

**STUDIES ON  
THE ANALYTICAL APPLICATIONS OF  
SOME ORGANIC REAGENTS AS LIGANDS**

**Thesis Submitted for the Degree of  
Doctor of Philosophy in Science ( Ph. D. )  
of the  
University of North Bengal  
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*Dedicated to*  
*The living memory of my uncle*  
*Shri Ful Kumar Thokdar.*

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## FOREWORD

Since the earliest days of analytical chemistry, organic reagents have been employed in various ways to facilitate the detection and determination of chemical substances. During the past few decades these compounds have been extensively used in analytical procedures. At present these are rapidly gaining in popularity because of their greater sensitivity and specificity as compared to inorganic reagents, and also because of greater convenience.

In this connection solvent extraction has come to the forefront as a unique technique because of its elegance, simplicity, speed and applicability to both tracer and macro amounts of metal ions. The objective of these analytical liquid-liquid extraction procedures developed in the laboratory lies in the extrapolation to full-scale commercial hydrometallurgical processes from the technical point of view. The methods are particularly applicable to the

solvent extraction processes of numerous systems in metallurgical separation from mine waste and dump leach liquors.

This thesis is the outcome of a series of investigations carried out to study the analytical potentialities of cetyl-trimethyl ammonium bromide (CTAB), 4-nitrosoresorcinol, diphenyl thiocarbazide and ninhydrinoxime as reagents for the spectrophotometric determination of iron, cobalt, palladium, platinum, gold, molybdenum, vanadium and copper. Auxiliary ligands namely iodide, thiocyanate, pyridine and some of its methyl substituted derivatives and solvents like chloroform, benzene, ethylacetate, 1,2-dichloroethane were made use of during the investigations.

The primary aim of this thesis is to develop analytical methods for the spectrophotometric determination of some heavy metals using some organic reagents. Some methods are promising from the view point of separation of the aforesaid metals from each other.

Attempts have been made to collect information relating to the analytical uses of a given compound and to present a discussion of the methods employing these reagents. References to the literature have been made so as to indicate, at least to some extent, the subject matter of each.

This thesis is divided into five chapters. A brief chapter-wise summary of the work done is as follows.

## CHAPTER I

Part I of the chapter opens with a general introduction of liquid-liquid extraction. Here the theoretical aspects of solvent-extraction are described with special reference to the method of extraction, classification into ion association and chelate extraction systems and the equilibria involved.

Cetyl trimethyl ammonium bromide, 4-nitrosoresorcinol, diphenylthiocarbazide and nihhydrinoxime produce characteristic colour reactions with the metal ions. This permits extraction of the metals under some optimum conditions followed by spectrophotometric determination in the organic phase.

Part 2 deals with absorption spectrophotometry in ultraviolet and visible region as applied to analytical chemistry. A description of the instruments used in the present investigations along with the application of spectrophotometry in determination of inorganic ions is given.

## CHAPTER II

In this chapter use of cetyltrimethylammonium bromide (CTAB) as a simple and sensitive reagent for the spectrophotometric determination of iron, cobalt, palladium, platinum gold, molybdenum and vanadium has been described.

In the beginning a literature survey on the use of CTAB in analytical chemistry is given. Use of other auxiliary ligands namely, thiocyanate and iodide has also been reviewed.

CTAB along with these auxiliary ligands produce characteristic colour reactions with the above metals, which is the basis of the extraction-spectrophotometric determination of the metals. The methods developed have been applied to the analysis of some synthetic mixtures with satisfactory results.

### CHAPTER III

This chapter describes the use of 4-nitrosoresorcinol as an analytical reagent. The reagent forms coloured complexes with palladium, cobalt and copper. In some cases pyridine and some of its methyl substituted derivatives have been used as auxiliary ligands. The methods developed find applications to the analysis of some synthetic mixtures.

### CHAPTER IV

Ninhydrinoxime has been used as an analytical reagent for the extraction-spectrophotometric determination of cobalt under some optimum conditions. Cobalt has been

determined in synthetic mixtures.

## CHAPTER V

A spectrophotometric method for the determination of copper has been presented. The reagent used is diphenylthiocarbazide. The method developed is very simple and rapid and extended to the analysis of synthetic and standard samples.

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 the future so 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 purposes.

CHAPTER I  
INTRODUCTION

## PART I

### General Discussion on Solvent Extraction

Solvent or liquid-liquid extraction is a technique in which a solution (usually aqueous) is brought into contact with a second solvent (usually organic), essentially immiscible with the first, in order to bring about a transfer of one or more solutes into the second solvent. It is necessary to make the fundamental principles of extractions clear particularly the various terms used for expressing the effectiveness of a separation.

#### Partition co-efficient :

For an analytical chemist the aqueous-organic solvent pair is of special interest since he is concerned with the analysis of the element present in the aqueous phase. If a solute is allowed to dissolve within two immisicible or

slightly 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 phase at equilibrium at particular temperature remains constant, provided that the molecular weight of the species will have the same in the both phases. This ratio is known as the distribution or partition coefficient ( $K_D$ ). Thus for aqueous and organic systems,

$$K_D = \frac{\text{Metal ion concentration in organic phase}}{\text{Metal ion concentration in aqueous phase}} \dots (1)$$

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

For an ideal case, the species distributes 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.

#### Distribution ratio or Extraction Co-efficient (D) :

In the solvent extraction technique analysts are interested primarily 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 necessary to introduce a reliable quantity to describe the extraction, called the distribution ratio (D).

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

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

$$D = \frac{\mathcal{L}^{M_1} I_{\text{org}} + \mathcal{L}^{M_2} I_{\text{org}} + \mathcal{L}^{M_3} I_{\text{org}} + \dots + \mathcal{L}^{M_n} I_{\text{org}}}{\mathcal{L}^{M_1} I_{\text{aq}} + \mathcal{L}^{M_2} I_{\text{aq}} + \mathcal{L}^{M_3} I_{\text{aq}} + \dots + \mathcal{L}^{M_n} I_{\text{aq}}} \dots (3)$$

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

#### Percentage extraction :

The percentage extraction (% E) is more useful. The relation between the distribution ratio and percentage extraction can be expressed as

$$\% E = \frac{100 D}{D + \left[ \frac{V_{aq}}{V_{org}} \right]} \dots (4)$$

$V_{aq}$  and  $V_{org}$  represents the volumes of the aqueous and organic phases respectively. The equation on simplification,

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

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

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

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

#### Multiple extraction :

This is applicable when the extraction efficiency is less than 100%.

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

$$L_A = \left( \frac{V_{aq}}{V_{aq} + V_{o,p}} \right)^n \dots (7)$$

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.,

$\underline{C}_{AO}/\underline{C}_{A_{aq}}$  =  $D$  which remains constant for any value of  $\underline{C}_A$ . To achieve good results  $V_o$  should be low and  $n$  should be of high value.

#### Separation factor :

It becomes necessary to introduce a term separation factor ( $\beta$ ), when the solution contains two species A and B. The separation factor ( $\beta$ ) is related to their individual distribution ratios. Thus

$$\beta = \frac{\underline{C}_A \underline{J}_o / \underline{C}_B \underline{J}_o}{\underline{C}_A \underline{J}_{aq} / \underline{C}_B \underline{J}_{aq}} \stackrel{(7)}{=} \frac{\underline{C}_A \underline{J}_o / \underline{C}_A \underline{J}_{aq}}{\underline{C}_B \underline{J}_o / \underline{C}_B \underline{J}_{aq}} = \frac{D_A}{D_B} \dots (8)$$

where  $\underline{C}_A \underline{J}_o$ ,  $\underline{C}_B \underline{J}_o$  are the concentrations of A and B in the organic phase and  $\underline{C}_A \underline{J}_{aq}$ ,  $\underline{C}_B \underline{J}_{aq}$  are the concentrations of A and B in the aqueous phase.

