and Williams R.T., Talanta, 1960, 5, 250.

5. Kumar N.P. Doklady, Akad. Nauk S.S.S.R., 1950, 72, 535.

6. Suzuki N. and Yoshida H., Nippon Kagaku Zasshi, 80, 1005, 2959.

7. U.K. At. Energy Authority, Rept. P.G. 509, (5), (1963), Anal Abstr. 11, 2618 (1964).

8. Kharsan R.S., Patel K.S., Mishra R.K. and Malewar L.R., Proc. Indian Acad. Sci. [Ser] Chem. Sci., 1980, 89 (5), 411.

9. Nakashima Kenichiro, Hirahara Hirohisa and Akiyama Suzo, Bunseki Kagaku, 1978, 27 (8), 529.

10. Rodrignes Rivaldo Alves, Cad. Omega, 1979, 3 (1-2), 189-99.

11. Casais Laino Maria del Carmen, Lorenzo Ferreira Rosa Antonia, ~~Bir~~mij Martinez Fransisco, Acta Quim. Cospostelana, 1979, 3 (4), 134-43.

12. Misc. Teneyoshi, Miyakonojo Kogyokoto Semmon Gakko Kenkyu Hokoku, 1980, 15, 35-9.

13. Reddy N. Subba Rani, Reddy D. Venkata, Anal. Chim. Acta., 1980, 120, 395-8.

14. Ilyas S.Q.R. & Joshi A.P., J. Indian Chem. Soc., 1981, 58 (4), 360.

15. Fresenius Z., Anal. Chem., 1981, 306 (2-3), 129.

16. Roman Ceba M., Mano Z Leyva J.A. and Jimenez Sanchez J.C., Afinidad, 1981, 38 (375), 431.

17. Urmanov N., Chaprasova L.V., Tashkhodzhaev A.T. & Mirzakasymov T.M., Amanov K., Deposited Doc., 1982, SPSTL-133, Khp-D82, 5pp.

18. Fukui Daigaku, Kogakubu Kenkyn Hokoku, 1982, 30 (1), 63.

19. Emeliyanova L.N., Kholevinskaya L.V. and Karavaeva E.S., abraztsy Tovarnye Znaki, 1984 (28), 128.

20. Deshmukh B.K., J. Indian Chem. Soc., 1983, 60 (2), 203.

21. Srinivasan S., Seshagiri V., Acta Cienc. Indica [Ser] Chem., 1983, 9(1-4), 97-101.

22. Reddy A.V., Reddy M.L.P., Reddy Y.K., J. Radio anal. Nucl. Chem., 1984, 86(6), 391.

23. Cano Pavon Jose M., Garcia de Torres Amparo and Bosch Ojida Catalina, Analyst (London), 1985, 110(9), 1137-40.

24. Yamamoto Daijiro, Washio Yoshifumi, Meiji Daigaku Nogakubu Kenkyu Hokoku, 1985, (70), 57-69.

25. Faria P.K. and Majumdar S.K., Ind. J. Chem., Sect. A, 1986, 25A (1), 103.

26. Salinas F., Jimenez -Arrabal M., Duran I., Michrochem. J., 1986, 33(2), 194.

27. Nakanishi Tsutomu, Otomo Makoto, Microchem J., 1987, 35(3), 328.

28. Rao D. Mallikarjuna, Reddy K. Hussain, Reddy D. Venkata, Mikro Chim. Acta, 1987, 2 (1-3), 57.

29. Salinas F., Forteza R. Estelu J.M., An. Quim. Ser. B, 1987, 83 (1), 109-10.

30. Soni H.K. & Shah J.R., Acta. Cienc-Indica Chem., 1985, 11(2), 122-3.

31. Katiyar G.S., Haldar B.C., J. Indian Chem. Soc., 1986, 63(10), 937-8.

32. Afeworki Selezion, Chandra Vanshi Bhagwan Singh, Mikrochim. Acta, 1987 (Pub. 1987), 2(4-6), 143-52.

33. Laila A.H. & Salim Radi, Spectrose Lett., 1988, 21(1), 35-44.

34. Li. Huanran, Rong. Qingxin, Fenxi Huaxue, 1988, 16(5), 464-6.

35. Zhang Guang & Han Quan, Yejin Fenxi, 1989, 9(3), 11-14.

36. Merthy G.V. Ramanna, Reddy T. Srinivasula, Chim. Acta Ture, 1989, 17 (2), 189-94.

37. Dawson Martin V., Lyle Samuel J., Talanta, 1990, 37(4), 443-6.

38. Zhang Zhengqi and Ding Yuping, Yankuang Ceshi, 1990, 9(3), 169-72.

39. Ji. Cuirong and Du. Hengkun, Lihua Jianyan, Huaxue Fence., 1990, 26(4), 240, 242.

40. Paria P.K., Thokdar T.K. & Majumdar S.K., J. Indian Chem. Soc., 1990, 67 (6), 532.

41. Nelcher F.J., Organic Analytical Reagents, Vol. IV, D. Van Nostrand, Princeton, 1965 (p-136).

42. Paria P.K., Thokdar T.K. and Majumdar S.K., J. Indian Chem. Soc., 1990, 67, 787-788.

43. Kato Takeshi and Kano Kiyoshi, Bunseki Kagaku, 1985, 34(1), 36-9.

44. Paria P.K. and Majumdar S.K., Ind. J. Chem., Sect. A, 1985, 24A(11), 989-990.

45. Ray Chandra (Miss) and Das Jyotirmoy, Ind. J. Chem., 1985, 24A, 40-47.

46. Kolthoff I.M., Elviny P.J. and Sandell E.B., "Treatise on analytical chemistry", Part-II, Vol. 8, Interscience, New York, 1963, p. 471.

47. Young R.S., Analyst, 1951, 76, 49.

48. Shehekochikhina R.L., Peshova V.M. and Shlenskaya V.I., Vestn. Moskov. Univ. Ser. Khim., 1962, 4, 38.

49. Cheng K.L., Anal. Chem., 1954, 26, 1895.

50. Dono T., Nakagawa G. and Hayashi M., Nippon Kagaku Zasshi, 1960, 81, 1703.

51. Gowda H. Sanke and Thimmaiah, Ind. J. Chem., 1976, 14A, 821-822.

52. Gowda H. Sanke and Ramappa P.G., Ind. J. Chem., 1976, 14A, 454-455.

53. P.O. Wei Hung Ha., Tse-Te, Fen Hsi Hue Hsueh, 1978, 6(2), 94-100.

54. Sikoraska-Tomicka Halima, Chem. Anal, 1979, 24 (40), 635.

55. Gimenez Plaza J., Becanegra Graces J.M., Afinidad, 1980, 37 (367), 237.

56. Meshcheryakova N.R. & Usatenko Yu. I., Vopr. Khim. Khim, Tekhnal, 1980, 59, 81-3.

57. Zhau Zhijie, Tong Shengyang, Fen Hsi Hua Hsuch, 1981, 9(3), 322-3.

58. Lal Kemti, Malhotra Sita Rani, Ann. Chim., 1981, 71(7-8), 479.

59. Yoda Reiko, Akiyama Kazuya, Yamamoto Yuchi, Mirakami Yukio, Bunseki Kagaku, 1981, 30(3), 160.

60. Hernandex Lopez M., Gercia Sanchez Fo, An. Quim. Ser. B, 1981, 77 (1), 112.

61. Kumar Avdesh, Hussain M.F., Satak Masatada and Puri B.K., Bull. Chem. Soc., 1982, 55 (11), 3455.

62. Lal Keemti, Katyal Mohan, Curr. Sci., 1982, 51 (23), 1115.

63. Sindhwani S.K. and Singh R.P., J. Chin. Chem. Soc., 1982, 29 (3), 201.

64. Bag S.P. and Bhattacharya B., J. Indian Chem. Soc., 1983, 60(2), 204.

65. Gregorowica Z., Gorka P., Kowalski S., Cebula J., Mikrochim. Acta, 1983, 2(3-4), 181.

66. Drille M., Barkane V. and Putnius J., Latu P.S.R., Zinat. Akad. Vestis, Khim., Ser., 1984, (3), 311-16.

67. Wasey A., Bansal R.K., Puri B.K. and Satake M., Analyst (London), 1984, 109 (5), 601-3.

68. Singh A.K. and Singh R.P., Chem. Anal. (Warsaw), 1983, 28 (5), 625-7.

69. Aggarwal Modhu, Bhargava Nandan, Jain R.K. and Mital R.L., Acta. Cienc. Indica., [Ser] Chem., 1983, 9(1-4), 75-6.

70. Bayan K.C. and Das H.K., Curr. Sci., 1984, 53 (17), 915-17.

71. Huang Muqiong and Kang Tingzhang Fenxi Huaxue, 1983, 11 (9), 660-4.

72. Issa Y.M., Shoukry A.F., E.L. Ansary A.L. and Okdah M.S., An. Quim, Ser. B, 1983, 79 (2), 207-10.

73. Sikorska-Tomicka Halina, Chem. Anal. (Warsaw), 1984, 29(2), 237-40.

74. Katami Takeo, Hayakawa Tomokuni, Furukawa Masamichi & Shibata Shozo, Bunsekikayaku, 1984, 33(12), 676-78.

75. Zhang Guang, Li Chengxue, Hu Yanrong, Fan Youlong and An. Min., Fenxi Huaxue, 1985, 13 (10), 775-8.

76. Majumdar S.K., Chattopadhyay P. and Paria P.K., J. Indian Chem. Soc., 1985, 62 (7), 544-5.

77. Kalinowski K. and Marczenko Z., Anal. Chem. Acta, 1986, 186, 331-5.

78. Kavlentis E., Microchem J., 1987, 36(3), 306-8.

79. Sharma K.N., Rastogi S.N., Jetley U.K., Shukla Hanu, Rehman F. and Singh Jai, Sci. Phys. Sci., 1989, 1(1), 46-7.

80. Hu. Shoukun, Huang Mei & Zeng Zhongzhi, Sichuan Daxue Xuebao, Ziran Kexueban, 1989, 26 (3), 336-9.

81. Zhang Guang & Han Quan, Guijinshu, 1989, 10(2), 28-33.

82. Siroki M., Maric L., Croat. Chem. Acta, 1990, 63(2), 255-62.

83. Gowda H. Sanke and Ramappa P.G., Ind. J. Chem., 1976, 14A, 454-455.

CHAPTER - III

2-HYDROXY-1-NAPHTHALDOXIME AS AN ANALYTICAL REAGENT

Literature reveals several oximes proposed for spectrophotometric determination of various metal ions. 2-Hydroxy-1-naphthaldoxime develops an intense forest-green colour with iron (III) at pH 2.3-2.7 and the reaction is highly sensitive and selection[39]. It has been noted that the analytical potentiality of the reagent may be extended for the spectrophotometric determination of nickel, cobalt and palladium.

Extraction and Spectrophotometric Determination of Nickel with 2-Hydroxy-1-naphthaldoxime

Introduction

A good number of methods are known for the separation and determination of nickel by liquid-liquid extraction. Chelate systems involve the utilization of reagents like monoximes, dioximes, β-diketones, naphthols, oxine and its derivatives, dithizone, dithiocarbamates and other miscellaneous reagents. The ion-association system consists of diethyl ether, thiocyanate, phenanthroline and other reagents.

The extraction of nickel by 8-quinolinol[1] was studied at pH range between 4.5 and 9.5. The complex was extractable into chloroform.

Dimethylglyoxime[2] has been used as a reagent for the extraction and separation of nickel. The pH was adjusted at 6.5 by using the AcOH-AcONa buffer solution. The complex was extracted into chloroform and did show absorbance at 366 nm. Other well known methods involve the utilisation of Furoyl trifluoroacetone[3], acetylacetone[4], thiothenoyl trifluoroacetone[5,6] for the determination of nickel.

Kamil F. et al[7] determined Ni(II) with phenanthraquinone monoxime. The complex was extracted into chloroform. The complex was stable in the pH range 4.9-8.5. The metal : ligand ratio was found to be 1:2.

Satake Masatada[8] proposed a method for spectrophotometric determination of nickel by absorption of Ni-DMG complex on naphthalene. The complex was extracted in to chloroform with absorbance at 375 nm. The pH was adjusted at 9.5. The Beer's law was obeyed for 20-170 μg Ni/10 ml chloroform.

Spectrophotometric determination of nickel was investigated by Riyazuddin P.[9] with bisbiacetylmonoxime-ethylenediimine and bisbiacetylmonoxime-o-phenylene diimine in presence of aqueous bromine. The metal : ligand ratio was found to be 1:2 and its absorbance was measured at 420 nm.

3-methoxy-7-methylpenon thiazine[10] was used to determine nickel spectrophotometrically. The 1:1 complex is formed at pH 2.5-6.0. The maximum absorbance was obtained at 425 nm.

Marishita and Katayanagi[11] developed the method based on using 6-chloro-3-hydrazinopyridiazine as a reagent. The maximum absorbance was obtained at 715 nm. with a molar absorptivity 1.86×10^{4} $1\ ml^{-1} cm^{-1}$.

Procedures based on the formation of Nickel(II) complexes with, 1-phenyl-3-methyl-4-p-nitrobenzoyl-5-pyrazolone[12], Dithizone and methyltrioctylammonium chloride[13], 2-(5-methyl-2-

isoxazol-3-ylazo)-4-chlorophenol[14], 1,3 cyclohexane dione bisthio semicarbazone monohydrochloride[15], biacetyl bis(4-phenyl3-thio) semicarbazone[16], 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-cyclotetradeca-4,11-diene and α -bromocaproic acid[17], 1-hydroxy-2-acetonaphthone oxime[18], 3-(O-acetophenyl)-1-methyltriazene -N-oxide[19], 7-(4,5-dimethylthiazolyl-2-azo)-8-hydroxy-quinoline-5-sulphonic acid[20], 2-thioorotic acid[21], sodium ethylthioxanthate[22], 5-(3,5-dibromo-2-pyridylazo)-2,4-diaminotoluene[23], 2,2'-dipyridylglyoxal bis (4,4'-diphenyl) semicarbazone[24], 2,2'-dipyridylketone-2-pyridylhydrazone[25], xanthatates[26], 2-(2-benzothiazolylazo)-5-dimethylaminophenol[27], 2-(5,5-dimethyl-4,5,6,7 -etrahydrobenzothiazolyl-2-azo)phenol[28], 2-mercapto-4-tert-butyl-phenol[29], 2-(2-thiazolylazo)-5-dimethylaminobenzoic acid[30], disodium-2-(1'-H'-1', 2', 4'-triazoyl-3'-azo)-1-naphthylamine-3, 6-disulphonate[31], dimethylglyoxime and diperoxysebacic acid[32], N,N'-diphenyldithiomalonamide[33] have been suggested by various workers.

Lizhem[34] developed a method for the spectrophotometric determination of nickel by using Eriochrome cyanine R-4, 4'-bipyridine and cetyltrimethyl ammonium bromide in the pH range of 9.3 to 10.8. The absorbance of the complex was constant at 650 nm.

Li Shengy et al[35] investigated on the spectrophotometric determination of nickel with O-chlorophenyl-fluorane and cetylpyridinium bromide. The complex was stable in the pH 11.6

that was adjusted by using the $Na_2B_4O_7$-NaOH buffer solution. The complex did show absorbance at 598 nm. The metal : ligand ratio was found to be 1:2.

Zhung Enmeng[36] found out a method for spectrophotometric determination of nickel by using xylenol orange and cetylpyridinium bromide. The metal:XO:CPB ratio was found to be 1:2:2. The absorbance of the complex was measured at 614 nm.

Ishii.Hayime et al[37] determined nickel(II) spectrophotometrically by using 5-nitro-2-pyridylhydrazones and α-(2-benzamidazolyl)α-(5-nitro-2-pyridyl) hydrazono-3-toluene sulphonic acid. The metal : ligand ratio was found to be 1:2. The complex was stable in the pH range 6.5-8.9 and showed absorbance at 498 nm.

Fernandez Liliana et al[38] were successful in divising a technique for the spectrophotometric determination of nickel(II) by using 5-phenylazo-8-quinolinol. The complex was extracted into benzene.

In the present investigation 2-hydroxy-1-naphthaldoxime has been used for the spectrophotometric determination of nickel.

EXPERIMENTAL

Apparatus and Reagents:

Absorbance measurements were carried out with a Shimadzu PR-1 model spectrophotometer equipped with stoppered quartz cells of 10 mm optical path length.

A stock solution of nickel (II) was prepared from $NiSO_4.7H_2O$ and standardized with dimethylglyoxime. A working solution of Ni(II) was prepared by appropriate dilution.

2-hydroxy-1-naphthaldoxime was prepared as reported[40]. Buffer solution (pH 8), prepared by standard method, was used to adjust the acidity of the aqueous phase.

3-picoline, carbon tetrachloride and other organic solvents were distilled before use. To study interference, standard solutions od diverse ions were prepared from their corresponding salts. All other chemicals used, were of analytical grade.

Determination of Nickel:

To an aliquot containing 39.5μg of nickel(II), were added 2.5 ml of 0.04% alcoholic solution of 2-hydroxy-1-naphthaldoxime and 0.2 ml of 3-picoline followed by adequate amount of buffer to make the volume of the aqueous phase upto 10 ml and left for 1 min to ensure complete comlexation. Finally it was equilibrated with carbon tetrachloride (10 ml) for 30 sec. The separated greenish organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the carbon-tetrachloride extract was read at 380 nm. against reagent blank. Amount of nickel was deduced from a calibration curve. To study the effects of diverse ions, the desired foreign ion was added to the system before addition of the reagents.

RESULTS AND DISCUSSION

Nickel (II) forms a greenish complex with 2-hydroxy-1-naphthaldoxime, extractable in to carbontetrachloride. Addition of traces of 3-picoline can lead to better sensitivity than the binary complex.

Absorption spectra :

The absorption spectrum of Ni(II) complex in carbon tetrachloride exhibits absorption maxima at 380 nm. With a shoulder at around 390 nm Fig. 1. The reagent blank does not absorb in this region. Wave length of 380 nm was selected for all analytical measurements.

Extraction as a function of pH :

The extraction of nickel in terms of absorbance was investigated in the pH range 0-13. Although extraction starts from PH-1, the organic extract showed a steady and maximum absorbance when the extractions were carried out from pH 7.0-12. In this pH range after a single extraction when the extraction process was repeated using the same aqueous phase, the organic extract virtually showed no absorbance. This indicated a complete and quantitative recovery of nickel in this condition. Absorbance as a function of pH is shown in Table 1, Fig. 2.

Effect of solvents :

Apart from carbontetrachloride, some other organic solvents like chloroform, benzene, and ethyl acetate were tested as extracting solvents; but those offered no special advantages over carbon-tetrachloride as seen from Table 2.

Stability of colour :

The absorbance of Ni(II)-2-hydroxy-1-naphthaldoxime complex in carbon tetrachloride was measured at elapsed intervals of time at 380 nm. The colour intensity was found to be stable for at least 12 hours as seen from Table 3.

Reagent concentration and Beer's law :

The optimum reagent concentration in the procedure was ascertained by extracting a known amount of nickel at various concentration of 2-hydroxy-1-naphthaldoxime, keeping the other variables constant. It was noted that 2.0 ml of 0.04% ethanolic solution of the reagent along with 0.2 ml of 3-picoline was sufficient to extract 39.5 μg of nickel in a single operation. Higher reagent concentration (upto 4 ml) had no adverse effect. Results are shown in Table 4.

The absorbance of the organic extract showed a linear response over a concentration of 10 ppm of nickel. The molar absorptivity of the complex (on the basis of metal content) was evaluated to be 1.202×10^4 l $ml^{-1}cm^{-1}$ with Sandell's sensitivity 0.048 $\mu g/cm^2$. Beer's law data are shown in Table 5, Fig. 3.

Although the nickel complex with 2-hydroxy-1-naphthaldoxime was extracted into carbon tetrachloride, the organic extract showed low absorbance. Addition of trace amount of nitrogenous bases like pyridine or some other substituted pyridines enhances the absorbance of the complex. Addition of 3-picoline offered maximum absorbance.

Interference :

To study the effect of diverse ions, nickel was determined as above in presence of the respective foreign ion in a binary mixture. Deviation of not more than ± 3% from the recovery of nickel, was taken as the tolerance limit for the diverse ion tested. In the estimation of 39.5 μg of nickel, the following ions did not interfere when present in amounts (μg) shown in Table 6.

Determination of nickel in synthetic mixtures :

In absence of real samples the proposed method was tested to estimate microgram amounts of nickel from some synthetic mixtures as shown in Table 7.

Precision and accuracy :

The proposed method was tested by analysing solutions containing a known amount of nickel(II). The experimental results are shown in Table 8. The method is fairly precise and reproducible, requiring hardly 10-15 min for each run.

Comparison of the present method

The proposed method is very simple and rapid and is comparable well with some other existing methods as seen from Table - 9.

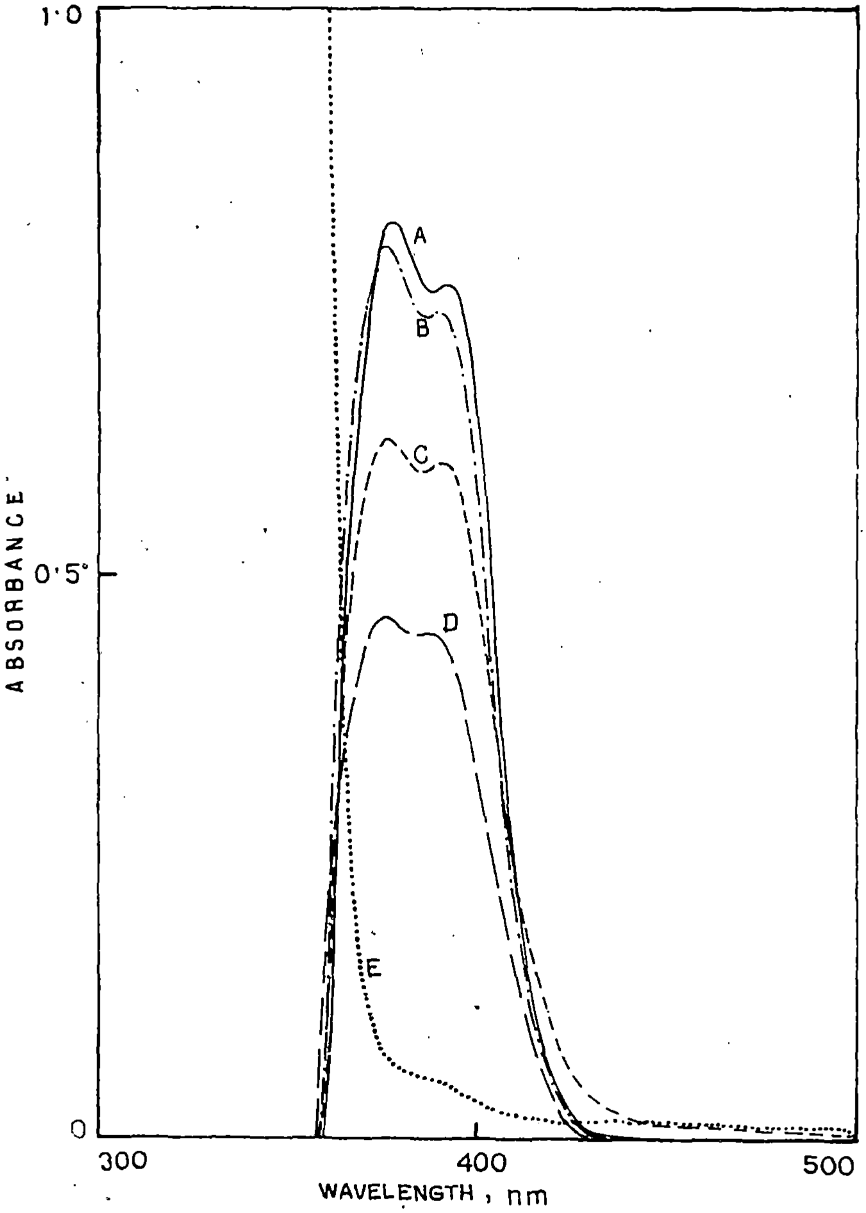


FIG : 1. ABSORPTION SPECTRUM OF Ni(II)-2-HYDROXY-1-NAPHTHALDOXIME COMPLEX (Ni - 3·95 ppm)

A - In carbontetrachloride , B - In Benzene ,
C - In Chloroform , D - In Ethylacetate , E - Reagent Blank

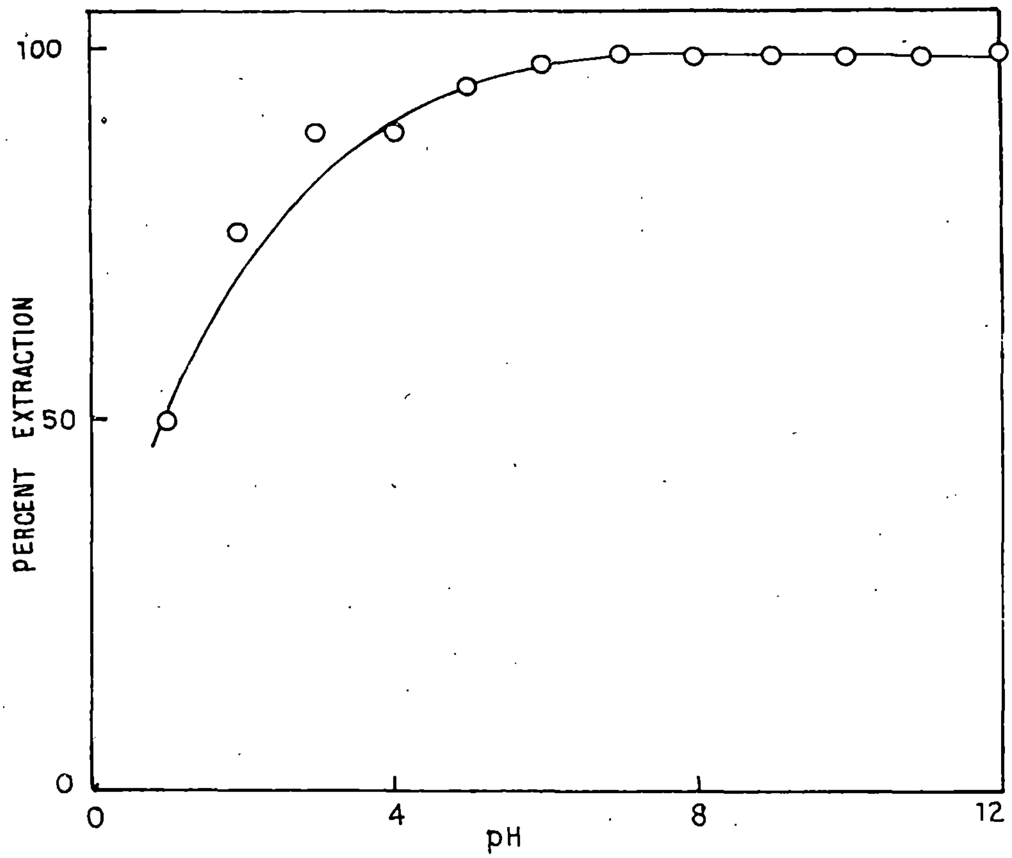


FIG : 2. EXTRACTION CURVE OF NICKEL

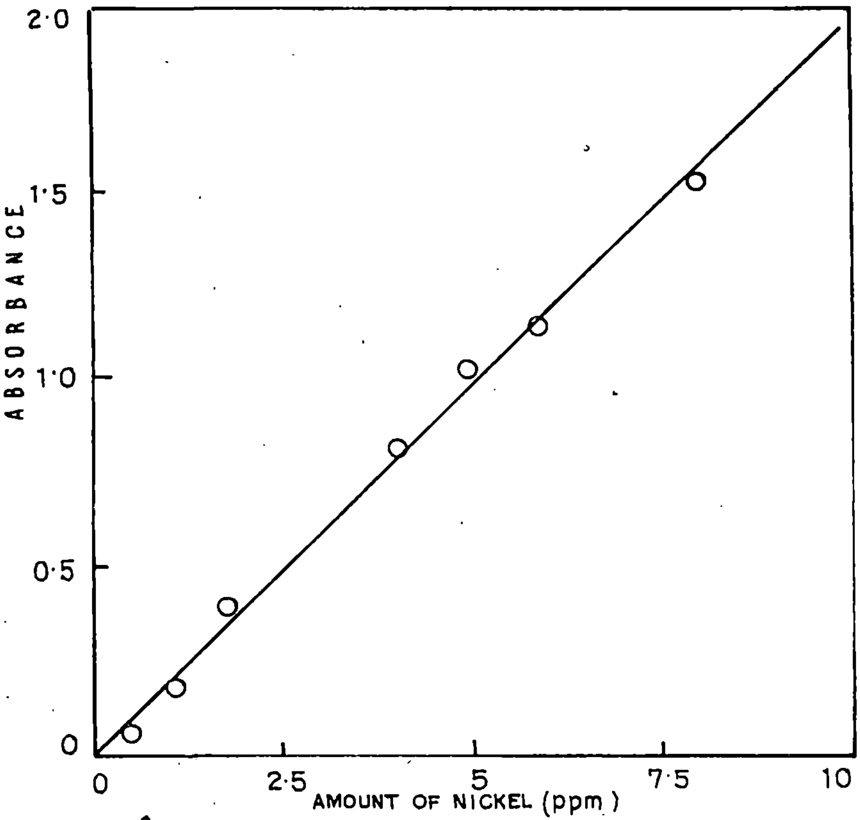


FIG: 3. CALIBRATION CURVE FOR DETERMINATION OF NICKEL

Table 1. Variation of absorbance with pH of the aqueous phase [The aqueous phase (10 ml) contains 39.5 μg of Ni(II), 2.5 ml ethanolic solution (0.04%) of the reagent and 0.2 ml of 3-picoline .]

pH	Absorbance at 380 nm	pH	Absorbance at 380 nm
1	0.406	8	0.812
2	0.608	9	0.810
3	0.720	10	0.812
4	0.720	11	0.812
5	0.768	12	0.810
6	0.786		
7	0.810		

Table 2. Effect of solvents on extraction of Nickel

Solvent used	Molar absorptivity ($l\ mol^{-1}cm^{-1}$)
Carbon tetrachloride	1.202×10^4
Benzene	1.172×10^4
Chloroform	0.920×10^4
Ethyl acetate	0.683×10^4

Table 3. Variation of absorbance of the carbontetrachloride extract containing Ni(II)-complex with time.

Time in hour after extraction	Absorance at 380 nm
0.25	0.810
0.5	0.810
1	0.812
2	0.812
4	0.810
8	0.810
12	0.812

Table 4. Effect of 2-hydroxy-1-naphthaldoxime concentration [The aqueous phase (10 ml) (pH 8) contains 39.5 μg of Ni(II) and 0.2 ml of 3-picoline] 0.04% ethanolic solution of the reagent was used.

Reagent added ml.	Absorbance at 380 nm.	Reagent added ml.	Absorbance at 380 nm.
0.05	-	1.5	0.810
0.1	0.120	1.75	0.812
0.25	0.330	2.0	0.814
0.5	0.660	2.5	0.818
0.75	0.706	3.0	0.820
1.0	0.780	3.5	0.816
1.25	0.810	4.0	0.820

Table 5. Beer's law data

Amount of Ni ppm	Absorbance at 380 nm.
0.49	0.080
0.88	0.180
1.97	0.400
3.95	0.810
4.90	1.002
5.90	1.140
7.90	1.520

Table 6 Effect of foreign ions on the determination of 39.5 μg of nickel

Foreign ion added	Amount tolerated (μg)	Foreign ion added	Amount tolerated (μg)
Thiocyanate	3000	Sr(II)	2000
Fluoride	3000	Ba(II)	2000
Phosphate	3000	Ca(II)	2000
Phthalate	3000	Cd(II)	2000
Thiosulphate	3000	Rh(III)	2000
Bromide	3000	Pt(IV)	2000
Iodide	3000	Pb(II)	2000
Nitrate	3000	Pd(II)	2000
Ascorbate	3000	Mo(VI)	2000
Tartrate	3000	Tn(IV)	500
Citrate	3000	Cu(II)*	2000
Oxalate	2000	Fe(III)**	2000
EDTA	nil	Co(II)	nil
Borate	2000	U(VI)	500
V(V)	2000	Zr(IV)	500
Sn(II)	2000	Hg(II)	500
Ag(I)	1000	Zn(II)	500
Bi(III)	2000	Au(III)	2000
Cr(III)	2000		

* In presence of citrate

** In presence of fluoride

Table 7. Determination of nickel in synthetic mixtures

	Composition (amount in µg)	Nickel found (µg)
1.	*Ni(39.5µg) + Cu(100) + Fe(100)	38.5, 38.0, 39.0
2.	Ni)39.5µg) + Pd(100) + Pt(100) + Rh(100)	40.0, 38.5, 38.5
3.	Ni(39.5µg) + Zr(100) + Th(100) + U(100)	38.0, 38.5, 40.0
4.	Ni(39.5µg) + Zn(100) + Hg(100) + Cd(100)	39.0, 39.0, 40.0
5.	Ni(39.5µg) + Mg(100) + Cr(100) + Mo(100)	38.5, 38.0, 38.5
6.	Ni(39.5µg) + Ag(100) + Pb(100)	38.5, 38.5, 40.0

* plus 2 ml each of citrate and fluoride.

Table 8. Reproducibility of nickel recovery

Nickel taken (μg)	Nickel found (μg)	Mean (μg)	Std. Dev. %
19.77	19.0, 18.5, 18.5 20.5, 20.0, 19.0	19.25	0.82
39.55	40.5, 38.5, 40.0 40.5, 39.5, 39.0	39.66	0.82
59.33	60.0, 61.5, 60.0 58.0, 58.5, 61.0	59.83	1.36

Table 9. Comparison of the present method

Ref.	Reagen	pH	λ_{max} (nm)	Molar absorptivity ($l\ mol^{-1}cm^{-1}$)	Interference
41.	2-(5-chloro-2-pyridylazo)-1,5-diaminobenzene	7.1	530-534	8.95×10^{4}	Fe
36.	Xylenol orange	10	614	5.6×10^{4}	-
42.	2-[2-(5-bromobenzothiazolyl) azo]-5-dimethyl aminobenzoic acid	-	655	1.47×10^{5}	Cu^{*}, Pd^{*}
26.	Xanthates	5-9	415,475	2.8×10^{3} -3.2×10^{3}	Fe(II)*, Pb(II)*, Co(II)*, Bi(III), Cu(II), Os(VIII), Vanadate, molybdate
7.	Phenanthroquinonemonoxime	4.9-8.5	450	5.95×10^{3}	Al^{+3*} Ca^{+2*}, Pb^{+2*}, Cu^{+2}, Ag^{+}, $^{*}Mn^{+2}$, Sb^{+3}
43.	2(p-sulphophenyl-azo) 1,8-dihydroxy naphthalene 3,6-disulphonic acid	2.5-7.0	575	7.0×10^{3}	nil (a large number of common ions do not interfere)
	Present method	7-12	380	1.202×10^{4}	-

* masking agents used.

Extraction and Spectrophotometric Determination of Cobalt with 2-hydroxy-1-napthaldoxime

EXPERIMENTAL

Apparatus and Reagents :

Absorbance measurements were made with a Shimadzu PR-1 model spectrophotometer equipped with stoppered quartz cells of 10 mm. optical path length.

A stock solution of cobalt (II) was prepared from $Co(NO_3)_2 \cdot 6H_2O$ and standardized. A working solution of Co(II) was prepared by appropriate dilution. 2-hydroxy-1-naphthaldoxime was prepared as reported earlier. Buffer solution (pH-8), prepared by standard method, was used to adjust the acidity of the aqueous phase.

3-picoline, benzene and other organic solvents were distilled before use. Standard solutions of diverse ions were prepared from this corresponding salts. All other chemicals used, were of analytical grade.

Determination of Cobalt :

To an aliquot containing 67 μg of cobalt (II), 1.2 ml of 0.04% alcoholic solution of 2-hydroxy-1-naphthaldoxime and 0.1 ml of 3-picoline followed by 5 ml of buffer were added. The aqueous phase was then diluted to 10 ml with distilled water and left for 1 min to ensure complete complexation. Finally, it was equilibrated with benzene (10 ml) for 30 sec. The separated orange-brown organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the benzene extract was read at 400 nm against a cobalt free reagent blank. Amount of cobalt was deduced from a calibration curve. To study the effects of diversions, the respective foreign ions were added to the aqueous solution before addition of the reagents.

RESULTS AND DISCUSSION

Absorption Spectra :

The absorption spectrum of the cobalt complex in benzene, taken against the reagent blank, shows maximum absorbance at 400 nm with shoulder around 380 and 420 nm (Fig. 1). The reagent blank does not absorb in this region. Wave-length of 400 nm was selected for all analytical measurements.

Extraction as a function of pH :

The extraction of cobalt in terms of absorbance was investigated in the pH range 0-12. Extraction of cobalt virtually starts from pH 1. The benzene extract showed steady and maximum absorbance when the extractions were carried out from aqueous solutions at pH 8-9. In this pH range, after a single operation when the extraction process was repeated using the same aqueous phase, the organic extract virtually showed no absorbance. This indicated a complete and quantitative recovery of cobalt in this condition. Extraction of the metal however decreases beyond pH 10. This has been shown in Table 1 (Fig. 2).

Effect of solvent :

Apart from benzene, some other solvents like chloroform, carbontetrachloride and ethylacetate were tested as extracting solvents, but those offered no special advantages over benzene as seen from Table 2. The pattern of the absorption spectra of the complex remains unchanged in all cases.

Stability of colour :

The absorbance of the Co(II)-2-hydroxy-1-naphthaldoxime complex in benzene was measured at elapsed intervals of time at 400 nm. The colour intensity is stable at least for 12 hours as seen from Table 3.

Reagent concentration and Beer's law :

The optimum reagent concentration was ascertained by extracting cobalt at various concentrations of 2-hydroxy-1-naphthaldoxime. It was noted that 1.5 ml of 0.04% ethanolic solution of the reagent along with 0.1 ml of 3-picoline was sufficient to extract 67 μg of cobalt in a single extraction. Higher reagent concentration (upto 3.0 ml of the oxime) had no adverse effect on the extraction. This has been shown in Table 4.

The system conforms to Beer's law over a concentration of 10 ppm of cobalt (Table 5, Fig. 3). The molar absorptivity of the complex (on the basis of metal content) was also evaluated (Table 2). The sensitivity of the method worked out to be 0.071 $\mu g/cm^2$.