It is possible to achieve complete separation when one of the distribution ratios is very small and the other relatively large. When the separation factor will be unity, it is very difficult to separate as the two distribution ratios are equal. In these cases to carry out separation, counter current extractions are generally used.

#### Classification of Extraction systems :

The most convenient way to classify the extraction systems is, on the basis of the nature of the extractable species because a particular system under certain conditions may be grouped under more than one class. Such a classification might be :

uncharged covalent species

simple molecules e.g.,  $I_2$ ,  $HgCl_2$ ,  $RuO_4$ ,  $C_6H_5COOH$

chelate complexes e.g., aluminium oxinate.

#### Uncharged electrovalent species (ion-association complexes)

Halometallic acids e.g.,  $HFeCl_4$

Amine-anionic complex compounds e.g.,  $R_3NH^+ \cdot FeCl_4^-$

Metal-acid ester complexes e.g.,  $La(DEHP)_3$ .

Solvated acids and salts e.g.,  $NHO_3 \cdot TBP$ ;  $VO_2(NO_3)_2(TBP)_2$

Non-solvated salts e.g.,  $(C_6H_5)_4As^+ \cdot FeCl_4^-$

(DEHP = di-2-ethyl hexylphosphate; TBP = tributyl phosphate)

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

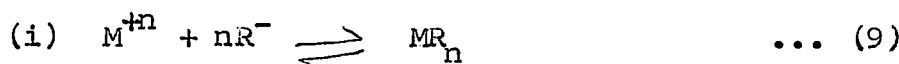
#### Extraction Process :

The three 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 .

Uncharged complex formation depends upon several factors.

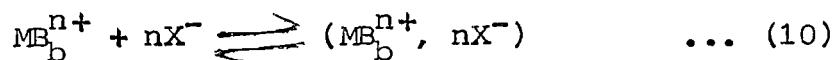
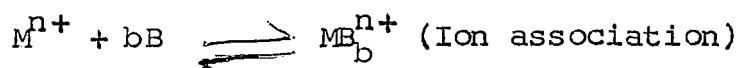
The complex may be of different types as (i) simple co-ordination complex, chelate complex or (ii) as ion association complex.



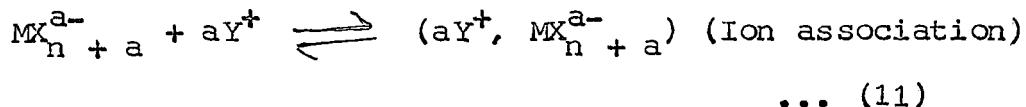
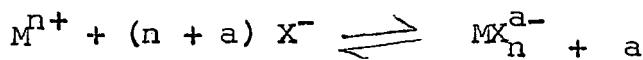
where  $\text{M}^{+n}$  is an  $n$  valent metal ion and  $\text{R}^-$  is an anion of a suitable chelating or co-ordinating agent.

Examples : Germanium tetrachloride (simple co-ordination)  
lead diethyldithiocarbamate (chelate)

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



Example :  $\left[ (n-C_4H_9)_4N^+, ReO_4^- \right]$



Example :  $\left[ H^+, FeCl_4^- \right]$

The stability of a metal co-ordination complex depends on (a) the acidity of the metal ion (b) basicity of the co-ordination ligand and (c) special factors related to the configuration of the resultant complex. In the simple co-ordination complex the monofunctional ligands take part and in the chelate complex polyfunctional ligands are acting which occupy more than one position in the co-ordination sphere. The chelate complexes are mostly soluble in organic

solvents and are 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-(phenanthroline)-iron(II).
- (ii) Chelates having one anionic and one uncharged basic group of the ligand i.e. neutral chelates e.g. Gallium 8-quinolate.
- (iii) Negatively charged chelates having negatively charged basic group of the ligand e.g. Alizarin derivatives of iron(III).

Ion association complexes e.g.  $\text{C}_6\text{H}_5\text{O}_2^- \text{As}^+$ ,  $\text{ReO}_4^- \text{Y}_2$  are soluble in organic solvents like chloroform, benzene etc. The extent of the 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) Interaction of the complex in the organic phase :

The chelate type complexes generally do not interact with the solvent. But in case of ion association complexes, polymerization (when concentration increases) and dissociation (in case of dilute solution) should be considered.

Methods of extraction :

In the analytical laboratory, three basic types of liquid-liquid extractions are generally utilized. They are :

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

(a) Batch extraction is the simplest extraction procedure and is the most used for analytical separation. The method 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) The continuous extraction makes use of a continuous flow of immiscible solvent through the solution or a continuous counter current flow of both phases. In continuous extraction the spent solvent is stripped and

recycled by distillation or fresh solvent is added continuously from a reservoir. This method is applicable when the distribution ratio is small.

(c) Craig<sup>1</sup> 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 is the direct evaporation of organic solvent if the solvent is volatile and then the solute is estimated. If the solvent is not so volatile, it may be removed by heating with concentrated nitric and perchloric acid followed by

estimation. Most recently the organic phase may be estimated by radiometric method<sup>2</sup>.

(iii) Selectivity :

Use of oxidising or reducing agents increases the selectivity of an extraction system. For example chromium (III) is not extracted with diphenyl carbazide but chromium (IV) can be extracted from its solution. Sometimes suitable masking agents like cyanide, citrate, tartarate, EDTA etc. are also used to prevent extractions of undesired element.

(iv) Salting-out agent :

The extent of extraction may be enhanced with the help of salting-out agents, especially in case of ion-association complexes. The most popularly 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 (solute) 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 difference 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.

Striping : Striping 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 determinated 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 necessary, 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 be 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 concentrations and of correct pH will result in the redistribution of the impurities in favour of the aqueous phase, since

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their distribution ratios are low; most of the desired element 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 in the salicylaldoxime complex in chloroform; the organic extract is

sprayed directly into an oxy-acetylene 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 et al<sup>3</sup> in 1958 in their report that when a dialkyl hydrogen phosphate  $(RO)_2PO.OH$ , is used in conjunction with certain neutral organophosphorous reagent e.g. TBP, the extracting powers of the mixture exceeds the sum of the  $\angle$  extracting powers of its components. This phenomenon of greatly enhanced  $\angle$  extraction or synergism due to a mixture of extractants has attracted considerable attention in recent years. The review articles by Marcus<sup>4</sup> and De<sup>5</sup> 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 ( $\beta$ -isopropyltropolone) and a solvating solvent such as TBP, IBMK (isobutylmethyl ketone), DBSO (dibutyl sulphoxide) and (2) a dialkylphosphoric acid and a neutral organophosphorous ester(s).

Chelating agent-solvating solvent system :

Considerable work has been done in this area. Irving and Edgington<sup>6</sup> postulated that the conditions for synergic extraction are :

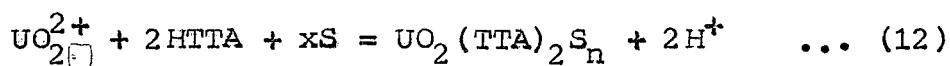
- (a) one of the active reagents (Hx) should be able to neutralize the charge on the metal ion, preferably by forming a chelate.
- (b) the solvent(s) should display any residual co-ordinated water from the neutral metal complex, rendering it less hydrophilic.
- (c) the solvent(s) should not itself be hydrophilic and co-ordinated less strongly than Hx.
- (d) the maximum co-ordination 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  $\text{UO}_2\text{X}_2\text{TBP}$  and  $\text{UO}_2\text{X}_2(\text{TBPO})_3$  respectively<sup>7-9</sup>, from isopiestic and infrared measurements. The studies were extended to plutonium(VI), americum(III), europium(III) and thorium, and the species indentified were

$\text{PuX}_3(\text{TBP})_2$ ,  $\text{AmX}_3(\text{TBP})_2$ ,  $\text{AmX}_3\text{TBPO}$ ,  $\text{ThX}_3(\text{NO}_3)_2\text{TBP}$  and  $\text{ThX}(\text{NO}_3)_3\text{TBPO}$ .