Although the cobalt complex with 2-hydroxy-1-naphthaldoxime was extracted into the benzene, addition of traces of nitrogenous bases like pyridine, 2-picoline, 3-picoline, 4-picoline, 2,4,6-collidine etc. could lead to better sensitivity than the binary complex. Among the bases used, addition of 3-picoline or 4-picoline gave maximum absorbance.

Interference :

In order to study the effects of diversions on the extraction behaviour, 67 μg of cobalt were extracted and determined according to the recommended procedure in presence of the respective foreign ions. Extraction pH was set at 8.0. An ion was considered to interfere if the recovery of cobalt differed by more than ± 3% from the actual amount taken. The results are shown in Table 6.

The interferences due to iron and copper were avoided using ammonium hydrogen fluoride and citrate respectively as the masking agents. However EDTA interfered seriously. Nickel must be absent. Presence of arsenate showed low recovery of cobalt.

Determination of cobalt in synthetic mixtures :

In absence of real samples, the proposed method was tested to estimate microgram amounts of cobalt in various synthetic mixtures (Table 7).

Precision and accuracy :

The proposed method was tested by analysing solutions containing a known amount of cobalt (II). The experimental results are shown in Table 8. The method is fairly precise and reproducible requiring 10-15 min for each run.

Comparison of the present method :

The proposed method is very simple and rapid. The method has been compared with some other existing methods as shown in Table 9. Microgram amounts of cobalt can be determined in presence of a number of diverse ions although EDTA and nickel interfered.

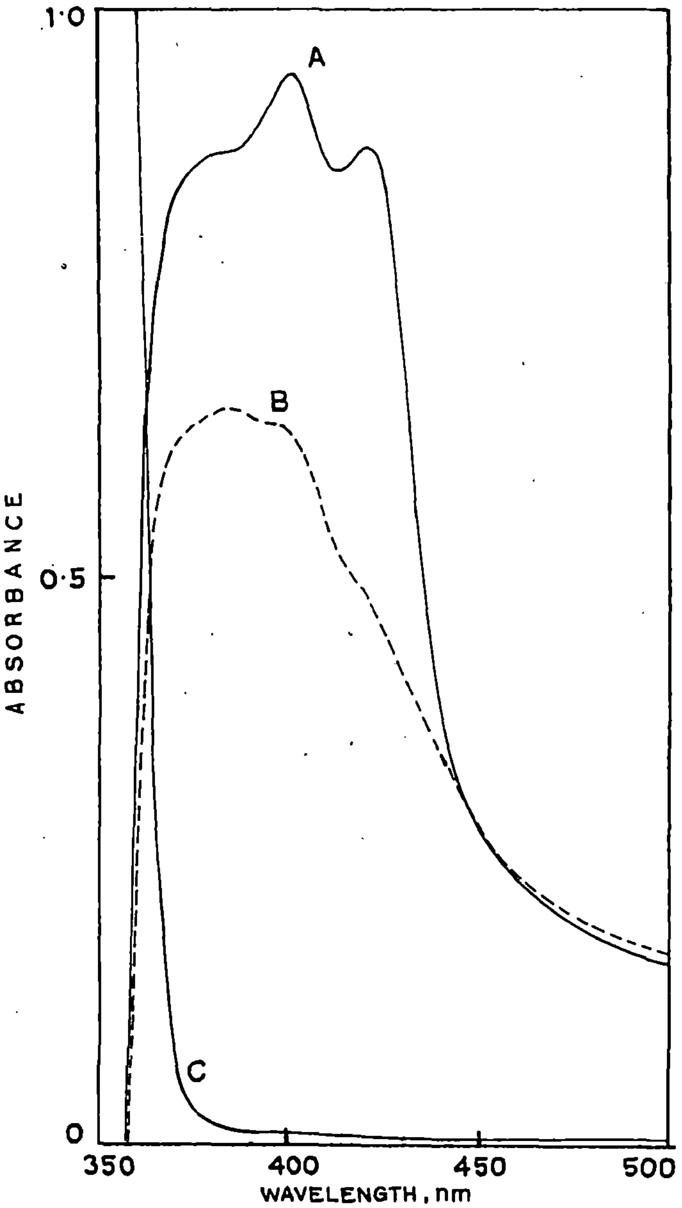


Fig: 1. Absorption spectrum of Co(II)-2-Hydroxy-1-Naphthaldoxime complex.

A - In presence of 3 picoline. B - In absence of 3 picoline. C - Reagent Blank

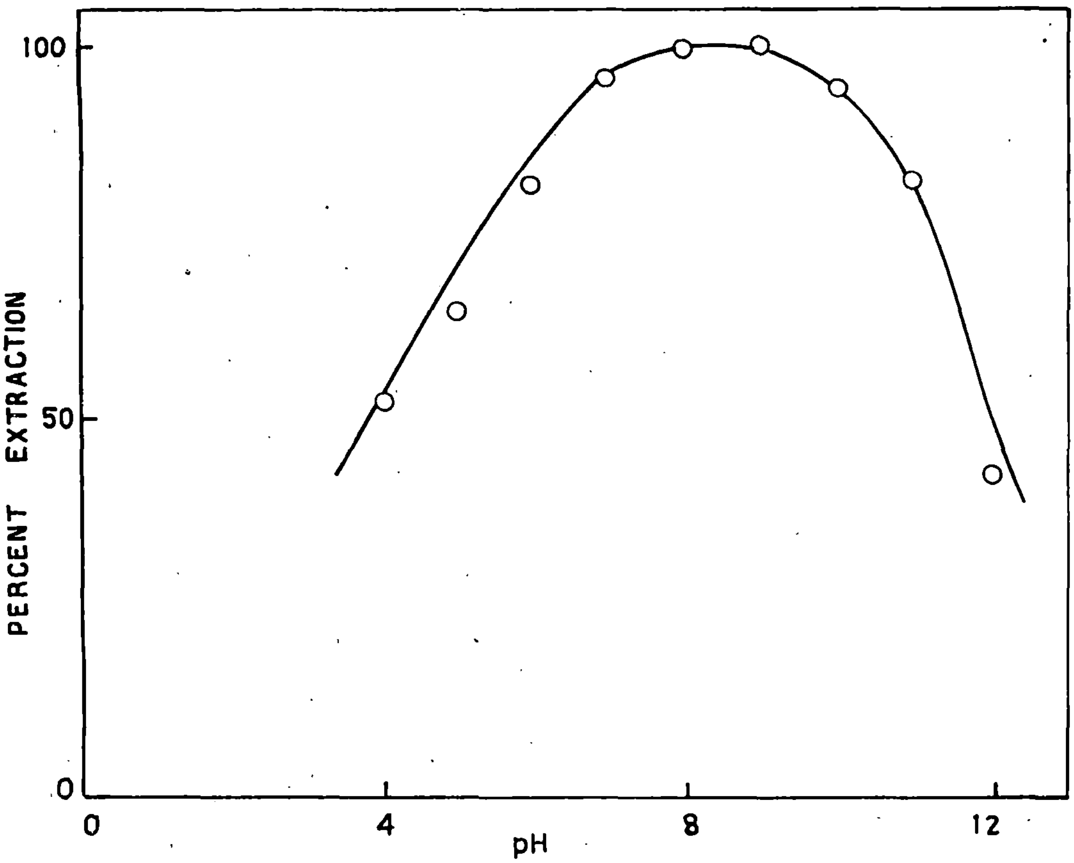


FIG. 2. EXTRACTION CURVE OF COBALT

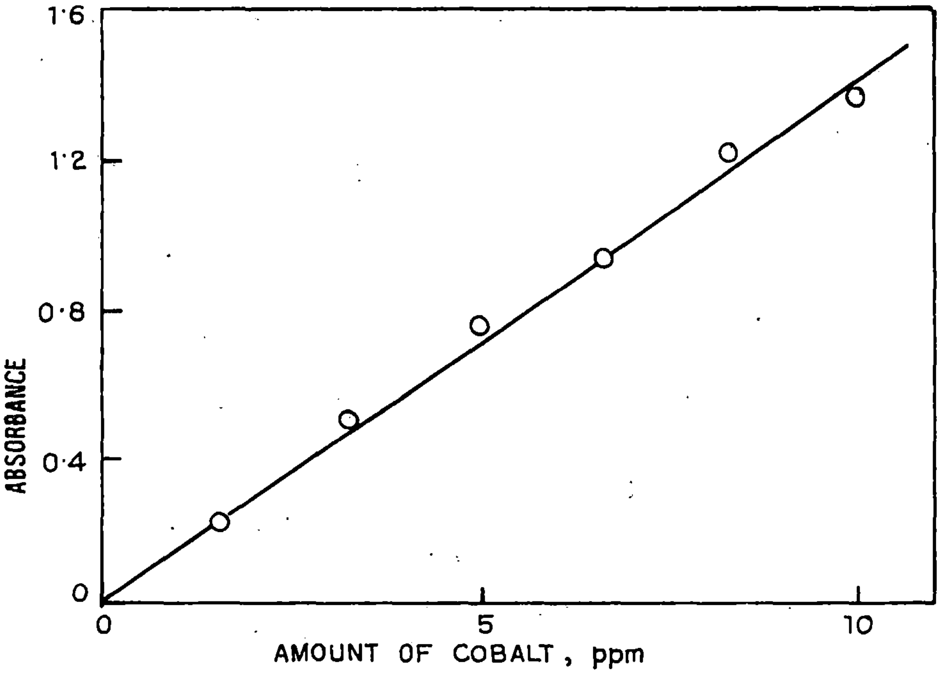


FIG. 3. CALIBRATION CURVE FOR COBALT

Table 1. Variation of absorbance with pH of the aqueous phase. [The aqueous phase (10 ml) contains 67 μg of Co(II), 1.2 ml of ethanolic solution (0.04%) of the reagent and 0.1 ml of 3-picoline].

pH	Absorbance at 400nm	pH	Absorbance at 400nm
4	0.490	9	0.940
5	0.600	10	0.880
6	0.760	11	0.760
7	0.900	12	0.400
8	0.940		

Table 2. Effects of solvents on extraction of cobalt

Solvent used	Molar absorptivity found ($l\ mol^{-1}cm^{-1}$)
Benzene	0.826×10^4
Carbon tetrachloride	0.782×10^4
Chloroform	0.774×10^4
Ethylacetate	0.703×10^4

Table 3. Variation of absorbance of the Co(II)-complex with time

Time in hour after extraction	Absorbance at 400 nm
0.25	0.940
0.5	0.942
1.0	0.940
2	0.940
4	0.942
8	0.938
12	0.938

Table 4. Effect of 2-hydroxy-1-naphthaldoxime concentration. [The aqueous phase (10 ml) (pH 8) contains 67 μg of Co(II) and 0.1 ml of 3-picoline]. 0.04% ethanolic solution of the reagent was used.

Reagent added ml	Absorbance at 400 nm	Reagent added ml	Absorbance at 400nm
0.2	0.130	1.6	0.940
0.4	0.332	1.8	0.955
0.6	0.520	2.0	0.950
0.8	0.660	2.5	0.950
1.0	0.860	3.0	0.940
1.2	0.922	4.0	0.910
1.4	0.922	5.0	0.896

Table 5. Beer's law data

Amount of Co(II) ppm	Absorbance at 400 nm
1.67	0.220
3.35	0.502
5.02	0.760
6.7	0.940
8.37	1.220
10.05	1.360

Table 6. Effect of diverse ions for determination of 67 μg of cobalt

Foreign ion added	Amount tolerated (μg)	Foreign ion added	Amount tolerated (μg)
Nitrate	3000	Hg(II)	1000
Ascorbate	3000	Pd(II)	1000
Tartrate	3000	Pt(IV)	1000
Citrate	3000	Ba(II)	3000
Borate	3000	Cd(II)	1000
Oxalate	500	Ca(II)	3000
Fluoride	3000	Th(IV)	500
Phthalate	3000	Sr(II)	3000
Phosphate	3000	Zn(II)	1000
Thiocyanate	3000	U(VI)	1000
Bromide	3000	Zr(IV)	750
Iodide	3000	Mo(VI)	1000
Thiosulphate	3000	Bi(III)	1000
Cu(II)*	750	Cr(III)	1000
Pb(II)	750	Ag(I)	500
Mg(II)	2000	V(V)	750
Sn(II)	1500		
Fe(III)**	1000		

*in presence of citrate

**in presence of fluoride

Table 7. Determination of cobalt in synthetic mixtures

Sl. No.	Composition (Amounts in μg)	Cobalt found (μg)
1.	Co(67 μg)* + Cu(100) + Fe (100)	69.0, 67.5, 67.5
2.	Co(67 μg) + Pd (100) + Pt(100) + Rh(100)	67.0, 67.5, 67.5
3.	Co(67 μg) + Zr(100) + Th(100) + U(100)	68.0, 68.0, 67.0
4.	Co(67 μg) + Zn(100) + Hg(100) + Cd(100)	67.0, 67.5, 68.5
5.	Co(67 μg) + Cr(100) + Mo(100)	68.5, 68.5, 67.0
6.	Co(67 μg) + Ag(100) + Pb(100)	67.0, 67.5, 69.0

* in presence of 2 mg each of citrate and fluoride.

Table 8. Reproducibility of cobalt recovery

Cobalt taken (μg)	Cobalt found (μg)	Mean (μg)	Std. Dev. (%)
33.5	32.0, 32.75, 33.5 33.0, 34.0, 33.75	33.16	0.818
67.0	65.5, 69.5, 68.0 68.0, 68.0, 67.75	67.75	1.29
100.5	101.5, 100.5, 98.5 98.5, 102, 102	100.5	1.64

Table 9. Comparison of the present method

Ref.	Reagent	pH	λ_{max}	Molar absorptivity	Interference
44	Ninhydrin oxime	3-6	330	1.97×10^4	Rh(III), nitrile
45	Cetyltrimethyl ammonium bromide + Thiocyanate	4M HCl to pH 8.0	625	1.9×10^3	Cu, Zn, Ag, EDTA*, Cd*
46	Isonitroso thiocamphor	1M HCl to 1M NaOH	240 295 325	1.7×10^4	Pd*, Cu* and EDTA*
47	Thioglycolic acid anilide	5.6-9.8	480-485	1.128×10^4	Be*(II), Fe*(III), Al*(III), Bi*(III), Th*(IV), Pb*(II), Cd*(II), As*(III), Cr*(III), Cu*(II), EDTA*, ascorbic acid and thioglycolic acid.
48	5-(3,5-dibromo-2-pyridylazo)-2,4-diamino toluene	5.5-7.7	580	1.16×10^5	EDTA, NO_3^-
	Present method	8-9	400	0.826×10^4	EDTA, Ni, Cu*, Fe*

*masking agents used.

Extraction and Spectrophotometric Determination of palladium with 2-Hydroxy-1-naphthaldoxime

EXPERIMENTAL

Apparatus and Reagents:

Absorbance measurements were carried out with a Shimadzu PR-1 model spectrophotometer equipped with stoppered quartz cells of 10 mm optical path length.

A stock solution of palladium (II) was prepared from palladium chloride (Johnson and Matthey) and standardised with dimethylglyoxime. A lower concentration of Pd(II) was prepared by appropriate dilution.

2-hydroxy-1-naphthaldoxime was prepared according to the procedure described by Vogel[40]. A 0.8% ethanolic solution of the reagent was used for the routine work. Buffer solution (pH-1), prepared by standard procedure was used to adjust the acidity of the aqueous phase solution.

2,4,6-collidine, chloroform, and other organic solvents were distilled before use. To study interferences, standard solutions of diverse ions were prepared from their corresponding salts. All other chemicals used, were of analytical grade.

Determination of palladium :

To an aliquot containing (120)μg of palladium(II) were added 2 ml of 0.08% ethanolic solution of 2-hydroxy-1-naphthaldoxime and 0.1 ml of 2,4,6-collidine followed by adequate amount of buffer to make the volume of the aqueous phase upto 10 ml and left for 1 min to ensure complete complexation. Finally it was equilibrated with chloroform (10 ml) for 30 sec. The separated organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the chloroform extract was read at 400 nm against a reagent blank. Amount of palladium was deduced from a calibration curve. To study the effects of diverse ions the desired foreign ion was added to the system before addition of the reagents.

RESULTS AND DISCUSSION

Palladium(II) forms yellowish green complex with 2-hydroxy-1-naphthaldoxime, extractable into chloroform. Addition of traces of 2,4,6-collidine enhanced the absorbance of the complex and thus leads to better sensitivity of the system.

Absorption spectrum :

The absorption spectrum of the palladium complex in chloroform exhibits absorption maximum at 400 nm. The reagent blank does not absorb in this region. Hence wave length of 400 nm was selected for all analytical measurements (Fig. 1).

Extraction as a function of pH :

The extraction of palladium in terms of absorbance was investigated in the pH range 0-12. Organic extracts showed steady and maximum absorbance when the extractions were carried out from aqueous solution of pH 0.5-3.5 indicating quantitative recovery of palladium in this range. Extraction of the metal however decreases at higher acidities and beyond pH 4.0. This has been shown in Table 1, Fig. 2.

Effects of solvents:

Apart from chloroform, some other organic solvents like benzene, ethyl acetate and carbon tetrachloride were tested as extracting solvents. Palladium(II) complex in ethyl acetate or carbon-tetra chloride showed low absorbances. Use of benzene offered no special advantages over chloroform.

Reagent concentration and Beer's law :

The optimum reagent concentration was ascertained by extracting palladium at various concentrations of 2-hydroxy-1-napththaldoxime keeping the other variables constant. It was noted that 2.0 ml of 0.08% ethanolic solution of the reagent along with 0.1 ml of 2,4,6-collidine was sufficient to extract 120 μg of palladium in a single operation. Higher reagent concentration (upto 4 ml) had no adverse effects on extraction. This has been presented in Table 2.

In the optimum conditions, the absorbance of the organic extract showed a linear response over a concentration of 15 ppm of palladium (Table 4, Fig. 3). The molar absorptivity of the complex (on the basis of metal content) was evaluated to be 0.865×10^4 l $mol^{-1}cm^{-1}$ with Sandell's sensitivity 0.012 $\mu g/cm^2$.

Although the palladium formed complex with 2-hydroxy-1-naphthaldoxime, extractable into chloroform, addition of traces of 2,4,6-collidine could lead to better sensitivity of the system. Other nitrogeneous bases like pyridine, α-picoline β-picoline or γ-picoline could also be used but 2,4,6-collidine showed maximum absorbance in this case.

Stability of colour :

The absorbance of the Pd(II)-2-hydroxy-1-naphthaldoxime complex in chloroform was measured at elapsed intervals of time at 400 nm. No change in the colour intensity was recorded upto 12 hours as seen from Table 3.

Interference :

To study the effects of diverse ions, palladium was determined as above in presence of the respective foreign ions in a binary mixture. Deviation of not more than ± 3% from the recovery of palladium was taken as the tolerance limit for the diverse ion tested. 120 μg of palladium could be determined without interference in presence of 25-fold excess of barium(II), cadmium(II), nickel(II), calcium(II), cobalt(II), thorium(IV), strontium(II), zinc(II), uranium(VI), mercury(II), platinum(IV), rhodium(III), gold(III), molybdenum(VI), vanadium(V), bismuth(III), lead(II), tin(II), magnesium(II). 15-fold excess of zirconium(IV), chromium(III(, silver(I); bromide, iodide and arsenate. 25-fold excess of iron(III), and copper (II), could be tolerated in presence of fluoride and citrate respectively. The system tolerated 50-fold excess of nitrate, ascorbate, tartrate, citrate, borate, oxalate, fluoride, phthalate, phosphate, thiocyanate and sulphate. However thiosulphate and EDTA interfered. The results are tabulated in Table 5.

Determination of palladium in synthetic mixtures :

In absence of real samples the proposed method was tested to estimate microgram amounts of palladium from some synthetic mixtures as shown in Table 6.

Precision and accuracy.

The proposed method was tested by analysing solutions containing a known amount of palladium(II). The experimental results are shown in Table 6, indicating the method to be fairly precise and reproducible requiring hardly 10-15 min for each run (Table 7).

Conclusion:

The present method for the spectrophotometric determination of palladium is simple and has been compared with some other existing methods. The sensitivity of the method is not as high as the other one (Table 8); but the method provides excellent recovery of palladium is microquantities in presence of almost all the common ions except thiosulphate and EDTA. Interference of the interfering ions like iron and copper can be easily overcome.

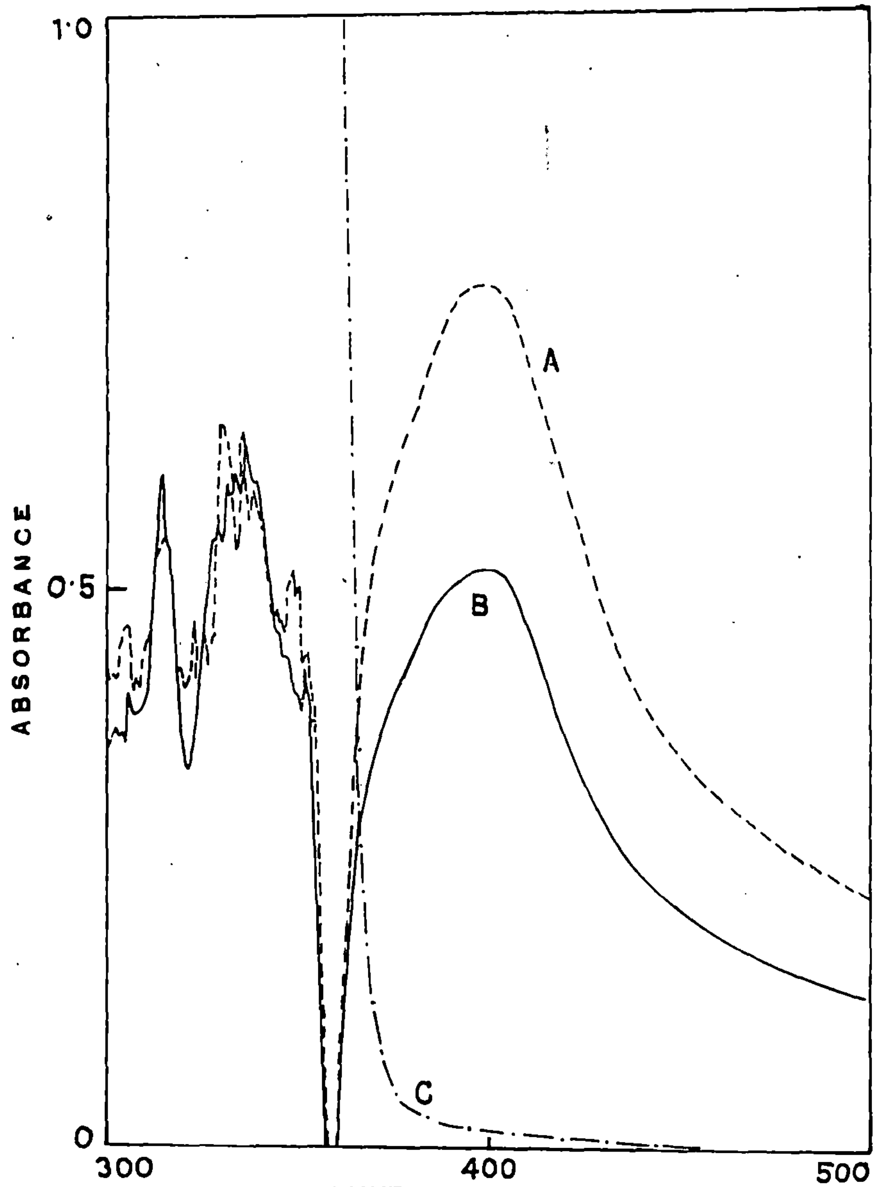


FIG. 1. Absorption spectrum of Pd(II)-2-Hydroxy-1-Naphthaldoxime complex (Pd-9·4 ppm) A- In presence of collidine, B- In absence of collidine, C- Reagent Blank

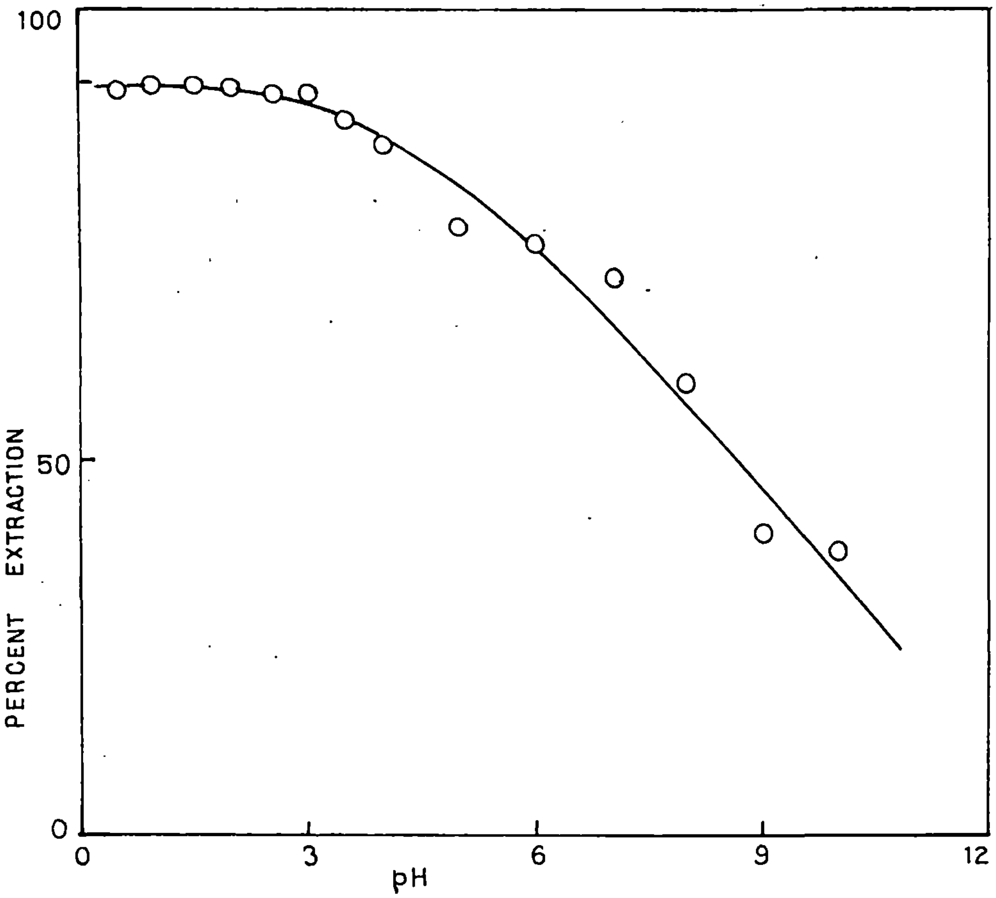


FIG: 2. EXTRACTION CURVE OF PALLADIUM

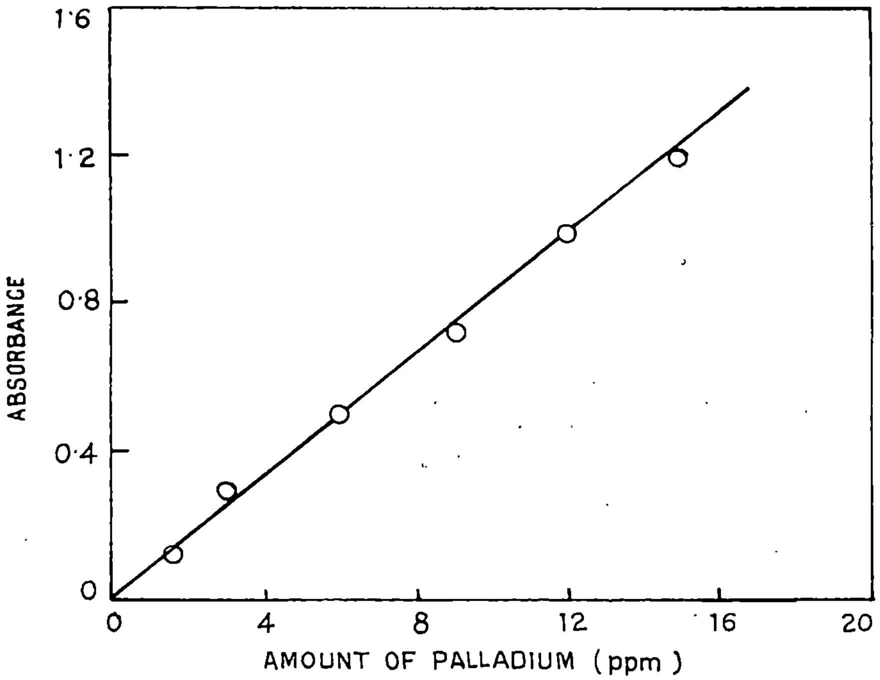


FIG : 3. CALIBRATION CURVE FOR DETERMINATION OF PALLADIUM

Table 1. Variation of absorbance with pH of the aqueous phase
[The aqueous phase contains 120 μg of Pd(II), 2 ml of 0.08% of the reagent and 0.1 ml of collidine. The volume is maintained at 10 ml].

pH	Absorbance at 400 nm	pH	Absorbance at 400 nm
0.5	0.988	4.0	0.922
1.0	0.988	4.5	0.900
1.5	0.988	5.0	0.804
2.0	0.988	6.0	0.780
2.5	0.984	7.0	0.742
3.0	0.988	8.0	0.602
3.5	0.970	9.0	0.400
		10.0	0.380

Table 2. Effect of 2-hydroxy-1- naphthaldoxime concentration
[the aqueous phase (10 ml) (pH-1) contains 120 μg of Pd(II) and 0.1 ml of collidine]. 0.08% ethanolic solution of the reagent was used.

Reagent added in ml	Absorbance at 400 nm	Reagent added in ml	Absorbance at 400 nm
0.25	0.420	2.0	1.000
0.5	0.490	2.25	0.988
0.75	0.582	2.5	0.986
1.0	0.662	2.75	0.988
1.25	0.804	3.00	0.988
1.50	0.870	3.5	0.986
1.75	0.984	4.0	0.986

Table 3. Variation of absorbance of the pd(II) complex with time.

Time in hour after extraction	Absorbance at 400 nm
0.25	0.988
0.5	0.988
1.0	0.986
2	0.988
4	0.988
8	0.986
12	0.988

Table 4. Beer's law data

Amount of Pd, in ppm	Absorbance at 400 nm
1.5	0.120
3	0.282
6	0.600
9	0.720
12	0.988
15	1.180

Table 5. Effects of diverse ions on the determination of 120 μg of palladium. Average of three determinations was taken in each case.

Ion added	Amount tolerated (μg)	Ion added	Amount tolerated (μg)
Nitrate	6000	Th(IV)	3000
Ascorbate	6000	Sr(II)	3000
Tartrate	6000	Zn(II)	3000
Citrate	6000	U(VI)	3000
Borate	6000	Hg(II)	3000
Oxalate	6000	Pt(IV)	3000
Fluoride	6000	Rh(III)	3000
Phthalate	6000	Au(III)	3000
Phosphate	6000	Mo(VI)	3000
Thiocyanate	6000	V(V)	3000
Sulphate	6000	Bi(III)	3000
Bromide	2000	Pb(II)	3000
Iodide	2000	Sn(II)	3000
Acetate	6000	Mg(II)	3000
Arsenate	2000	Zr(IV)	2000
Ba(II)	3000	Cr(III)	2000
Cd(II)	3000	Ag(I)	2000
Ni(II)	3000	Fe(III)*	3000
Ca(II)	3000	Cu(II)**	3000
Co(II)	3000		

*in presence of fluoride

**in presence of citrate.

Table 6. Determination of palladium in synthetic mixtures (Average of three determinations)

Composition (amount in μg)	Palladium found (μg)
1. Pd(120) + Fe(250) +Cu(250)	118.5
2. Pd(120) + Pt(250) + Rh(250)	120.5
3. Pd(120) + Ni(250) + Co(250)	121.0
4. Pd(120) + Zn(250) + Cd(250)	120.0
5. Pd(120) + Mo(250) + V(250)	119.0
6. Pd(120) + Hg(250) + Cr(250)	119.0

Table 7. Reproducibility of palladium Recovery

Palladium taken (μg)	Palladium found (μg)	Mean (μg)	Std. Dev. %
60	61.5, 60.0, 58.0 59.0, 60.0, 58.0	59.42	1.35
120	122, 122.5, 120.5 119, 119, 120	120.5	1.20
180	182, 180.5, 180 181, 178.5, 177.5	179.92	1.65

Table 8. Comparison of the present method

Ref.	Reagent	pH	λ_{max}	Molar absorptivity	Interference
49.	Isonitrosothiocamphor	pH 2.0-5M HCl	450	3.90×10^3	Cu*, Hg, Co*, Pt* and S_2O_3
50.	2-(2-benzothiazolylazo)-5-dimethylamino)-benzoic acid	2-6	695	4.96×10^4	Ag*(I), CO*(II), Ni*(II), Os*(VIII), Pt*(IV) and V*(V)
51.	Benzyl dimethylphenylammonium-chloride	3.4 to 5.8	450	0.534×10^4	- (common ions do not interfere)
52.	3-Acetoxy-7-methyl phenothiazine	0.5-4.0	550	7.4×10^3	- (common cations and anions do not interfere)
53.	O-Mercaptoacetoacetanilide	lower pH in HCl medium	518	7.57×10^3	nil (for noble and base metals)
	Present method	0.5-3.5	400	8.65×10^3	Fe*(III), Cu*, S_2O_3, EDTA

* masking agents used.

REFERENCES

1. Gentry C.H.R. and Sherrington L.G., Analyst, 1950, 75 , 17.

2. Nielsch W., Z. Anal. Chem., 1956, 150, 114.

3. McIntyre R.T., Berg E.W. and Campbell D.N., Anal. Chem., 1956, 28, 1316.

4. Stary J. and Headky E., Anal. Chim. Acta, 1963, 28, 227.

5. Shinde V.M. and Khopkar S.M., Chem. Ind. London, 1967, 1785.

6. Berg E.W. and Reed K.P., Anal. Chim. Acta, 1966, 36, 372.

7. Kamil F., Sindhwani S.K. and Singh R.P., Ind. J. Chem., 1978, 16A, 365-367.

8. Satake Masatada,
Fukui Daigaku Kogakubu Kenkyu Hokoku, 1979, 27(1), 17-24.

9. Riyazuddin P., Ind. J. Chem., 1981, 20A, 312-313.

10. Jain R.K. and Mital R.L., J. Inst. Chem. (India), 1981, 53(1), 38-40.

11. Morishita Muneo and Katayanagi Mosa, Buneski Kagaku, 1981, 30(7), 460-4.

12. Arora H.C., Ind. J. Chem., 1982, 21A, 335-336.

13. Hideo Akaiwa, Hiroshi Kawamoto and Etsuo Hiyamuta, Buneski Kagaku, 1982, 31(3), E117-E122.

14. Armas A. Gonzalex Diaz V. Gonzolex, Trujillo J.P. Perez and Montelongo F. Garcia., An. Guim., Ser. B., 1982, 78(3), 351-5.

15. Reddy K. Hussain and Reddy D. Venkata, Ind. J. Chem., 1983, 22A , 824-826.

16. Suero A.G.A., Microchem. J., 1983, 28(2), 198-202.

17. Sukhan V.U., Gorloch V.F., Nazarenko A. Yu., Pilipenko L.E. and Klod N.V., Ukr. Khim. Zh. (Russ. Ed.), 1983, 49(9), 956-60.

18. Reddy K.V. and Paul Agnes, Ind. J. Chem., Sect. A, 1984, 23A(9), 790-1.

19. Biswas N.R., Ray B.C. and Lahiri S., J. Indian. Chem. Soc., 1983, 60 (8), 775-8.

20. Xilin Liu, Garg Gu, Tongyue Chen and Jialong Gao, Fenxi Huaxue, 1984, 12 (4), 246-50.

21. Shrivastava Madhulika and Pandey G.S., Ind. J. Chem., Sect. A, 1984, 23A(4), 357-8.

22. Rao A.L. and Sekhar Chander J., Microchem. J., 1984, 30(3), 283-8.

23. Nengyoung Xie, Zuting Pan, Mineyi Xu and Mengwei Ye, Fenxi Huaxue, 1985, 13(8), 616-18.

24. Kato Takeshi, Hamada Makoto and Inoshita Hiroyasu, Buneski Kagaku, 1985, 34(3), 124-8.

25. Di Tera Michael R. and Schilt Alfred A., Microchem. J., 1985, 32(1), 44-9.

26. Paria P.K. and Majumdar S.K., Ind. J. Chem., Sect A., 1985, 24A (7), 629-30.

27. Dayong Qi, Fenggin Miao, Rongju Xie and Xiaoxuan Sun., Huaxue Shiji, 1986, 8(1), 10-13.

28. Kandrac J. and Szalo A., Acta Fac. Rerum. Nat. Univ. Comenianae Chim., 1985, 33 127-35.

29. Bashirov E.A. and Mamedov M.M., Azerb. Khim. Zh., 1987 (1), 128-32.

30. Youju Zhu and Yiqi Wang, Fenxi Huaxue, 1988, 16 (4), 347-50.

31. Arias J.J., Jimenez F. and Jimenez A.I., An. Quim. Ser. B., 1987, 83 (2), 211-16.

32. Zinchuk V.K., Mal'tseva G.S. and Grishchuk G.V., Zavod. Lab., 1988, 54(8), 11-12.

33. Pal Tarasankar, Ganguly Ashes and Pal Anjali, J. Indian. Chem. Soc., 1988, 65 (9), 655-7.

34. Li Zhem, Yejin Fenxi, 1988, 8(1), 23-26.

35. Li Shengy., Qin. Yongchao, Zhong Ping and Zhang Yuqing,

36. Zheng Enming, Yejin Fenxi, 1989, 9(6), 54-5.

37. Ishii Hayime, Odashima Rsugikatsu and Kawamonzen Yoshiaki, Bull. Chem. Soc., Jpn.,1990, 63 (12), 3405-9.

38. Fernandez Liliana, Marchevsky Eduardo and Olsina Roberto, An. Quim., 1991, 87 (2), 243-7.

39. Sautha K.S., Lakshmi, R.R. Naidu and Krishnan, V.R., J. Ind. Chem. Soc., 62 (1985) 79.

40. Vegel, A.I., A Text Book of Practical Organic Chemistry, Longmans, London, 1968, p. 171.

41. Yang Kejian and Sun Chengyao, Yejin Fenxi, 1988, 8(5), 13-15.

42. Zheng Guang and Yang Heqing, Fenxi Huaxue, 1990, 18(10), 933-6.

43. Bhattacharjee A.K. and Mahanti M.K., Ind. J. Chem., 1981, 20A, 427-428.

44. Paria P.K., Thokdar T.K. and Majumdar S.K., J. Indian Chem. Soc., 1990, 67, 532.

45. Paria P.K., Thokdar T.K. and Majumdar S.K., J. Indian Chem. Soc., 1990, 67, 787-788.

46. Paria P.K. and Majumdar S.K., Ind. J. Chem., 1985, 24A, 989-990.

47. Ray Chandrima (Miss) and Das Jyotirmoy, Ind. J. Chem., 1985, 24A, 40-42.

48. Jinfer Wang, Fenxi Huaxue, 1983, 11 (3), 203-5.

49. Majumdar S.K., Chattopadhayay P. and Paria P.K., J. Indian Chem. Soc., 1985, 62 (7), 544-5.

50. Katami Takeo, Hayakawa Tomokuni, Furukawa Masamichi and Shibata Shozo, Bunseki Kagaku, 1984, 33 (12), 676-78.

51. Bayan K.C. and Das H.K., Curr. Sci., 1984, 53 (17), 915-17.

52. Aggarwal Modhu, Bhargava Nandan, Jain R.K. and Mital R.L., Acta Cienc. Indica, [Ser.]Chem., 1983, 9(1-4), 75-6.

53. Das Arabinda K. and Das Jyotirmoy, Indian J. Chem., 1983, 22A, 93-94.

CHAPTER - IV

CETYLTRIMETHYLAMMONIUM BROMIDE AS AN ANALYTICAL REAGENT

Quaternary ammonium salts are very popular analytical reagents for the spectrophotometric determination and detection of a good number of metals. Quarternary ammonium salts with long carbon chain have an affinity to form ion-pairs with large anions and these ion-pairs are soluble in organic solvents. This property has been applied to the separation of number of metal ions. Cetyl-trimethyl ammonium bromide (CTAB) belongs to this category.