Healy<sup>10</sup> reported on 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<sup>11</sup> further suggested that the reaction for the system uranium(VI) HTTA-S can be expressed as (S = organo-phosphorus ester) :



Sekine and Dyrssen<sup>12-17</sup> 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 carbontetrachloride.

#### Dialkylphosphoric acid (Hx) - neutral phosphorous ester(s) system :

Important cases in this category are : di(2-ethylhexyl) phosphoric acid (HDEPH)-TBP, which was the first reported case of synergic extraction<sup>3,18,19</sup>; mono (2-ethylhexyl) phosphoric acid ( $\text{H}_2\text{MEHP}$ )-TBP<sup>20</sup>; dibutyl phosphoric acid

(HDBP)-TBP<sup>21</sup> and HDBP-TOPO<sup>22</sup>.

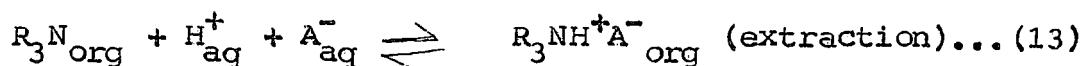
Peppard et al<sup>20</sup> investigated the system lanthanide(III), Y(III), Am(III), Cen(III), Th, U(VI)-H<sub>2</sub>MEHP-S-diluent, where the synergic agent S was n-decanol, TBP or TOPO and the diluent was toluene, cyclohexane or n-decanol.

#### Substoichiometric extraction :

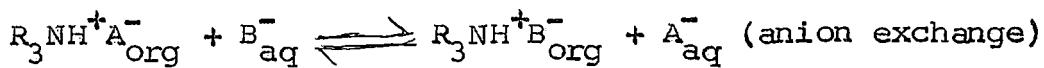
Ruzicka and Stary<sup>23,24</sup> first proposed this new technique of substoichiometric extraction and determination of metals, which is applicable to activation analysis and isotope dilution analysis.

#### Liquid Ion-exchangers :

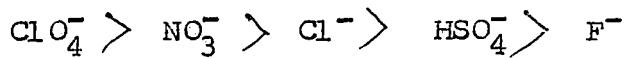
The use of liquid ion-exchange dates back to 1948 when Page<sup>25</sup> reported that high molecular-weight amines (HMWA) can be used for extraction of acids because their acid salts are insoluble in water but readily soluble in organic solvent such as chloroform, benzene or kerosene :



where A<sup>-</sup> = anion of simple acid or complex metal acid e.g., FeCl<sub>4</sub><sup>-</sup>, and



The amine salt<sup>13</sup> 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.



The earlier work for liquid anion-exchangers (HMWA) has been reviewed by Moore, Green and Prabhu<sup>26-29</sup>.

#### Reversed-Phase chromatography :

In reversed phase chromatography the organic extractant is immobilized on some stationary inert support such as kieselguhr, styrene-divinylbenzene copolymer or simply filter paper. The technique was introduced by Fidelis and Siekierski<sup>30</sup> 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<sup>31</sup> to the heavier rare earths, which are usually difficult to separate.

Combined ion-exchange-solvent extraction (CIESE) :

Korkisch<sup>32</sup> 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 complex :

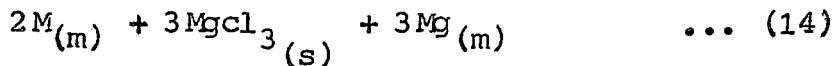
Betteridge and West<sup>33</sup> described the selective extraction of microgram amounts of dibutylamine silver(I) with an ion-association complex (or ternary complex) with salicylic acid. Dagnall and West<sup>34</sup> described the extraction of a blue ternary complex Ag(I)-1,10, phenanthroline-Bromopyrogallol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

Ternary complexes have been reviewed by Babko<sup>35</sup>.

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 produce from reactor fuel by

extraction with magnesium chloride<sup>36,37</sup> according to the reaction (for a tetravalent metal such as a lanthanide).



where the subscripts (m) and (s) denotes the metal and salt phase.

The use of organic solvents in conjunction with molten salt was reported by Gruen and co-workers<sup>38</sup>. Marcus<sup>39</sup> has given an excellent review of the 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, molybdenum, platinum, gold, copper, vanadium and palladium :

Numerous methods on spectrophotometric determination of iron, cobalt, molybdenum, gold, copper, vanadium and

palladium 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.
- (v) Choice of convenient and easier method of 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 variation of the colour of a system with change in concentration of some component forms the basis of what the chemist commonly terms colorimetric analysis. The colour is usually due to the formation of a coloured compound by the addition of an appropriate 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 generally used as a light source, and the determinations are usually made with a simple

instrument termed a colorimeter or colour comparator. When the eye is replaced by a photoelectric cell (to eliminate the errors due to the personal characteristics of each observer) the instrument is termed a photoelectric colorimeter. In spectrophotometric analysis a source of radiation is used that extends into the ultraviolet region of the spectrum. For this, definite wavelength of radiations are chosen possessing a bandwidth of less than 1 nm. The process necessitates the use of a more complicated and consequently more expensive instrument. The instrument employed for this purpose is a spectrophotometer, which is actually 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 the light absorbed. Incident radiation is emitted from a suitable source and is passed via an optical system, which isolates a narrow band of wavelengths, through a homogeneous layer of the absorbing medium.

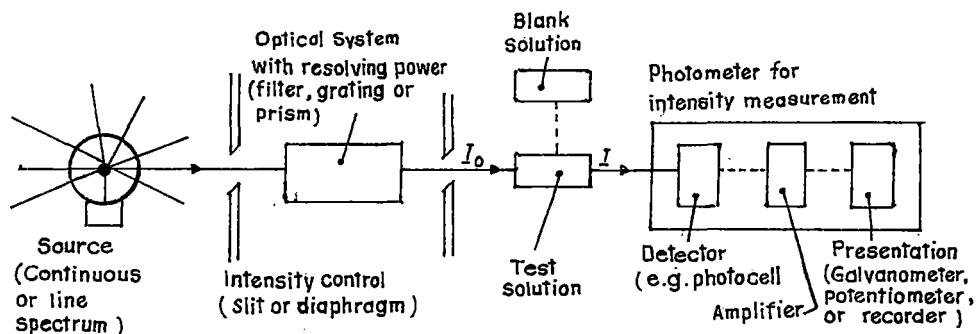


FIG. BASIC ELEMENTS OF ABSORPTIOMETRIC INSTRUMENTS ( SINGLE-BEAM OPERATION )

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,  $I_0$ , 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  $I_0$ . The detection is often a photoelectric cell (photo cell) sensitive in the required wavelength 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,  $I/I_0$ , termed the transmittance,  $T$ . The detection signal may be amplified and presented in various forms, such as percentage transmittance ( $100 T$ ) or  $100 I/I_0$  or absorbance,  $A(-\log T)$ .

Two important properties are concerned in absorption measurements, wavelength and degree of absorption. The wavelength at which absorption occurs are determined by the energy difference,  $\Delta E$ , 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 Bouguer's) law deals with optical path length. It states that the intensity of a beam of parallel monochromatic radiation decreases exponentially i.e., in geometric progression, as it traverses a thickness (or path length) of homogeneous absorbing medium.

$$I = I_0 e^{-Kl}$$

where  $l$  is the thickness,  $e$  the natural logarithm base and  $K$  is a constant for the medium at the particular wavelength. Rearranging the above equation

$$\ln I_0/I \text{ or } 2.303 \log I_0/I = Kl$$

$$\text{or } \log I_0/I = Kl/2.303$$

$$\log I_0/I = Kl$$

where  $K = Kl/2.303$  and is termed the extinction coefficient 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 parallel monochromatic beam decreases exponentially with the number of absorbing molecules encountered i.e., the concentration of the absorbing substance in a homogeneous solution. The solvent is assumed to be non-absorbing, in the simplest case. For general use the two laws are combined and, using the above mathematical treatment, the Beer-Lambert law may be expressed in the form

$$\log \frac{I_0}{I} = K' cl$$

or  $A = K' cl$

where  $c$  is the concentration of the absorbing solute  $l$  is the thickness and  $K'$ , the extinction coefficient, is a combination of constants. The property  $\log \frac{I_0}{I}$  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 wavelengths. Both laws are held to be generally valid, though Kortum considered Beer's law to be a limiting law, valid only at low concentrations.

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

$$c \propto \log \frac{I_0}{I}$$

$$\text{or } c \propto \log \frac{1}{T}$$

$$\text{or, } c \propto A$$

Hence by plotting A (or  $\log \frac{1}{T}$ ) as ordinate, 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 coefficient

(European system) or molar absorptivity (U.S. system) and is written as  $\epsilon$ , 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 dissolve 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  $\log I_0/I$  or  $\log T$  against the concentration : a straight line passing through the origin indicates the conformity to the law.

Some aspects of colorimetric Determination :

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

1. A colourimetric 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.

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## CHAPTER II

Cetyltrimethyl ammonium Bromide as an Analytical Reagent

Section 1 : Literature Survey on the Use of Cetyltrimethyl-  
ammonium Bromide

Quaternary ammonium salts have long been used as extracting reagents in analytical chemistry for detection and determination of a number of metal ions. There are water soluble large ionic compounds. The quaternary ammonium salt specially those with long carbon chain have a tendency to form an ion-pair with large anions. These ion-pairs are soluble in organic solvents. This fact have been applied to the separation of number of metal ions. Cetyl trimethyl ammonium bromide (CTAB) belongs to this category.

A.I.Kirlov et al<sup>1</sup> determined uranium(VI) by using bromopyrogallol red and CTAB bromide at pH 6-7. The complex absorbs maximum at 635 nm. Niobium(V) was determined<sup>2</sup> spectrophotometrically by using various organic dyes in presence of CTA bromide. A sensitive method was

suggested by Jadav and Venkateswarlu<sup>3</sup> for the determination of niobium. The molar absorbtivity of the niobium - Bromopyrogallol red-IDTA system with CTA bromide was  $1.55 \times 10^5$  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<sup>4</sup>. Tellurium(IV) was determined<sup>5</sup> spectrophotometrically with the help of iodide and CTA bromide. The complex was extractable into chloroform from 0.3M H<sub>2</sub>SO<sub>4</sub> medium. The absorbtion maximum of the complex was at 630 nm, with molar absorborpticity  $5.9 \times 10^4$  l mol<sup>-1</sup>cm<sup>-1</sup>. Lin, Jingrong<sup>6</sup> determined tungsten in pure iron and steel with bromopyrogallol red and CTAB after chromatographic separation. The spectrophotometric determination of bismuth was studied by Wyganowski<sup>7</sup> using bromopyrogallol red and CTA bromide. The absorbance was measured at 615 nm. Bismuth was first separated by extraction with dithizone in carbon tetra chloride or sodiumdiethyl dithiocarbamate in chloroform because many metal ions interfered.

A spectrophotometric method was carried out by Gordeva and Meshcher Yakova<sup>8</sup> for vanadium(IV). The reagents used are Pyrocatechol violet and CTA bromide. The method was applied to the determination of vanadium in bauxites and

silicates and the absorbance of the ion-association complex was measured at 670 nm at pH 5.0 in the presence of ascorbic and tartaric acid.

Hanxishen<sup>9</sup> proposed a very sensitive method for the determination of molybdenum using dibromoalizarin violet and CTA bromide. The 1:1.5:3 Mo(VI)-dibromoalizarin violet -CTA bromide absorbs maximum at 635 nm in HCl medium.

Guanghui et al<sup>10</sup> determined tin spectrophotometrically with salicylfluorone and CTA bromide in metallic materials. The complex exhibits maximum absorbance at 510 nm (in 0.5 -3.5N H<sub>2</sub>SO<sub>4</sub>).

Shen, Hanxi<sup>11</sup> determined zirconium spectrophotometrically with salicylfluorone and CTA bromide. The complex have absorption maximum at 512 nm with molar absorptivity 1.38 x 10<sup>5</sup> (in 0.3 M HCl).

Hanxi<sup>14</sup> determined tungsten spectrophotometrically by using dibromo alizarin violet and CTA bromide. In 1 M HCl medium tungsten dibromoalizarin violet and CTA bromide react to form a 2:3:6 blue complex with maximum absorption at 620 nm. The molar absorptivity of the complex is 8.2 x 10<sup>4</sup>.

Chromium(VI) - bromopyrogallol red - CTA bromide system has been investigated by Huigong and Guoquan<sup>15</sup>. Chromium (VI) forms a 1:3 complex with bromopyrogallol red in

presence of CTA bromide. The blue complex absorbs maximum at 635 nm with molar absorptivity  $3.64 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1}$ .

Guohong<sup>16</sup> applied erichrome cyanine R and CTA bromide for the spectrophotometric determination of uranium. Uranium forms 1:2:2 complex with erichrome cyanine R and CTA bromide at pH 4.4-5.8. The absorption maximum of the complex is at 585 nm (molar absorptivity  $9.4 \times 10^4$ )  $\text{l mol}^{-1} \text{cm}^{-1}$ .

Weiwei et al<sup>17</sup> proposed a spectrophotometric method for the determination of titatinum using o-nitrophenyl fluorone and CTA bromide. The complex exhibits absorption maximum at 535 nm (pH 1.5-2.0) with molar absorptivity  $1.3 \times 10^5$   $\text{l mol}^{-1} \text{cm}^{-1}$ .

Daopei<sup>18</sup> presented a method for the spectrophotometric determination of vanadium with Erichrome Cyanine R and CTA bromide. At pH 5.0-6.0 Erichrome Cyanine R and CTA bromide forms 1:3:3 complex. The molar absorptivity of the complex was  $6.63 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1}$  at 585 nm.

Qiheng<sup>19</sup> determined hafnium spectrophotometrically using bromopyrogallol red and cationic surfactant as the reagents. In a 0.2 M HCl medium Hf-bromopyrogallol red and CTA bromide or cetylpyridinium bromide forms a 3 component colour complex of molar absorptivity of  $6.3 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1}$  at 670 nm with CTA bromide and pyridine bromide.

Jun et al<sup>20</sup> employed CTA bromide in the spectrophotometric determination of calcium and magnesium by using xylene orange at pH 10.5. The blue complex of calcium with xylene orange and CTA bromide has  $\lambda_{\text{max}}$  at 505 nm with molar absorptivity  $4.5 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1}$  and the red complex of magnesium has  $\lambda_{\text{max}}$  at 570 nm with molar absorptivity  $2.5 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1}$ .

Xue Guang<sup>21</sup> studied the colour reaction of thorium with semixylene orange in presence of CTA bromide. At pH 1.5 - 4.0 the complex thorium-semixylene orange ratio was found to be 1:2 with molar absorptivity  $5.5 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1}$  at 550 nm.

A highly sensitive method for the spectrophotometric determination of molybdenum has been suggested by Dongjin et al<sup>22</sup> with 4,5-dibromophenyl fluorone and CTA bromide. The orange red complex was formed in 1.2-2.1 M HCl and the ratio of Mo-4,5-dicrophephenyl fluorone was found to be 1:2. The apparent molar absorptivity was  $1.2 \times 10^5 \text{ l mol}^{-1} \text{cm}^{-1}$  at 538 nm.