A.I. Kirlov et al[1] determined uranium (VI) by using bromopyrogallol red and CTAB at pH 6-7. The complex absorbs maximum at 635 nm. Niobium (V) was determined[2] spectrophotometrically by using various organic dyes in presence of CTAB. A sensitive method was suggested by Jadav and Venkateswarlu[3] for the determination of niobium. The molar absorptivity of the niobium-Bromopyrogallol red-IDTA system with CTAB was 1.55×10^5 at 620 nm. This method was applied to the analysis of steel.

The 1:2 ion-association complex of rare earth metal -m-cresolphthalexon complex with CTAB has been investigated by Shanlina and Kirilov[4]. Chrome Azural and CTAB[5] were used for the photometric determination of Ruthenium at pH 4.6-5.6. The complex absorbed maximum at 610 nm. Tellurium (IV) was determined[6] spectrophotometrically with the help of iodide and CTAB. The complex, extractable in to $CHCl_3$ absorbed at 630 nm with molar absorptivity 5.9×10^4 l $mol^{-1} cm^{-1}$. A spectrophotometric method was devised by Gordeva et al[7] for vanadium (V). The reagents used were pyrocatechol violet and CTAB. The complex showed maximum absorbance at 670 nm with pH at 5.0.

Shen. Hanxi[8] determined zirconium spectrophotometrically with salicylfluorone and CTAB. The complex absorbed at 512 nm with molar absorptivity 1.38 x 10^5 (in 0.3 M HCl).

Guanghui et al[9] determined tin spectrophotometrically with salicylfluorone and CTAB in metallic materials. The complex exhibits maximum absorbance at 510 nm (in 0.5-7.5 N H_2SO_4).

Hanxi[10] determined tungsten by dibromo alizarin violet and CTAB. In 1M HCl medium the W:DBA:CTAB ratio was found to be 2:3:6. The blue complex absorbed maximum at 620 nm. The molar absorptivity was 8.2 x 10^4.

Cr(VI)-bromopyrogallol red-CTAB system has been investigated by Huaigang and Guoquan[11]. Cr(VI) forms a 1:3 complex with Bromopyrogallol red in presence of CTAB. The absorbance was measured at 635 nm with molar absorptivity 3.64 x 10^4 l $mol^{-1}cm^{-1}$.

Weiwa et al[12] proposed a photometric method for the determination of titanium using O-nitrophenyl fluorone and CTAB. The absorbance of the complex was measured at 535 nm (pH 1.5-2.0) with molar absorptivity 1.3 x 10^5 l $mol^{-1}cm^{-1}$.

Daopei[13] determined Vanadium with Erichrome cyanine R and CTAB, at pH 5–6. Absorbance was measured at 585 nm with molar absorptivity 6.63×10^4 l $mol^{-1} cm^{-1}$. Oiheng[14] determined Hf spectrophotometrically with bromopyrogallol red and CTAB or cetylpyridinium bromide in 0.2 M HCl medium. The absorbance of the complex was found at 670 nm with molar absorptivity 6.3×10^4 l mol^{-1} cm^{-1}.

Xue Guang[15] studied the colour reaction of thorium with semixylenol orange in presence of CTAB. At pH 1.5–4.0 the complex thorium-semixylenol orange ratio was found to be 1:2 with molar absorptivity 5.5×10^4 l mol^{-1} cm^{-1} at 550 nm.

Bismuth in tin was determined spectrophotometrically by A.T. Pilipenko et al[16] using polysulphide ion and CTAB. The complex absorbed maximum at 440 nm. The solvent used was $CHCl_3$.

Aluminium was determined spectrophotometrically by Zhe and Shuisheng[17] using salicyl fluorone and CTAB. The complex exhibits maximum absorbance at 559 nm with molar absorptivity 1.4×10^5 l $mol^{-1} cm^{-1}$ at pH 5.7–6.5.

The reaction of Al(III)[18] with sodium 2-bromo-4, 5 dihydroxy benzene-4'-sulphonate in the presence of CTAB has been studied spectrophotometrically. Maximum absorbance was found at 527 nm in the pH range of 6.7–8.0.

Li Shaoqing et al[19] have made an investigation on the spectrophotometric determination of Vanadium (IV) with diphenylcarbazide and CTAB. The met : DPC:CTAB ratio was found to be 1:2:2.

The molar absorptivity of the complex was calculated to be 5 x 10^4 l mol^{-1} cm^{-1}. The method was applied in the determination of V(IV) in minerals, rocks and coal.

Rhodium was determined spectrophotometrically by the Hu Shokum et al[20] using salicylfluorone and CTAB. The complex has maximum absorbance at 595 nm.

Jiang Shufa et al[21] determined scandium using 7-iodo-8-hydroxyquinoline-5-sulphonic acid and CTAB. The complex exhibits its maximum absorbance at 505 nm in the pH range 4.5-6.0.

Clun Ziruo[22] described a spectrophotometric method for the determination of tin with o-chlorophenylfluorone and CTAB. The complex has an absorption peak at 520 nm with molar absorption coefficient 0.97 x 10^5.

Zinc was determined[23] with chrome zyral-s-semi-xylenol orange-CTAB spectrophotometrically. The absorbance was measured at 525 nm. The molar absorptivity was 1.18 x 10^2 l $mol^{-1}cm^{-1}$.

Yang Suqing et al[24] determined micro amounts of Cu with 4,5-dibromophenyl fluorone in presence of CTAB. The complex absorbed maximum at 590 nm (pH 5.0). The molar absorptivity was 1.5 x 10^5 l $mol^{-1}cm^{-1}$.

Hu Shoukun et al[25] carried out the spectrophotometric determination of Pd(II) with p-aminophenyl fluorone and CTAB. The Pd(II):PAPF was found to be 1:3. The absorbance was measured at 583 nm (pH 6.9-7.8) with molar absorptivity 8.56×10^4 l $mol^{-1} cm^{-1}$.

Cao-Shiti et al[26] used 5-nitrosalicyl fluorone in presence of CTAB to determine spectrophotometrically Ga. The complex showed maximum absorbance at 555 nm with molar absorptivity 1.91×10^5 l $mol^{-1} cm^{-1}$.

Ren Xing et al[27] have suggested a method for photometric determination of Zr with chlorophosphonazo-DBC and CTAB. The complex absorbed well at 650 nm with molar absorptivity 6.3×10^4 l $mol^{-1} cm^{-1}$.

9-(p-fluorophenyl) fluorone[28] and CTAB were used as reagents for the determination of Ge at 505 nm. The molar absorptivity was calculated to be 1.5×10^5 l $mol^{-1} cm^{-1}$.

Mo. Weiming et al[29] spectrophotometrically determined molybdenum using O-hydroxynaphthylfluorone and CTAB. The complex absorbs at 514 nm and has molar absorptivity of 1.17×10^5. Beer's law is obeyed in the range 0 to 10 μg Mo/25 ml.

Tang. Yangqiang[30] devised a method for determination of Ge with vanillyl fluorone and CTAB in 0.48-1.92 mol HCl/L. The complex showed maximum absorbance at 510 nm. The molar absorptivity was found to be 1.24×10^5 l $mol^{-1} cm^{-1}$.

Here CTAB finds applications in the extraction and spectrophotometric determination of bismuth and copper in optimum conditions.

Extraction and Spectrophotometric Determination of Bismuth with Cetyltrimethylammonium bromide (CTAB)

Introduction

From the literature survey it has been observed that Bismuth has an affinity to form complexes with different organic reagents like dithizone, dithiocarbamates, 8-quinolinol, bromopyrogallol red etc. In most of the cases, the after-extraction organic phases have been used for the colourimetric determination of the metal. Some of the methods are mentioned here.

Dithizone[31] has been used as a reagent for the spectrophotometric determination of bismuth. The bismuth-dithizone complex was extractable into chloroform showing its absorbance at 500 nm.

8-quinolinol[32] is another reagent that was utilised for the determination of bismuth at a pH of 4.0. The complex was extracted into chloroform and absorbed well at 395 nm.

Diethyldithiocarbamate[33] forms a complex with bismuth which is extractable into carbontetrachloride. The complex showed strong absorbance at 370 nm and 400 nm.

2-mercapto-4,4,6-trimethyl-1H, 4H-pyrimidine has been chosen as a spectrophotometric reagent for Bi(III) by Singh Ajai K. et al[34]. The orange red complex was extractable into chloroform from 1.5-3.0N perchloric acid. The complex absorbed well at 500 nm.

Kotelyanskaya L. I. et al[35] carried out the solvent extraction of Bismuth using lumogallion and diphenylguanidine. The metal: ligand:ligand ratio was found to be 1:1:1. The pH was adjusted between 1.8 and 2.0. The complex absorbed well at 490 nm.

Gorene D. et al[36] prepared a method for the spectrophotometric determination of bismuth using ammonium tetramethylene dithiocarbamate in excess. The spectrophotometric determination of bismuth with diacetyl monoxime-4-phenyl-3-thiosemicarbazone was carried out by Cano Pavan J.M. et al[37]. The metal : ligand ratio was found to be 1:2 and the complex was extracted into amyl alcohol with an absorbance at 385 nm. The Beer's law was obeyed upto 1-10 ppm Bismuth.

Nenova P. et al[38] investigated the spectrophotometric determination of bismuth with diethylene triamine pentaacetic acid. The complex was stable in 1.6 M aqueous $HClO_4$. The complex absorbed well at 270 nm. Beer's law was obeyed over the range 1-40 μ g/ml.

Bismuth (III) was extracted by coprecipitation of its 2-mercaptobenzothiazole complex with naphthalene by Satake Mosatada et al[39]. The absorbance of the complex was measured at 394 nm at the pH 4.5. Beer's law was obeyed over the range from 10 to 100 μg Bi/10 ml.

Procedures based on the formation of Bismuth(III) complexes with chlorophosphonazo III and cetyl pyridinium chloride[40], bromopyrogallol red[41], dipyrazolonylhexyl methanol[42], diethyl dithiocarbamate[43], 3-methyl-1, 2-cyclopentanedione dithiosemicarbazone[44], iodide and rhodamine B[45], pyrocatechol violet and tridodecyl ethyl ammonium bromide[46], N-benzoyl-N-phenyl hydroxyl amine[47], have been suggested by various workers.

Vakhsyshiva L.E. et al[48] photometrically determined bismuth in nonferrous metallury products. Serrol F. Bosch et al[49] determined bismuth by using 0.5M Sn(II), 0.1M Sn(IV), 1M HCl, 2 ml polyvinylalcohol and 2 ml Se(IV) solutions at pH 0.8-1.3. The absorbance was measured at 380 nm. Agrawal et al[50] used N-m-tolyl-p-chlorobenzohydroxamic acid and xylenol orange for Bi(III) determination at pH 4.5 with λ_{max} 530 nm for the spectrophotometric determination of bismuth in the pH range 2.2-6.6 with absorbance at 362 nm. Salim Rodi et al[51] carried out the photometric determination of Bi(III) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol with its absorbance at 583 nm. The spectrophotometric determination of Bi(III) with pyrocatechol derivatives was investigated by Guseinov J.K. et al[52] at pH 2, showing the absorbance at 540 nm. Bismuth was determined spectrophotometrically by Shchemeleva G.G. et al[53] with the phenyl hydrazones of 1,3,3-trimethyl-2-formylindolinium perchlorate. Zhang Rende et al[54] provided a method for determination of bismuth with alizarine violet in presence of N-cetylpyridinium chloride in the pH range 5-5.8. The absorbance was found at 620 nm. N-n-cetyl aniline was used for spectrophotometric determination of Bi(III) from HCl media in benzene solvent by Mulik G.N. et al[55].

Extraction photometric determination of Bismuth was worked out by Presnyak I.S. et al[56] with tetramethylene thiourea and iodide from 1 mol. H_2SO_4/L solution into chloroform at 485 nm. Beer's law was obeyed for 2-50 μg Bi.

Burns D. Thorburn et al[57] determined bismuth spectrophotometrically using hexadryl tributyl phosphonium tetraiodide and microcrystalline benzophenone. The complex extractable into carbontetrachloride. The absorbance of the complex was measured at 495 nm.

Rakhamatullaev K. et al[58] used 2-(2-pyridylazo)-5-diethyl-m-aminophenol, Singh Ishwar et al[59] used 2,4,6-tris (2-hydroxy-4-sulpho-1 naphthylazo)-1,3,5-triazine trisodium salt and Honova Dagmar et al[60] utilised pyrocatechol violet and septonex for the spectrophotometric determination of Bi(III). The absorbances of the complexes were measured at 580 nm, 530 nm and 612 nm respectively.

Spectrophotometric determination of bismuth with O-nitrophenylfluorone was investigated by Zuoshiyu et al[61]. The pH range was chosen between 1.84-2.34 and the absorbance was found at 532 nm.

Zhang Guang et al[62] devised a method for spectrophotometric determination of Bi(III) with 2-(3,5-dichloro-2-pyridylazo)-5-(diethyl amino)-phenol, in the pH range of 8.5 to 9.5 and showing the absorbance at 580 nm. The metal : ligand ratio was found to be 1:4 and the molar absorptivity was calculated to be 1.32×10^5.

Zhou Nan et al[63] investigated a study on the spectrophotometric determination of bismuth by using semixylenol orange. It formed a 1:2 complex at 1.8 M $HClO_4$ with absorbance at 540 nm. The molar absorptivity was calculated to be 4.2×10^4 l $mol^{-1}cm^{-1}$.

Nonova D. et al[64] suggested a spectrophotometric procedure for the determination of bismuth with phenyl fluorescene and quaternary ammonium salts. It was a red coloured 1:1:2 complex (Bi:PF: GAS) with absorbance in the region 550-560 nm. The molar absorptivity value was 4.67×10^4 $dm^3mol^{-1}cm^{-1}$.

In the present investigation bismuth has been extracted and determined spectrophotometrically with CTAB.

EXPERIMENTAL

Apparatus and Reagents:

Absorbance measurements were carried out with a Shimadzu PR-1 model spectrophotometer equipped with stoppered quartz cells of 10 mm. optical path length.

A stock solution of bismuth was prepared from bismuth trichloride and standardised. A working solution of Bi(III) (123.24 ppm) was prepared by appropriate dilution. Aqueous solutions of cetyl trimethyl ammonium bromide (CTAB) (0.1%) and potassium iodide (2%) were used.

Chloroform and other solvents were distilled before use. Buffer solution (pH 5), prepared by the standard method, was used to adjust the acidity of the aqueous phase. To study the inteferences, standard solutions of diverse ions were prepared from their corresponding salts. All other chemicals used, were of analytical grade.

Determination of bismuth:

To an aliquot containing 160.2 μg of bismuth(III) were added 2.5 ml of potassium iodide, 0.2 ml of cetyl trimethyl ammonium bromide followed by adequate amount of buffer to make the volume of the aqueous phase up to 10 ml and left for 1 min to ensure complete complexation. Finally it was equilibrated with chloroform (10 ml) for 30 sec. The orange organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the chloroform extract was read at 490 nm. against a blank. Amount of bismuth was deduced from a previously prepared calibration curve. To study the effects of diverse ions the desired foreign ion was added to the system before addition of the reagents.

RESULTS AND DISCUSSION

When potassium iodide in excess is added to an acid solution of bismuth(III), a yellow to orange colouration due to the formation of tetraiodobismuthate(III), $[BiI_4]^-$ is produced. This complex is not extractable into chloroform. On adding to it an aqueous solution of cetyl trimethyl ammonium bromide (CTAB), an orange precipitate completely soluble in chloroform is obtained. The precipitate is an ion-association complex of the type $[CTA]^+$ $[BiI_4]^-$.

Absorption spectra:

The absorption spectrum of the bismuth(III) complex in chloroform against a blank was taken. Maximum absorption of the complex, as seen from the spectrum, takes place at 490 nm Fig. 1.

The reagent blank prepared under similar condition does not have any absorption at this wave length.

Extraction as a function of pH :

The extraction of bismuth in terms of absorbance was investigated in the pH range 0-12. Although extraction starts from pH 1, the organic extracts showed maximum absorption when the extractions were carried out from aqueous solution and adjusted to pH 4-5. The aqueous phases, after extraction, were free from bismuth. This indicated a complete and quantitative recovery of bismuth in this condition. Extraction of the metal however decreases beyond pH 5.5. This has been shown in Table 1, Fig. 2.

Effects of solvents:

Apart from chloroform, some other organic solvents like carbon tetrachloride, benzene and ethylacetate were tested as extracting solvents. The bismuth(III) complex when extracted into chloroform showed maximum absorbance. The complex was not extractable into carbon tetrachloride. Hence chloroform was used for the purpose.

Reagent concentration and Beer's law:

The effect of reagent concentration on the extraction behaviour of bismuth was studied by using different concentrations of cetyl trimethyl ammonium bromide (CTAB) or potassium iodide. One variable was varied, while keeping others constant. It was noted that 1.5 ml of cetyl trimethyl ammonium bromide (0.1%) along with 2 ml of potassium iodide (2%) was sufficient to extract 160 μg of bismuth in a single operation. Use of less than 1 ml of cetyl trimethyl ammonium bromide showed low absorbance of the complex, although increased concentration of cetyl trimethyl ammonium bromide (upto 5 ml) produced no significant effect on maximum colour development. Results are shown in Table 2 and 3. The absorbance of the chloroform extract showed a linear response over a concentration of 25 ppm of bismuth. The molar absorptivity of the complex (on the basis of metal content) was calculated to be 0.822×10^4 l mol^{-1}cm^{-1} with Sandell's sensitivity 0.025 μg/cm^2. Beer's law data are tabulated in Table 4, Fig. 3.

Stability of colour:

The absorbance of Bi(III)-CTAB complex in chloroform was measured at elapsed intervals of time and the colour intensity was found to be stable for at least 6 hours. This has been shown in Table 5.

Interference:

The effect of foreign ions was studied by adding different amounts of foreign ions to 160 μg bismuth(III) and determining the bismuth following the recommended procedure. It was found that the following ions did not interfere when present in mg mentioned in the parenthesis. Fe(III)(2), Ba(II)(2), Cu(II)(1.0), Cd(II)(1.2), Ni(II)(2.0), Ca(II)(2.0), Co(II)(2.0), Th(IV)(2.0), Sr(II)(2.0), Zn(II)(2.0), U(VI)(2.0), Hg(II)(2.0), Pd(II)(1.0), Pt(IV)(1.0), Rh(III)(1.0), Zr(IV)(2.0), Mo(VI)(2.0), Au(III)(1.5), V(V)(1.5), Ag(I)(1.0), Sn(II)(2.0), Mg(II)(2.0), Pb(II)(2.0), Cr(III)(2.0), Nitrate (4.0), fluoride (4.0), arsenate (3.0), ascorbate (3.0), tartrate (3.0), citrate (3.0), borate (3.0), thiocyanate (3.0), bromide (1.5) and phosphate (1.5). However oxalate and EDTA interfered. This has been shown in Table 6.

Determination of bismuth in synthetic mixtures :

In absence of real samples the proposed method was tested to estimate microgram amounts of bismuth from some synthetic mixtures, as shown in Table 7.

Precision and accuracy :

The proposed method was tested by analysing solutions containing a known amount of bismuth (III). From the results shown in Table 8, the method seems to be fairly precise and reproducible, requiring hardly 10-15 min. for each run. The method has also been compared with some other existing methods.

Comparison of the method

The proposed method is simple, rapid and comparable well with some other existing methods as shown in Table 9.

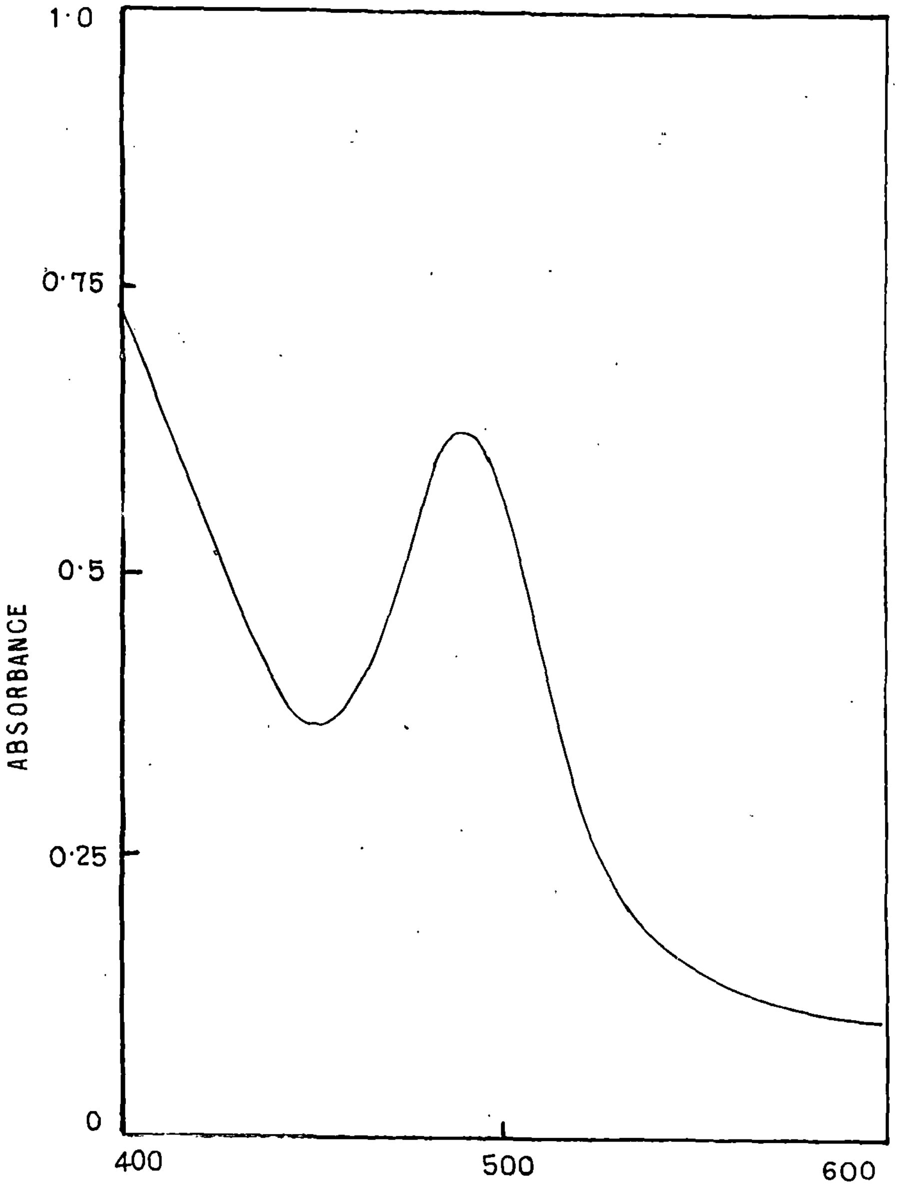


FIG. 1. ABSORPTION SPECTRUM OF Bi(III)-CTAB COMPLEX (Bi-16 ppm).

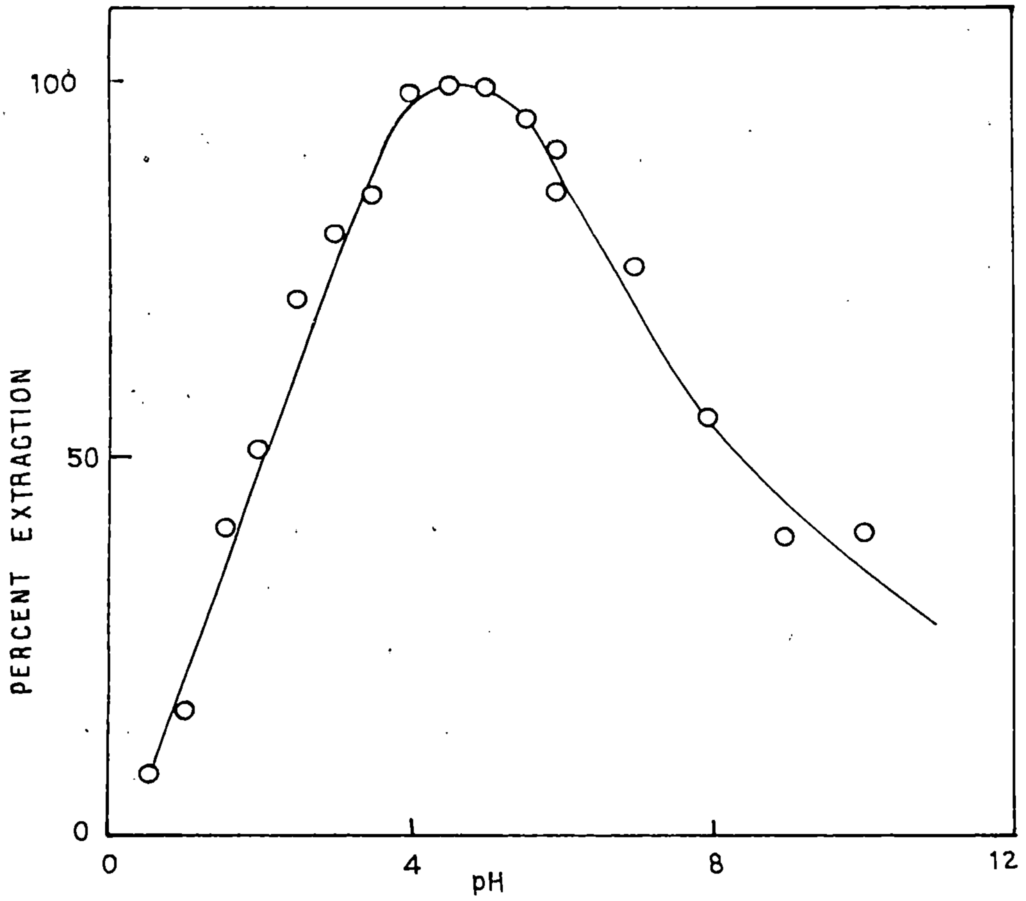


FIG. 2. EXTRACTION CURVE OF Bi(III) - CTAB COMPLEX

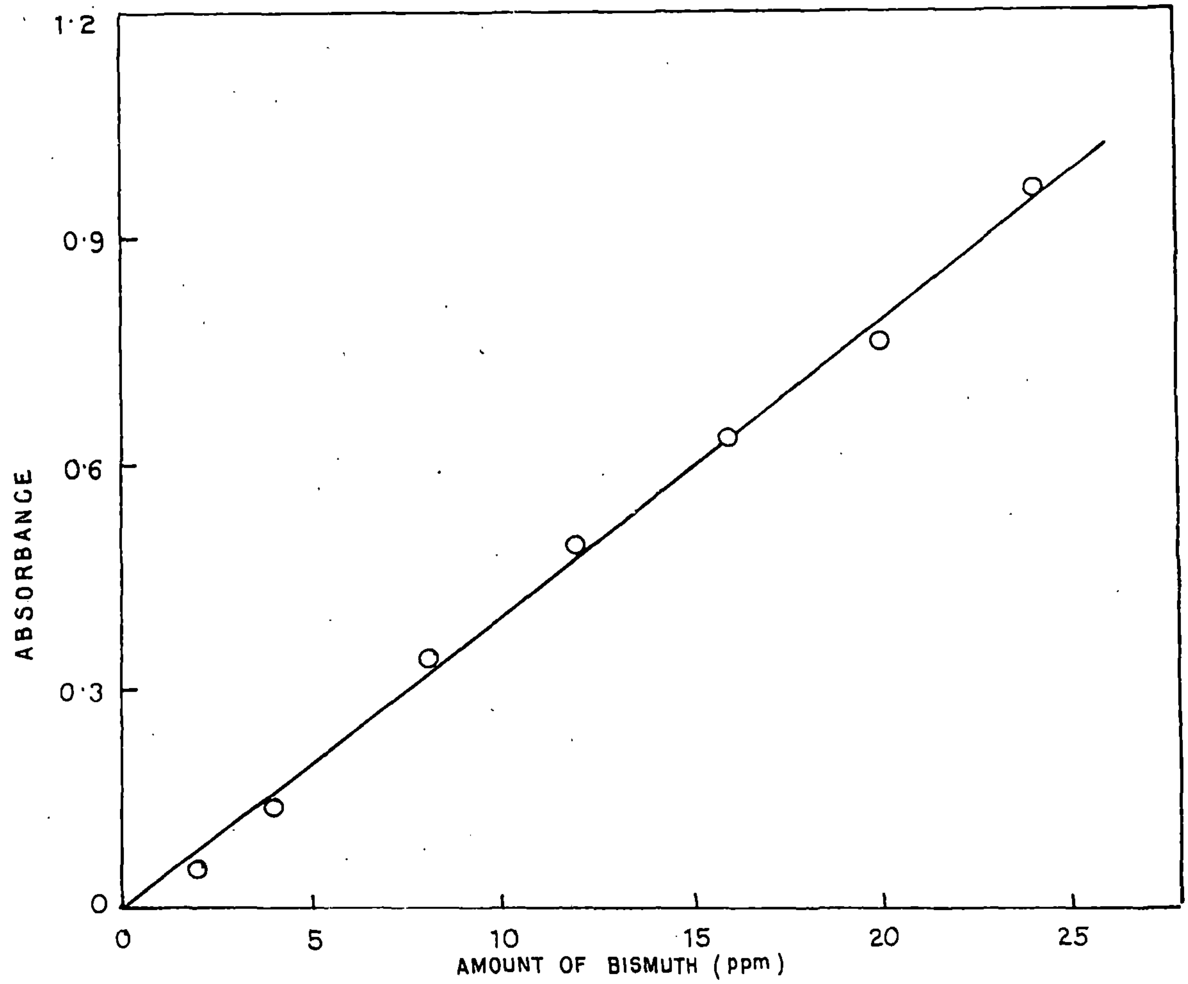


FIG: 3. CALIBRATION CURVE FOR DETERMINATION OF BISMUTH.

Table 1. Variation of absorbance with pH of the aqueous phase [The aqueous phase (10 ml) contains 160.2 μg of Bi(III), 2.5 ml aqueous solution (2%) of KI and 0.2 ml CTAB (0.1%)]

pH	Absorbance at 490 nm	pH	Absorbance at 490 nm
0.5	–	4.5	0.632
1.0	0.108	5.0	0.632
1.5	0.252	5.5	0.598
2.0	0.322	6.0	0.536
2.5	0.442	7.0	0.472
3.0	0.504	8.0	0.346
3.5	0.508	9.0	0.252
4.0	0.630		

Table 2. Effect of cetyl trimethyl ammonium bromide concentration. [The aqueous phase (10 ml) (pH-5) contains 160.2 μg of Bi(III) and 2.5 ml aqueous KI (2%)] Aqueous solution of CTAB (0.1%) was used.

CTAB added (ml.)	Absorbance at 490 nm	CTAB added (ml.)	Absorbance at 490 nm
0.1	–	1.8	0.632
0.2	0.108	2.0	0.630
0.3	0.150	2.25	0.632
0.4	0.250	2.5	0.632
0.6	0.360	3.0	0.630
0.8	0.460	3.5	0.632
1.0	0.504	4.0	0.630
1.2	0.600	4.5	0.632
1.4	0.630	5.0	0.630
1.6	0.634		

Table 3. Effect of potassium iodide concentration [The aqueous phase (10 ml) (pH-5) contains 160.2 μg of Bi(III) and 2 ml of CTAB (0.1%)] Aqueous KI (2%) was used

KI added (ml)	Absorbance at 490 nm	KI added (ml)	Absorbance at 490 nm
0.1	0.105	1.75	0.632
0.25	0.250	2.0	0.632
0.5	0.400	2.25	0.632
0.75	0.450	2.5	0.630
1.0	0.500	3.0	0.632
1.25	0.566	3.5	0.632
1.5	0.600	4.0	0.630

Table 4. Beer's law data

Amount of Bi ppm	Absorbance at 490 nm.
2	0.055
4	0.135
8	0.345
12	0.495
16	0.630
20	0.765
24	0.965

Table 5. Variation of absorbance of the Bi(III)-CTAB complex with time

Time in hours after extraction	Absorbance at 490 nm
0.25	0.630
0.5	0.630
1	0.632
2	0.630
4	0.628
6	0.628

Table 6. Effect of diverse ions for the determination of 160 μ g of bismuth (III)

Foreignion added	Amount tolerated (μg)	Foreign ion added	Amount tolerated (μg)
Nitrate	4000	Th(IV)	3000
Fluoride	4000	Sr(II)	3000
Arsenate	4000	Zn(II)	3000
Ascorbate	4000	U(VI)	3000
Tartrate	4000	Hg(II)	3000
Citrate	4000	Pd(II)	1500
Borate	4000	Pt(IV)	1500
Thiocyanate	3500	Rh(III)	1500
Bromide	3000	Zr(IV)	3000
Phosphate	3000	Mo(VI)	3000
Fe(III)	3000	Au(III)	2000
Ba(II)	3000	V(V)	2000
Cd(II)	1500	Hg(II)	3000
Ni(II)	3000	Mg(II)	3000
Ca(II)	3000	Pb(II)	3000
Cu(II)	1500	Cr(III)	3000
Ag(I)	1500	Co(II)	3000

Table 7. Determination of bismuth in synthetic mixtures (average of three determinations)

Composition with amounts in (μ g)	Bismuth found in (μg)
1. Bi(123.2), Fe(200), Ni(200)	122.5
2. Bi(123.2), Cu(200), Pb(200)	120.5
3. Bi(123.2), Zn(200), Mn(200)	121.0
4. Bi(123.2), Co(200), Pb(200)	124.5
5. Bi(123.2), Pd(200), Pt(200)	122.5

Table 8. Reproducibility of bismuth recovery

Bismuth taken (μ g)	Bismuth found (μ g)	Mean (μ g)	Std. Dev. (%)
61.62	60.5, 60.5, 62.0	61.66	1.03
	61.5, 62.5, 63.0		
123.24	120.5, 122.5, 124.0	122.16	1.29
	122.0, 121.0 123.0		
160.2	161.5, 158.5, 160.5	160.75	1.33
	161.0, 162.5, 160.5		
221.8	220.5, 222.0, 223.0	221.42	1.11
	221.0, 222.0 220.0		

Bi(III)

Table 9. Comparison of the present method

Ref.	Reagent	pH	λ_{max} (nm)	Molar absorptivity ($l\ mol^{-1} cm^{-1}$)	Interference
34.	2-mercapto-4,4,6-trimethyl-1H, 4H-pyrimidine	1.5-3.0N perchloric acid	500	12700	Nil
61.	O-nitrophenyl fluorone	1.84-2.34	532	7.08×10^4	Nil (interference of most of the cases of metal ions has been eliminated)
63.	Semixylenol orange	1.8M $HClO_4$	540	4.2×10^4	Ni^{*+2}
65.	Tribromo-chlorophosphonazo	2.4	640	1.05×10^5	-
66.	Arsenazo-DBC	1.2N $HClO_4$	632	9.0×10^4	Nil (The common ions do not interfere)
	Present method	4.5	490	8220	Oxalate, EDTA

* masking agents used

Extraction and Spectrophotometric Determination of Copper with Cetyltrimethylammonium Bromide.

Introduction

There are numerous methods which have been suggested for the separation and determination of copper by liquid-liquid extraction. The principal method used for such extraction procedures involved the utilization of various organic reagents like β-diketone, monoxime, dioxime, nitrosophenol, dithizone, dithiocarbamate and other miscellaneous reagents as the chelating agents, followed by photometric determination of the metal. The ion association system involved the utilization of thiocyanate, halide, phenanthroline and other organic reagents.

The extraction of copper by diethyl dithiocarbamate[67] was investigated at pH 8.5. The absorbance of the complex was measured at 560 nm in butyl acetate. Other well-known methods involved the utilization of neo-cuproin[68] and bis cyclohexane oxalyl-dihydrazone[69] for the determination of copper.

The reaction of copper with pyridine and thiocyanate has been investigated. The greenish-white precipitate, soluble in chloroform, carbontetrachloride and ether, gives an intense blue colour[70].

Arora H.C. et al and Talra R.K.[71] have performed the solvent extraction of Cu(II) by using 4-Isonitroso-3-methyl-1-phenyl-5-pyrazolone. The complex was extractable into benzene. Gonzaley et al[72] determined copper(II) spectrophotometrically at 680 nm as its 1:2 (metal:ligand) complex with nucic acid at pH 10.0.

Reddy et al[73] determined copper(II) by making use of 2-hydroxy acetophenone oxime. The complex was extractable into iso-Bu COMe at pH 5.5. The absorbance of the organic layer was measured at 355 nm. Copper(II) was determined spectrophotometrically using monoethyl ester of n-butyl-amino-o-hydroxy benzyl phosphonic acid[74]. The 1:1 green complex was soluble in methyl alcohol and the absorbance of the complex was measured at 400 nm.

More recently, procedures based on the formation of copper complexes with bis(4-hydroxypent-2-ylidene) diaminoethane[75], 2-(5,5-dimethyl-4,5,6,7 tetrahydrobenzthiazolyl-2-azo)-4-ethyl phenol[76], 5-methyl-1,10-phenanthroline and Eriochrome cyanine R[77], 1-phenyl-3 thiobenzoylthiocarbamide[78], ammonium (2-amino-3-hydroxy-4-pyridylazo) benzene-4-arsonate[79], citric acid or EDTA[80], biacetyl monoquinolyl hydrazone[81], substituted pyridines and thiocyanate[82], 4-methyl tetrahydrobenzofurano (6,7,6) coumarin[83], 5-(3,5-dibromo-2-pyridylazo)-2,4 diamino tolune[84], meso-tetrakis (p-sulfonyl-phenyl) porphyrin[85], 4-methyl-2-(2-hydroxy-1-naphthylazo) thiazole and 4-adamantyl-2-(2-hydroxy-1-naphthylazo) thiazole[86], 2-(5,5-dimethyl, 4,5,6,7-tetrahydrobenzothiazolyl-2-azo)-4-chloro-5-methyl phenol[87], 2-(5,5-dimethyl-4,5,6,7-tetrahydro-2-benzothiazolylazo)-4 bromophenol[88], 2-hydroxy-1-acetonaphthoneoxime[89], bis (acetyl acetone) ethylenediamine[90], 2,2'-biquinolyl and tetrabromophenolphthalein ethyl ester[91], 1,3-bis [di(2-pyridyl) methylene amino] urea[92], 2-(2-benzothiazolylazo)-5-dimethyl aminobenzoic acid[93], cetyltrimethyl ammonium chloride-chromal blue G[94], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol[95], N-(α-pyridyl)-2-thioquinaldinamide[96], cuprizone[97], N-(4-hydroxy-3-methoxy benzylidene) hydrazine carbothioamide[98], have been investigated for the spectrophotometric determination of copper.

Alonso Rodriguez Elia et al[99] have developed a method for the spectrophotometric determination of Cu(II) by using triethylene tetramine hexamethylene phosphonic acid. The absorbance of the complex was measured at 680 nm.

Huang Yechu[100] presented an extractive photometric technique to determine copper with 1,2-cyclohexanediamine tetra acetic acid in the pH 2.5. Phthalate-HCl buffer was used. The absorbance of the complex was measured at 700 nm.

Bajkin Dubravka P et al[101] made an investigation spectrophotometrically for the determination of copper(II) by using 4,4'-dimethoxy-benzilmonoxime.

In the present investigation CTAB has been used for the extraction and spectrophotometric determination of copper.

EXPERIMETNAL

Apparatus and Reagents :

Absorbance measurements were carried out with a Shimadzu PR-1 model spectrophotometer fitted with stoppered quartz cells of 10 mm optical path length.

A stock solution of copper(II) was prepared from $CuSO_4 \cdot 5H_2O$ and standardised. A working solution of copper(II) was prepared by appropriate dilution. Aqueous solution of cetyl trimethyl ammonium bromide (CTAB) (SISCO) (0.2%) and potassium iodide (BDH) (2%) were used for the purpose.

Chloroform and other solvents were distilled before use. Buffer solution (pH 2.0), prepared by the standard method was used to adjust the acidity of the aqueous phase. To study the interferences, standard solutions of respective diverse ions were prepared from their corresponding salts. All other chemicals used, were of analytical grade.

Determination of copper :

To an aliquot containing 52.5 μg of copper(II), were added 2 ml of potassium iodide, 2 ml of cetyl trimethyl ammonium bromide followed by adequate amount of buffer (KCl-HCl buffer) to make the volume of the aqueous solution to 10 ml and left for 1 min to ensure complete complexation. Finally it was equilibrated with chloroform (10 ml) for 30 sec. The organic layer was separated and poured over anhydrous sodium sulphate to remove any water droplets. The absorbance of the chloroform extract was read at 360 nm against a blank and the amount of copper was deduced from a calibration curve. To study the effect of interference, the desired diverse ion was added to the system before addition of the reagents.

RESULTS AND DISCUSSION

In presence of potassium iodide and cetyltrimethyl ammonium bromide copper forms a yellowish complex extractable into chloroform. But separately either in presence of potassium iodide or cetyl trimethyl ammonium bromide the method does not form any extractable complex.

Absorption spectra :

The absorption spectrum of the copper(II) complex in chloroform against a blank showed absorption maximum at 360 nm (Fig. 1). The reagent blank prepared under identical condition did not absorb in the region. Hence the wave-length of 360 nm was selected for all analytical measurements.

Extraction as a function of pH :

Extraction of copper in terms of absorbance was investigated in the pH range 0–10. The complex exhibited constant and maximum absorbance in the pH range 0.5–3.5 which indicated a complete and quantitative recovery of the metal. Absorbance decreases when the extractions were carried out beyond pH 4.0 or at higher acidities. For our purpose, acidity of the aqueous phase was maintained at pH 2.0 with the buffer. The variation of absorbance with pH of the aqueous phase has been shown in Table 1.

Effect of solvent :

Apart from chloroform, some other organic solvents like carbon tetrachloride, benzene or ethylacetate were tested as extracting solvents. It was found that the complex in chloroform gives the maximum absorbance and hence this solvent was used for our purpose.

Stability of colour :

The absorbance of the Cu(II)-CTAB complex in chloroform is stable for at least 12 hours as measured at elapsed intervals of time shown in Table 4.

Reagent concentration and Beer's law :

In the process, the concentrations of potasssium iodide and cetyl trimethyl ammonium bromide were varied in order to ascertain the optimum condition for quantitative extraction of the metal. It was noted that 2 ml potassium iodide along with 2 ml of cetyl trimethyl ammonium bromide was sufficient to extract 52.5 μg of copper(II) in a simple operation. Use of excess potassium iodide (over 4 ml) has a tendency to lower the absorbance of the chloroform extract, while higher concentration of cetyl trimethyl ammonium bromide (upto 4 ml) had no adverse effects (Fig. 2). The results have been shown in Table 2 and 3.

Different amounts of copper were extracted by the recommended procedure and absorbances of the chloroform extracts measured. The system obeyed Beer's law over a concentration of 10 ppm of copper. The molar absorptivity of the complex (based on copper content) was evaluated to be 1.064×10^4 lit $mol^{-1}cm^{-1}$ and Sandell's sensitivity 0.059 μ g/cm^2. Beer's law data have been tabulated in Table 5 (Fig. 3).

Interference :

To study the effects of diverse ions on the extraction behaviour, copper was determined as above in presence of the respective foreign ions. Deviation of not more than ± 3% from the recovery of copper was taken as the tolerance limit for the diverse ions tested. Copper (52.5 μ g) could be determined without interference in presence of the following ions shown in Table 6.

Determination of copper in synthetic mixtures :

In absence of real samples the proposed method was extended to various synthetic mixtures to estimate microgram amounts of copper as shown in Table 7.

Precision and Accuracy :

Precision and accuracy of the method was tested by analysing solutions containing a known amount of copper. The results in Table 8 show that the method is fairly precise and reproducible requiring hardly 10-15 min for each run.

Conclusion :

The present method for the spectrophotometric determination of copper is simple and rapid. Copper can be determined without interference in presence of all the common ions tested except thiosulphate. The method is well comparable with some other existing methods as shown in Table 9.

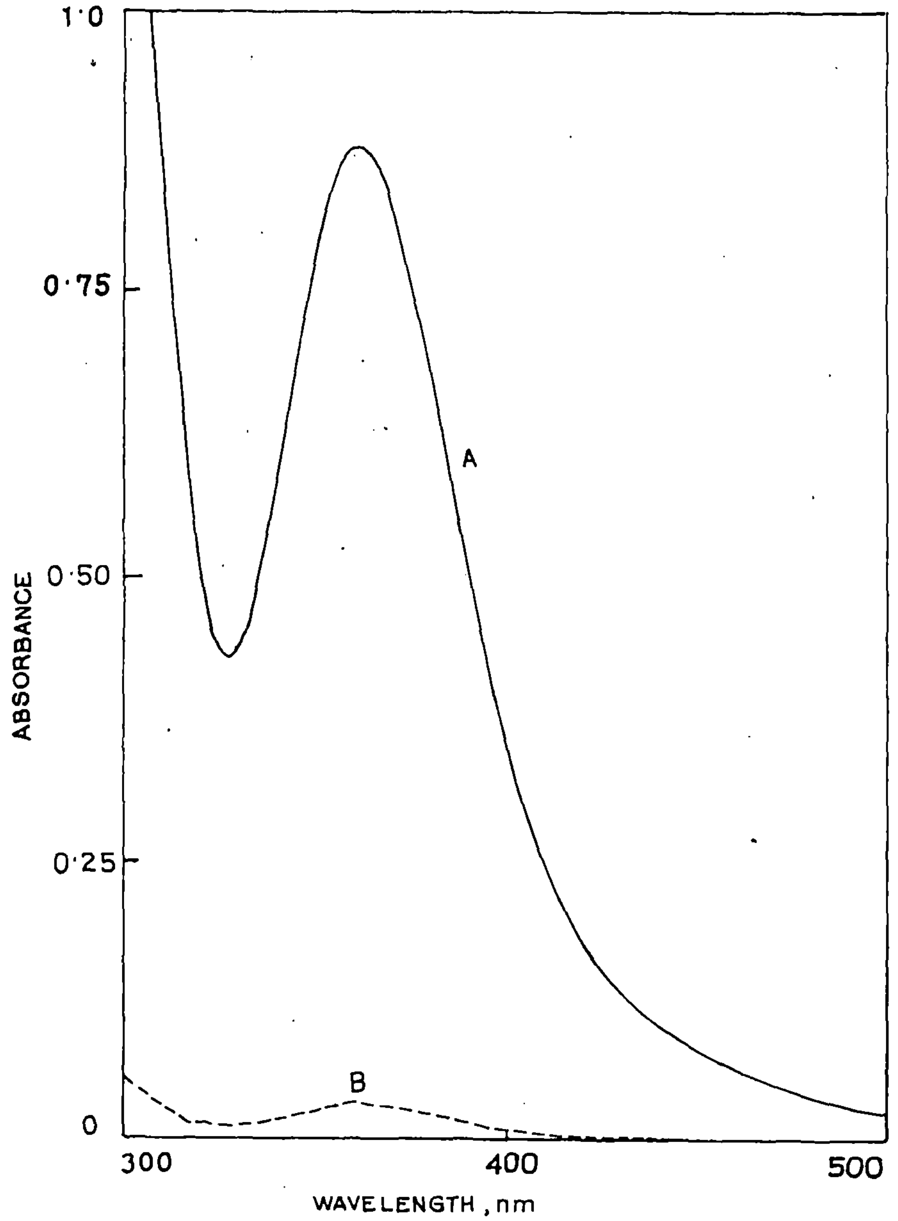


FIG: 1. ABSORPTION SPECTRUM OF Cu(II)-CTAB COMPLEX (A) AND REAGENT BLANK (B) (Cu- 5·2 ppm)

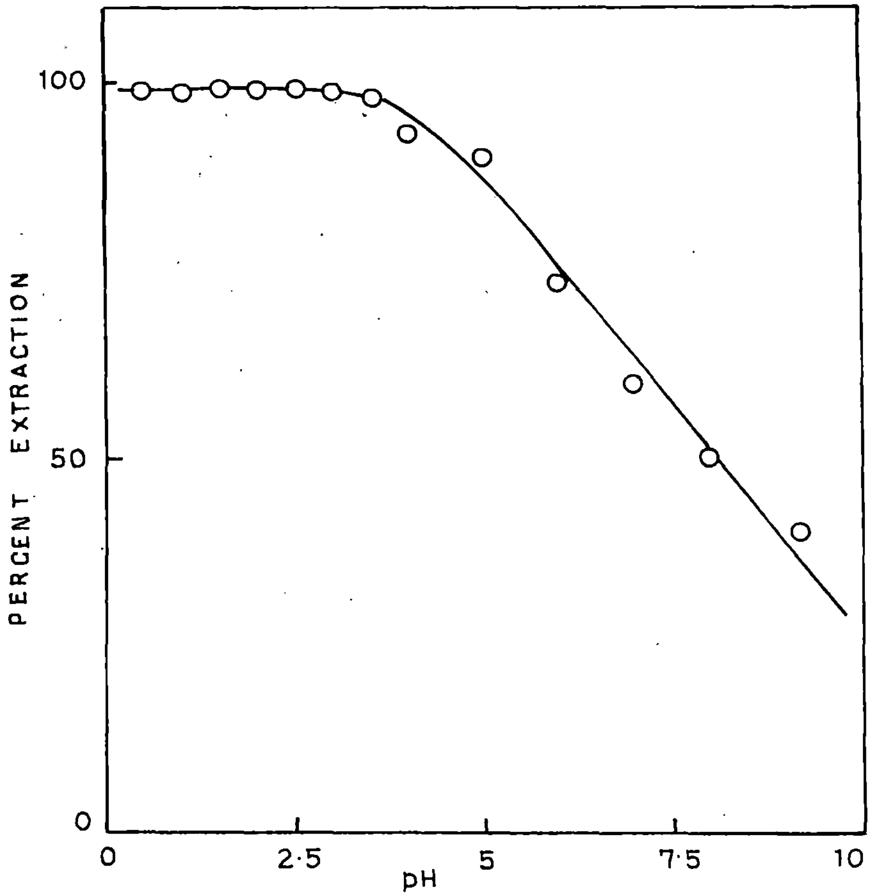


FIG. 2. EXTRACTION CURVE OF Cu(II)-CTAB COMPLEX

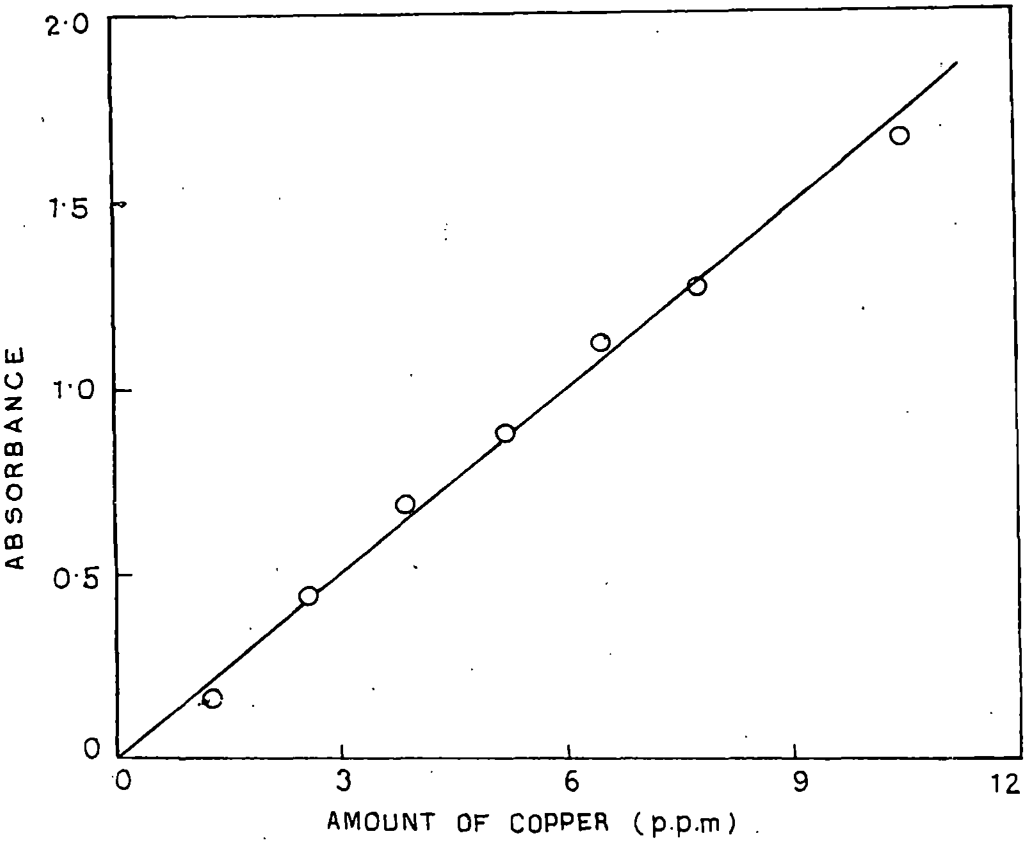


FIG. 3. CALIBRATION CURVE FOR DETERMINATION OF COPPER

Table 1 . Variation of absorbance with pH of the aqueous phase [The aqueous phase (10 ml) containing 52.5 μg of Cu(II), 2 ml of KI(2%) and 2 ml of CTAB (0.2%)

pH	Absorbance	pH	Absorbance
0.5	0.878	4.5	0.800
1.0	0.880	5.0	0.792
1.5	0.882	6.0	0.650
2.0	0.880	7.0	0.528
2.5	0.882	8.0	0.440
3.0	0.882	9.0	0.352
3.5	0.860		
4.0	0.878		

Table 2. Effect of potassium iodide concentration [The aqueous phase (10 ml) (pH 2) contains 52.5 μg of Cu(II), 2 ml of CTAB (0.2%)] 2% KI solution was added for the purpose.

KI solution added, ml	Absorbance at 360 nm	KI solution added, ml	Absorbance at 360 nm
0.1	-	2.0	0.882
0.25	0.140	2.25	0.880
0.5	0.262	2.5	0.882
0.75	0.600	2.75	0.880
1.0	0.650	3.0	0.878
1.25	0.710	3.5	0.878
1.75	0.780	4.0	0.865
		5.0	0.860

Table 3. Effect of cetyltrimethyl ammonium bromide concentration [The aqueous phase (pH 2) containing 52.5 μ g Cu(II) and 2 ml of KI (2%) was maintained at 10 ml in volume] 0.2% of cetyl trimethyl ammonium bromide was used.

CTAB added ml	Absorbance at 360 nm	CTAB added, ml	Absorbance at 360 nm
0.25	0.150	1.75	0.840
0.5	0.352	2.0	0.882
0.75	0.515	2.5	0.880
1.0	0.616	3.0	0.882
1.25	0.680	3.5	0.880
1.5	0.800	4.0	0.880

Table 4. Variation of absorbance with time

Time in hours after extraction	Absorbance at 360 nm
0.25	0.882
0.5	0.880
1	0.880
2	0.880
4	0.880
8	0.882
12	0.880
16	0.870
24	0.850

Table 5. Beer's law data

Amount of copper, ppm	Absorbance at 360 nm
1.3	0.180
2.6	0.422
3.9	0.682
5.2	0.880
6.5	1.120
7.8	1.260
10.5	1.672

Table 6. Effect of diverse ions on determination of 52.5 μ g of copper

Foreign ion added	Amount tolerated (μg)	Foreign ion added	Amount tolerated (μg)
Thiocyanate	3000	Calcium	2000
Fluoride	3000	Cobalt	2000
Nitrate	3000	Thorium	2000
Ascorbate	3000	Strontium	2000
Tartrate	3000	Palladium	500
Citrate	3000	Platinum	500
Phthalate	3000	Rhodium	1000
Phosphate	3000	Zirconium	2000
Bromide	3000	Molybdenum	2000
Borate	60	Gold	2000
Oxalate	60	Vanadium	2000
Thiosulphate	nil	Bismuth	2000
Barium	2000	Iron*	1000
Cadmium	2000	Mercury	500
Nickel	2000	Uranium	2000
Lead	2000	Tin	2000
Chromium	2000	Magnesium	2000
		Silver	500
		Zinc	1000

* Masking agents used.

Table 7. Determination of copper in synthetic mixtures

Composition with amounts in (μg)	Copper found in (μg)
1. Cu(52.5), Fe(200) Ni(200) + F(2000)	50.5
2. Cu(52.5), Pb(200) Bi(200)	52.0
3. Cu(52.5), Ni(200) Co(200)	52.0
4. Cu(52.5), Zn(200) Pb(200)	53.0
5. Cu(52.5), Pb(200) Pt(200)	53.5

Table 8. Reproducibility of copper recovery

Copper taken (μg)		Copper found (μg)	Mean (μg)	Std. Dev. %
1.	13.12	12.0, 15.5, 12.5 13.0, 13.0, 14.0	13.33	1.25
2.	26.25	25.0, 26.5, 28.5 29.0, 25.0, 26.0	26.66	1.72
3.	52.50	50.5, 52.5, 53.5 53.5, 50.5, 53.5	52.16	1.32
4.	78.74	80.0, 78.0, 77.5 77.0, 81.0, 80.5	79.0	1.70

Table 9. Comparison of the Present Method

Ref.	Reagent	pH	λ_{max}	Molar absorptivity	Interference
102.	Diphenylthiocarbazide	4-8	540	5.04×10^4	Pd*, Pb*, Bi*, Borate and nitrite
103.	4-nitroso-resorcinal and pyridines bases	1.5-2.5	365-375	0.71×10^4 0.45×10^4 0.89×10^4 1.06×10^4 0.21×10^4	Hg, Co(II), Pd(II), Fe(III), Zr(IV), SCN, S_2O_3, C_2O_4, EDTA, tartrate, citrate, F and ascorbate.
104.	Pyridine bases and bromide/Iodide	1.5-2.5 and 0.5-1.5	320-355 and 350-360	2.17×10^3 3.07×10^3 3.23×10^3 2.33×10^3 5.13×10^3 and 2.38×10^3 2.65×10^3 4.28×10^3 4.76×10^3 6.77×10^3	Pd(II), Pt(IV), S_2O_3, EDTA, F, C_2O_4, tartrate, citrate, ascorbate and SCN

Contd..

Table 9 (Contd..)

Ref.	Reagent	pH	λ_{max}	Molar absorptivity	Interference
105.	N-(4-hydroxy-3-methoxybenzylidene) hydrazine carbothioamide	11.2	410	1.23×10^4	-
106.	3-thiobenzoyl-1-p-tolyl thiocarbamide		520	1.0×10^4	Co, Ni
	Present method	0.5-3.5	360	1.064×10^4	Fe*, S_2O_3

*masking agents used

REFERENCES

1. Kirov A.I., Golentovskaya I.P. and Vlasov N.A., Zavod. Lab., 1975, 41(5), 523.

2. Vasilev Kh., Karagosov L., Kunev D. and Chimbulev M., God. Vissu. Khim., Tekhnol. Inst, Sofia, 1978, 24(1), 135.

3. Jadhav S.G. and Venkateswarlu C., Indian J. Chem., 1978, 16A(3), 263.

4. Shaulina L.P., Kirrilov A.I., Deppposited Doc., 1980, SPSTL 776 Khp-D80, 9.

5. Ravi Kant., Om Prakash, Sanjay Kumar and S.P. Mushran, Proc. Natl. Acad. Sci., India, Sect A, 1981, 51(2), 221-227.

6. Mamzenko Zygmut, Krasiejko Maria, Stec. Judwiga; Chem. Anal., 1981, 26 (6), 1051.

7. Gorduva M.N. and Meshcheryakova D.N., Probl Sovrem, Anal. Khim., 1981, 3(16).

8. Shen Hanxi, Wang Zhenquing, Huaxue Shiji; 1982, 4(5), 257.

9. Xu. Guanghui, Shen Hanxi, Fenxi Huaxue, 1982, 10(5), 334.

10. Shen Hanxi, Huaxue Shiji, 1982, (2), 79.
11. Wang Huaxue, 1983, 11(4), 291.
12. Xia Daopei, Fenxi Huaxne, 1983, 11(11), 845.
13. Xu. Qiheng, Huaxin Shiji, 1984, 6(3), 191.
14. Pilipenko A.J., Demutskaya L.N., Ryabuskno O.P., Zh. Analkhim. 1984, 39(b), 1081.
15. Li Weiwu, Xi. Gangquing. Dexin, Kuangye. Gongeheng, 1983, 3(3), 48.
16. Xue Guang; Fenxi Huaxue., 1984, 12(10), 928.

17. Ten. Zhe, Wu. Shuisheng; Huaxne Shiji, 1985, 7(6), 319.
18. Zhang Zengrui, Yang Qi, Huaxne Shiji, 1985, 7(6), 311.
19. Li Shaoqing, Guo Tongzhang, Hu. Wengqing, Fenxi Huaque, 1986, 14(2), 129-31.
20. Hu. Shcuun, Shu. Changhua; Li Qingyi; Cheng Shlin Yin Anzhong, Fenxi Huaxne, 1987, 15(9), 814.
21. Jiang Shufa, Jie Nianquin, Cheng Chuange, Fenxi Huaxne, 1988, 16(3), 236.
22. Chen. Ziruo, Kuangye Gongcheng, 1989, 9(2), 45.
23. Den. Huixiang, Huanjing Wuran Yu Fangzhi, 1989, 11(4), 40.
24. Yang Suqing & Tan. Dahua, Lihua Jianyan, Huaxue Fence, 1989, 25(5), 311-12
25. Hu. Shorkun, Huang Mei, Zeng Zhongzhi, Sichuan Daxue Xuebao, Ziran Kexueban, 1989, 26(3), 336-9.
26. Ishii Hayime, Odashima Tsugikatsu, Kawamonzen Yoshiaki, Bull. Chem. Soc., Jpn., 1990, 63(12), 3405-9.
27. Zhou Nan., Yu. Renqing, Yao. Xuzhang, Fenxi Shiyanshi, 1990, 9(5), 25-6, 44.
28. Paria P.K., Thokdar T.K., Majumdar S.K., J. Indian Chem. Soc., 1990, 67(6), 532.
29. Mo. Weiming, Li Shengyi, Yu. Ximao, Chem. Abst., Vol. 114, No. 13, p. 835.
30. Tang Yangqiang, Chem. Abst., Vol. 114, p. 870.
31. Haddock L.A., Analyst, 59, 163, 1934.
32. T. Moeller, Ind. Eng. Chem., Anal. Ed., 1943, 15, 346.
33. Cheng K.L., Bray R.H. and Meloted S.W., Anal. Chem., 1955, 27, 24.
34. Singh Ajai K. and Singh R.P., Ind. J. Chem., 1977, 15A, pp 257-258.

35. Kotelyanskaya, L.I., Shestidesyanaya N.L., Zh. Anal. Khem, 1978, 33(6), 1095-8.

36. Gorenc D., Kosta L., J. Radio anal. Chem., 1978, 44(2), 279-84.

37. Cano Pavon J.M., Garcia de Tornes A., Pino F., An. Quim., 1978, 74(1), 24-27.

38. Nenova P., Kantcheva D. and Karadakov B., Talanta, 1978, 25(11-12), 691-2.

39. Satake Masatada and Suzuki Tsutomu, Fukui Daigaku Kogakubu Kenkyu Hokoku, 1979, 27(1), 1-10.

40. Mise Teruyoshi, Miyakonoyo Kogyo Koto Semmon Gakko Kenkyu Hokoku, 1980, 14, 73-7.

41. Chang Tao-kun, Chiang Tse-Mei and Kao Li-Chun, Fen Hsi Hua Hsueh, 1978, 6(4) 268-71.

42. Khor'kova M.A., Degtev M.I. and Zhivopistsev V.P., Izu. Vyssh. Uchebn., Zaved., Khim. Khim., Tekhonol., 1981, 24(9), 1102-5.

43. Wang, Zhenpu and Cheng K.L., Talanta, 1982, 29(7), 551-6.

44. Rojas J., Lopez Fernandez J.M. and Valcarcel M., Microchem. J., 1982, 27(3), 445-53.

45. Liu. Shaopu, Liu. Zhongfang, Fenxi, Huaxue, 1982, 10(6), 321-4.

46. Shijo Yoshio, Shimizu Tokuo, Sakai Kaoru., Bull. Chem. Soc., Jpn., 1983, 56(1), 105-7.

47. Chem. Kuochem, Qian. Quizhang, Huaxue Xuebao, 1981, (Zengkan), 120-4.

48. Vakhrysheva L.E. and Sayun M.G., Tsv. Metallurgiya, 1984, 137, 44-6.

49. Serrot F. Bosh, Perez M.J. Savall, Diaz. Hernandez and Vinuesa J. Manes, Afinidad, 1984, 41(394), 546-8.

50. Agrawal Yadvendra Kand Bhatt Vinay J., Analyst (London), 1984, 109(10), 1287-9.

51. Salim Rodi, Suraydeh Bassem, Microchem. J., 1985, 32(1), 83-8.

52. Guseinov I.K., Azerb. Khim. Zn., 1984, (1), 146-52.

53. Shchemeleva G.G., Chechushkova N.E., Bagdasarov K.N and Shelepin N.E., Izv. Vyssh. Uchebn. Zaved, Khim. Khim. Tekhnol, 1985, 28 (10), 41-5.

54. Zhang Rende and Wang Huaigang, Lanzhau Doxue Xuebao, Ziran Kexueban, 1986, 22(2), 71-75.

55. Mulik G.N., Kuchekar S.R., Chavan M.B., Ind. J. Chem., Sect. A, 1986, 25A(II), 1073-4.

56. Presnyak I.S., Antonovich V.P. and Nazarenkov A., Zavod. Lab., 1987, 53(1), 13.

57. Burns D. Thorburn and Tungkananuruk K., Anal. Chim. Acta., 1987, 197, 285-9.

58. Rakhmatullaev K., Giyasov A. Sh. and Zakirov B.G., Uzb. Khim. Zh., 1988, (6), 10-13.

59. Singh Ishwar and Kadyan Pratap Singh, Bull. Chem. Soc., Jpn., 1988, 61(10), 3689-92.

60. Honova Dagmar, Nemcova Irena and Suk Vaclav, Talanta, 1988, 35(10), 803-4.

61. Zuo. Shiyu, Guo. Jingman and Liu. Hong., Yejin Fenni, 1988, 8(1), 18-20.

62. Zhang Guang, Liu Bin and Li. Kejuan, Yejin Fenxi, 1989, 9(2), 43-4.

63. Zhou Nan, Yu. Renqing, Yao. Xuzhang and Lu. Zhiren., Huaxue Shiji, 1990, 12(5), 280-2, 311.

64. Nonova D., Vasibva E. and Mincheva V., God Sofii Univ. 'Kliment Okhridski', Khim. Fak., 1985 (Pub. 1990), 79, 373-98.

65. Sun Xi and Yi Youhang, Yejin Fenxi, 1990, 10(3), 10-12.
66. Yang Dailing, Wang Hon Wei and Yu Ximao, Wuhan Daxue Xuebao, Ziran Kexueban, 1986, (3), 68-72.

67. Hague J.L., Brow E.D. and Bright H.A., J. Research Nath. Standards, 1951, 47, 380; Classen A. and Bastings, L., Z. anal Chem., 1956, 153, 30.

68. Gaher A.R., Anal Chem., 1954, 26, 577.
69. Vogel I., Text book of Quantitative Inorganic Analysis, ELBS, London, 1978.

70. Gordieyff V.A., Analyt. Chem., 1950, 22, 116.
71. Malik Wahid V. and Salahuddin, Ind. J. Chem., 1963, 1, 203-207.

72. Gonzalez Portal, Aurora Bermejo Marinez F., Baluza Santos C., Act. Quim. Compostelena, 1978, 2(2-3), 54.

73. Reddy T., Sreenivasula and Rao S. Brahmaji, Current Science, 1979, 48 (10), 439.

74. Zuchi Gand Rev. Roum. Chim., 1979, 24(3), 497.
75. Kafor O., Emmanuel Chakwuemeka, Talanta, 1980, 27(11A), 887.
76. Kandrae J., Chem. Zvesti, 1980, 34(5), 645-52.
77. Ishidu Ryoei, Tonosaki Koichi, Sci. Rep. Hirosaki Univ., 1980, 27(2), 123-9.

78. Ilyas Q.R. & Joshi A.P., Mikrochim. Acta., 1980, 2(3-4), 263.

79. Varma Yashbir Singh, Barua Sudarshan, Singh Ishwar, Garg Bhagwan Singh, Singh Rajendra Pal, Ann. Chim., 1981, 71(5-6), 343.

80. Zaki M.T.M., Alquasmi R. and Fresenius Z., Anal. Chem., 1981, 306, 5, 400.

81. Anipindi A.R., Jain P. & Singh R.P., J. Chin. Chem., Soc., 1981, 28 (3), 165.

82. Chattopadhyay Partha and Majumdar Santosh Kumar, Ind. J. Chem., 1982, 21A, 857-858.

83. Tyagi Ani., Tyagi R.P., & Joshi B.C., Bull. Inst. Chem. Acad. Sin., 1982, 29, 47.

84. Ma. Zhicheng Rang. Qingxin & Pan Qinyhong, Yankuangeeshi, 1983, 2(1), 61-2, 24.

85. Chen. Bingrong, Fenxi Huaxue, 1983, 11(6), 459-61.

86. Pilipenko A.T., Karetnikova E.A. and Trachevskii V.V., Zh. Anal. Khim., 1983, 38(10), 1787-92.

87. Kandrae J. and Zalo A., Acta. Fac. Rerum-Nat. Univ. Comenianae Chim., 1984, 31, 95-104.

88. Szalo Anton and Kandrac Jan., Fiz. - Khim. Issled. Ravnovesii, V. Rastvorakh, Yaroslavl, 1983, (202), 83-9.

89. Reddy K.V. and Hussain R.C., Curr. Sci., 1984, 53(15), 798-99.

90. Gambarov D.G. and Babaev A.K., Zn. Anal. Khim., 1984, 39(5), 801-3.

91. Sakai Tadao., Ohno Noriko., Tsuruboshigekazu, Tanaka Masaya and Horigome, Analyst (London), 1984, 109(8), 1043-5.

92. Gomez Ariza J.L., Barragan de la Rasa F.J. and Montana Gonzalez M.T., Mikrochim. Acta, 1984, 2(5-6), 407-16.

93. Katami Takeo, Hayakawa Tomokuni, Furukawa Maramichi and Shibata Shozo, Analyst (London), 1984, 109(11), 1511-12.

94. Vesugi Katsuya, Miyawaki Mitsuo and Nagahiro Tohru, Microchem. J., 1985, 32(3), 332-7.

95. Sakai Yukio, Anal. Sci., 1985, 1(4), 373-6.

96. Chakraborti Anil K., Ind. J. Chem., Sect. A., 1986, 25A (9), 886.

97. Rudometkina T.F., Chernova I.B. and Orlov V.V., Zavod Lag, 1987, 53(9), 18-20.

98. Gowda H. Sanke, Ahmed S. Maqbool and Jagadeesh K.S., J. Indian Chem. Soc., 1989, 66(12), 915-7.

99. Alonso Rodriguez Elia., Rermejo Barrera Adela and Bermejo Martinez F., An. Quim, 1990, 86(4), 436-8.

100. Huang Yechu, Yejin Fenxi, 1990, 10(3), 54-5.

101. Bajkin Dubravka P., Perisic-Janjic Nadav and Nikolic Aleksander D., Zb. Rad. Pris-Mat Fak, Univ. Nov., Sadu. Ser. Hem. 1989 (Pub. 1991), 19, 19-24.

102. Paria P.K., Thokdar T.K. and Majumdar S.K., J. Ind. Chem. Soc., 1990, 67, 263-264.

103. Sarkar A., Thokdar T.K., Paria P.K. and Majumdar S.K., J. Ind. Chem. Soc., 1988, LXV, 742-743.

104. Thokdar T.K., Sarkar A., Paria P.K. and Majumdar S.K., J. Ind. Chem. Soc., 1988, LXV, 386-388.

105. Hu. Shoukun, Huang Mei, Zeng Zhongzhi, Sichuan Daxue Xuebao, Ziran Kexueban, 1989, 26(3), 336-9.

106. Ambhore D.M. and Joshi A.P., J. Ind. Chem. Soc., 1991, 68(3), 175-7.

CHAPTER - V

IODIDE, BROMIDE AND PYRIDINE BASES AS ANALYTICAL REAGENTS

The use of iodide, bromide and pyridine as auxiliary ligands is known. Among the elements that are extracted as iodide and bromide complexes are gold (III), mercury(II), lead(II), cadmium, antimony(III), and Au(III), Co(III), Cu(II), Fe(II), Fe(III), platinum, zinc, Mn(II), etc. respectively. The solvents that have been used include ethyl ether, methyl isobutyl ketone, methyl isopropylketone, methyl ethyl ketone, isopropyl ether, carbontetrachloride, ethylacetate, diethyl ether etc.

The nitrogeneous base like pyridine acts like a neutral ligand coordinated to the metal. Copper, nickel and cobalt in presence of pyridine form water-insoluble complexes that dissolve in chloroform to give rise to green, blue and pink colouration of which the first containing $Cu(Py)_2(SCN)_2$ has been utilised in colorimetry[1]. Similar complexes are formed by zinc, cadmium and many other metals which can serve as the basis for thier solvent extraction[2].

Umezake[3] extracted iron into isobutyl methyl ketone from acid media with a solution of 0.5% dibenzoylmethane in mixture of pyridine and methanol. The absorbance was measured at 410 nm.

During the extraction of uranium with 8-hydroquinoline Koppiker and Ganjankush[4] observed that the addition of pyridine and acetone enhances the colour intensity of the uranium oxinate complex.

Akaiwa and Kawamoto[5] studied the 2-theonyltrifluoro acetone-pyridine bases complex of cobalt for the spectrophotometric determination of cobalt. The solvent employed was benzene and the absorbance was measured at 430 nm.

Kuroda et al[6] studied the formation of cobalt complex with pyridine and azide which was used for the colorimetric determination of cobalt.

Extraction behaviour of some bivalent metals with methyl substituted pyridines has been studied[7,8,9].

The complex formation of ruthenium(III) was based on its reaction with 6-amino-5-nitroso-2,4-pyrimidinediol and pyridine[10] in acetate buffer at pH 3.0 by heating on a steam bath. Its absorbance was measured at 530 nm.

Extractive spectrophotometric determination of vanadium as vanadium(III) -pyridine dibenzoyl methane complex is proposed by Ary and Yatiranjan[11].

Sharmah Kabita et al[12] studied spectrophotometric determination of zinc with diphenylcarbazone in presence of pyridine. The pH range was 9-10 and the absorbance was measured at 520 nm.