Bismuth in tin was determined spectrophotometrically by A.T.Pilipenko et al<sup>23</sup> using polysulfide ion and CTA bromide. The complex was extractable into  $\text{CHCl}_3$  and the absorbance was measured at 440 nm. A spectro photometric method for the determination of manganese(II) with chrome

Azurobs, 1,10-phenanthroline and CTA bromide<sup>24</sup> has been devised. The ratio was found to be 1:1:1:3 at pH 10.5. The absorbance of the green complex was measured at 618 nm with molar absorptivity  $9.6 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1}$  at 618 nm and  $1.21 \times 10^5 \text{ l mol}^{-1} \text{cm}^{-1}$  by dual wave length method.

Fan and Zhiping<sup>25</sup> devised a spectrophotometric method for the determination of zirconium(IV) using 6,7-dihydroxy-2-phenylbenzopyrylium chloride 4-carboxylic acid(I) and CTA bromide. In presence of excess zirconium the ratio (Zr:I) was found to be 1:1 with molar absorptivity  $2.6 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1}$  at 480 nm. In presence of excess I the ratio Zr:I:CTA bromide was found to be 1:5:3 with molar absorptivity  $1.21 \times 10^5 \text{ l mol}^{-1} \text{cm}^{-1}$  at 560 nm.

Aluminium was determined spectrophotometrically by Zhe and Shuisheng<sup>26</sup> using salicyl fluorone and CTA bromide. The aluminium-salicyl fluorone ratio was found to be 1:2. The complex exhibits maximum absorbance at 559 nm with molar absorptivity  $1.4 \times 10^5 \text{ l mol}^{-1} \text{cm}^{-1}$  at pH 5.7-6.5.

The reaction of aluminium(III)<sup>28</sup> with sodium 2-bromo-4,5 dihydroxy benzene-4'-sulfonate in the presence of CTA bromide has been studied spectrophotometrically. Maximum absorbance occurred at 527 nm in the pH range 6.7-8.0.

9-(4'-aldehydophenyl)-2,3,7-trihydroxyl-6-fluorone and CTA bromide were used as reagents by Rongnong et al<sup>29</sup> for the spectrophotometric determination of tantalum.

Abu Zuhri and Ali <sup>30</sup> determined lead spectrophotometrically at 575 nm as its complex with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and CTA bromide at pH-7.00. The molar absorptivity was  $5.1 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1}$ .

Wang, Dongjin et al<sup>31</sup> studied the use of 4,5 dibromo-phenyl fluorone (Br PF) and CTA bromide in spectrophotometric determination of gallium. The molar absorptivity of the complex was  $2.59 \times 10^5 \text{ l mol}^{-1} \text{cm}^{-1}$  at 588 nm. The ratio of the Ga/Br-PF/CTAB was established as 1:3:5.

Tantalum was determined spectrophotometrically by Xi, Ganquing et al<sup>32</sup> using 2,4-dichlorophenyl fluorone and CTA bromide. The optimum acidity range, maximum wavelengths molar absorptivities, ranges in which Beer's law is obeyed are given.

Xi Ganging and Liang Dexice<sup>33</sup> carried out a spectrophotometric method for the determination of germanium with 2,4-dichlorophenyl fluorone in presence of CTA bromide. The maximum absorbance was measured at 513 nm with molar absorptivity  $1.7 \times 10^5 \text{ l mol}^{-1} \text{cm}^{-1}$ .

Nengxin et al<sup>34</sup> determined tin spectrophotometrically using 2,4-dichloro spacetrophotometrically using 2,4-dichloro phenyl fluorone and CTA bromide. The absorbance was measured at 514 nm from 0.6-2.1 (M)  $\text{H}_2\text{SO}_4$  medium.

Rhodium was determined spectrophotometrically by Shokum et al<sup>35</sup> using salicylfluorone and CTA bromide. The complex has maximum absorbance at 595 nm.

A spectrophotometric study of complex formation of molybdenum with P-amino phenyl fluorone (PAF) in presence of CTA bromide was carried out by Xi, Gangning et al<sup>36</sup>. The molybdenum complex has an absorption maximum at 527 nm. The molar absorptivity is  $8.5 \times 10^4$  in the presence of  $H_3PO_4$  while only  $4.8 \times 10^4$  in the absence of  $H_3PO_4$ . The Mo:P AF ratio of the complex is 1:2 in the presence of  $H_3PO_4$ .

An extractive spectrophotometric method for the determination of iron(II) has been described by M. Zaki et al<sup>37</sup> using Pyrocatechol violet and CTA bromide. The iron(II)-Pyrocatechol CTA bromide ratio was found to be 1:2:2. The molar absorptivity of the complex is  $1.35 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$  at 595 nm.

Jiang, Shufa et al<sup>38</sup> determined scandian using 7-iodo-8-hydroxyquinoline-5 sulfonic acid and CTA bromide. The complex exhibits its maximum absorbance at 505 nm in the pH range 4.5-6.0.

Chen, Ziruo<sup>39</sup> described a spectrophotometric method for the determination of tin with o-chlorophenylfluonone and CTMAB. The complex has an absorption peak at 520 nm with

molar absorption coefficient  $0.97 \times 10^5$ .

Zinc was determined<sup>40</sup> with chrome zyrol-s-semixylenol orange-CTAB spectrophotometrically. The absorbance was measured at 525 nm. The ratio of Zn(II):chromeayurols:semixylenol:CTAB was found to be 1:2:1.5:1. and the molar absorptivity is  $1.18 \times 10^2 \text{ l mol}^{-1}\text{cm}^{-1}$ .

Keeping in view the potentiality of cetyltrimethylammonium bromide as an extracting agent, a programme has been taken to develop methods for spectrophotometric determination of some metal ions in microquantities with the help of this agent.

Section 2 : Literature Survey on the Use of Thiocyanate, Iodide and Pyridine Bases as Auxiliary Ligands

The use of thiocyanate as a reagent for the extraction and estimation of many metals is known since long back. The metals like iron(III), cobalt(II), bismuth, uranium(VI), niobium, rhenium etc. form coloured complexes with thiocyanate. Generally these complexes are extractable into oxygen-containing solvents like ethyl ether, acetone, etc.

Thiocyanate have a tendency to form a series of consecutive complexes with a given metal (e.g. iron, bismuth, molybdenum), depending upon the thiocyanate concentration. For example, formation of di, tri and hexathiocyanate complexes of cobalt, depends on the thiocyanate concentration and the medium used<sup>41-44</sup>. Iron also forms a series of complexes like  $\text{Fe}(\text{SCN})_2^+$ ,  $\text{Fe}(\text{SCN})_3$ , ... etc. depending on thiocyanate concentration<sup>45</sup>. The coloured thiocyanate complexes are stable in organic

solvents and they can be applied in mineral acid medium.

Certain organic cations of large size viz. tetraphenylarsonium<sup>46</sup>, triphenylmethylarsonium<sup>47</sup>, tributyl ammonium<sup>48</sup>, etc. form ion-pairs with the thiocyanate complex of cobalt which are extractable into organic solvents like chloroform. These extracts are useful for determination of cobalt.

Zhan and Liu<sup>49</sup> determined cobalt using thiocyanate and some basic triphenylmethane dyes.

The thiocyanate method for the determination of iron has been studied by various workers<sup>50-54</sup>. Dwyer and Gibson<sup>55</sup> extracted the thiocyanate complex of iron with triphenylmethylarsonium cation at pH 1-2 into o-dichloro benzene.

Babko studied<sup>56</sup> the various complexes of quinquevalent molybdenum with different thiocyanate concentration. Bayan and Das<sup>57</sup> determined molybdenum using thiocyanate and benzyl trimethyl ammonium chloride. They used thiourea to reduce molybdenum. The complex was extractable into 1,2 dichloroethane with maximum absorbance at 465 nm.

Cimpu Viorica<sup>58</sup> made a study on the spectrophotometric determination of palladium with thiocyanate and thiourea. The yellow complex absorbs maximum at 350 nm.

Vanadium(II) was determined<sup>59</sup> spectrophotometrically using thiocyanate and diantipyrylmethane. The 1:2:3

V-SCN-diantipyrylmethane complex was extractable into chloroform.