Izquierdo A. et al[13] investigated the formation of Mo(VI) complex with 3-phenyl-3-methyl-2-mercaptopropenoic acid in the presence of pyridine. The solvent used was chloroform and the molar absorptivity was found to be 1.14×10^4 l $mol^{-1} cm^{-1}$.

Iodide complexes are more coloured compared to the chloro and bromo complexes. In presence of excess iodide platinum(IV), palladium, tellurium etc. yield strongly coloured soluble complexes in acid solutions.

Sudo used[14] potassium iodided in presence of antipyrine solution to determine mercury. The absorbance of the chloroform extract was measured at 330 nm. Yamamato and Kotsuji[15] extracted HgI_4^{2-} complex with $Fe(dipy)_3^{+}$ at pH 6.5 into 1,2-dichloromethane and measured its absorbance at 526 nm.

Rao S.P. et al[16] extracted Cd(II) with N-butyl aniline in chloroform from a mixture of potassium iodide and sulphuric acid. The pH was adjusted at 10. Marczenko et al[17] determined tellurium spectrophotometrically using iodides and cetyltrimethyl ammonium ion. The ion-association complex was soluble in chloroform. Another spectrophotometric method for the determination of lead with iodide and 1,4-dimethyl-1,2,4-trizolinium (3-azo-4)-N-N-diethyl-aniline was investigated by Kish et al[18].

In a weakly acidic solution (0.016-0.064N HCl) lead(II) and potassium iodide form $(PbI_4)^{2-}$ which in turn reacts with crystal violet[19] to give a stable complex having the maximum absorption at 540 nm. Jaya Sambamoorthy et al[20] determined platinum spectrophotometrically with iodide and pyronine G. Marczenko Zygmunt et al[21] used dithizone to determine Pd(II) and platinum spectrophotometrically in an iodide medium.

Bismuth could be determined[22] photometrically by using potassium iodide and Rhodamine 6 G. Lopez Erroz et al[23] spectrophotometrically determined bismuth using iodide and rivanol. It formed an ion-association complex with absorbance at 375 nm.

Deb ManasKanti and Mishra R.K.[24] studied spectrophotometric determination of Bi(III) in soil and ore using iodide and amidines. The solvent used was chloroform.

Bromide complexes impart better colouration than the chloride complexes but lesser than the iodide complexes. Elements like, mercury, arsenic, antimony, platinum etc. form soluble complexes in presence of bromide in acid solution. A number of studies on the separation of specific elements by bromide extraction have been performed by various investigators.

L. Wohler and A. Spengel[25] carried out the extraction of platinum into ethyl ether using bromide solutions followed by addition of $SnCl_2$.

McBryde and Yoe[26] found that Au(III) is completely extracted into isopropyl ether using 2.5 to 3M HBr solution. Under these conditions small amounts of Fe and Os can also be extracted.

Bock R. et al[27] were successful in extracting 58% of mercury(II) into diethyl ether from 1M HBr solution, while the per cent extraction reduces to $\angle$4% on using >2M HBr solution.

Bock R. et al[27] investigated that molybdenum is extracted (99%) into diethyl ether from 6M HBr solution. They also could extract Sb(III) (38%) from 2M HBr solution.

The extractability of the bromides of Cu(I), Cu(II), Zn, Ni, Co(II), Fe(II), Fe(III), Al(III), Mn(II), Sn(II) and Sn(IV), using methyl ethyl ketone and methyl isobutyl ketone as solvents, has been studied using aqueous solutions containing HBr and/or NH_4Br[28].

Poluektov N.S. et al[29] suggested that $InBr_4^-$ is extracted with Rhodamine C into benzene using 2.5 M HBr containing acetone.

Denaro A.R. and Occleshaw V.J.[30] found that IBMK extracts Sn(II) (99%) from 3-4 M HBr solution and Sn(IV) (99%) from 4.5 M HBr.

Cu(II) is (80%) extracted into IBMK from 5-6M HBr solution while Cu(I) is (80%) extracred into ethyl methyl ketone using 1-4M HBr solution[31].

Zn(II) is 80% extractable into IBMK with the help of 5M HBr solution[31].

Studler K.[31] made an investigation that As(V) is extracted into carbon tetrachloride using 7-8.5M H_2SO_4 containing potassium bromide (8g/l).

Miketukova V. and Khlicek J.Z.[32] used rhodamine B or counter-ion in extraction of $TlBr_4^-$ into benzene. The absorbance of the bromide complex was measured at 560 nm.

In the present investigations, iodide/bromide and pyridine or some of its methyl substitutes have been used for extraction and spectrophotometric determination of palladium, platinum and copper.

Extractive Spectrophotometric Determination of Palladium(II) using Mixed Ligand Complex Formation with Pyridine/α-Picoline/β-picoline/γ-picoline/2,4,6-Collidine and Iodide.

EXPERIMENTAL

Apparatus and Reagents :

Absorbance measurements were made witn a Shimadzu PR-1 spectrophotometer equipped with stoppered quartz cells of 10 mm optical path length. An ECL 5651 digital pH meter was used to measure the acidities of the aqueous solutions.

Palladium(II) chloride (Johnson and Matthey) (1g) was dissolved in 1 ml hot conc. HCl and diluted to 250 ml with distilled water followed by standardisation by dimethylglyoxime[33]. A working solution (41.75 ppm Pd) was prepared by dilution.

Chloroform (E. Merck), pyridine (B.D.H), α-picoline (Reidel), β-picoline (BDH), γ-picoline (Fluka) and 2,4,6-collidine (BDH) were distilled before use. Potassium iodide (BDH) and all the other reagents used were of analytical reagent grade. Stock solutions of desired diverse ions were prepared from their nitrates, chlorides or sulphates by dissolving pure samples in dilute acid or pure water. Sodium/ammonium salts were used in the case of anions. The metal contents were determined by a standard methods[33]. To adjust pH of the aquecus phase KCl-HCl buffer was used unless otherwise mentioned.

Determination of palladium :

To an aliquot containing 10-100 μg of palladium was added 1 ml of 0.015 M aqueous potassium iodide and 0.02 ml of pyridine/ α-picoline/ β-picoline/ γ-picoline/ 2,4,6-collidine followed by addition of adequate amount of buffer to make up the volume upto 10 ml. The aqueous phase was then allowed to stand for 1 min to ensure complete complexation. The mixture thus obtained was equilibrated with 10 ml of chloroform for 30 sec. The two layers were allowed to settle for 1 min. The separated organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. pH of the aqueous solution, after extraction, was measured. Finally the absorbances of the chloroform extracts were measured at the respective absorption maxima against palladium free reagent blanks. Amount of palladium(II) was determined from a previously prepared calibration curve. To study the effect of foreign ions, the respective diverse ions were added to the system prior to the addition of reagents.

RESULTS AND DISCUSSION

It has been noted that iodo-palladium(II) forms complexes with pyridine or its methyl substituted derivatives in aqueous solution. These mixed ligand complexes are found to be extracted into chloroform.

Absorption spectra of palladium complexes :

The absorption spectra of palladium(II)-complexes in chloroform, extracted as above, show absorption maxima at around 355 nm. The absorbance steadily decreases and becomes negligible beyond 500 nm. The reagent blanks show insignificant absorbances in 300-500 nm wave length region. For simplicity all the absorption measurements were carried out against chloroform as reference. One of the spectra has been shown in Fgi. 1.

Extraction as a function of pH :

The liquid-liquid extraction behaviour of palladium(II)-complexes was investigated in the pH range 0-14.0. Extraction of palladium virtually starts from pH 1.0. The chloroform extracts showed steady and maximum absorbances when the extractions were carried out in presence of pyridine bases from aqueous solution in the pH range 3.5-10.0. FIG.2 In this pH range, after single operation when the extraction processes were repeated using the same aqueous phase, the organic extracts showed no absorbances. This indicated a complete and quantitative recovery of palladium in this condition. From the graph $pH_{\frac{1}{2}}$ values were evaluated to be 1.6 and 10.7.

Effect of solvents:

Apart from chloroform, other common organic solvents such as carbon tetrachloride, benzene and ethyl acetate were tested as extracting solvents; but those offered no special advantages over chloroform as seen from Table 1. The pattern of the absorption spectra of the complexes remained unchanged in all cases.

Stability of colour :

The absorbances of the palladium complexes in chloroform were measured at elapsed intervals of time after extraction. The colour intensity was stable for at least 48 hours, as seen from Table 2.

Reagent concentration and Beer's law :

The optimum reagent concentrations were found by extracting palladium at various concentrations of potassium iodide and pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine. It was noted that 1 ml of 0.015 M potassium iodide solution and 0.02 ml of pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine were sufficient to extract 41.75 μg of palladium in a single extraction. Higher concentrations of the reagents (upto 4 ml of 0.015 MKI and 0.1 ml of pyridine bases) had no adverse effects on the extraction behaviour. Different amounts of palladium were extracted by the general procedure and the absorbance of the chloroform extracts was measured at the respective absorption maxima. In all cases, Beer's law was found to be valid over the concentration range of 1-10 μg Pd/ml (Table 3) and FIG-3. The molar absorptivities of the palladium(II) complexes (on the basis of Pd content) at the respective absorption maxima were evaluated (Table 1).

Interference :

In order to study the effect of diverse ions on the extraction behaviour, a definite amount of palladium(II) was extracted and determined according to the general procedure in presence of the respective foreign ions. All the bases i.e. pyridine, α-picoline, β-picoline, γ-picoline and 2,4,6-collidine showed similar behaviour towards the extraction of palladium. In each case an average of three determinations was taken. An ion was considered to interfere if the recovery of Pd(II) differed by more than ± 3% from the actual amount taken.

It was found that 41.75 μg of palladium could easily be determined without any interference in presence of the following cations and anions, the amounts (mg) taken being mentioned in parentheses : Co(II), (5.1), Ni(II)(5.3), Cd(II)(4.9), Zn(II)(6.7), V(V)(5.2), Rh(III)(2.4), Zr(IV)(1.2), U(VI)(5.1), Mn(II)(3.9), Cr(III)(4.8), La(III)(4.2), Al(III)(3.9), Th(IV)(4.1), Be(II) (6.9), Pb(II)(1.3), and Bi(III)(1.1), Iron(III)(1.2) and Cu(II) (0.2) were kept in the aqueous phase by masking them with ammonium hydrogen fluoride and citrate respectively. All attempts to remove the intereference due to Hg(II) failed, Pt(IV) interfered in all cases except in the 2,4,6-collidine system where the interference was avoided by extracting palladium at pH 10.0. Among the anions tested the following (10 mg each) did not interfere: EDTA, borate, phosphate, tartrate, citrate, fluoride, bromide, ascorbate, phthalate. However, thiocyanate and thiosulphate, even in trace amounts interfered seriously. The results are shown in Table 4.

Determination of palladium in synthetic mixtures :

In absence of real samples, the proposed method was tested to estimate microgram amounts of palladium in various synthetic mixtures (Table 5).

Precision and accuracy :

Among the bases used, 2,4,6-collidine is found to be most sensitive. With this reagent the precision and accuracy of the method was tested by analysing solutions containing a known amount of palladium following the recommended procedure. The experimental results are shown in Table 6. The method is fairly precise and reproducible requiring 10-15 min for each run.

Conclusion:

The present method for the spectrophotometric determination or palladium is simple and has been compared with some other existing methods. The sensitivity of the method is not as high as the other ones (Table 6); but the method provides excellent recovery of palladium in micro quantities in presence of almost all the common ions except thiocyanate, thiosulphate. Influence of the interfering ions like iron and copper can easily be overcome. The method is comparable well with some other existing methods (Table 7).

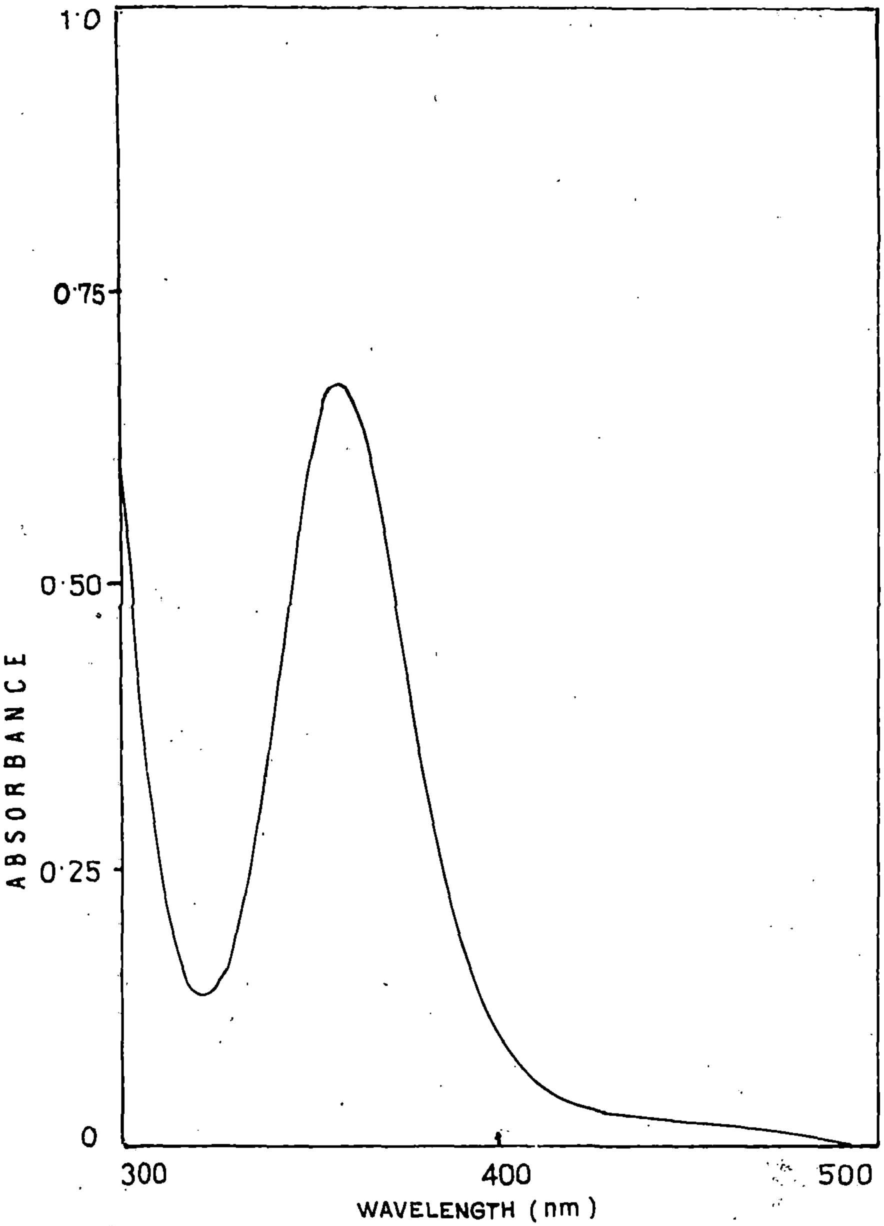


FIG. 1. ABSORPTION SPECTRUM OF
Pd (II)-I-Py COMPLEX (Pd-4·17 ppm)

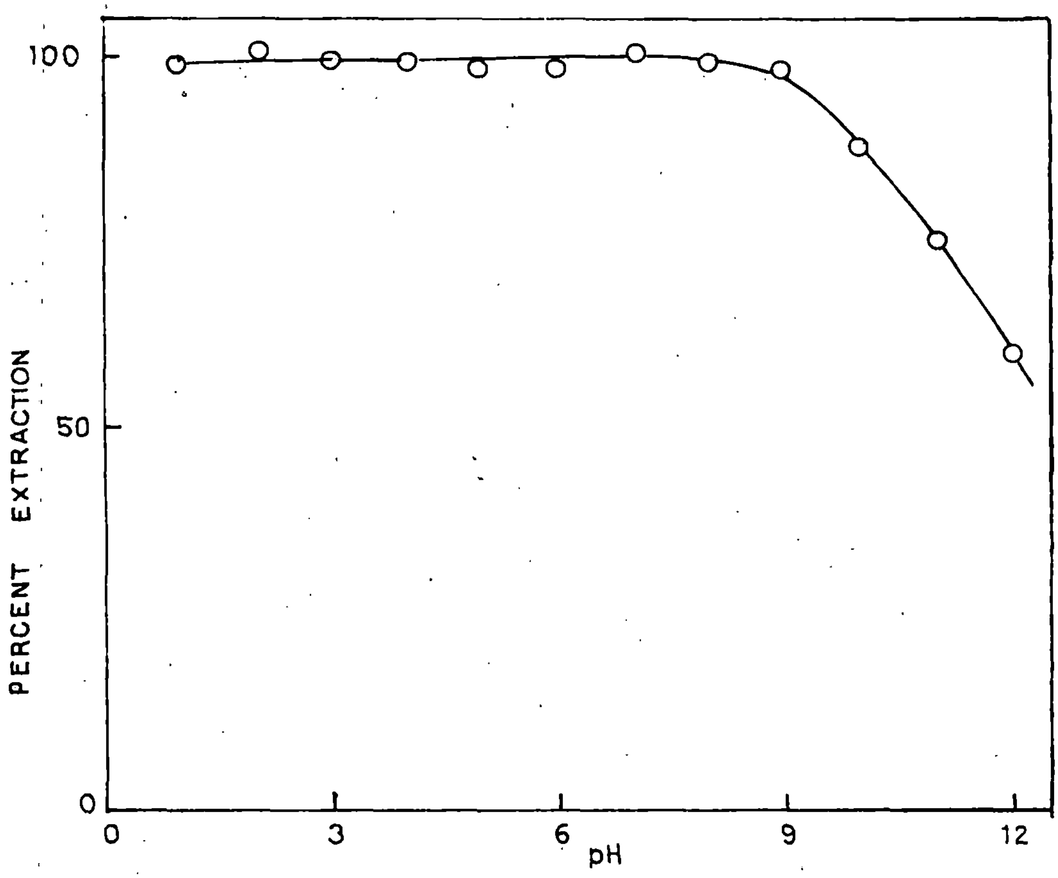


FIG. 2. EXTRACTION CURVE OF Pd(II)-I-Py COMPLEX

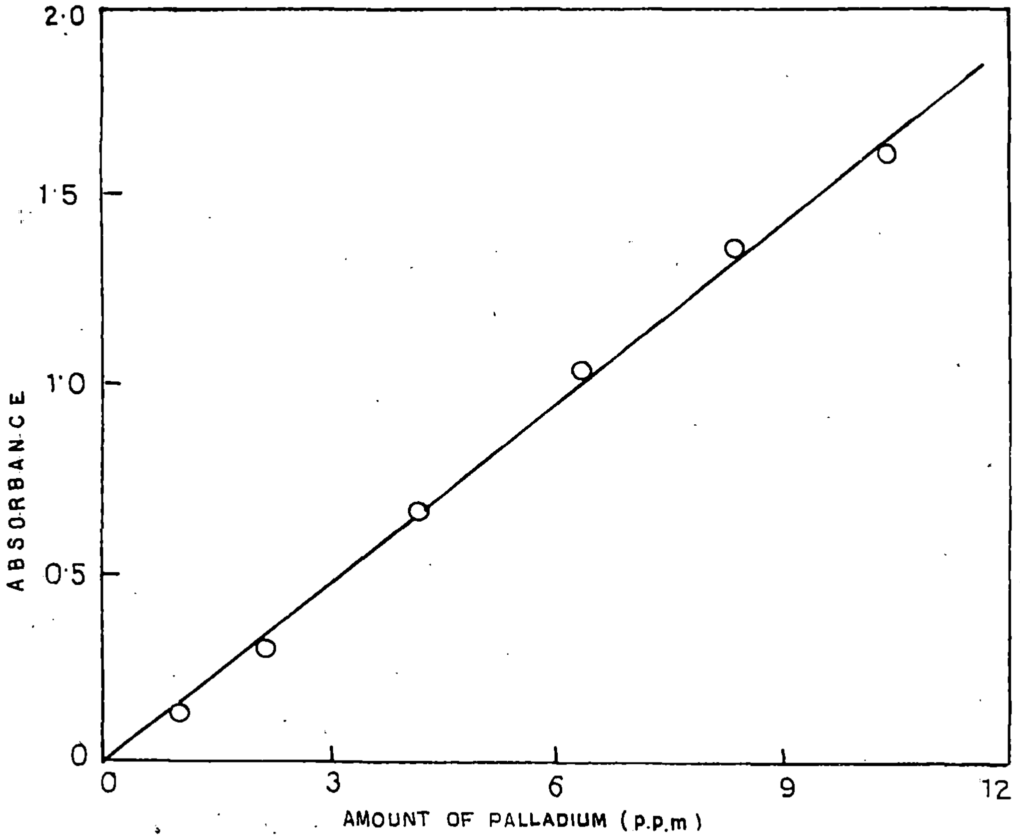


FIG. 3. CALIBRATION CURVE FOR DETERMINATION OF PALLADIUM.

Table 1. Details of Extractive Methods

Parameter	Base employed				
	Pyridine	α-Picoline	β-Picoline	γ-Picoline	2,4,6-Collidine
λ_{max} (nm)	359^a	355^a	356^a	356^a	354^a
	366^b	360^b	365^b	363^b	360^b
	365^c	360^c	362^c	361^c	360^c
	355^d	355^d	356^d	359^d	359^d
Molar absorptivity* ($mol^{-1} cm^{-1}$)	$1.68 \times 10^{4\,a}$	$1.79 \times 10^{4\,a}$	$1.70 \times 10^{4\,a}$	$1.75 \times 10^{4\,a}$	$1.98 \times 10^{4\,a}$
	$1.63 \times 10^{4\,b}$	$1.94 \times 10^{4\,b}$	$1.78 \times 10^{4\,b}$	$1.88 \times 10^{4\,b}$	$1.78 \times 10^{4\,b}$
	$1.78 \times 10^{4\,c}$	$2.19 \times 10^{4\,c}$	$1.73 \times 10^{4\,c}$	$1.98 \times 10^{4\,c}$	$1.83 \times 10^{4\,c}$
	$1.78 \times 10^{4\,d}$	$2.04 \times 10^{4\,d}$	$2.08 \times 10^{4\,d}$	$1.88 \times 10^{4\,d}$	$1.83 \times 10^{4\,d}$

Extracting solvents: a- Chloroform, b- carbon tetrachloride, c-benzene and d-ethylacetate

* Measured at corresponding absorption maxima.

Table 2. Variation of absorbance with time
(Pd taken 41.75 μg)

Time in hour after extraction	Absorbance
0.25	0.670
0.5	0.670
1	0.672
4	0.670
8	0.670
12	0.672
24	0.668

Table 3. Beer's law data

Amount of Pd in (ppm)	Absorbance
1.04	0.118
2.08	0.304
4.17	0.670
6.26	1.032
8.35	1.350
10.44	1.610

Table 4. Effect of diverse ions on the determination of 41.75 µg of palladium, (Average of three determinations was taken)

Ion added	Amount tolerated (mg)	Ion added	Amount tolerated (mg)
EDTA	10	Rh(III)	2.4
Borate	10	Zr(IV)	1.2
Phosphate	10	U(VI)	5.1
Tartrate	10	Mn(II)	3.9
Citrate	10	Cr(III)	4.8
Fluoride	10	La(III)	4.2
Bromide	10	Al(III)	3.9
Ascorbate	10	Th(IV)	4.1
Phthalate	10	Be(II)	6.9
Co(II)	5.1	Pb(II)	1.3
Ni(II)	5.3	Bi(III)	1.1
Cd(II)	4.9	Fe(III)	1.2*
Zn(II)	6.7	Cu(II)	0.2**
V(V)	5.2	Pt(IV)	1.0+

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* in presence of fluoride

** in presence of citrate

\+ with 2,4,6-collidine.

Table 5. Analysis of synthetic mixtures (with collidine)

Composition with amounts in µg	Palladium found in µg
1. Pd(41.75), Pt(200), Rh(200)	42.25
2. Pd(41.75)*, Fe(200), Cu(100)	42.0
3. Pd(41.75), Ni(200), Co(200)	41.5
4. Pd(41.75), Al(200), Cr(200)	41.5
5. Pd(41.75), Zn(200), Cd(200)	42.0
6. Pd(41.75), U(200), V(200)	41.5

*plus fluoride and citrate.

Table . Reproducibility of palladium recovery using collidine

Pd taken µg	Pd found µg	Relative mean deviation (%)
10.44	10.5	3.8
20.88	20.7	1.7
41.75	41.9	1.2
62.62	62.1	0.77
83.50	83.3	0.91

Table 7. Comparison after the Present Method

Ref.	Reagen	pH	λ_{max}	Molar absorptivity	Interference
34.	Isonitroso thiocamphor	2.0 to 5M HCl	450	3.9×10^3	Cu*, Hg, Co*, S_2O_3, Pt*
35.	Sodium ethyl trithiocarbonate	1.0–10.0	370 and 448	1.277×10^4	Mn*(II), Zn*(II), Cd*(II), Fe*(III), Ni*(II), Co*(II) and Pt.
36.	Promethazine hydrochloride	1.3–4.0	470	3.86×10^3	Ru(III) [When $>$ 0.6 μg/ml] and I^- (when $>$ 0.8 μg/ml)
37.	2'-hydroxy-4-methoxy-5'-methyl-chalkone oxime	0.5–2.5	380	3.38×10^3	Fe(III), Ru(III), Zro(II), citrate, tartrate and EDTA
38.	Prochlorpenazine	0.1–3.0	480	4.63×10^3	Ag(I), Au(III) and S_2O_3
39.	Present method	(Vide Table – 1)			Fe*, Cu*(II) and Pt*(IV)

* masking agents used.

Extraction and Spectrophotometric Determination of Platinum using Mixed ligand Complex Formation with Pyridine, α-Picoline, β-Picoline, γ-Picoline or 2,4,6-Collidine and Iodide.

Introduction

The prime methods used for the liquid-liquid extraction of platinum involved the utilisation of different organic reagents such as dithizone, tributylphosphate, dithiocarbamates, dithiophosphoric acid, high molecular weight amines etc. In most of the procedures the after-extraction-organic-phases have been used for the colourimetric determination of the metal. Some of the methods are cited below:

Khopkar S.M[40] utilised molecular and ion-association compounds for the spectrophotometric determination of platinum from 5 M HCl medium into mesityloxide. In presence of iodide or thiocyanate platinum gets extracted into tributyl phosphate[41]. In the process the metal has been separated from rhodium and iridium.

In HCl-ACONa buffer, Pt(IV) forms a blue green cationic complex with trifluoperazine hydrochloride where Cu^{+2} acted as catalyst. This 1:1 (metal:ligand) complex can be used for the determination[42] of the metal. The absorbance was measured at 504 nm.

Gowda H. Sanke et al[43], determined platinum spectrophotometically using profenamine hydrochloride. The yellow-green 1:1

(metal : ligand) complex absorbed maximum at 400 nm. Beer's law was obeyed from 0.5-9 μg Pt/ml.

Ivanov V.M. et al[44] suggested method for the determination of platinum(IV) using 4-(2-pyridylazo) resorcinol as a selective reagent.

Sabartova J. et al[45] proposed a spectrophotometric technique for determination of platinum(IV) with chromazurol(S) in presence of cetyl pyridinium or 1-(ethoxycarbonyl) pentadecyl trimethyl ammonium bromide. The absorbance of the complex was determined at 640-50 nm.

Gorbunova G.N. et al[46] utilised thiazolylazo compounds as reagents for determination of platinum (II).

Gowda H. Sanke et al[47] determined platinum by using promethazine hydrochloride. The metal : ligand ratio was found to be 1:1 and the pH was adjusted to be at 2.3. The absorbance of the complex was measured at 406 nm.

Some other methods involve the utilization of N-phenyl-N'-(2-pyridyl) thiourea[48], p-dimethyl aminobenzylidene rhodamine[49], methyl green[50], propionylpromazine phosphate[51], O-mercaptoacetanilide[52], 2-furancarbothioic acid hydrazide[53], methoxypromazine maleate[54], dithiozone and stannous chloride[55], hexachloroiridate (IV)[56], ferriin[57], dithizone and iodide[58], ethylisobutrazine hydrochloride[59], 1,3-cyclohexanedione bis thiosemicarbazone monohydrochloride[60], thiocyanate and malachite green[61], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol[62], potassiumbutylxanthate[63], 1,5-diphenylcarbazide[64], Mandelazol[65], 4-(3,5-dibromo-2-pyridylazo)-2-methyl 1,5-diaminobenzene[66], Nile blue B[67], for the spectrophotometric determination of platinum.

Isonitroso thiocamphor has been used as a reagent for the spectrophotometric determination of Pt by Paria P.K. et al[68]. The complex attained stability at the pH range 6-9. The absorbance of the complex was measured at 369 nm.

Nitrosulfonazo III was utilised by Li Youfur et al[69] for the determination of Pt. The metal : ligand ratio was found to be 1:2. The pH was adjusted at 8.6, by using the buffer NH_3-NH_4Cl. The complex showed an absorbance at 579 nm.

In our laboratory it has been observed that iodo-platinum (IV) with pyridine or its methyl substituted derivatives forms ring-ligand complexes, extractable into chloroform. These properties of Pt-complexes led to further studies of the systems for the development of a simple spectrophotometric method for the determination of platinum, as described below.

EXPERIMENTAL

Apparatus and Reagents :

Spectral curves and analytical measurements were made with a Shimadzu PR-1 model spectrophotometer, and a ECL 5651 digital pH meter was used for the measurement of acidities of aqueous solutions.

Chloroplatinic acid (Johnson and Matthey) (1g) was dissolved in distilled water (100 ml) followed by standardisation as elemental platinum[70]. A working solution (392μg Pt/ml) was prepared by appropriate dilution. Chloroform (E. Merck), pyridine (BDH), α-picoline (Riedel), β-picoline (BDH), γ-picoline (Fluka) and 2,4,6-collidine (BDH) were distilled before use. Potassium iodide (BDH) and all other reagents used were of analytical grade. Different buffer solutions were prepared by standard procedures. Standard solutions of diverse ions were prepared from their corresponding salts.

Determination of Platinum:

An aliquot containing 100-500μg of platinum was mixed with 0.05M aqueous potassium iodide (2 ml) and pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine (0.05 ml). Volume of the final aqueous phase was made upto 10 ml with buffer solution of desired pH and it was left for 1 min to ensure complete complexation.

The mixture was then equilibrated with chloroform (10 ml) for 30 sec. The separated organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. pH of the aqueous solution, after extraction, was measured. The absorbance of the chloroform extracts were read at respective absorptions maxima against chloroform. Amount of platinum (IV) was determined from a previously prepared calibration curve. To test the effect of diverse ions, the respective foreign ions were added to the system before addition of the reagents.

RESULTS AND DISCUSSION

Absorption Spectra :

The platinum complexes in chloroform taken against the reagent blanks, showed absorption maxima at 345-360 nm (Table 1). The reagent blanks show insignificant absorbances in the aforesaid wave length region (Fig. 1). Wave-length region 345-360 nm was selected for all analytical measurements.

Extraction as a function of pH :

The extraction of platinum in terms of absorbance was investigated in the pH range 0-12. Extraction of platinum virtually starts from pH 1. The chloroform extracts showed steady and maximum absorbances when the extractions were carried out from aqueous solution at pH 2-8, 2-9, 8-9, 2-9 and 3-4 for pyridine, α-picoline, β-picoline, γ-picoline and 2,4,6-collidine, respectively. In these pH ranges, after single operation when the extraction processes were repeated using the same aqueous phases, the organic extracts virtually showed no absorbance. This indicated a complete and quantitative recovery of platinum in this condition. Extraction of the metal as a function of pH has been shown in Fig. 2 .

Effects of solvents :

Apart from chloroform, some other solvents like benzene, carbontetrachloride and ethylacetate were tested as extracting solvents; but those offered no special advantages over chloroform. The pattern of the absorption spectra of the complexes remain unchanged in all cases.

Stability of colour :

The absorbances of the platinum complexes in chloroform were measured at elapsed intervals of time at 345-360 nm. The colour intensity was stable for at least 24 hours.

Reagent concentration and Beer's law :

The optimum reagent concentrations were ascertained by extracting platinum at various concentrations of potassium iodide along with pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine. It was noted that 2 ml of 0.05 M aqueous potassium iodide solution together with 0.5 ml of pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine was sufficient to extract 100-500 μg of platinum in a single extraction.

In all cases, Beer's law was found to be valid over the concentration range 5-50 ppm of platinum. The molar absorptivities of the complexes (on the basis of metal content) were also evaluated (Table 1). The sensitivities of the methods with pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine worked out to be 0.10 $\mu g/cm^2$, 0.11 $\mu g/cm^2$, 0.10 $\mu g/cm^2$, 0.05 $\mu g/cm^2$ and 0.018 $\mu g/cm^2$ respectively.

<u>Interference</u> :

In order to study the effects of diverse ions on the extraction behaviour, 392 μg of platinum (117.6 μg for collidine) were extracted and determined according to the recommended procedure in presence of the respective foreign ions. An ion was considered to interfere if the recovery of platinum differed by more than ± 3% from the actual amount taken. The results are shown in Table 2. A 25-fold excess of Co(II), Ni(II), Zn(II), Mo(VI), U(VI), Pb(II), Mn(II), Ca(II), V(V), Ba(II), Sr(II), Cr(III), La(III), Be(II) and Al(III) did not interfere. A 10-fold excess of Cd(II), Zr(IV), Th(IV) and a 5-fold excess of Rh(III) were tolerable. A 5-fold excess of Fe(III) and Cu(II) could be kept in the aqueous phase with ammonium hydrogenfluoride and citrate respectively. Hg(II) and Pd(II) interfered. Among the anions tested, the following (50-fold excess) did not interfere : oxalate, borate, phosphate, tartrate, citrate, fluoride, bromide, phthalate, acetate. However, thiocyanate, thiosulphate and ascorbate interfered seriously. The lower concentration of EDTA is permissible. This has been shown in Table 2.

Determination of platinum in synthetic mixtures :

In absence of real samples, the proposed method was tested to estimate microgram amounts of platinum in various synthetic mixtures (Table 3).

Precision and accuracy :

2,4,6-collidine was found to be most sensitive among the pyridine bases used. With this reagent the precision and accuracy of the proposed method was tested by analysing solutions containing a known amount of platinum following the recommended procedure. The experimental results are shown in Table 4. The method is fairly precise and reproducible requiring 10-15 min for each run.

Comparison of the present method :

The proposed method is very simple and rapid. The method has been compared with some other existing methods as shown in Table 5. Microgram amounts of platinum can be determined in presence of a number of diverse ions althougn thiocyanate, thiosulphate, ascorbate, mercury and palladium interfered.

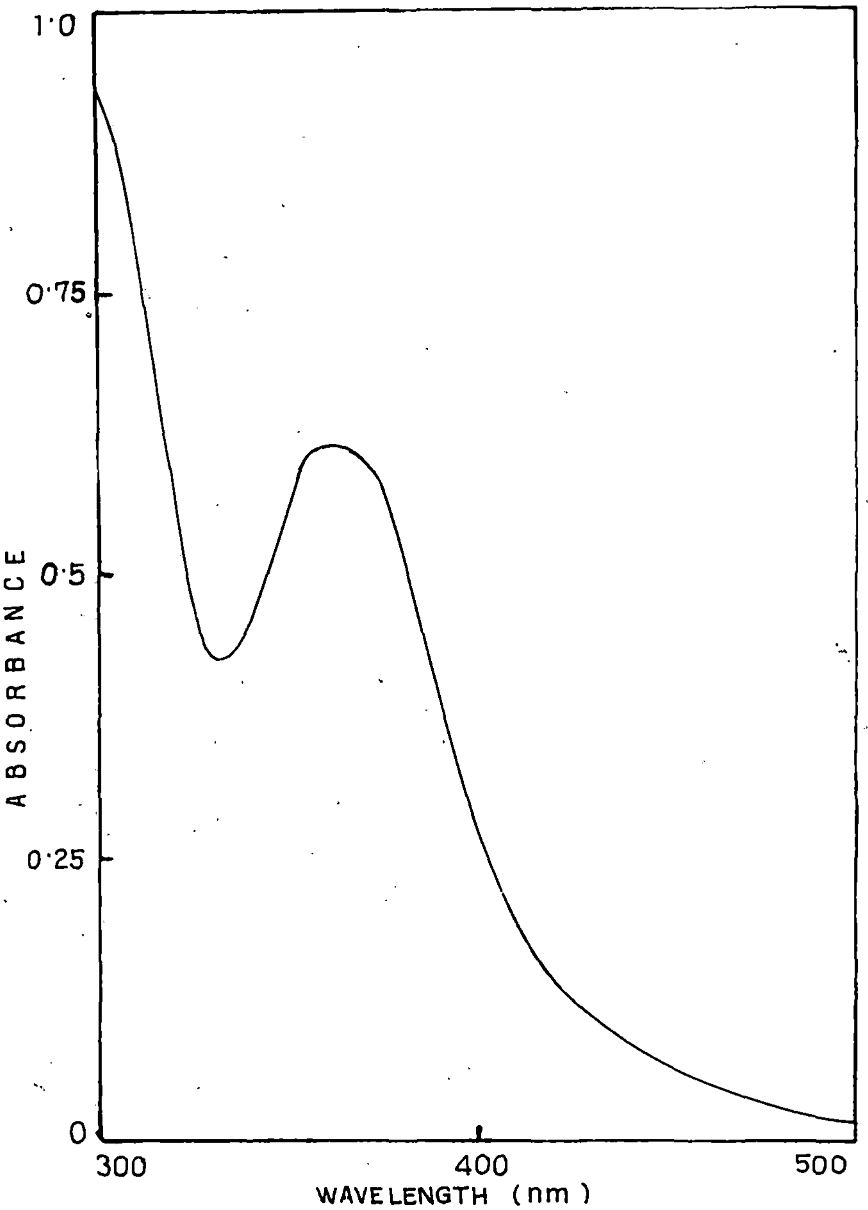

FIG. 1. ABSORPTION SPECTRUM OF
Pt(IV)-I-COLLIDINE COMPLEX (Pt-1·17 ppm)

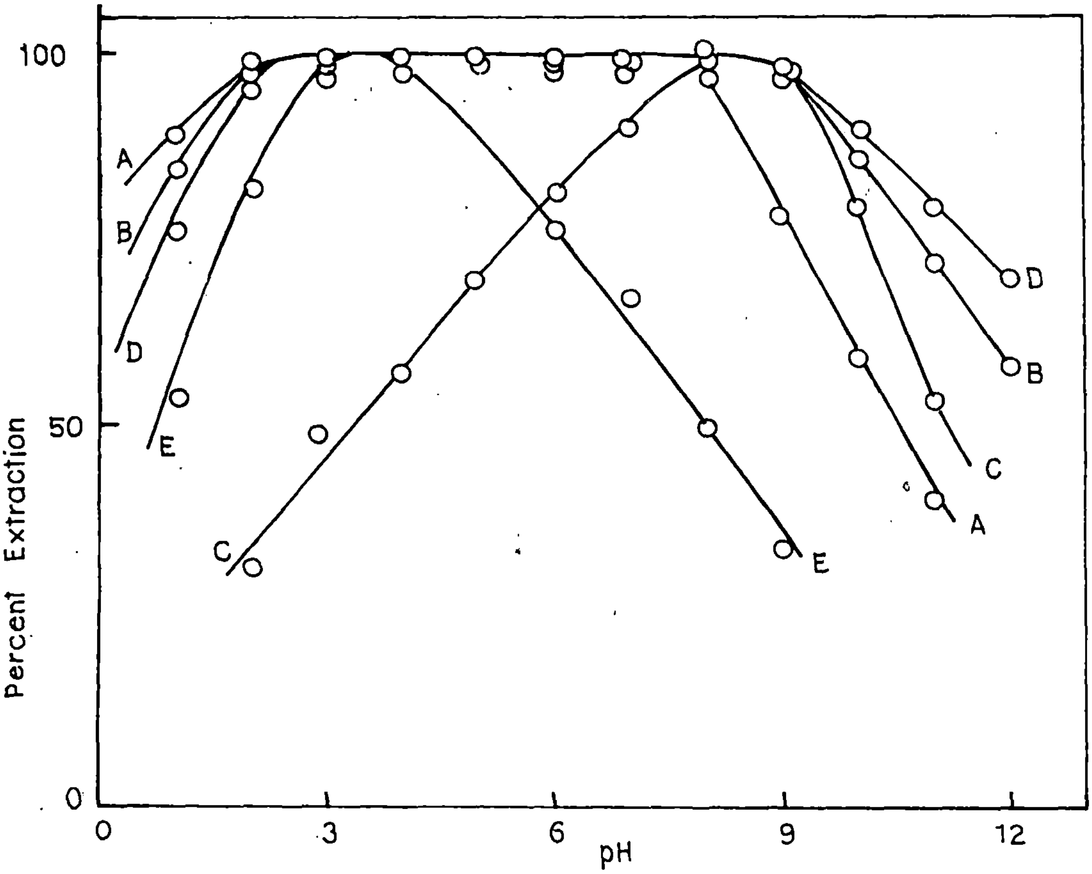

FIG. 2. EXTRACTION OF Pt-COMPLEX IN PRESENCE OF (A)- Pyridine, (B)-α-Picoline, (C)-β-Picoline, (D)-γ-Picoline, (E)-2,4,6-Collidine.