Kharsan and Mishra<sup>60</sup> proposed a selective method for the determination molybdenum spectrophotometrically by extracting the molybdenum-N-hydroxy-N-P-tolyl-N-(3,4 dimethyl-phenyl) benzamidine in present of thiocyanate. The complex absorbs maximum at 470 nm.

The mixed ligand complex formation of vanadium(V) with N-p-cin-amoyl-N-pmethylphenyl hydroxyl amine and thiocyanate have been investigated by Bag and Saha<sup>61</sup>. The complex is extractable into chloroform and was used for the spectrophotometric determination of vanadium.

Niobium was determined<sup>62</sup> spectrophotometrically from 3 M HCl medium with dibenzo-18-crown-6 and thiocyanate. Benzene was used as an extracting solvent. The ion-association complex of U(VI)-thiocyanate-1-ethoxycarbonyl pentadecyl trimethylammonium was extracted<sup>63</sup> into chloroform for the spectrophotometric determination of uranium(VI).

Jaya et al<sup>64</sup> devised a spectrophotometric method for the determination of rhodium(III) in thermocouple wires using thiocyanate and rhodamine 6G. The complex in aqueous solution was stabilized by adding gelatin.

Lopez et al<sup>65</sup> determined silver in lead and lead concentrates with thiocyanate and Rhodamine B. Copper(II)

was extracted from thiocyanate solution into chloroform solution containing 2-benzoylpyridine-2-Pyridyl hydrazone or 2,2'-dipyridyl ketone-2 pyridylhydrazone by Stratis et al<sup>66</sup> for the determination of copper photometrically.

Shiraliева and Iskenderov<sup>67</sup> determined titanium photometrically by extracting of its 1:4:2 complex with SCN<sup>-</sup> and amine from 2.4-4.8 M HCl into chloroform. The absorbance was measured at 400 nm.

Chandrakar and Mishra<sup>68</sup> proposed a new spectrophotometric method for the determination of Mo(V). Mo(V) forms a ternary complex with N-hydroxy-N-P-chlorophenyl-N'-p-chlorophenyl-o-chlorobenzamidine hydrochloride in presence of thiocyanate. Another method for the spectrophotometric determination of Mo(V) is based on it formation of green complex with thiocyanate and malachite green<sup>69</sup>. In our present investigation thiocyanate has been used as an auxiliary ligand to develop some spectrophotometric methods.

#### Use of Iodide and Pyridine bases as reagents :

The use of iodide and pyridine as auxiliaries ligands is known. Among the elements that are extracted as iodide complexes are antimony(III), cadmium, gold(III), indium(III), lead(II), mercury(II) etc. The solvents that have been

used are, ethyl ether, methyl isobutyl ketone and methyl isopropyl ketone.

The base like pyridine behaves like a neutral ligand co-ordinated to the metal. Cobalt, nickel and copper in the presence of pyridine give water insoluble complexes which dissolve in chloroform to give pink, blue and green solutions of which the last, containing  $\text{Cu}(\text{Py})_2(\text{SCN})_2$  has been used in colorimetry<sup>70</sup>. Similar complexes are formed by zinc, cadmium and many other metals which can serve as the basis for their solvent extraction<sup>71</sup>.

Umezaki<sup>72</sup> 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. Umezaki<sup>73</sup> also extracted U(VI) with dibenzoylmethane into tributyl phosphate from nitric acid containing aluminium nitrate as the salting-out agent. He found that in presence of pyridine the system gives a bright yellow colour, stable for 20 hours.

During the extraction of uranium with 8-hydroquinoline Koppiker and Ganjankush<sup>74</sup> observed that the addition of pyridine and acetone enhances the colour intensity of the uranium oxinate complex.

Copper forms a green complex in the presence of pyridine and thiocyanate. This has been used in developing

gravimetric as well as colorimetric methods for estimation of copper<sup>75-78</sup>. Ayres et al<sup>79</sup> studied the extraction of thiocyanate complex of cobalt with chloroform in the presence of pyridine and worked out the optimum conditions for the colorimetric determination. Akaiwa and Kawamoto<sup>80</sup> 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<sup>81</sup> studied the formation of cobalt complex with pyridine and azide which was used for the colorimetric determination of cobalt.

Palladium can be determined colorimetrically with o-mercaptopbenzoic acid in the presence of pyridine<sup>82</sup>.

Extraction behaviour of some bivalent metals with methyl substituted pyridines in thiocyanate system has been studied<sup>83, 84, 85</sup>. Soni and Shah<sup>86</sup> studied the solvent extraction behaviour of cobalt(II) chelate of 4-formyl-1-phenyl-3-methyl-2-pyrazoline-5-one in presence of pyridine. Extractive spectrophotometric determination of vanadium as Vanadium(III)-Pyridine-dibenzoyl methane complex is proposed by Ary and Yatiranjan<sup>87</sup>.

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

reaction of bismuth with iodide provides an excellent sensitive methods for the determination this element.

Sudo used<sup>88</sup> Potassium iodide in presence of antipyrine solution to determine mercury. Absorbance of the chloroform extract was measured at 330 nm. Yamamoto and Kotsuji<sup>89</sup> extracted  $HgI_4^{2-}$  complex with  $Fe(dipy)_3^+$  at pH 6.5 into 1,2 dichloromethane and measured its absorbance at 526 nm.

According to Figgis and Gibson<sup>90</sup> antimony could be determined spectrophotometrically as  $SbI_4^-$  from 2 M HCl with  $Ph_3MeAs^+$ ,  $(P\text{-tolyl})_2MeAs^+$  and  $(P\text{-tolyl})_3Me_2As^+$ . The complex was extractable into o-dichlorobenzene.

An indirect colorimetric method for the determination of calcium was proposed by Sendroy<sup>91</sup> by using iodide.

Matano, and Kawase<sup>92</sup> studied spectrophotometric determination of bismuth with iodide and tetraphenyl phosphonium chloride. The complex  $\langle Ph_4P^+ \rangle \langle BiI_4^- \rangle$  was extractable into chloroform from 1M  $H_2SO_4$  and the absorbance measured at 505 nm.

Dembinski<sup>93</sup> found that imipramine hydrochloride(HI) in acid medium reacts with iodo complex of palladium to form the species  $(IH)_2 PdI_4$ , which is soluble in chloroform. This compound is utilized for the determination of the metal spectrophotometrically.

Marczenko et al<sup>94</sup> determined tellurium spectrophotometrically using iodides and cetyltrimethyl ammonium ion. The ion-association complex was soluble in chloroform.

An ion-association complex of lead with iodide and 1,4-dimethyl-1,2,4-trizolinium (3-azo-4)-N-N-diethylaniline was investigated by Kish et al<sup>95</sup> for the spectrophotometric determination of the metal. Another spectrophotometric method for the determination of cadmium have been proposed by Rao and Ranakrishna<sup>96</sup>. They used iodide and pyronine G and determined cadmium in pure zinc materials.

A hypersensitive method for the determination of rhodium is described by Ci and Wang<sup>97</sup>. They studied the Rhodium(III) --- Potassium iodide --- butyl Rhodamine B-arabic gum-Triton x 100 system. Bismuth could be determined<sup>98</sup> photometrically by using potassium iodide and Rhodamine 6G.

In the present investigations, thiocyanate, pyridine and iodide have been used as auxiliary ligands when necessary.

### Section 3 : Extraction and Spectrophotometric Determination of Iron

#### INTRODUCTION

The extensively used complexing agent thiocyanate, for the colorimetric determination of iron is well known. The red colour of  $\text{FeSCN}^{+2}$ <sup>99</sup> has long been employed for the colorimetric estimation of iron(III) and in presence of excess thiocyanate iron can be extracted into oxygen containing solvents. Other reagents may have also been used. The metal can be determined spectrophotometrically by using chromeazurols and hexadecyltrimethyl ammonium bromide<sup>100</sup>.

Gonzalez Portal et al<sup>101</sup> determined iron(III) spectrophotometrically by using music acid at pH 8.6. The absorbance was measured at 290 nm. Mathur S.P<sup>102</sup> determined iron(III) spectrophotometrically by measuring the

absorbance of its complex with N-quinolyl-N'-phenyl thiourea at 475 nm.

Ethylene diaminetetra methylene phosphonic acid<sup>103</sup> forms complex at pH 4.0 which was used for the determination of iron, absorbance was read at 255 nm. Other reported methods for the determination of iron involve the application of di-2-Pyridyl-glyoxal-2-quinolyl hydrazone<sup>104</sup>, poly-N-methylene-4,4'-dipyridylum chloride<sup>105</sup>, 3-hydroxy flavone<sup>106</sup>.

Akama Yoshifumi et al<sup>107</sup> determined iron in solar salt sample with 4-capryl-3-methyl-1-phenyl-5-Pyrazoline at pH 3.5. The complex was extracted into butyl alcohol and the absorbance was measured at 450 nm. Taketatsu Tomitsugu et al<sup>108</sup> used 2-theonyl-trifluoroacetone as a spectrophotometric reagent for the determination of iron(III). The molar absorptivity were measured at 338, 388 and 500 nm. The 4-hydroxy-1, 10, phenanthroline<sup>109</sup> complex of iron(II) was investigated at pH 10 - 2(M)NaOH. The maximum absorbance was observed at 545 nm. Mehra M.C. et al<sup>110</sup> used hexacyanoruthenate as an analytical reagent for the detection of iron. The complex absorbs maximum at 550 nm. At pH 4-5 ferric iron forms with 3-aldehydo salicylidene lyano acetyl hydrazone<sup>111</sup>, a red brown complex which absorbs maximum at 370 nm.

2-2' dipyridyl-2-quinolyl hydrazone<sup>112</sup> forms a complex with iron(II) at pH 3.4-4.5, which was used for the

determination of iron. The complex was extracted with benzene with maximum absorbance at 473, 504 and 644 nm.

The characteristics of the iron(II)-biacetyl monoxime<sup>113</sup> complex in the presence of ascorbic acid and ammonia or methylamine were studied and a spectrophotometric method for the determination of iron was described. The absorbance was measured at 505 or 510 nm with ammonia or methylamine respectively.

In the pH range 4.8-10.0 a brown complex formed by iron with 2-(2-thiazolylazo)-4-methylphenol<sup>114</sup> has been investigated. The complex was extracted with CHCl<sub>3</sub>. The absorbances were measured at 527, 628 and 762 nm.

Some other reagents have also been studied for the spectrophotometric determination of iron which includes 2,6 diacetyl pyridine and ethylene diamine<sup>115</sup>, 2,2' dipyridyl ketoxime<sup>116</sup>, salicyloyl-hydrazide<sup>117</sup>, Pyridine-2-acetaldehyde salicyloylhydrazone<sup>118</sup>, 3-hydroxy-2-methyl-1-4-napthoquinone monoxime<sup>119</sup>, methyl-1-3-indadione-2-carboxylate<sup>120</sup>, 7-(2-thiazolylazo) resorcinol<sup>121</sup>, isophthalodihydroxamic acid<sup>122</sup>, dipicolinyl dihydroxamic acid<sup>123</sup>, 4-(4-methyl-2-thiazolylazo) resorcinol<sup>124</sup>, 1,3-bis[ $\gamma$ -(2-Pyridyl)-methylene amino] thiourea and 1,3-bis[ $\gamma$ -(2-Pyridyl)-methylene amino] thiourea and 1,3-bis[ $\gamma$ -(2-Pyridyl)-methylene amino] guanidine<sup>125</sup>.

Chandravanshi et al<sup>126</sup> found that, iron(III) formed an orange complex with N-phenyl cinnamohydroxamic acid. The complex was extracted quantitatively into benzene from acidic medium. The complex shows absorption maximum around 440 nm. Iron(II) complex with bromopyrogallol red and pyrogallol red in the presence of tetradecyl trimethylamino bromide was used<sup>127</sup> for the photometric determination of iron. A violet complex formed by iron(III) with N-hydroxy -N-N'-diphenyl<sup>128</sup> benzanide in the presence of azide has been investigated. The mixed ligand complex was extracted into chloroform at pH 2-5. The absorbance was measured at 530 nm. Ammonium thiocyanate and tetrabutyl and ammonium chloride<sup>129</sup> form an ion-pair with iron(III) which was used for the spectrophotometric determination of iron. The complex was extracted into chloroform and the absorbance was measured at 475 nm.

Iron can also be determined spectrophotometrically by using 4-(2 thiazolylazo)-6-chlororesorcinol<sup>130</sup>, chloroderivatives of phenyl azo chromotropic acid<sup>131</sup>, neotetrazolium chloride<sup>132</sup>, monobutyl ester of  $\alpha$ -(N-benzyl amino)-salicyl phosphonic acid<sup>133</sup>, 1,10-phenanthroline-thiocyanate<sup>134</sup>, 2-(2'-benzothiazolylazo)-4,6-dimethyl phenol<sup>135</sup>, theonyl-trifluoro acetone<sup>136</sup>, salicylate and purpurin<sup>137</sup>, 2-acetyl pyridine thiosemi carbazone<sup>138</sup>.

Bayan K.C<sup>139</sup> determined iron(III) by extraction of its ion-pair with benzyltrimethyl ammonium chloride and thiocyanate in presence of ethyl methyl ketone into 1-2 dichloroethane. The absorbance was measured at 475 nm. Another spectrophotometric method involves the use of 2-(3'-sulfonylbenzoyl) Pyridine benzoyl hydrazone<sup>140</sup>. The absorbance of the complex was measured at 646 nm at pH 7-11. Salinas F. et al<sup>141</sup> determined iron(III) using 2-Pyrilidine imino benzohydroxamic acid. The absorbance of the red complex was measured at 475 nm.

Another procedure for iron(II) determination has been investigated by using pyrocatechol violet and cetyl trimethyl ammonium bromide<sup>142</sup>. The absorbance of the complex was read at 595 nm.

Lin, Jeun Lin<sup>143</sup> recently devised a method for the determination of trace amounts of iron(III) through enrichment of its acenaphthenequinone dioximate with microcrystalline naphthalin. Absorbance was measured at 470 nm. P.K.Paria and S.K.Majumdar<sup>144</sup> used potassium butyl xanthate for the spectrophotometric determination of iron. The absorbance was measured at 460 nm. Both ferrous and ferric iron forms complex with 9,10-phenanthroquinone monoxime<sup>145</sup>. This complex was used for the photometric

determination of iron. The absorbances were measured at 747 nm for iron(II) and 425 nm for iron(III).

In our present investigation it has been observed that iron(II) forms a stable complex with thiocyanate which by itself is not extractable into organic solvents like benzene, chloroform, ethylacetate. But in presence of cetyltrimethyl ammonium bromide the complex is extractable into above mentioned organic solvents. This fact has been used<sup>146</sup> in developing a photometric method for estimation of iron in microquantities. Further, the sensitivity is raised by addition of borate.

## EXPERIMENTAL

Apparatus and reagents : Spectral curves and absorbance measurements were made on a Shimadzu PR-1 model recording spectrophotometer, equipped with matched quartz cells of 10 mm optical path length. An ECL 5651 digital pH meter was used to measure the acidity of the aqueous solutions. Separating funnels (corning; 50 ml capacity) were used for extraction purpose.

3.532 gm of ferrous ammonium sulphate was dissolved in distilled water, acidified with 2-3 drops of conc HCl, to prepare 250 ml of the stock solution. This was then standardised<sup>147</sup>. Solutions of lower concentrations were prepared by appropriate dilution.