Table 1. Details of Extraction Methods

Parameter	Base				
	Pyridine	α-Picoline	β-Picoline	γ-Picoline	2,4,6-collidine
pH	2-8	2-9	8-9	2-9	3-4
λ_{max} (nm)	345	370	485	365	360
Molar absorptivity ($dm^3 mol^{-1} cm^{-1}$)	1.95×10^3	1.75×10^3	1.85×10^3	3.70×10^3	1.09×10^4
Sandell's sensitivity ($\mu g\ cm^{-2}$)	0.10	0.11	0.10	0.05	0.018

Table 2. Effect of diverse ions on the determination of 392 μg of platinum (117.6 μg for collidine). Average of three determinations was taken

Ion added	Amount tolerated (mg)	Ion added	Amount tolerated (mg)
Oxalate	20 (6)	Mn(II)	10 (3)
Borate	20 (6)	V(V)	10 (3)
Phosphate	20 (6)	Ca(II)	10 (3)
Tartrate	20 (6)	Ba(II)	10 (3)
Citrate	20 (6)	Sr(II)	10 (3)
Fluoride	20 (6)	Cr(III)	10 (3)
Bromide	20 (6)	Be(II)	10 (3)
Phthalate	20 (6)	Al(III)	10 (3)
Acetate	20 (6)	Cd(II)	4 (1)
EDTA	2 (0.5)	Zr(IV)	4 (1)
Co(II)	10 (3)	Th(IV)	4 (1)
Ni(II)	10 (3)	Rh(III)	2 (0.5)
Zn(II)	10 (3)	Fe(III)*	2 (0.5)
Mo(VI)	10 (3)	Cu(II)**	2 (0.5)
U(VI)	10 (3)		
Pb(II)	10 (3)		

*in presence of fluoride

**in presence of citrate

( ) for collidine system

Table 3. Determination of platinum in synthetic mixtures (with collidine)

Composition with amounts in μg	Platinum found μg
1. Pt(117.6), Rh(200), Co(200)	115, 116.5, 115
2. Pt(117.6), Co(200), Ni(200)	116.5, 116, 116
3. Pt(117.6)*, Fe(200), Cu(200)	115.0, 114.0, 115.5
4. Pt(117.6), Mo(200), V(200)	116, 116, 115.5
5. Pt(117.6), Zn(200), Pb(200)	117.5, 116, 115
6. Pt(117.6), U(200), Cr(200)	116.5, 117, 115

*Plus 2 mg each of fluoride and citrate.

Table 4. Reproducibility of Platinum Recovery (with collidine)

Platinum taken in μg	Platinum found μg	Mean μg	Std. Dev. %
58.8	57.5, 57, 58.5 58, 58, 56	57.5	0.89
117.6	114.5, 117, 115.5 115, 115.5, 114.5	115.5	1.05
176.4	175.5, 175.5, 177.5 176, 176, 175	175.9	0.86
235.2	234.5, 235.5, 233 234, 233.5, 236	234.4	1.16

Table 5. Comparison of the present method

Ref.	Reagent	pH	λ_{max} (nm)	Molar absorptivity ($l\ mol^{-1}cm^{-1}$)	Interference
71.	Thioridazine hydrochloride	1. 6-4.0M H_3PO_4	640-664	$3.41x10^4$ ($dm^3mol^{-1}cm^{-1}$)	$Pd^*(II)$, $Ru^*(III)$
72.	Mepazine hydrochloride	1.5-4.1	512-516	$1.44x10^4$	$Fe^*(III)$, $Ru^*(III)$
73.	Benzin-α-monoxime	3.0	440	$6.67x10^3$	Co(II), Ni(II),W, Th, Zr, EDTA, Br^-, F^-, SCN^-, S_2O_3 , I^-
74.	Propionyl promazine phosphate	1-3M phosphoric acid	512-516	$5.95x10^3$	nil
75.	2-oximino-1-indanone	5.4-8.0	342	$1.06x10^4$	-
76.	O-mercapto-acetoacetanilide	At lower pH in HCl	593	$9.56x10^3$ ($dm^3mol^{-1}cm^{-1}$)	Nil (free from the interference of noble and base metals)
77.	Phenothiazine	-	660	$1.353x10^4$	Pd(II),Au(III),Ru(III), Fe(III), Cu(II), Ag(I), Hg(II)
78.	Present method (Collidine)	3-4	360	$1.09x10^4$	Hg, Pd, thiocyanate, thiosulphate, ascorbate

*masking agents were used.

Solvent Extraction and Spectrophotometric Determination of Copper using Mixed Ligand Complex Formation with Pyridine, α-Picoline, β-Picoline, γ-picoline or 2,4,6-Collidine and Bromide/Iodide

EXPERIMENTAL

Apparatus and Reagents :

Spectral curves and analytical measurements were made with a Shimadzu-PR-1 model spectrophotometer. Stoppered quartz cells of 10 mm optical path length were used for absorbance measurements.

A stock solution of copper(II) was prepared by dissolving $CuSO_4.5H_2O$ in distilled water followed by its standardisation as benzoin-α-oximate[79]. A working solution of Cu(II)(120 μg ml^{-1}) was prepared by appropriate dilution. Chloroform (E. Merck), pyridine (BDH), α-picoline (Riedel), β -picoline (BDH) γ -picoline (Fluka) and 2,4,6-collidine (BDH) were distilled before use. All other chemicals were of analytical grade. Stock solutions of desired diverse ions were prepared from their corresponding salts. Potassium chloride-hydrochloric acid buffer was used to adjust pH of the aqueous solution.

Determination of copper : Bromide System:

An aliquot containing 50-300 μg of copper was mixed with 8M aqueous potassium bromide (1 ml) followed by the addition of 0.5 ml of pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine. Buffer solution (5 ml) of pH 2.0 was then added to it and the volume of the aqueous phase was made upto 10 ml with distilled water and left for 1 min to ensure complete complexation. The mixture was then equilibrated with chloroform (10 ml) for 30 sec. The separated organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the organic extract was measured at corresponding absorption maxima against a blank. The amount of copper(II) was determined from a calibration curve. To test the effect of foreign ions, the respective ions were added to the system before addition of the reagents.

<u>Iodide system</u> :

An aqueous solution containing 50-30μg copper was mixed with 0.05M potassium iodide (3 ml) and 0.5 ml of pyridine/α-piccoline/β-picoline/γ-picoline/2,4,6-collidine. Buffer solution (5 ml) of pH 1.0 was then added followed by distilled water to make the volume of the aqueous phase up to 10 ml. The aqueous phase was left for 1 min, to ensure complete complexation. The mixture was then equilibrated with chloroform (10 ml) for 30 sec. The separated organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the chloroform extract was measured at corresponding absorption maxima against copper free reagent blank. Amount of copper(II) was deduced from a previously prepared calibration curve. To study the effect of diverse ions, the respective foreign ions were added to the system prior to the addition of the reagents.

RESULTS AND DISCUSSION

In presence of pyridine and alkali thiocyanate, copper forms an insoluble complex[80] of formula $CuPy_2(SCN)_2$, where thiocyanate behaves as a pseudo-halogen. In presence of bromide/Iodide and pyridine bases copper(II) probably forms complexes of the type CuP_2X_2 (P = Pyridine base; X = Br/I). These complexes are extractable into chloroform.

Absorption Spectra :

The absorption spectra of the copper(II)-bromide-pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine complexes in chloroform showed maximum absorbances at 320-355 nm with a shoulder at around 380 nm in each case (Fig. 1).

In the copper(II)-iodide-pyridine/β-picoline/γ-picoline/2,4,6-collidine systems, the absorption maxima were at 350-360 nm.(FIG. 2) The copper(II)-iodide-α-picoline complex exhibited no absorption maxima in the region 300-600 nm; in this case the analytical measurements were carried out at 350 nm. The reagent blanks did not absorb in the aforesaid wave-length regions. Hence for simplicity all analytical measurements were carried out at respective absorption maxima against chloroform.

Effect of pH :

Effect of pH on the extractability of Cu(II) into chloroform was examined in terms of absorbance of the mixed-ligand complex. In the bromide system, in presence of pyridine bases, maximum absorbance was obtained in the pH range 1.5-2.5. In a second consecutive operation the chloroform extract virtually showed no absorbance. This indicated a complete and quantitative extraction of copper(II) into chloroform in this condition. However in case of iodide system, in presence of pyridine bases, quantitative extraction of copper(II) was accomplished from pH 0.5-1.5.

Effect of solvents :

Apart from chloroform, some other solvents like benzene, ethylacetate, carbontetrachloride were tested as extracting solvents; but those offered no special advantage over chloroform. The pattern of the absorption spectra of the complexes remain unchanged in all cases.

Stability of colour:

The absorbances of the copper (II) complexes in chloroform were measured at elapsed intervals of time. The colour intensity was stable for at least 24 hours.

Reagent concentration and Beer's law :

The optimum reagent concentrations were ascertained by extracting copper at various concentrations of potassium bromide or potassium iodide along with pyridine bases. It was found that for bromide complexes, 1 ml of 8M aqueous solution of potassium bromide along with 0.5 ml of pyridine bases was sufficient to extract 240 μg of copper(II) at pH 2.0. For iodide complexes, the amounts of reagents required were 3 ml of 0.05M aqueous solution of potassium iodide and 0.5 ml of pyridine bases to extract the same amount of copper(II); the extraction was carried out at pH 1.0. Higher reagent concentration (of the bromide or of the iodide) had no adverse effect on extraction.

In the optimum conditions, the absorbance of the organic extract showed a linear response over a concentration range of 5-50 ppm of copper. The corresponding molar absorptivities of the complexes (on the basis of copper content) and Sandell's sensitivities were calculated as shown in Table 1.

Interference :

In order to study the effects of diverse ions on the extraction behaviour, 240 μg of copper (II) was extracted and determined according to the general procedure in presence of the respective foreign ions. Deviation of not more than ± 3% from the recovery of copper was taken as the tolerance limit for the diverse ions tested. For bromide complexes the system tolerates 10-25 fold excess of the following ions: Fe(III), Co(II), Pb(II), Ni(II), Zn(II), V(V), Rh(III), Ca(II), Ba(II), Sr(II), Be(II), Tl(I), U(VI), Zr(IV), La(III), Al(III), Th(IV), Mg(II), Cd(II), Mo(IV), Pt(IV) and Hg(II) are permissible at lower concentrations. Pd(II) however shows strong interference even at trace level. Among the anions tested, most of them are susceptible to the procedure, although phthalate, borate and phosphate do not interfere. In case of iodo-complexes, 10-25 fold excess of the following ions are permissible : Co(II), Ni(II), Pb(II), Zn(II), Mo(IV), V(V), Rh(III), Ca(II), Ba(II), Sr(II), Zr(IV), U(VI), Al(III), Be(II), La(III), Tl(I). The system tolerates lower concentration of Cd(II), Hg(II), and Fe(III). However, Pd(II) and Pt(IV) must be absent. Among the anions tested borate, bromide, phthalate, phosphate do not interfere. The presence of thiosulphate, EDTA, tartrate, oxalate, citrate, fluoride, ascorbate restricts the extraction of copper. High results are obtained in presence of thiocyanate. The results are presented in Table 2.

Determination of copper in synthetic mixtures :

In absence of real samples, the proposed method was tested to estimate microgram amounts of copper in various synthetic mixtures (Table 3).

Precision and accuracy :

Among the bases used 2,4,6-collidine was found to be most sensitive in both the bromide and iodide systems. With this reagent the precision and accuracy of the method was tested by analysing solution containing a known amount of copper(II) following the recommended procefure. The average of six determinations indicated the proposed method to be fairly precise and reproducible in either of the systems. The results are shown in Table 4.

Comparison of the present method:

The proposed method is very simple and rapid. The method has been compared with some other existing methods as shown in Table 5. Microgram amounts of copper can be determined in presence of a number of diverse ions although palladium(II) and platinum(IV) interfered.

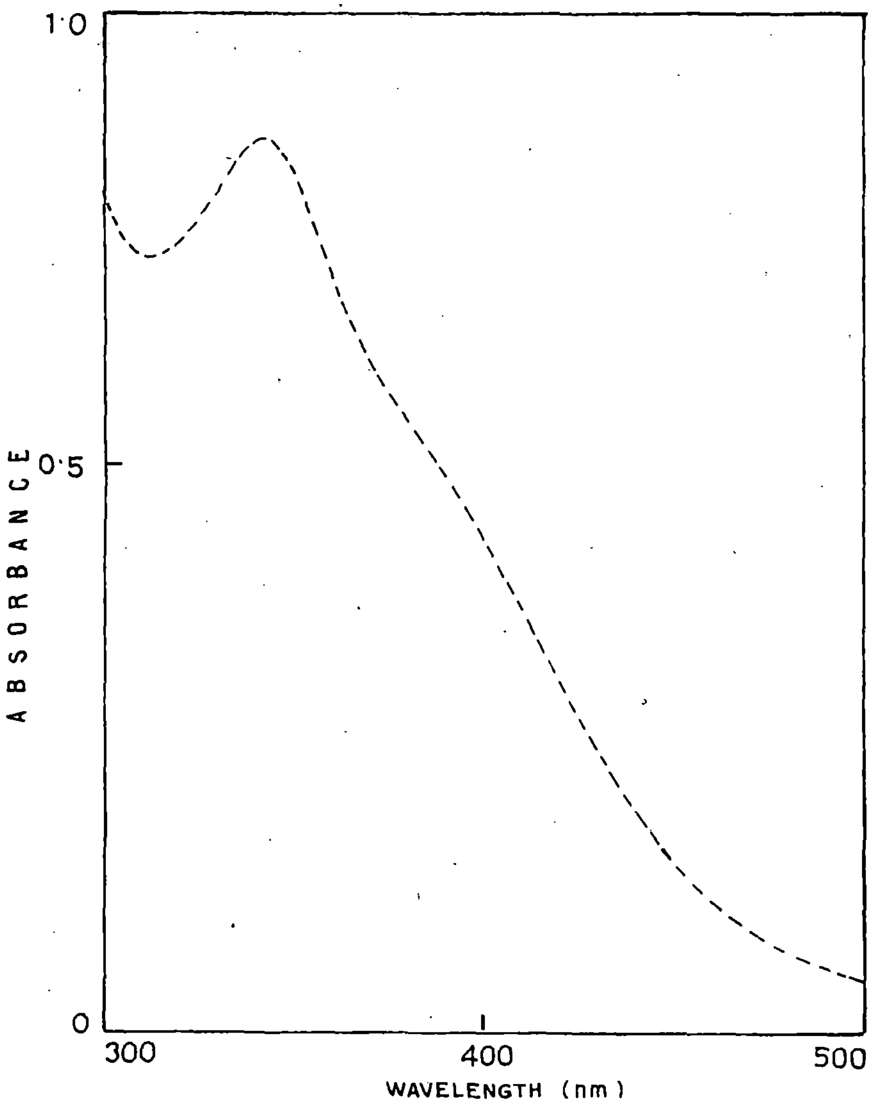

FIG. 1. ABSORPTION SPECTRUM OF
Cu(II)-Br-γ-Picoline COMPLEX (Cu-24 ppm)

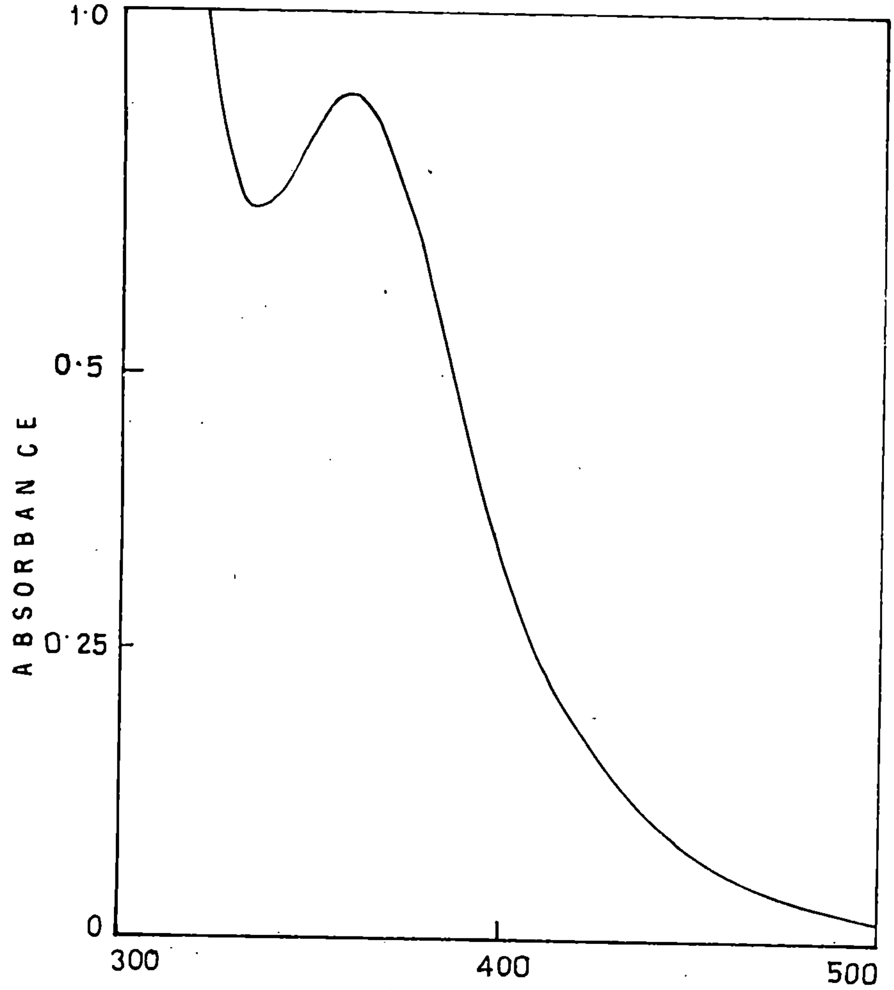

FIG. 2. ABSORPTION SPECTRUM OF
Cu(II)-I-γ-Picoline-COMPLEX (Cu-12 ppm)

Table 1. Parameters of Extractive Methods

Parameter	Base employed				
	Pyridine	α-Picoline	β-Picoline	γ-Picoline	2,4,6-collidine
		Bromide system			
pH	1.5-2.5	1.5-2.5	1.5-2.5	1.5-2.5	1.5-2.5
λ_{max} (nm)	340	320	340	340	355
Molar absorptivity ($\times 10^3 dm^3 mol^{-1} cm^{-1}$)	2.17	3.07	3.23	2.33	5.13
Sandell's sensitivity ($\mu g\ cm^{-2}$)	0.029	0.021	0.018	0.027	0.012
		Iodide system			
pH	0.5-1.5	0.5-1.5	0.5-1.5	0.5-1.5	0.5-1.5
λ_{max} (nm)	355	350	350	360	360
Molar absorptivity ($\times 10^3 dm^3 mol^{-1} cm^{-1}$)	2.38	2.65	4.23	4.76	6.77
Sandell's sensitivity ($\mu g\ cm^{-2}$)	0.027	0.024	0.015	0.013	0.009

Table 2. Effect of diverse ions on the determination of 240 μg of copper. Average of three determinations was taken

Ion added	Amount tolerated (μg)	
	Bromide system	Iodide system
Fe(III)	5000	2000
Co(II)	6000	6000
Pb(II)	6000	6000
Ni(II)	6000	6000
Zn(II)	3000	3000
V(V)	6000	6000
Rh(III)	4000	4000
Ca(II)	6000	6000
Ba(II)	6000	6000
Sr(II)	6000	6000
Be(II)	4000	4000
Tl(I)	4000	4000
U(VI)	3000	3000
Zr(IV)	2000	2000
La(III)	4000	4000
Al(III)	4000	4000
Th(IV)	4000	4000
Mg(II)	60000	6000
Cd(II)	3000	1000
Mo(IV)	3000	3000
Pt(IV)	500	-
Hg(II)	500	500

Table 3. Determination of copper in synthetic mixtures. (Average of three determinations)

Composition with amounts (μg)	Copper found (μg)
1. Cu(120), Fe(300), Ni(300)	121.5
2. Cu(120), Ni(300(, Co(300)	119.5
3. Cu(120), Pb(300), Zn(300)	120
4. Cu(120), Hg(200), Rh(200)	122
5. Cu(120), Mo(200), V(200)	121

Table 4. Reproducibility of copper recovery

Copper taken (μg)	Copper found (μg)	Mean (μg)	Std. Dev. %
	Bromide system		
60	58, 60.5, 61 61, 61.5, 60	60.33	1.24
120	120.5, 122, 121 120, 121, 120.5	120.8	0.22
180	181, 182.5, 181 180, 181.5, 180	181	0.94
240	240.5, 242.5, 242 241, 242, 241	241.5	0.77
	Iiodide system		
60	58.5, 60, 61.5 60.5, 61, 58	59.9	1.39
120	121.5, 120, 119 120.5, 120, 118	119.8	1.21
180	180.5, 181.5, 180 182, 182, 181	181.16	0.81
240	242.5, 241 239 240, 242, 242	241	1.36

Table 5. Comparison of the Present Method

Ref.	Reagent	pH	λ_{max}	Molar absorptivity	Interference
81.	Diphenyl thiocarbazide	4-8	540	5.04×10^4	Fe^*(III), Sn^*(II), Pd^*(II), Hg^*(II), Pb^*(II), Bi^*(III), borate and nitrite
82.	4-nitroso-resorcinal and pyridine bases	1.0-11.0	365-375	0.71×10^4 0.45×10^4 0.89×10^4 1.06×10^4 0.21×10^4	Co(II), Pd(II), Hg(II), Fe(III), Zr(IV), SCN, S_2O_3, EDTA, F^-, C_2O_4, tartrate, citrate and ascorbate
83.	N-(α-pyridyl)-2-thioquinaldinamide	10.5-11.0	520	5.2×10^3	-
84.	10-(2-benzoxazolylazo)-9-pehanthrol	5.1 ± 0.1	542	5.1×10^4	Al^*(III), Fe^*, Pb^*, Cr^*(III), Zn^*, Co^*, Ni^*, Cd^* and Hg^*(II)
85.	8-(nonylbenzene) sulfonylamino-quinoline	Weakly acidic (<5)	375	6.78×10^3	Hg(II)
86.	Diphenyl-carbazide	8.4	540	1.5×10^5	-
87.	Present method	(Vide-Table 1)			Pd(II), Pt(IV) and SCN^-

*masking agents used.

REFERENCES

1. Moeller T. and Zogg R.E., Anal. Chem., 1950, 22, 612.
2. Hinter J.A. and Miller C.C., Analyst, 1956, 81, 79.
3. Umezaki Y., Bull. Chem. Soc., Japan, 1964, 37, 70.
4. Koppiker K.S. and Gajankush K.S., Rept. At. Energy Comm., India, AEET-225 (1965).
5. Akaiwa H, Kawamoto H., Anal. Chim. Acta, 1969, 48(2), 438.
6. Kuroda R., Matsusue H., Oguma K., Fresenius Z., Anal. Chem., 1979, 294(3), 413.
7. Saha M.B. and Chakraborty A.K., J. Indian Chem. Soc., 1983, 60(3), 281-2.
8. Das Arabinda K. and Das Jyotirmoy, Ind. J. Chem., Sect. A, 1984, 23A(4), 359-60.
9. Das Arabinda K. and Das Jyotirmoy, Chem. Anal. (Warsaw), 1984, 29(4), 403-408.
10. Sindhu R.S. and Singh R.P., J. Indian Chem. Soc., 1985, 62(1), 80-81.
11. Arya S.P., Yatiranjan V., Acta Ciene Indica. Chem., 1986, 12(2), 67.
12. Sun. Xi, Yi. Youhang, Jejin Fenxi, 1990, 10(3), 10-12.
13. Zhang Guang & Han Quan, Guijinshu, 1989, 10(2), 28-33.
14. Sudo E., Sci. Repts. Research Inst., Tohoku Univ. Ser. A, 1956, 8, 367.
15. Yamamoto Y. and Katsuji K., Bull. Chem. Soc., Japan, 1964, 37, 594.
16. Rao S.P., Sharma R.C. and Khosla M.M.L., Ind. J. Chem., 1976, 14A, 819-820.
17. Zygmunt Marenzenko, Maria Krasiejko, Stec Jadwiga, Chem. Anal (Warsaw), 1981, 26(6), 1051.

18. Kish P.P., Bazel Ya. R., Balog I.S., Ukr., Khim. Zh., 1982, 48(9), 966.

19. Ciqing Zhan, Huaxue Shijie, 1984, 25(1), 12-14.

20. Sambamoorthy Jya, Rao Talasila Prasad, Ramakrishna Tiruvesaloor Venkatrama, Analyst (London), 1984, 109(11), 1405-7.

21. Marczenko Zygmunt and Kus Stanislaw, Analyst (London), 1985, 110(8), 1005-8.

22. Mianyl Xuj Zutung Pan, Shujan Nia, Fenxi Huaxue, 1988, 16(4), 363.

23. Lopez Erroz C. and Hernandez Cordoba M., An. Cienc., 1987, 46(1-4), 25-8.

24. Siroki M. and Maric L., Croat. Chem. Acta, 1990, 63(2), 255-62.

25. L. Wohler and A. Spengel, Z. Chem. U. Ind. Kalloide, 7, 243 (1910).

26. W.A.E. McBryde and J.H. Yoe, Anal. Chem., 20, 1094, (1948).

27. Denaro A.R. and Occleshaw V.J., Anal. Chim. Acta, 13, 239(1955).

28. Bock R., Kusche H. and Boc E.Z., Anal. Chem., 138, 167(1953)

29. Poluecktov N.S., Kononenko L.I. and Lauer R.S., Zh. Analit. Khim., 13, 396, (1958).

30. Denaro A.R. and Occleshaw V.J., Anal. Chim. Acta., 13, 239, (1959).

31. Studlar K., Talanta, 8, 272(1961).

32. Miketukova V. and Kohlicek J.Z., Anal. Chem., 208, 7(1965).

33. Vogel's Text book of Quantitative Inorganic Analysis, fourth edition, English Language, Book Society, Longman Group, 1978, p. 474.

34. Majumdar S.K., Chattopadhayay P. and Paria P.K., J. Indian Chem. Soc., 1985, 62(7), 544-5.

35. Rao A.L.J. and Shekhar Chander, Ind. J. Chem., 16A, 1978, 463-464.

36. Gowda H. Sanke and Keshavan B., Ind. J. Chem., 1976, 14A, 293.

37. Deshmukh B.K. and Kharal R.B., Ind. J. Chem., 1976, 14A, 214-215.

38. Murti M.V.R. and Khopkar S.M., Ind. J. Chem., 1976, 14A, 454-455.

39. Thokdar T.K., Sarkar A., Paria P.K. and Majumdar S.K., Ind. J. Chem., 1989, 28A, 181-182.

40. Khapkar S.M., Anal. Chem., 1966, 38, 360.

41. Berg E.W. and Lan E.Y., Anal. Chim. Acta, 1962, 27, 248.

42. Gowda H. Sanke and Jagadeesh K.S., Talanta, 1978, 25(7), 416.

43. Gowda H. Sanke and Padmaji K.A., Curr. Sci., 1979, 48(12), 520-1.

44. Ivanov V.M. and Gorbunova G.N., Sovrem Metody Khim. analit. Kontrolya M. 1980, 20-4.

45. Sabartova J., Herramannova M., Malat M. and Cermakova L., Chem. Zresti, 1980, 34(1), 111-17.

46. Gorbunova G.N. and Ivanov V.M., Zn. Anal Khim., 1980, 35(4), 705.

47. Gowda H. Sanke and Padmaji K.A., Microchem. J., 1980, 25(3), 396.

48. Meshcheryakova N.R., Usatenko Yu. I. and Izv. Vyas R. Uchebu., Zaved Khim. Khim Tekhnal, 1981, 24(8), 980.

49. Mosheva P., Borisova R. and Dakl Bolg., Akad. Nauk, 1982, 35(8), 1085.

50. Ovsepyan E.N., Chen. Kim Tien and Mikaelyan D.A., Zh. Anal Khim., 1983, 38(7), 1277.

51. Keshavan B. and Nagarajan P., Ind. J. Chem., Sect. A, 1983, 22A(8), 725.

52. Das Arabinda K., and Das Jyotirmoy, Ind. J. Chem., Sect A, 1983, 22A(1), 93.

53. Mote N.A., Anuse M.A. and Chavan, M.B., Curr. Sci., 1983, 52(2), 69.

54. Thimmegowda Ankapura, Sankegowda Halukuru and Gowda Netkal M. Mode., Anal. Chem., 1984, 56(3), 358-63.

55. Cacho J., Nerin C. and Gonzalex Mateo P., An. Quin., Ser. B., 1983, 79(3), 406-12.

56. Khan Hasan M., J. Chem. Soc., Pak., 1985, 7(2), 129-31.

57. Novak Josef, Vyhlicka Paul and Zemanova Dogmar, Chem. Listy, 1985, 79(5), 530-3.

58. Marenzenko Zygmunt and Kus Stanillaw, Analyst (London), 1985, 110(8), 1005-8.

59. Gowda A. Thimme, Gowda N. MMade and Gowda H. Sanke., Microchem., J., 1985, 32 (2), 211-19.

60. Reddy K. Hussain, Prakash K.M.M.S., Reddy K. Giridhara and Reddy D. Venkata, J. Ind. Inst. Sci., 1984, 65(5), 119-26.

61. Pilipenko A.T., Khvatkov, Z.M. and Golvina U.V., Zn. Anal. Khim., 1986, 41(11), 2045-9.

62. Fang Guozhen and Liu Xin, Gooding Huaxiao Huaxue Xuebao, 1986, 7(4), 315-18.

63. Singh Nepal and Garg Arvind K., Analyst (London), 1987, 112(5), 693-5.

64. Brajter Krystyna, Kozicka Urszula and Chmurska Joanna, Fresenius Z., Anal. Chem., 1987, 328(7), 598.

65. Rakha T.H., Khalifa, M.E. & Moussa M.N.H., Anal. Lett., 1987, 20(10), 1557-65.

66. Chen. Huifeng, Dong Zhiming & Rovg Gingxin., Fexi Ceshi Tongbao, 1989, 8(3) 42-4.

67. Goekchyan N.O., Ovsepyan E.N. and Khachatryan, A.G., Arm Khim. Zh., 1989, 42(5), 289-94.

68. Paria P.K., Thokdar T.K. and Majumdar S.K., Curr. Sci., 1989, 58(13), 739-40.

69. Li Youfur, Fenxi Huaxue, 1989, 17(11), 1004-6.

70. Vogel's Text book of Quantitative Inorganic Analysis, fourth edition, English Language Book Society, Longman Group, 1978, pp. 474-475.

71. Gowda H. Sanke and Raj J.B., Ind. J. Chem., 1986, 25A, 1167-1168.

72. Gowda H. Sanke and Padmaji K.A., Ind. J. Chem., 1979, 17A, 208.

73. Paria P.K. and Majundar S.K., Ind. J. Chem., 1976, 14A, 916.

74. Keshavan B. and Nagaraya P., Ind. J. Chem., 1983, 22A 725-726.

75. Kim Jack C., You Mi Kyung, Won Mi Soak, Shim You Bo and Koh Young Sim, Yakhak Haechi, 1984, 28(2), 61-7.

76. Das Arabinda K. and Das Jyotirmoy, Ind. J. Chem., 1983, 22A, 93-94.

77. D'Souza Jayarama M.V., Yathirajan H.S. and Rangaswamy, Ind. J. Chem., 1985, 24A, 987-988.

78. Thokdar T.K., Sarkar A., Paria P.K. and Majumdar S.K., J. Indian Chem. Soc., 1988, LXV, 743-744.

79. Vogel's Text book of Quantitative Inorganic Analysis, Fourth edition, ELBS, Longman Group, 1978, 463-464.

80. Vogel, A.I., A Text book of Quantitative Inorganic Analysis, ELBS, fourth edition, 1978, Longman, p. 427.

81. Paria P.K., Thokdar T.K. and Majumdar S.K., J. Ind. Chem. Soc., 1990, 67, 263-264.

82. Sarkar A., Thokdar T.K., Paria P.K. and Majumdar S.K., J. Ind. Chem. Soc., 1988, LXV, 742-743.

83. Chakrabarti Anil K., Ind. J. Chem., Sect. A, 1986, 25A(9), 886.

84. Okawa Shinichiro; Bunseki Kagaku, 1986, 35(10), T101- T 105.

85. Stainslaw Przeszlakowski and Jodwiga Iwaniuk, Ann. Univ. Mariae Curie Sklodowska, Sect. 4A, Chem., 1980(Pub 1982), 35, 85-97.

86. Huang Xuan Zhong, Lihua Jianyan, Huaxue Fence, 1991, 27(1), 51, 53.

87. Thokdar T.K., Sarkar A., Paria P.K. and Majumdar S.K., J. Ind. Chem. Soc., 1988, 386-388.

CHAPTER - VI

2-MERCAPTOBENZOIC ACID AS AN ANALYTICAL REAGENT

Literature reveals a number of complexing agents for spectrophotometric determination of palladium. In our laboratory 2-mercaptobenzoic acid is under investigation to study its analytical potentiality. A method has been reported to determine palladium spectrophotometrically in microgram levels with the reagent.

Spectrophotometric Determination of Palladium

EXPERIMENTAL

Apparatus and Reagents :

Absorbance measurements were carried out with a Shimadzu PR-1 model spectrophotometer fitted with a pair of matched quartz cells of 10 nm optical path length.

Palladium chloride (Johnson and Matthey) (1 g) was dissolved in conc. HCl (1 ml) and diluted to 250 ml with distilled water. This was standardised with dimethyl glyoxime[1]. A working solution of palladium(II) was prepared by approximate dilution of the stock solution.

A 0.1% ethanolic solution of 2-mercapto benzoic acid (E. Merck) was used for the purpose. Adjustment of pH in the aqueous phase was done by using 0.2 N acetic acid and 0.2 M sodium acetate solution.

Standard solutions of diverse ions were prepared from chlorides nitrates as sulphates of metals (in case of cations); and from sodium, potassium or ammonium salts of the species concerned (in case of anions) to study this interfering effects.

All other chemicals used were of analytical grade.

Determination of palladium :

An appropriate amount of palladium solution (20-100 μg) was taken in a 10 ml volumetric flask. To this was added 0.1% ethanolic solution (1 ml) of 2-mercaptobenzoic acid followed by the acetate buffer (5 ml) (pH 3.5). The volume was made up with distilled water and left for 1 min to ensure complete complexation and maximum colour development. Absorbance of the solution was measured at 420 nm against a reagent blank. Amount of palladium present was computed from a calibration curve. To study the interference, the respective foreign ions were added prior to the addition of reagent and volume make up.

RESULTS AND DISCUSSION

Absorption and Spectra :

The absorption spectrum of the Pd(II)-2-mercaptobenzoic acid complex in aqueous solution against the reagent blank taken as reference is shown in Fig. 1. Maximum absorbance as seen from the spectrum, occurs at 420 nm. The reagent blank prepared under conditions of the experiment absorbs considerably below 380 nm but the absorbance became insignificant from 400 nm onwards. Hence the wave length of 420 nm was selected for all analytical measurements.

Effect of pH :

The effect of pH on colour development was examined by measuring at 420 nm the absorbance of the palladium complex over the pH range 0-12. Various buffers were employed for the purpose. The complex exhibits constant and maximum absorbance when the acidity of the aqueous phase was maintained at pH 3-4, showing a gradual decrease in value with increase or decrease in pH. The variation of absorbance with change in pH of the aqueous phase is shown in Table 1 and 4 in Fig. 2.

Effect of reagent concentration :

The effect of 2-mercapto benzoic acid on the colour development of the Pd(II) complex in the aqueous phase was studied by adding different amounts of the reagents. Use of 0.4 ml of 0.1% ethanolic solution of the reagent was sufficient for maximum colour development of the aqueous phase (10 ml) containing 43 μg of palladium. Use of less than 0.25 ml of the reagent probably render the complexation incomplete and low absorbance values of the aqueous solution are obtained. Increased concentrations, on the other hand, do not bring about any significant change in the maximum value of absorbance. However, use of 1 ml of 0.1% ethanolic solution of the reagent is preferred in the proposed method as a part of the added reagent may be consumed - if foreign ions are present. Results obtained in respect of reagent concentration are presented in Table 2.

Stability of colour:

The absorbance of the palladium complex in the aqueous phase was measured at elapsed intervals of .25, 0.5, 1, 2, 4, 8, 12 and 24 hours after the colour development at 420 nm against the reagent blank was measured. No change in the colour intensity was recorded upto 24 hours (Table 3). The complex is thus, sufficiently stable.

Calibration curves sensitivity and precision :

Calibration curve was prepared by standard procedure. Different amounts of palladium were allowed to interact with 2-mercapto benzoic acid maintaining all conditions of the given procedure. Absorption of the Pd-complex was measured at 420 nm against a blank. A standard calibration curve was obtained by plotting absorbance values against corresponding palladium concentrations (Table 4, Fig. 3).

The system conforms to Beer's law over concentrations of 10 ppm of palladium (Table 4, Fi.g 3). Sandell's sensitivity and molar absorptivity of the complex (on the basis of palladium content) are 0.006 $\mu g/cm^2$ and 1.725×10^4 l $mol^{-1} cm^{-1}$ respectively at 420 nm. This classifies the colour reaction as one of the most sensitive for palladium compared with some other existing methods (Table 5).

Precision and accuracy :

The precision and accuracy of the proposed method was tested by analysing solutions containing a known amount of palladium (II). The results in Table 6 indicated the method to be fairly precise and reproducible. The total operation time for each run required 10-15 min.

Interference :

In a separate set of experiments a standard palladium(II) solution containing 43 μ g of palladium in each case was mixed with an aqueous solution of one of the foreign species. Determination of palladium was then computed following the recommended procedure. The tolerance limit was set at that amount of the foreign material for which approximately ± 3 per cent error would be achieved. The upper limit of concentration investigated was, however, restricted to the amount around 100 fold excess (w/w) of the palladium concentration. The results showing tolerance limits of the foreign materials investigated, are given in Table 7.

Tolerance limits of some ions having serious interference were improved by using masking agents, e.g., iron(III) was masked with fluoride, lead(II) with excess acetate. Among the ions tested mercury(II) has very low tolerance limit.

Application to the analysis of synthetic mixtures :

In absence of real samples the proposed method was extended to some synthetic mixtures to estimate microgram amounts of palladium. Five different synthetic mixtures were prepared by mixing solutions of palladium(II) with those of platinum(II), Rhodium (III), iron(III), copper(II), nickel(II), cobalt(II), zinc(II), cadmium(I), molybdenum(VI) and vanadium(V) in the manner as given in Table 8. The amount of palladium present in each sample was then determined by following the recommended procedure. Masking agent was used wherever necessary.

Conclusion :

The present method for the spectrophotometric determination of palladium is simple, rapid and sensitive. The metal in micro quantities can be estimated in presence of most of the common ions. Influence of some interfering ions can be overcome. The method is, therefore, a selective one. Furthermore, the method is precise and reproducible. The proposed method is thus worthy of finding application for determination of palladium whenver high degree of precision and sensitivity is desired.

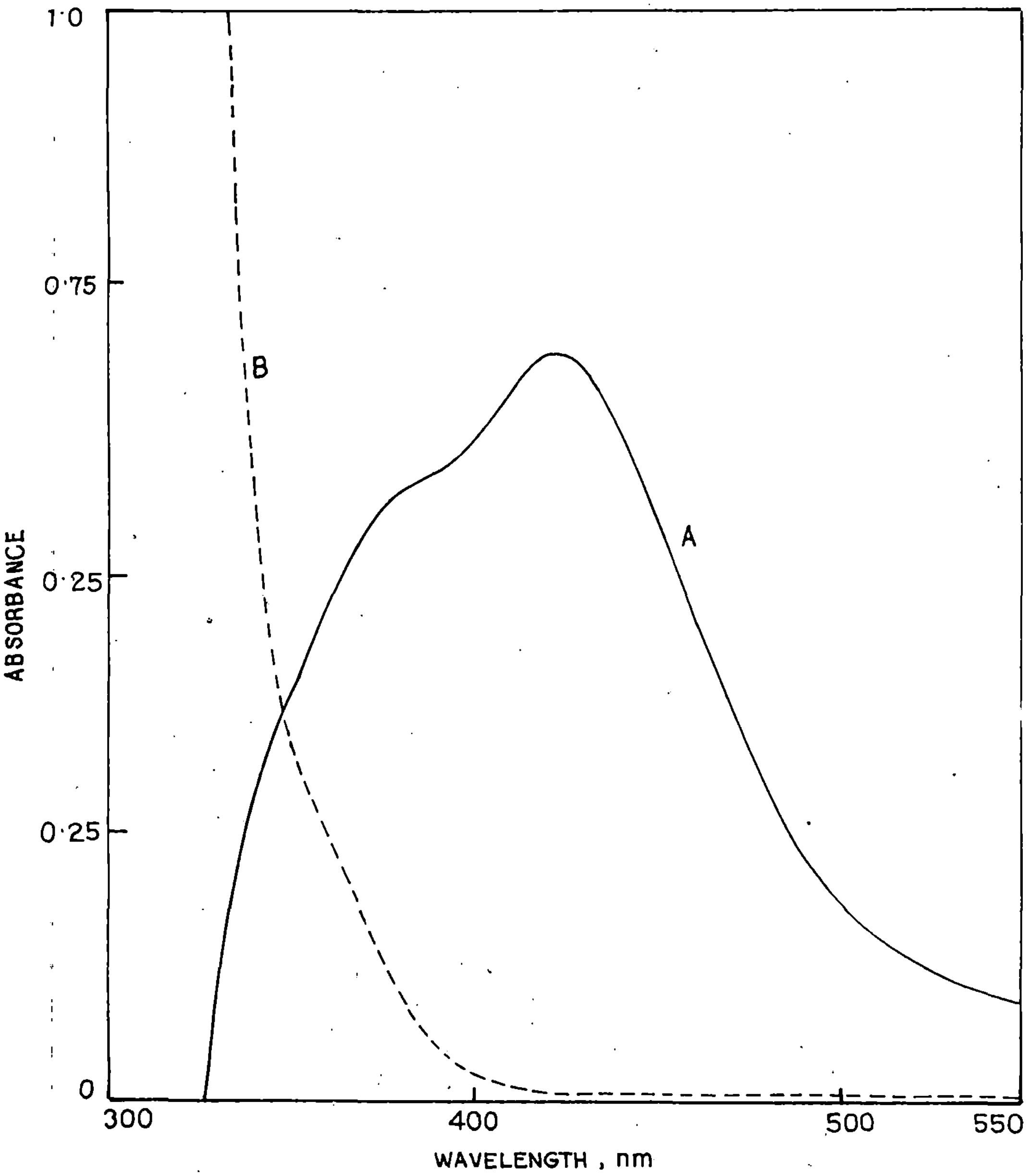

FIG: 1. ABSORPTION SPECTRUM OF Pd(II)-2-MERCAPTOBENZOIC ACID COMPLEX (A) AND REAGENT BLANK (B).(Pd-4·3 ppm)

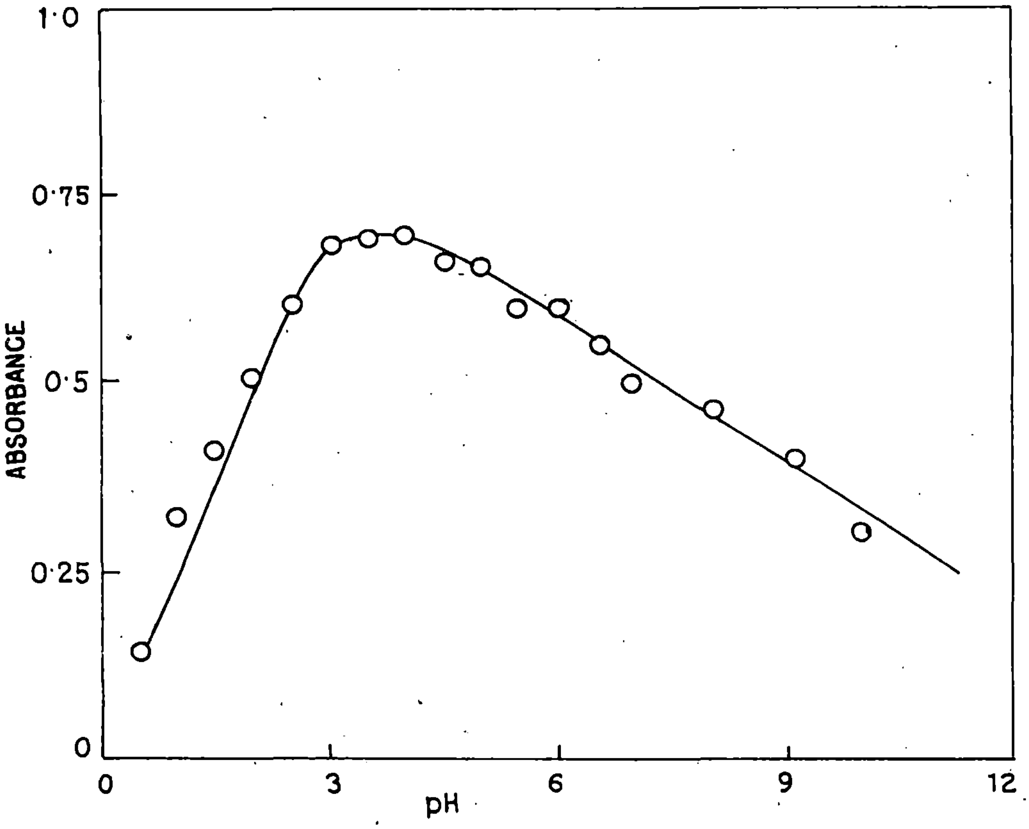

FIG. 2. ABSORBANCE OF PALLADIUM (II) COMPLEX AS A FUNCTION OF pH .

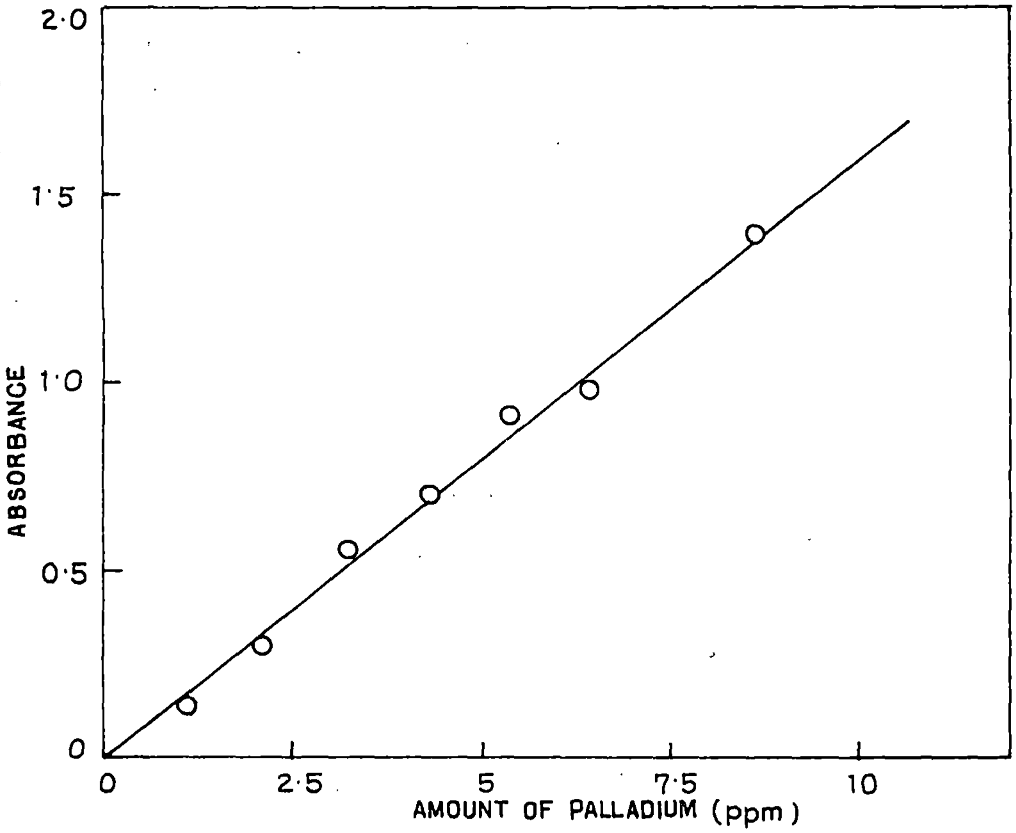

FIG: 3. CALIBRATION CURVE FOR DETERMINATION OF PALLADIUM .

Table 1 : Variation of absorbance with pH of the aqueous phase (The aqueous phase (10 ml) contains 43 μg of Pd(II) and 2 ml of 0.1% ethanolic solution of 2-mercaptobenzoic acid

pH	Absorbance	pH	Absorbance
0.5	0.140	4.5	0.660
1.0	0.322	5.0	0.650
1.5	0.410	5.5	0.600
2.0	0.500	6.0	0.600
2.5	0.610	6.5	0.550
3.0	0.688	7.0	0.510
3.5	0.695	8.0	0.470
4.0	0.695	9.0	0.410
		10.0	0.310

Table 2. Effect of 2-mercaptobenzoic acid. The aqueous phase (10 ml) (pH 3.5) contains 43 μg of Pd. 0.1% ethanolic solution of the reagent was used

Addition of reagent added in ml	Absorbance	Addition of reagent added in ml.	Absorbance
0.05	0.340	0.5	0.695
0.10	0.395	0.6	0.692
0.15	0.430	0.8	0.692
0.2	0.480	1.0	0.695
0.25	0.532	1.5	0.695
0.3	0.430	2.0	0.695
0.35	0.680	4.0	0.695
0.40	0.690	6.0	0.692

Table 3. Variation of absorbance with time

Time in hour	Absorbance
0.25	0.695
0.5	0.695
1	0.692
2	0.695
4	0.695
8	0.695
12	0.695
24	0.695

Table 4. Beer's law data

Concentration of palladium(ppm)	Absorbance at 420 nm
1.07	0.140
2.15	0.322
3.22	0.550
4.30	0.695
5.38	0.890
6.45	0.982
8.60	1.380

Table 5. Comparison of the Method

Ref.	Reagent	pH	λ_{max}	Molar absorptivity	Interference
1.	Isonitroso thiocamphor	5M HCl to pH 2.0	450	3.90×10^3	Cu*, Co*, Pt*, Hg and S_2O_3
3.	Phenothiazine and Promazine	Ethanol medium	551 and 450	3.542×10^3 and 9.213×10^3	Pt(IV), Au(III), Fe(III), Cu(II), Ag(I) and Hg(II)
4.	Sodium Ethyl-trithiocarbonate	1.0-10.0	370	1.277×10^4	Mn*(II), Zn*(II), Cd*(III), Fe*(III), Ni*(II), Co*(II) and Pt.
5.	Xanthates	10M HCl to pH 2.0, pH 1.7 and 2M HCl to pH 7.0	460 and 465	1.9×10^2 1.9×10^2 1.76×10^2 1.82×10^2 1.80×10^2	Fe*, Pb*, Bi(III), Au, Pt(IV), Os(VIII), S_2O_3, vanadate, molybdate, Ni*(II), Co*(II), Cu(II)
6.	2'-Hydroxy-4-methoxy-5'-methylchalkone-oxime	0.5 to 2.5	380	3.38×10^3	Be(III), Ru(III), ZrO(II), citrate, tartrate and EDTA
	Present method	3-4	420	1.725×10^4	Fe*(III), Pb*(II),

* masking agents used

Table 6. Reproducibility of the method

Palladium taken (μg)	Palladium found (μg)			Mean μg	Std. Dev. %
21.5	19.5	21.5	21.0	20.25	0.98
	20.0	20.5	19.0		
43.0	41.5	43.0	42.5	42.25	0.68
	41.5	42.0	43.0		
64.5	64.5	66.0	65.0	65.25	0.52
	65.5	65.0	65.5		
86.0	85.5	84.5	86.5	86.33	1.63
	88.5	88.0	85.0		

Table 7. Effects of diverse ions on the determination of 43 μg of palladium. Average of three determinations was taken in each case

Ion added	Amount tolerated μg	Ion added	Amount tolerated μg
Ascorbate	4000	Fe(III)*	400
Tartrate	4000	Cu(II)	200
Citrate	4000	Cr(III)	4000
Borate	4000	Tu(IV)	1000
Fluoride	4000	Zr(IV)	1000
Oralate	4000	Mo(VI)	2000
EDTA	2000	Pb(II)*	400
Thiosulfate	200	Hg(II)	100
Thiocyanate	2000	Sn(II)	4000
Iodide	400	V(V)	4000
Phthalate	2000	Au(III)	4000
Arsenate	4000	Mg(II)	4000
Bromide	4000	Ag(I)	1000
Phosphate	4000	Cd(II)	4000
Nitrate	4000	Co(II)	4000
Zn(II)	4000	Sr(II)	4000
Ba(II)	4000	U(VI)	4000
Ni(II)	4000	Bi(III)	4000
		Pt(IV)	4000
		Rh(III)	4000

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* in presence of fluoride

*In presence of excess acetate.

Table 8. Analysis of Synthetic Mixtures

No.	Composition with amount (in μg) of each constituent	Palladium found (μg)
1	Pd(43), Pt(200), Rh(200)	43.5, 44.0, 43.5
2	Pd(43), Fe(100)*, Cu(100)	43.5, 44.0, 44.0
3	Pd(43), Ni(200), Co(200)	43.5, 43.5, 43.0
4	Pd(43), Zn(200), Cd(200)	42.5, 44.0, 43.0
5	Pd(43), Mo(200), V(200)	43.0, 43.0, 43.5

* in presence of fluoride.

REFERENCES

1. Vogel's Text book of Quantitative Inorganic Analysis. (Including Elementary Instrumental Analysis), Fourth Edition, English Language Book Society, Longman.

2. Majumdar S.K., Chattopadhyay P. and Paria P.K., J. Indian Chem. Soc., 1985, 62 (7), 544-5.

3. Jayarama H.S. Yathirajan, M.V.D'scuza and Rangaswamy, Ind. J. Chem., 1986, 25A, 703.

4. Rao A.L.J. and Shekhar Chander, Ind. J. Chem., 1978, 16A, 463-464.

5. Paria P.K. and Majumdar S.K., Ind. J. Chem., 1985, 24A, 629-630.

6. Deshmukh B.K. and Kharat R.B., Ind. J. Chem., 1976, 14A, 214-215.

CHAPTER - VII

CACOTHELINE AS A SPECTROPHOTOMETRIC REAGENT

Cacotheline is to be the nitrate of the bisdimethylmononitrobrucine hydrate[55] and have the formula, $C_{20}H_{20}(OH)_2(NO_2)N_2O_3 \cdot HNO_3$. Aqueous solution of cacotheline gives a violet colour with stannous ions due to the formation of a reduction product of cacotheline of unknown composition[56]. Potluri[57] used cacotheline as an indicator in estimating Pb(IV) and Cr(VI) with Ti(III). The present authors noted that Fe(II) gives a violet colour with aqueous solution of cacotheline in presence of phosphoric acid, and which lead to the development of a simple spectrophotometric method for iron(II) determination.

Spectrophotometric Determination of Iron(II) with Cacotheline

Introduction

Literature survey shows that use of thiocyanate, as a complexing agent for colorimetric determination of iron is very popular. The red colour of $FeSCN^{+2}$[1] has long been employed for the colorimetric estimation of iron(III) and in presence of excess thiocyanate, the extraction of iron is possible in to oxygen bearing solvents. The metal can be determined spectrophotometrically by using chromeazurals and hexadecyl trimethyl ammonium bromide[2].

Gonzalez Portal et al[3] determined iron (III) spectrophotometrically by using music acid at pH 8.6. The absorbance was measured at 290 nm. Mathur S.P[4] determined iron(III) spectrophotometrically by measuring the absorbance of its complex with N-quinolyl-N-phenyl thiourea at 475 nm. Other reported methods for the determination of iron involve the application of ascorbic acid[5], 3-hydroxy flavone[6], N-benzyl-N-phenyl hydroxyl-amine and naphthalene[7], 2,2'-dipyridyl ketone-2-pyrimidyl hydrazone[8], 4-capryl-3-methyl-1-phenyl-5-pyrazoline[9], 2-theonyltrifluoroacetone[10], 4-hydroxy-1,10-phenanthroline[11], N-hydroxy-N-phenyl-N'-(2- methylphenyl) benzamidine hydrochloride and thiocyanate and azide[12], 2,2'-dipyridyl-2-quinolyl hydrazone[13], biacetyl monoxime[14], 2-(2-thiozolyl-azo)-4-methylphenol[15], 2,6 diacetyl pyridine and ethylene diamine[16], 2,2'-dipyridyl ketoxime[17], salicyloyl-hydrazide[18], pyridine-2-acetaldehyde salicyloylhydrazone[19], 3-hydroxy-2-methyl-1,4-napthoquinone monoxime[20], 7-(2-thiazolylazo) resorcinol[21], isophthalodihydroxamic acid[22], 5 or 4-nitro-2-benzyl-1,3, indandione[23], 4,5,7-trihydroxy-3-(p-methoxy phenyl)-coumarin[24].

Simonenko V.I. et al[25] proposed a method for photometric determination of iron(III) using methyl 1,3-indan-dione 2-carboxylate. It was a 1:3 complex extractable in to chloroform. The pH was adjusted at 3-4. The complex absorbed well at 490 nm.

Some other reagents which have also been studied for the spectrophotometric determination of iron include 2-hydroxy-3-methyl-2-cyclopenten-1-one[26], quinoline-2-aldehyde thiosemicarbazone[27], crystal violet and malachite green[28], 5-(2-thiazolylazo)-salicylic acid[29], bromopyrogallol red[30], antipyrine and chloro acetic acid[31], 8-quinolinol and monionic surfactant and sodium thiosulphate[32], 3-(2-pyridyl)-5-6-diphenyl-1,2,4-triazine and tetraphenyl borate[33], 5,5-dimethyl-1,2,3-cyclohexane trione 1,2-dioxime-3-thiosemicarbazone[34], silicates and 1,10 phenanthroline[35], methylethylene diamine tetra acetic acid[36], amines and thiocyanate[37], 2-benzylideniminobenzohydroxamic acid[38], bipyridyl glyoxal bis (4-phenyl-3-thiosemicarbazone)[39], 3-hydroxypicolinaldehydeazine[40], sulfochrome and cetylpyridinium chloride[41], N-(4-methylphenyl)-3-oxobutanamide[42], thiocyanate and chloropromazine[43].

Xiang Yuan et al[44] developed a method for the photometric determination of iron(III) using oxytetracyline. The complex was stable at the pH range 3-5 and showed an absorbance at 420 nm.

Spectrophotometric determination of iron by using 2-[2-(5-bromobenzo thiazolyl)azo]-5-dimethyl amino benzoic acid was carried out by Zhang Guang et al[45]. The 1:2 complex had a $_{max}$ at 646 nm with molar absorptivity of 8.0×10^4 l mol^{-1} cm^{-1}.

Zhang Zhenya et al[46] have determined iron(II) using 1,10 phenanthroline and picrate in pH 2-9 medium in presence of $NH_2OH.HCl$ and AcONa. The complex was extracted with CH_2Cl_2. Its absorbance was measured at 510 nm.

Salinas F. et al[47] was successful in determining ion(II) with thiosalicylic acid with λ_{max} at 658 nm. Beer's law was obeyed between 0.3 and 2.9 ppm of Fe(II).

Ambhore D.M. et al[48] suggested a method for the spectrophotometric determination of iron using 3-thiobenzoyl 1-p-tolylthiocarbamide. The complex absorbed at 520 nm. The sensitivity of the method was determined to be 0.014 and Beer's law was obeyed in the range of 1.0-7.5 µg of iron.

In the present investigation a programme has been undertaken for the spectrophotometric determination of iron with cacotheline.

EXPERIMENTAL

1. Apparatus and Reagents:

Absorbance measurements were carried out with a Shimadzu PR-1 model spectrophotometer fitted with a pair of matched quartz cells of 10 mm optical path length.

Stock solution of iron (II) was prepared from $FeSO_4$, $(NH_4)_2SO_4$ and standardised[58]. A working solution of iron (II) was prepared by appropriate dilution of the stock solution.

A 0.2% aqueous solution of cacotheline was used for colour development. Adjustment of molarity in the aqueous phase was done by using phosphoric acid.

Standard solutions of diverse ions were prepared from chlorides, nitrates or sulphates of metals (in case of cations); and from sodium, potassium or ammonium salts of the species concerned (in case of anions) to study the interfering effects. All other reagents were of anlytical reagent grade.

2. Determination of Iron:

An appropriate amount of iron(II) solution (100-500 μg) was taken in a 10 ml volumetric flask. To this was added phosphoric acid (5 ml) and the aqueous solution of cacotheline (0.5 ml). Volume of the mixture was made up to 10 ml with distilled water and left for 1 min to ensure complete complexation and maximum colour development. Absorbance of the solution was measured at 530 nm against a reagent blank. Amount of iron(II) was computed from a calibration curve. To tent the interference, the respective foreign ions were added to the system before addition of the reagents and volume make up.

RESULT AND DISCUSSION

3. Absorption and Spectra:

In presence of fluoride or phosphate, iron (II) gives a violet colour. In the former, the colour is very unstable and fades away within 5 min. But in presence of phosphoric acid the system gives a stable colour. The absorption spectrum of the Iron(II) cacotheline complex in aqueous solution against the reagent blank taken as reference is shown in Fig. 1 . Maximum absorbance as seen from the spectrum, occurs at 530 nm. The reagent blank prepared under the experimental conditions did not show any absorbance in the aforesaid region of wave-length. Hence the wave length of 530 nm was selected for all analytical measurements.

4. Effect of molarity:

The effect of molarity on colour development was examined by measuring at 530 nm the absorbance of the iron(II) complex over the range of molarity 0-12. The complex exhibits constant and maximum absorbance along with maximum colour development when the acidity of the aqueous phase was maintained at 6-10 M with respect to phosphoric acid, showing a gradual decrease in value with decrease in molarity. The variation of absorbance with change in molarity of the aqueous phase is shown in Table 1.

5. Effect of reagent concentration:

The effect of cacotheline on the colour development of the Iron(II) complex, in the aqueous phase was studied by adding different amounts of the reagents. Use of 0.5 ml of 0.2% aqueous solution of cacotheline was sufficient for maximum colour development of the aqueous phase (10 ml) containing upto 500 μg of iron (II). Use of less than 0.3ml of the reagent probably render the complexation incomplete and low absorbance values of the aqueous solution are obtained. Higher concentrations of the reagent, on the other hand, do not bring about any significant change in the maximum value of absorbance. However, use of 1.0 ml of 0.2% aqueous solution of the reagent was preferred in the proposed method as a part of the added reagent may be consumed - if foreign ions are present. Results obtained in respect of reagent concentration are presented in Table 2.

6. Stability of colour:

The absorbance of the iron complex in the aqueous phase was measured at elapsed intervals of 0.25, 0.5, 1,2,4, 8, 12 hours after the colour development at 530 nm against the reagent blank was measured. No change in the colour intensity was recorded up to 12 hours (Table 3). The complex is thus sufficiently stable.

7. Calibration curve, sensitivity and precision:

Calibration curve was prepared by standard procedure. Different amounts of iron were allowed to interact with cacotheline maintaining all conditions of the given procedure. Absorption of the iron-complex was measured at 530 nm against a blank. A standard calibration curve was obtained by plotting absorbance values against corresponding iron concentration (Table - 4, Fig.2.).

The system conforms to Beer's law over concentration range of 2-50 ppm of iron(II) (Table 4, Fig. 1.). Sandell's sensitivity and molar absorptivity of the complex (on the basis of iron content) were found to be $0.05 \mu g/cm^2$ and 1.49×10^3 $l\ mol^{-1} cm^{-1}$ respectively at 530 nm.

8. Interference:

In a separate set of experiments a standard iron(II) solution containing $300 \mu g$ of iron in each case was mixed with an aqueous solution of one of the foreign species. Determination of iron has been computed following the recommended procedure. The tolerance limit was set at that amount of the foreign material for which approximately ± 3% error would be achieved. It was found that 300 μg of iron(II) could easily be determined without any interference in presence of 5 mg of each of the following cations: Mn(II), Co(II), Ni(II), Mo(VI), Pd(II), Pt(IV), Rh(III), Cd(II), Ca(II), Ba(II), Sr(II), Zr(II), Th(IV), Be(II), Zn(II), Hg(II), Mg(II), Pb(II), Tl(I), U(VI), La(III) and Al(III). Cu(II) and V(V) must be absent as the system gives no colour in presence of the said cations. Presence of less than 2 mg of Cr(III) is harmless. In presence of Fe(III) low absorbance is obtained. The system tolerates 50 mg of each of the following anions :EDTA, thiosulphate, iodide, bromide, fluoride, citrate, tartrate, ascorbate, oxalate, acetate, phthalate, borate. There is no colour development if nitrate is present. The results shwoing tolerance limits of the foreign materials investigated, are given in Table 5.

9. Comparison of the present method:

The present method for spectrophotometric determination of iron is very simple and rapid and comparable with some other existing methods (Table 7).

10. Application to the analysis of Synthetic Mixtures:

In absence of real samples the proposed method was extended to some synthetic mixtures to estimate microgram amounts of iron. Four different synthetic mixtures were prepared by mixing solution of iron(II) with 500 μg each of platinum(II), Rhodium(III), palladium(II), nickel(II), Cobalt(II), Zinc(II), cadmium(II) and molybdenum(VI), in the manner as given in Table 6. The amount of iron present in each sample was then determined by following the recommended procedure.

11. Precision and accuracy :

The precision and accuracy of the proposed method was tested by analysing solutions containing a known amount of iron(II). The results indicated the method to be fairly precise and reproducible. The total operation time for each run required 10-15 min.

12. Conclusion :

The present method for the spectrophotometric determination of iron is simple and rapid. The metal in microquantities can be estimated in presence of most of the common ions. The method is, precise and reproducible.

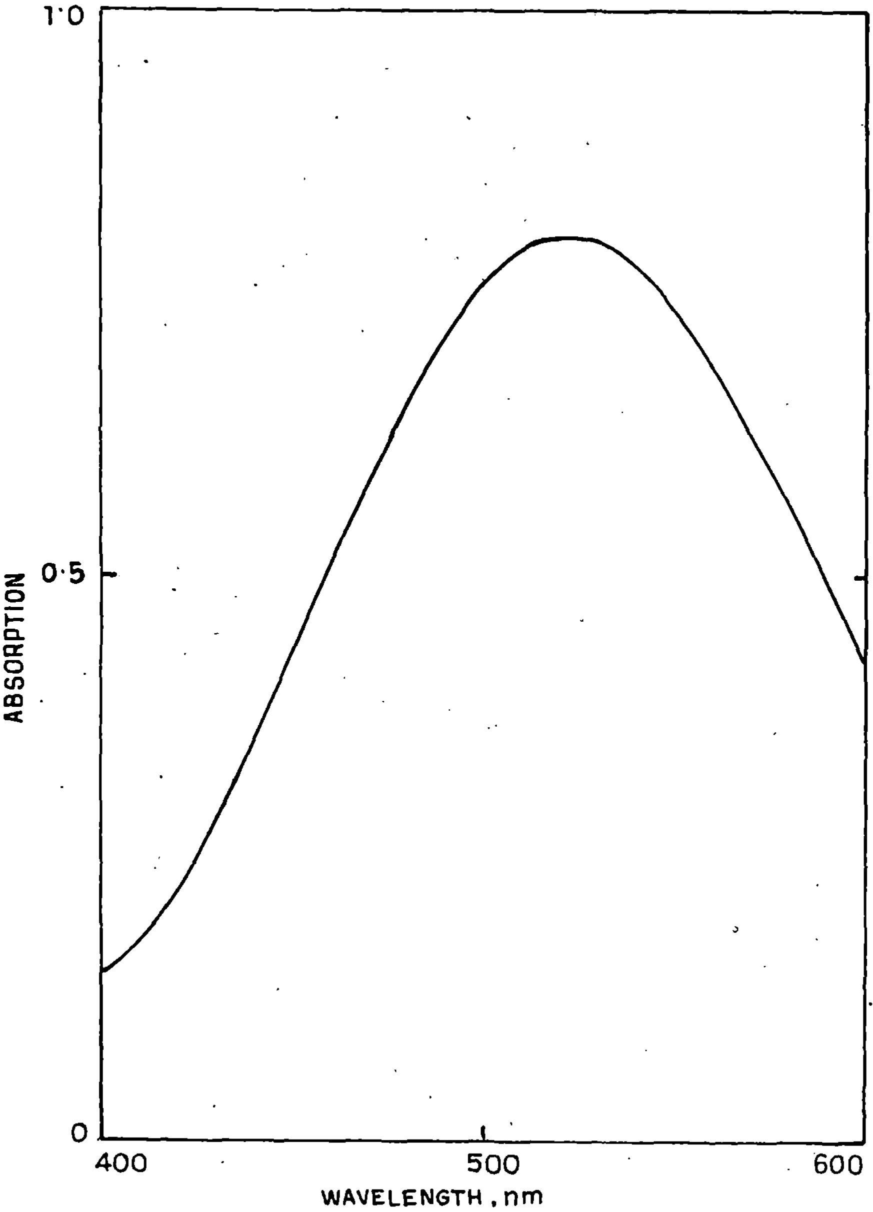

FIG.1. ABSORPTION SPECTRUM OF Fe(II)-Cacotheline system.

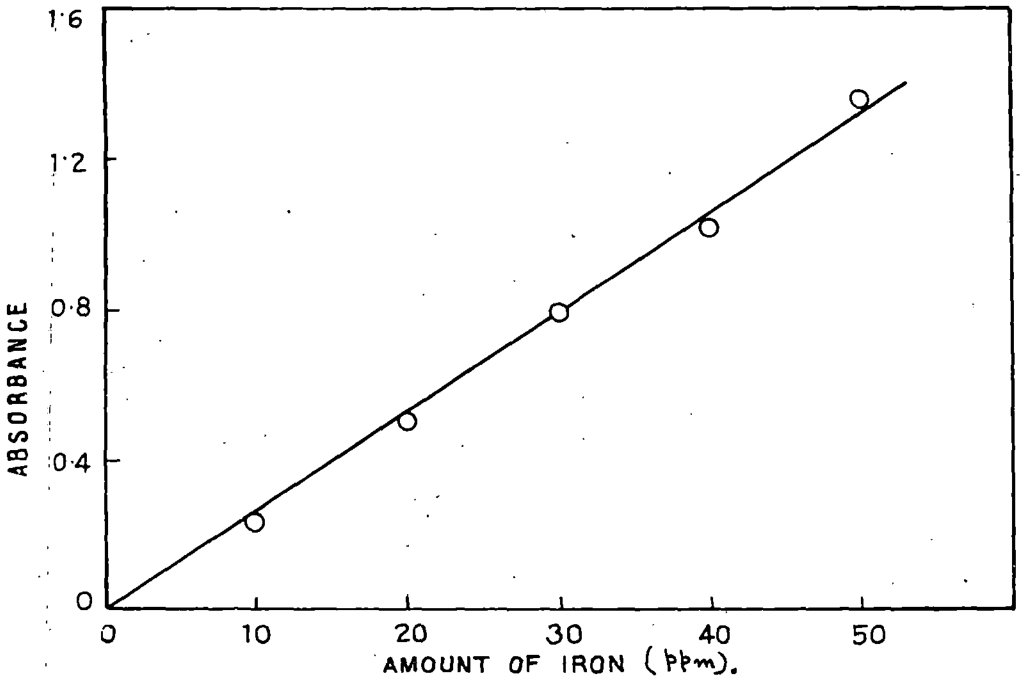

FIG. 2. CALIBRATION CURVE FOR DETERMINATION OF IRON

Table - 1. Variation of absorbance with acid concentration of the aqueous phase[The aqueous phase (10 ml) contains 300μg of iron(II) and 0.5 ml of cacotheline 0.2%]

H_3PO_4 Concen. in M	Absorbance	H_3PO_4 Concen. in M	Absorbance at 530 nm.
1	-		
1.5	0.105	5	0.795
2	0.350	6	0.800
2.5	0.650	7	0.802
3	0.700	8	0.798
3.5	0.750	9	0.800
4	0.790	10	0.800

Table 2- Effect of Cacotheline concentration. The aqueous phase (10 ml) contains 300μg of iron (II) and 5 ml of H_3PO_4 [0.2% Aqueous solution of cacotheline used for variation

Vol of aq. Cacotheline	Absorbance	Vol of aq. Cacotheline	Absorbances at 530 nm
0.05	0.250	0.8	0.800
0.1	0.650	1.0	0.802
0.2	0.750	1.2	0.798
0.3	0.795	1.4	0.800
0.4	0.800	1.6	0.800
0.5	0.800	1.8	0.798
0.6	0.798	2.0	0.800
0.7	0.798		

Table - 3 Variation of absorbance with time

Time in hour	Absorbances at 530 nm
0.25	0.800
0.5	0.798
1	0.800
2	0.800
4	0.800
8	0.800
12	0.800

Table - 4 Beer's law Data

Amount of iron (ppm)	Absorbances at 530 nm
10	0.240
20	0.490
30	0.798
40	1.030
50	1.370

Table - 5 Effect of diverse ions on the determination of 94.7μg of Cobalt. Average of them determinations was taken

Ion added	Amount (mg) tolerated	Ion added	Amount tolerated (mg)
Mn(II)	5	Zn(II)	5
Co(II)	5	Hg(II)	5
Ni(II)	5	Mg(II)	5
Mo(VI)	5	Pb(II)	5
Pd(II)	5	Tl(I)	5
Pt(IV)	5	U(VI)	5
Rh(III)	5	La(III)	5
Cd(II)	5	Al(III)	5
Ca(II)	5	Cu(II)	5
Ba(II)	5	V(V)	5
Sr(II)	5	Cr(III)	2
Zr(II)	5	EDTA	50
Th(IV)	5	Thiosulphate	50
Be(II)	5	Iodide	50
		Bromide	50
		Fluoride	50

Table-6 Analysis of synthetic mixtures

No.	Composition with amounts taken in μg	Iron found in μg
1.	Fe(300), Pd(500), Pt(500), Rh(500)	301.5
2.	Fe(300), Cu(500), Ni(500), Co(500)	302
3.	Fe(300), Zn(500), Cd(500)	301
4.	Fe(300), Ni(500), Mo(500)	300.5

Table - 7 Comparison of the present method

Ref.	Reagent	pH	λ_{max}	Molar absorptivity ($1\ mol^{-1} cm^{-1}$)	Interference
49.	2-Acetyl pyridine-thiosemicarbazone	2.5 and 8.5	550 and 610	5.32×10^3 and 7.0×10^3	Cu*, Ag*, EDTA, CN^-, SCN^-
50.	5-bromo-2-(2-pyridylazo)-5-(diethylamino)-phenol	3.5-10	558	7.64×10^4	Ti*, W*, Co*
51.	8-hydroxy-7-nitrosoquinoline-5-sulphonic Acid	3.5-6.0	705	1.8×10^4	Co(II)*
52.	1,10-phenanthroline and 2,2'-bipyridine	1.0-1.5	515, 518	22500, 21700	F^-*, Cr^{+3}*
8.	2,2'-dipyridyl ketone-2-pyrimidylhydrazone	1.5-2.5 and 5.0-13	540, 580	11500, 12500	EDTA, CN^-, persulphate, Pd(II)
53.	5-(3,5-dibromo-2-pyridylazo)-2-4-diamino toluene	4-6.5	556	4×10^4	Co(II) (when>0.01 mg) Cu(II) (when > 0.05 mg)
54.	Present method	6-10M H_3PO_4	530	1.49×10^3	Cu(II), V(V) nitrate

* masking agents used.

REFERENCES

1. Solvent extraction in Analytical Chemistry, Freiser, Morrison, New York, John Wiley & Sons., London, 1957.

2. Nakamura Y. Nagai H., Kubota D. and Himeno S., Jpn., Analyst, 1973, 22, 1156.

3. Aurora Gonzalez Portal, Bermejo Martinez F., Baluja Santosh C., Acta Quin Compostelana, 1978, 2 (2-3), 37.

4. Mathur S.P., An. Quim., 1978, 74(6), 1020.

5. Maslowska Joanna, Owczarek Alina, Chem Anal (Warsaw), 1978, 23 (5), 825-9.

6. Velasevic Kse nijia, Radovic Zorica and Dukanovic Andelijia, Arh. Farm, 1979, 29(4), 239-45 (Serbo-croatian).

7. Satake Masatada, Yokota Toshihiko and Yoshida Nobasate, Fukui Daigaku Kogakubu Kenkyu Hokoku, 1979, 27(2), 271-8.

8. Singh R.B., Garg B.S. and Singh R.P., Ind. J. Chem., 1979, 17A, 318-320.

9. Akama Yoshifumi, Sato Kenji Makai Toshio and Kawamura Fumikazu, Nippon Kaisui Gakkaishi, 1980, 34 (189), 200.

10. Taketatsu Tomitsugu & Sato Atsuko, Bull. Chem. Soc., Jpn., 1980, 53 (12), 3713.

11. Poe Donald P., Eppen Alan D. and Whoolery Stephen P., Talanta, 1980, 27(4), 368.

12. Mohabey Hemlata, Sharma Parmod Kumar, Mishra Rajindra K., Proc. Indian Acad. Sci., [Ser]; Chem. Sci., 1980, 89(2), 95-9.

13. Otomo Makoto, Ano Srichiro and Kako Hiroyuki, Microchem J., 1981, 26(2), 228.

14. Azrina M, Riyazuddin P.,Curr. Sci., 1981, 50(12), 531.

15. Ueda Kazumasa, Sakamoto Shunji and Yamamoto Toshikaza, Nippon Kagaku Kaisi, 1981, 7, 1111.

16. Kato Takeshi, Honda Keaji, Kinki Daigaku and Rikogakubu Kenkyn Ho Ko Ku, 1981, 16, 37.

17. Kato Takeshi & Ikuwawa Katsuhiko, Bunseki Kugaku, 1981, 30(4), 256.

18. Savindra Randhawa & Sekhon B.S., J. Indian Chem. Soc., 1981, 58 (4), 412.

19. Garcia-Vargos M., Rodrigenz Bautista J.M. and Avila Novas S., Microchem J., 1982, 27(4), 519.

20. Kamini Kamil F. & Sindhwani S.K., J. Chin. Chem. Soc., (Taipei), 1982, 29(3), 209.

21. Rudometkine T.F. and Ivamov V.M., Zh. Anal. Khim., 1982, 37(11), 2021.

22. Salinas F. and Jemenez Arrabal M., Bol. Soc. Quim., Peru, 1983, 49 (3), 161.

23. Apsitis A. & Ratbergs J., Latv. PSR. Zinat. Akad. Vestis, Kim. Ser., 1983, (2), 207-9.

24. Dhar M.L. and Pandita Kuldeep, Curr. Sci., 1983, 52(11), 544-6.

25. Simonenko V.I. & Valovenko Yu. M., Ukr. Khim. Zh. (Russ. Ed.), 1982, 48 (12), 1291-2.

26. Martos I., Rojar J., Lopez Fernandex J.M. and Valcarcet M., Afinidad, 1984, 41 (390), 173-5.

27. Khasnis D.V. and Shinde V.M., J. Indian Chem. Soc., 1984, 61 (3), 275-7.

28. Arstamyan Zh. M., Uch. Zap. Erevan Un-t. Estertv N., 1983, (1), 99-103.

29. Murty R.N., Dash R.N. and Rao D.V. Ramana, J. Inst. Chem. (India), 1984, 56 (2), 104-6.

30. Batasheva N.A., Organ Reaktrivity V. Anal. Teoriya Deistviya i Primenenie V. Fotometri, Saratov, 1983, 93-7.

31. Retrov B.I. and Rogozhnikov S.I., Zh. Anal. Khim., 1984, 39 (10), 1848-52.

32. Nishida Hiroshi and Nishida Tacko, Bunseki Kagaku, 1984, 33 (11), 627-9.

33. Lin Jenn Lin and Chang Li Fen, J. Chim. Chem. Soc. (Taipei), 1984, 31(3), 229-34.

34. Yamaguchi Shigeroku and Vesugi Katsuya, Analyst (London), 1984, 109 (11), 1391-5.

35. Salinas Francisco, Jimenez Sanchez Juan Carlos and Galeano Diaz Teresa, Anal. Chem., 1986, 58 (40), 824-7.

36. Uchida Tetsuo, Mitsumatsu Masato, Kojima Isao and Iida Chuzo, Bunseki Kagaku, 1986, 35 (1), 42-6.

37. Castro Romero J.M., Fernandez Salis J.M., Bollain Rodriguez M.H., Bermejo Martinez F., Acta Quim. Compostelana, 1984, 8 (4), 86-96.

38. Hayashi Kenjiro, Saraki Yoshiaki, Tagashira Shoji, Soma Yoshiko and Ichinose Tomohide, Anal. Sci., 1986, 2(5), 457-60.

39. Salinas F., Mahedero M.C. and Garcia Martin J.P., Bull. Soc. Chem., Belg., 1987, 96(1), 75-76.

40. Gonzalez Balairon M. and Cano Pavon J.M., An. Quim., Ser. B., 1986, 82 (3), 347.

41. Bosh Ojeda C. and De Torres A. Garcia, Afinidad, 1987, 44 (411), 434.

42. Amelin V.G., Andreev P.A. and Kiseleva T.I., Zh. Anal. Khim., 1987, 42(3), 506-10.

43. Gupta A.K. & De K., Ind. J. Technol., 1987, 25 (5), 249-50.

44. Ranappa P.G. and Manjappa S., Curr. Sci., 1989, 58(14), 797-8.

45. Xiang Yuan, Wu. Ziliang, Wu. Xingcao, Hao Xinling, Chem. Abst., 1990, 113, 731.

46. Zhang Guang, Yang Hiqing Wu. Huiji, Lihua Jianyan, Huaxue Fence, 1990, 26(1), 3-5.

47. Zhang Zhenyu, Yao Jinzhu, Yejin Fenxi, 1990, 10(6), 48-50.

48. Salinas F. & Martinez Vidal J.L., Quim. Anal. (Barcelona), 1990, 9(2), 157-62.

49. Devi Surekha, Ind. J. Chem., 1986, 25A , 205-206.

50. Jin Yang, Yejim Fenxi, 1988, 8(5), 56-7.

51. Abbasi Sahid Abbas, Bhat B.G. and Singh R.S., Ind. J. Chem., 1976, 14A, 215-216.

52. Bhadra Amal Kanti and Banerjee Siddheswar, Ind. J. Chem., 1969, 7, 936.

53. Chen Xiangbin, Fenxi Hua Xue, 1983, 11(4), 284-5.

54. Sarkar A., Paria P.K. and Majumdar S.K., J. Indian Chem., 1989, 66, 428-429.

55. Moufang N. and Tafel J., Ann., 1898, 304, 47.

56. Welcher F.J., "Organic Analytical Reagents", Van Nostrand, Princeton, Vol. 3, 1962.

57. Potluri V.K.R., Rao V.R. and Kumar A., "Proceedings of the 24th Annual Convention of Chemists", Indian Chemical Society, Calcutta, 1987, p. D2.

58. Vogel A.I., "A Textbook of Quantitative Inorganic Analysis", Longmans, London, 1978.

LIST OF PUBLICATIONS

1. Extractive Spectrophotometric Determination of Palladium(II) Using Mixed Ligand Complex Formation with Pyridine/α-Picoline /β-Picoline/γ-Picoline/2,4,6-Collidine and Iodide, Indian Journal of Chem., 28A, (1989), 181-182.

2. Extraction of Spectrophotometric Determination of Platinum Using Mixed ligand Complex Formation with Pyridine, α-Picoline, β-Picoline, γ-Picoline or 2,4,6-Collidine and Iodide, J. Indian Chem. Soc., 65, (1988), 743-744.

3. Solvent Extraction and Spectrophotometric Determination of Copper using Mixed Ligand Complex Fomration with Pyridine, α-Picoline, β-Picoline, γ-Picoline or 2,4,6-Collidine and Bromide/Iodide, J. Indian Chem. Soc., 65, (1988), 386-388.

4. Spectrophotometric Determination of Iron(II) using Cacotheline, J. Indian Chem. Soc., 66, (1989), 428-429.

5. Spectrophotometric Determination of Palladium with 2-Mercaptobenzoic Acid, Z. Anal. Chem. (Communicated for publication).

6. Phenylthiohydantoic Acid as an Analytical Reagent for Spectrophotometric Determination of Cobalt, Z. Anal. Chem. (Communicated for publication).

7. Extraction Spectrophotometric Determination of Bismuth with Cetyltrimethylammonium Bromide, Current Science (Communicated for publication).

8. 2-Hydroxy-1-naphthaldoxime as a Reagent for Spectrophotometric Determination of Palladium, Current Science, (Communicated for publication).

9. Extraction Spectrophotometric Determination of Nickel with 2-Hydroxy-1-naphthaldoxime, J. Indian Chem. Soc. (Accepted for publication).

10. Extraction and Spectrophotometric Determination of Copper with Cetyltrimethylammonium Bromide in presence of Iodide, J. Indian Chem. Soc., (Accepted for publication).

11. Phenylthiohydantoic Acid a Selective Reagent for Extraction Spectrophotometric Determination of Palladium. Indian Journal of Chem., (Accepted for publication

12. Extraction Spectrophotometric Determination of Cobalt with 2-Hydroxy-1-naphthaldoxime, Indian Journal of Chem., (Accepted for publication).

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Extractive Spectrophotometric Determination of Palladium(II) Using Mixed Ligand Complex Formation with Pyridine/α-Picoline/β-Picoline/γ-Picoline/2, 4, 6-Collidine & Iodide

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Palladium(II) forms complexes with pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine in presence of potassium iodide. These are extractable into chloroform and absorb at 354-360 nm. The molar absorptivities of the complexes are in the range $1.6\text{-}1.9 \times 10^4$ l mol^{-1}cm^{-1}. The formation of these complexes has been utilized to propose an extractive spectrophotometric method of determination of palladium. The notable metal interference is due to mercury. Use of other common organic solvents provides no special advantages.

There are reports on extraction of iodide complexes of platinum metals with tributylphosphate in hexane as the coordinating solvent, and using this method the platinum metals have been separated from each other[1,2]. It has been noted that palladium(II) iodide forms complexes with pyridine or its methyl substituted derivatives in aqueous solution. These mixed ligand complexes are extractable into chloroform. These systems have been studied now to develop a simple spectrophotometric method for the determination of palladium. Apart from pyridine, other bases used are α-picoline, β-picoline, γ-picoline and 2, 4, 6-collidine.

Absorbance measurements were made with a Shimadzu PR1 model spectrophotometer with stoppered quartz cells of 10 mm optical path length. An ECL 5651 digital *p*H meter was used to measure the acidities of the aqueous solutions.

Palladium(II) chloride (Johnson & Matthey) (1g) was dissolved in 1 ml hot conc. HCl and diluted to 250 ml with distilled water followed by standardisation by dimethylglyoxime[3]. A working solution (41.75 ppm Pd) was prepared by dilution.

Chloroform (E. Merck), pyridine (BDH), α-picoline (Reidel), β-picoline (BDH), γ-picoline (Fluka) and 2, 4, 6-collidine (BDH) were distilled before use. Potassium iodide (BDH) and all the other reagents used were of analytical reagent grade. Stock solutions of desired diverse ions were prepared from their nitrates, chlorides or sulphates by dissolving pure samples in dilute acid or pure water. Sodium/ammonium salts were used in the case of anions. The metal contents were determined by standard methods[3].

General procedure

To an aliquot containing 10-100 μg of palladium was added 1 ml of 0.015 *M* aqueous potassium iodide and 0.02 ml of pyridine/α-picoline/β-picoline/γ-picoline/2, 4, 6-collidine followed by addition of adequate amount of distilled water to make up the volume upto 10 ml. The mixture thus obtained was equilibrated with 10 ml of chloroform for 30 sec. The two layers were allowed to settle for 1 min. The separated organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. *p*H of the aqueous solution, after extraction, was measured. Finally the absorbance of the chloroform extract was measured at the λ_{max} of the complex against a reagent blank. Amount of palladium(II) was determined from a previously prepared calibration curve.

The absorption spectra of palladium(II) complexes in chloroform, extracted as above, exhibit maxima as indicated in Table 1. The reagent blanks show insignificant absorbances from 300 nm onwards. Beer's law is obeyed at the respective absorption maxima. All the absorption measurements were carried out against respective reagent blanks. The systems are stable for at least 48 hr.

The liquid-liquid extraction behaviour of Pd(II)-complexes was investigated in the *p*H range 0-14.0. After extraction, *p*H of the aqueous solution was measured in each case. In presence of pyridine bases, quantitative extraction of palladium(II) was found to be achieved in the *p*H range 3.5-10.0. From the graph $pH_{1/2}$ values were evaluated to be 1.6 & 10.7.

The optimum reagent concentrations were found to be 1 ml of 0.015 *M* KI and 0.02 ml of pyridine/α-picoline/β-picoline/γ-picoline/2, 4, 6-collidine for quantitative extraction of 41.75 μg of palladium. Higher concentrations of the reagents (upto 4 ml of 0.015 *M* KI and 0.1 ml of pyridine bases) had no adverse effects on the extraction behaviour.

Apart from chloroform, other common organic solvents such as carbon tetrachloride, benzene and ethyl acetate were tested as extracting solvents. The molar absorptivities of the palladium(II) complexes (on the basis of Pd content) at the respective absorption maxima in various solvents are shown in Table 1. It has been found that use of other organic solvents of-

Table 1—Details of Extractive Methods

Parameter	Base employed				
	Pyridine	α-Picoline	β-Picoline	γ-Picoline	2,4,6-Collidine
λ_{max}(nm)	359^{a}	355^{a}	356^{a}	356^{a}	354^{a}
	366^{b}	360^{b}	365^{b}	363^{b}	360^{b}
	365^{c}	360^{c}	362^{c}	361^{c}	360^{c}
	355^{d}	355^{d}	356^{d}	356^{d}	359^{d}
Molar absorptivity* ($mol^{-1}cm^{-1}$)	1.68×10^{4a}	1.79×10^{4a}	1.70×10^{4a}	1.75×10^{4a}	1.98×10^{4a}
	1.63×10^{4b}	1.94×10^{4b}	1.78×10^{4b}	1.88×10^{4b}	1.78×10^{4b}
	1.78×10^{4c}	2.19×10^{4c}	1.73×10^{4c}	1.98×10^{4c}	1.83×10^{4c}
	1.78×10^{4d}	2.04×10^{4d}	2.08×10^{4d}	1.88×10^{4d}	1.83×10^{4d}

Extracting solvents: a-chloroform, b-carbon tetrachloride, c-benzene & d-ethyl acetate.
* Measured at corresponding absorption maxima

fers no special advantages. Chloroform was used as the extracting solvent in the present investigation.

Different amounts of palladium were extracted by the general procedure and the absorbance of the chloroform extracts was measured at the respective absorption maxima. In all the cases Beer's law was found to be valid over the concentration range 1-10 µg Pd/ml.

Effect of diverse ions—In order to study the effect of diverse ions on the extraction behaviour, a definite amount of palladium(II) was extracted and determined according to the general procedure in presence of the respective foreign ions. All the bases i.e., pyridine, α-picoline, β-picoline, γ-picoline and 2, 4, 6-collidine showed similar behaviour towards the extraction of palladium. In each case an average of three determinations was taken. An ion was considered to interfere if the recovery of Pd(II) differed by more than ± 3% from the actual amount taken.

It was found that 41.75 µg of palladium could easily be determined without any interference in presence of the following cations and anions, the amounts (mg) taken being mentioned in parentheses: Co(II) (5.1), Ni(II) (5.3), Cd(II) (4.9), Zn(II) (6.7), V(V) (5.2), Rh(III) (2.4), Zr(IV) (1.2), U(VI) (5.1), Mn(II) (3.9), Cr(III) (4.8), La(III) (4.2), Al(III) (3.9), Th(IV) (4.1), Be(II) (6.9), Pb(II) (1.3) and Bi(III) (1.1). Iron(III) (1.2) and Cu(II) (0.2) were kept in the aqueous phase by masking them with ammonium hydrogen fluoride and citrate respectively. All attempts to remove the interference due to Hg(II) failed. Pt(IV) interfered in all cases except in the 2, 4, 6-collidine system where the interference was avoided by extracting Pd at *p*H 10.0. Among the anions tested the following (10 mg each) did not interfere: EDTA, borate, phosphate, tartrate, citrate, fluoride, bromide, ascorbate, phthalate. However, thiocyanate and thiosulphate, even in trace amounts interfered seriously.

Table 2—Reproducibility of the Method Using 2,4,6-Collidine

Palladium taken (µg)	Palladium found (µg)	Relative mean deviation (%)
10.44	10.5	3.8
20.88	20.7	1.7
41.75	41.9	1.2
62.62	62.1	0.77
83.50	83.3	0.91

Among the based used, 2, 4, 6-collidine is found to be most sensitive. With this reagent the precision and accuracy of the method were tested (Table 2) by analysing solutions containing a known amount of Pd following the recommended procedure. Average of six determinations was taken in each case.

References

1 Faye G H & Inman W R, *Analyt Chem*, **35** (1963) 985.
2 Berg E W & Lau E Y, *Analyt chim Acta*, **27** (1962) 248.
3 Vogel A I, *A textbook of quantitative inorganic analysis* (ELBS, London), 1962.

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Extraction and Spectrophotometric Determination of Platinum using Mixed-ligand Complex Formation with Pyridine, α-Picoline, β-Picoline, γ-Picoline or 2,4,6-Collidine and Iodide

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THERE are reports[1,2] on the extraction and separation of iodide complexes of platinum metals using tributylphosphate. In our laboratory, it has been noted that iodoplatinum(IV) with pyridine or its methyl substituted derivatives, forms mixed-ligand complexes which are extractable into chloroform. These properties of the Pt-complexes suggested that further studies of the systems might lead to the development of simple spectrophotometric method for platinum. Apart from pyridine, other bases used are α-picoline, β-picoline, γ-picoline and 2,4,6-collidine.

Experimental

Spectral curves and analytical measurements were made with a Shimadzu PR1 spectrophotometer, and a ECL 5651 digital pH meter was used for the measurement of acidities of aqueous solutions.

Chloroplatinic acid (Johnson & Matthey) (1 g) was dissolved in distilled water (100 ml) followed by standardisation as elemental platinum[3]. A working solution (392 μg Pt/ml) was prepared by appropriate dilution. Chloroform (E. Merck), pyridine (B.D.H.), α-picoline (Riedel), β-picoline (B.D.H.), γ-picoline (Fluka) and 2,4,6-collidine (B.D.H.) were distilled before use. Potassium iodide (B.D.H.) and all other reagents used were of A.R. grade. Different buffer solutions were prepared by standard procedures.

General procedure : An aliquot containing 100 – 500 μg of platinum was mixed with 0.05 *M* aqueous potassium iodide (2 ml) and pyridine/α-picoline/β-picoline/γ-picoline/collidine (0.5 ml). Volume of the final aqueous phase was made upto 10 ml with buffer solution of desired pH. The mixture was then equilibrated with chloroform (10 ml) for 30 s. The separated organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. Finally, the absorbance of the organic extract was measured at respective absorption maxima against chloroform, and platinum(IV) was determined from a previously prepared calibration curve. To test the effect of diverse ions, the respective foreign ions were added to the system before addition of the reagents.

Results and Discussion

The platinum complexes absorb maximum at 345 – 360 nm. The reagent blanks show insignificant absorbances in the aforesaid wavelength region. The systems show steady absorbances for at least 24 h. Maximum absorbances were found to be achieved when the extractions were carried out at pH 2 – 8, 2 – 9, 8 – 9, 2 – 9 and 3 – 4 for pyridine, α-picoline, β-picoline, γ-picoline and 2,4,6-collidine, respectively. Chloroform extracts obtained in the second consecutive operations in the respective pH range virtually showed no absorbance. This indicate a complete and quantitative extraction of platinum.

The optimum reagent concentrations were 2 ml of 0.05 *M* aqueous potassium iodide along with 0.5 ml of pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine to extract 100 – 500 μg of platinum. In all cases, Beer's law was found to be valid over the concentration range 5 – 50 ppm of Pt. The Ringbom's optimum concentration range for the measurement was found to be from 8 – 50 ppm of Pt^{IV}. The molar absorptivities of the complexes (on the basis of Pt content) and the respective Sandell's sensitivities were calculated as shown in Table 1.

TABLE 1 – DETAILS OF EXTRACTION METHODS

Parameter	Base				
	Pyridine	α-Picoline	β-Picoline	γ-Picoline	2,4,6-Collidine
pH	2 – 8	2 – 9	8 – 9	2 – 9	3 – 4
λ_{max} (nm)	345	370	485	365	360
Molar absorptivity ($dm^3\ mol^{-1}\ cm^{-1}$)	1.95×10^3	1.75×10^3	1.85×10^3	3.70×10^3	1.09×10^4
Sandell's sensitivity ($\mu g\ cm^{-2}$)	0.10	0.11	0.10	0.05	0.018

Platinum(iv) was determined in presence of other diverse ions. In fact all the bases, i.e. pyridine, α-picoline, β-picoline, γ-picoline and 2,4,6-collidine showed similar behaviour towards the extraction of platinum. An ion was considered to interfere if the recovery of platinum(iv) differed by more than ±3% from the actual amount taken.

For the determination of 392 μg of Pt^{IV} (117.6 μg for collidine) a 25-fold excess of Co^{II}, Ni^{II}, Zn^{II}, Mo^{VI}, U^{VI}, Pb^{II}, Mn^{II}, V^{V}, Ca^{II}, Ba^{II}, Sr^{II}, Cr^{III}, La^{III}; Be^{II} and Al^{III} did not interfere. A 10-fold excess of Cd^{II}, Zr^{IV}, Th^{IV} and a 5-fold excess of Rh^{III} were tolerable. A 5-fold excess of Fe^{III} and Cu^{II} could be kept in the aqueous phase with ammonium hydrogenfluoride and citrate, respectively. Hg^{II} and Pd^{II} interfered. Among the anions tested, the followings (50-fold excess) did not interfere: oxalate, borate, phosphate, tartrate, citrate, fluoride, bromide, phthalate, acetate. Lower concentration of EDTA is permissible. However, thiocyanate, thiosulphate and ascorbate interfered seriously.

2,4,6-Collidine was found to be most sensitive among the pyridine bases used. With this reagent the precision and accuracy of the proposed method were tested by analysing solutions containing a known amount of platinum following the recommended procedure. The average of six determinations containing 117.6 μg of Pt^{IV} gives a value of 115.5 μg, which varies between 114.52 to 116.44 at 95% confidence limit. The standard deviation is 0.92 μg.

References

1. G. H. FAYE and W. R. INMAN, *Anal. Chem.*, 1963, **35**, 985.
2. E. W. BERG and E. Y. LAU, *Anal. Chim. Acta*, 1962, **27**, 248.
3. A. I. VOGEL, "A Textbook of Quantitative Inorganic Analysis", ELBS, London, 1962.

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Solvent Extraction and Spectrophotometric Determination of Copper using Mixed Ligand Complex Formation with Pyridine, α-Picoline, β-Picoline, γ-Picoline or 2,4,6-Collidine and Bromide/Iodide

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REFERENCE to pyridine as an auxiliary ligand in the solvent extraction of metals is not new in the literature. Use of pyridine – thiocyanate for extractive-photometric determination of various metals is well known[1-6]. It has been noted that copper(II) forms complexes with pyridine bases in presence of potassium bromide or potassium iodide. The mixed ligand complexes are extractable into chloroform. These properties of the copper complexes suggested that further studies of the systems might lead to the development of a simple spectrophotometric method for the determination of copper. Apart from pyridine, some of its methyl-substituted derivatives used are α-picoline, β-picoline, γ-picoline and 2,4,6-collidine.

Experimental

Spectral curves and analytical measurements were made with a Shimadzu PR1 spectrophotometer. Stoppered quartz cells of 10 mm optical path length were used for absorbance measurements.

A stock solution of copper(II) was prepared by dissolving $CuSO_4.5H_2O$ in distilled water followed by its standardisation as benzoin-α-oximate[7]. A working solution of Cu^{II} (120 μg ml^{-1}) was prepared by dilution. Chloroform (E. Merck), pyridine (B.D.H), α-picoline (Riedel), β-picoline (B.D.H), γ-picoline (Fluka) and 2,4,6-collidine (B.D.H.) were distilled before use. All other chemicals were of A.R. grade. Stock solutions of desired diverse ions were prepared from their corresponding salts. Potassium chloride – hydrochloric acid buffer was used to adjust pH of the aqueous solution.

General procedure :

Bromide system : An aliquot containing 50 – 300 μg of copper was mixed with 8 *M* aqueous potassium bromide (1 ml) followed by the addition of 0 5 ml of pyridine/α-picoline, β-picoline/γ-picoline/2,4,6-collidine. Buffer solution (5 ml) of pH 2.0 was then added to it and the volume of the aqueous phase was made upto 10 ml with distilled water. The mixture was then equilibrated with chloroform (10 ml) for 1 min. The separated organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. Finally the absorbance of the organic extract was measured at corresponding absorption maxima against chloroform. The amount of copper(II) was determined from a calibration curve. To test the effect of foreign ions, the respective ions were added to the system before addition of the reagents.

Iodide system : An aqueous solution containing 50 – 300 μg Cu was mixed with 0.05 *M* potassium iodide (3 ml) and 0.5 ml of pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine. Buffer solution (5 ml) of pH 1.0 was then added followed by distilled water to make the volume of the aqueous phase upto 10 ml. The other part of the procedure was the same as for the bromide system.

Results and Discussion

In presence of pyridine and alkali thiocyanate, copper forms an insoluble complex[7] of formula

TABLE 1—PARAMETERS OF EXTRACTIVE METHODS

Parameter	Base employed				
	Pyridine	α-Picoline	β-Picoline	γ-Picoline	2,4,6-Collidine
			Bromide system		
pH	1.5 – 2.5	1.5 – 2.5	1.5 – 2.5	1.5 – 2.5	1.5 – 2.5
λ_{max} (nm)	340	320	340	340	355
Molar absorptivity ($\times 10^3$ dm^3 mol^{-1} cm^{-1})	2.17	3.07	3.23	2.33	5.13
Sandell's sensitivity (μg cm^{-2})	0.029	0.021	0.018	0.027	0.012
			Iodide system		
pH	0.5 – 1.5	0.5 – 1.5	0.5 – 1.5	0.5 – 1.5	0.5 – 1.5
λ_{max} (nm)	355	*	350	360	360
Molar absorptivity ($\times 10^3$ dm^3 mol^{-1} cm^{-1})	2.38	2.65	4.23	4.76	6.77
Sandell's sensitivity (μg cm^{-2})	0.027	0.024	0.015	0.013	0.009

*Absorbance measured at 350 nm.

$CuPy_2.(SCN)_2$, where thiocyanate behaves as a pseudo-halogen. In presence of bromide/iodide and pyridine bases copper(II) probably forms complexes of the type CuP_2X_2 (P=pyridine base ; X=Br/I). These complexes are extractable into chloroform.

The effect of pH on the extractibility of copper(II) into chloroform was examined in terms of absorbance of the mixed ligand complex. The optimum pH of extraction for bromide system was 1.5 – 2.5 and for iodide system, 0.5 – 1.5. In both the cases, after a second consecutive operation, the chloroform extract showed virtually no absorbance. This indicated a complete and quantitative extraction of copper in these conditions.

The spectra were scanned in the region 300 – 600 nm against chloroform. The copper(II)-bromide-pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine complexes in chloroform showed absorption maxima at 320 – 355 nm (Table 1) with a shoulder at around 380 nm in each case.

In the copper(II)-iodide-pyridine/β-picoline/γ-picoline/2,4,6-collidine systems, the absorption maxima were at 350 – 360 nm (Table 1). The copper(II)-iodide-α-picoline complex exhibited no absorption maxima in the region 300 – 600 nm ; in this case the analytical measurements were carried out at 350 nm. The reagent blanks did not absorb in the aforesaid wavelength region. Hence for simplicity all the absorbance measurements were carried out at respective absorption maxima against chloroform.

The systems conformed to Beer's law over a concentration range of 5 – 50 ppm of copper. The corresponding molar absorptivities of the complexes (on the basis of copper content) and Sandell's sensitivities were calculated (Table 1).

For bromide complexes, 1 ml of 8 *M* aqueous solution of potassium bromide along with 0.5 ml of pyridine bases was sufficient to extract 240 μg of copper(II) at pH 2.0. For iodide complexes the amounts of reagents required were 3 ml of 0.05 *M* potassium iodide along with 0.5 ml of pyridine bases to extract the same amount of copper ; in this case the extraction was carried out at pH 1.0. In all cases the organic extracts produced a steady absorbance for at least 24 h.

In order to study the effects of diverse ions on the extraction behaviour, 240 μg of copper(II) was extracted and determined according to the general procedure in presence of the respective foreign ions. For bromide complexes the system tolerates 10 – 25-fold excess of the following ions : Fe^{III}, Co^{II}, Pb^{II}, Ni^{II}, Zn^{II}, V^{V}, Rh^{III}, Ca^{II}, Ba^{II}, Sr^{II}, Be^{II}, Tl^{I}, U^{VI}, Zr^{IV}, La^{III}, Al^{III}, Th^{IV}, Mg^{II}, Cd^{II}, Mo^{IV}. Pt^{IV} and Hg^{II} are permissible at lower concentrations. Pd^{II} however shows strong interference even at trace level. Among the anions tested, most of them are susceptible to the procedure, although phthalate, borate and phosphate do not interfere. In case of iodo complexes, 10 – 25-fold excess of the following ions are permissible : Co^{II}, Ni^{II}, Pb^{II}, Zn^{II}, Mo^{IV}, V^{V}, Rh^{III}, Ca^{II}, Ba^{II}, Sr^{II}, Zr^{IV}, U^{VI}, Al^{III}, Be^{II}, La^{III}, Tl^{I}. The system tolerates lower concentration of Cd^{II}, Hg^{II} and Fe^{III}. However, Pd^{II} and Pt^{IV} must be absent. Among the anions tested borate, bromide, phthalate, phosphate do not interfere. The presence of thiosulphate, EDTA, tartrate, oxalate, citrate, fluoride, ascorbate restricts the extraction of copper. High results are obtained in presence of thiocyanate.

Among the bases used 2,4,6-collidine was found to be most sensitive in both the bromide and iodide systems. With this reagent the precision and accuracy of the method was tested by analysing solutions containing a known amount of copper(II) following the recommended procedure. The average of six determinations indicated the proposed method to be fairly precise and reproducible in either of the systems.

References

1. P. Chattopadhyay and S. K. Majumdar, *Indian J. Chem., Sect. A*, 1983, **22**, 91.
2. J. H. W. Forsythe, R. J. Magee and C. L. Wilson, *Talanta*, 1958, **1**, 249.
3. T. Moeller and R. E. Zogg, *Anal. Chem.*, 1950, **22**, 612.
4. V. Yatirajan and S. P. Arya, *Talanta*, 1975, **22**, 861.
5. G. H. Ayres and I. E. Scroggie, *Anal. Chim. Acta*, 1962, **26**, 470.
6. G. S. Deshmukh and S. Y. Tatwawadi, *J. Sci. Ind. Res., Sect. B*, 1961, **20**, 506.
7. A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", ELBS, London, 1962.

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Spectrophotometric Determination of Iron(II) using Cacotheline

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CACOTHELINE is to be the nitrate of the bisdimethylmononitrobrucine hydrate[1] and have the formula, $C_{20}H_{20}(OH)_2(NO_2)N_2O_8.HNO_3$. Aqueous solution of cacotheline gives a violet colour with stannous ions due to the formation of a reduction product of cacotheline of unknown composition[2]. Potluri[3] used cacotheline as an indicator in estimating Pb^{IV} and Cr^{VI} with Ti^{III}. The present authors noted that Fe^{II} gives a violet colour with aqueous solution of cacotheline in presence of phosphoric acid, and which lead to the development of a simple spectrophotometric method for iron(II) determination.

Experimental

Spectral curves and analytical measurements were made with a Shimadzu PR1 spectrophotometer fitted with quartz cells of 10 mm optical pathlength.

Stock solution of iron(II) was prepared from $FeSO_4.(NH_4)_2SO_4$ and standardised[4]; a working solution was prepared by appropriate dilution. Aqueous solution of cacotheline (0.2%) was used for colour development. All other reagents were of analytical grade. Stock solutions of diverse ions were prepared from their corresponding salts.

General procedure: To an aliquot containing 100 - 500 μg iron(II), was added phosphoric acid (5 ml) and the aqueous solution of cacotheline (0.5 ml). Volume of the mixture was made up to 10 ml with distilled water and the absorbance of the solution was measured at 530 nm against pure water as blank. Amount of iron(II) was computed from a calibration curve. To test the interference, the respective foreign ions were added to the system before addition of the reagents.

Results and Discussion

In presence of fluoride or phosphate, iron(II) gives a violet colour with cacotheline. In the former, the colour is very unstable and fades away within 5 min. But in presence of phosphoric acid the system gives a stable colour for at least 12 h showing a broad band of absorption maxima around 530 nm. The reagent blank does not absorb in this region.

It has been noted that 0.5 ml of 0.2% cacotheline is sufficient for maximum colour development of the sample solution containing upto 500 μg of iron(II) provided the aqueous solution be made $6-10$ *M* with respect to phosphoric acid. Lower values in absorbance were obtained when the aqueous phase was less than 5 *M* with respect to phosphoric acid. Higher concentration of the reagent or the acidity of the aqueous phase were devoid of any significant change in the maximum value of absorbance. The system conforms to Beer's law over the concentration range $2-50$ ppm of Fe^{II} with Sandell's sensitivity of 0.05 $\mu g\ cm^{-2}$ at 530 nm.

To test the interferences, iron(II) was determined in presence of the respective foreign ions. Deviation of not more than $\pm 3\%$ from the expected absorbance was taken as the standard tolerance limit for the system. It was found that 300 μg of Fe^{II} could easily be determined without any interference in presence of 5 mg of each of the following cations: Mn^{II}, Co^{II}, Ni^{II}, Mo^{VI}, Pd^{II}, Pt^{IV}, Rh^{III}, Cd^{II}, Ca^{II}, Ba^{II}, Sr^{II}, Zr^{II}, Th^{IV}, Be^{II}, Zn^{II}, Hg^{II}, Mg^{II}, Pb^{II}, Tl^{I}, U^{VI}, La^{III} and Al^{III}. Cu^{II} and V^{V} must be absent as the system gives no colour in presence of the said cations. Presence of less than 2 mg of Cr^{III} is harmless. In presence of Fe^{III} low absorbance is obtained. The system tolerates 50 mg of each of the following anions: EDTA, thiosulphate, iodide, bromide, fluoride, citrate, tartrate, ascorbate, oxalate, acetate, phthalate, borate. There is no colour development if nitrate is present.

The method is very simple and rapid. Precision and accuracy of the proposed method were tested by analysing solutions containing a known amount of iron(II). The average of six determimations of 300 μg Fe was found to be 300.5 μg with the relative mean deviation of 1.27%.

References

1. N. MOUFANG and J. TAFEL, *Ann.*, 1898, **304**, 47.
2. F. J. WELCHER, "Organic Analytical Reagents", Van Nostrand, Princeton, Vol. 3, 1962.
3. V. K. R. POTLURI, V. R. RAO and A. KUMAR, "Proceedings of the 24th Annual Convention of Chemists", Indian Chemical Society, Calcutta, 1987, p. D2.
4. A. I. VOGEL, "A Textbook of Quantitative Inorganic Analysis", Longmans, London, 1978.