Solutions of ammonium thiocyanate (0.2 M), cetyltrimethylammonium bromide (CTAB) (0.1 M), sodium tetraborate (0.025) and hydroxylamine hydrochloride (1%) were prepared from distilled water. KCl-HCl buffer (pH-1) was used to adjust the pH of the aqueous phase.

Standard solutions of diverse ions were prepared from chlorides, nitrates or sulphates (in case of cations) and from sodium, potassium or ammonium salts (in case of anions) of the species concerned, followed by standardisation, to study interferences.

All other chemicals and solvents used, were of analytical grade. Benzene, chloroform, ethyl acetate, carbon tetrachloride, and butyl alcohol were distilled before use.

Determination of iron : To an aliquot of standard solution or sample containing up<sup>to</sup> 15  $\mu\text{g}$  of iron(II), were added 0.2 M ammonium thiocyanate (0.5 ml), 0.1 M cetyltrimethylammonium bromide (0.1 ml) and 0.025 M sodium tetraborate solution (0.5 ml). 0.5 ml of hydroxylamine hydrochloride was added if iron(III) is present. KCl-HCl buffer (pH-1.0; 5 ml) and water, as necessary, were added to the above solution to give a total volume of 10 ml. The resulting mixture was equilibrated with benzene (10 ml) for 30 sec. After phase separation, organic layer was poured over anhydrous sodium sulphate to remove any retained water globules. The absorbance of the organic extract was measured against a blank at 475 mm and the metal concentration computed from a calibration curve. To test the inference, the respective foreign ion was added to the aqueous solution before addition of the reagents.

#### RESULTS AND DISCUSSION

Absorption spectra : The spectrum of the iron(II) complex in benzene, taken against reagent blank as the reference, has been shown in Fig.1. The complex exhibits

absorption maximum at 475 nm. The reagent blank itself shows insignificant absorbance in the aforesaid wave-length region. The pattern of the absorption spectrum of the complex, extracted throughout the entire range i.e., from 4 (M) HCl medium to pH 1.0, remains unchanged. This indicates the presence of a single variety of the complex species in the system.

Beer's law and calibration curve : Different amounts of iron(II) were taken and extracted as in the procedure at pH-1.0 and the corresponding absorbances were measured against the blank in order to observe the adherence of the colour system to Beer's law. The absorbance shows a linear response over a concentration range of 1.5 ppm of iron, as seen from Table 1 and Fig.3. In each case in remaining aqueous phase after a single extraction was clear and colourless. Furthermore, the aqueous phase was free from iron as tested by an independent method.

Effect of thiocyanate concentration : Keeping other variables constant, the amount of aqueous ammonium thiocyanate (0.2 M) was varried to study its effect on absorbance. It was found that 0.5 ml of 0.2 M ammonium thiocyanate along with 0.1 ml of 0.1 M cetyltrimethylammonium bromide and 0.5 ml of 0.025 M sodium tetra borate was sufficient to extract 9  $\mu$ g of iron in a single operation. Increased concentration of thiocyanate, however, did not

bring about any significant change in the maximum absorbance as seen from Table 2.

Effect of cetyltrimethylammonium bromide (CTAB)

concentration : As regards, 0.1 ml of 0.1 M CTAB was quite adequate for quantitative extraction of 9  $\mu\text{g}$  of iron. Below 0.05 ml of 0.05 M CTAB, absorbance of the benzene extract was found to give values. Increased concentration could not produce any significant change in the maximum colour intensity. Experimental results in respect of CTAB concentration are presented in Table 3.

Effect of the presence of sodium tetraborate : Presence of sodium tetraborate in the reaction mixture was found to play a significant role in enhancing the colour intensity of the extracted species. Spectral curves of the benzene extracts obtained by applying the procedure to solutions initially containing iron as iron(II) were identical in nature to those obtained from iron(III) solutions. In the procedure addition of borate raised the intensity of the colour when iron was present initially as iron(II). To a solution containing iron as iron(III), addition to borate had no effect (Fig.2). The effect of varying amounts of sodium tetraborate is shown in Table 4.

Effect of acidity : Effect of acidity on the system was examined in terms of absorbance of the Fe(II)-SCN-CTAB

complex in the organic phase. Maximum absorbance was obtained when the extractions were carried out from 4 M HCl medium to pH-1.0. In each case the remaining aqueous phase, after the extraction, was clear and colourless. Complete and quantitative extraction of iron occurred from this entire range. At higher acid concentrations difficulty arises in separating the organic layer due to formation of some imulsion in between the organic and the aqueous phase. Beyond pH-2 iron shows no colour reaction with the reagents in the aqueous phase. The reagent blank absorbs minimum at pH-1.0 where the extractions were carried out for our investigations, unless otherwise mentioned.

Effect of solvents : Among the various solvents used, benzene was found to be most suitable to extract the iron complex, as seen from the Table 5 & Fig.1, shows that the spectral curves of the iron complex in various water immiscible solvents are identical in nature, although the complex is not extractable into carbon tetrachloride or butyl alcohol.

Addition of reagents : Addition of reagents is important in the procedure. One must follow the sequence of adding the reagents as - thiocyanate, CTAB and borate followed by addition of buffer. No colour development was there if borate was added before thiocyanate.

Stability of colour : The rapid development of the maximum colour intensity and its constancy with time indicates that time is not a critical factor in iron determination. The absorbance of the Fe(II)-SCN-CTAB complex in benzene was measured at elapsed intervals of time and the results are shown in Table 6.

Interference : To test the effects of diverse ions, iron(II) was extracted and determined according to the recommended procedure in presence of the desired foreign ions. Extraction pH was set at 1.0, unless otherwise mentioned. An ion was considered to interfere if the recovery of iron differed by more than  $\pm$  3% from the actual amount taken. Iron(II) (9  $\mu\text{g}$ ) could be determined in presence of aluminium(III), barium(II), beryllium(II), calcium(II), strontium(II), cerium(III), cadmium(II), chromium(III), lanthanum(III), lead(II), magnesium(II), nickel(II), rhodium(III), bismuth(III), thallium(I), thorium(IV), uranium(VI), girconium(IV), silver(I), cobalt(II), manganese(II), molybdenum(VI) and platinum(IV). Vanadium(VI) could be tolerated if the extraction be carried from 3 M HCl medium. In presence of copper(II), the benzene extract becomes hazy and the absorbance of the organic layer could not be measured. Authors failed to remove this interference. Zinc(II), mercury(II) and tin must be absent as iron(II) showed no colour reaction

with the reagents in presence of them. Presence of palladium(II) resulted low recovery of iron.

Among the anions tested, the system tolerated the followings : citrate, tartrate, acetate, phthalate, phosphate and nitrate. Extraction should be carried out from 3 M HCl medium to avoid the interference due to EDTA, fluoride and oxalate. The system however was found to be susceptible to the presence of iodide, nitrite and ascorbate. In 3 M HCl medium, thiourea could be tolerated. Results are shown in Table 7.

Precision and accuracy : The proposed method was tested by analysing solutions containing a known amount of iron(II). The experimental results for the determination of 3-12  $\mu$ g of iron(II) are shown in Table 8. The method is fairly precise and reproducible requiring hardly 10-15 min for each run. The sensitivity of the method has also been compared to those of some other existing methods as seen from Table 9..

Analysis of Synthetic mixtures : The method has been tested on a number of synthetic mixtures comprising different metal ions to determine iron. The results are shown in Table 10.

The method finds its application in the analysis of the following standard samples obtained from the Bureau

of Analysed Samples Limited, England.

Portland cement : An weighed amount (0.2143 gm) of the substance was dissolved in the minimum volume of 1:1 hydrochloric acid. The mixture was boiled and filtered. The volume of the filtrate was made up to 100 ml with distilled water. The solution after proper dilution was used to determine the amount of iron present in the sample.

Dolomite : 0.2135 gm of dolomite was dissolved exactly as portland cement to give 100 ml of test solution. Iron present was determined similarly as described earlier. The results obtained from three determinations in each case, are presented in Table 11.

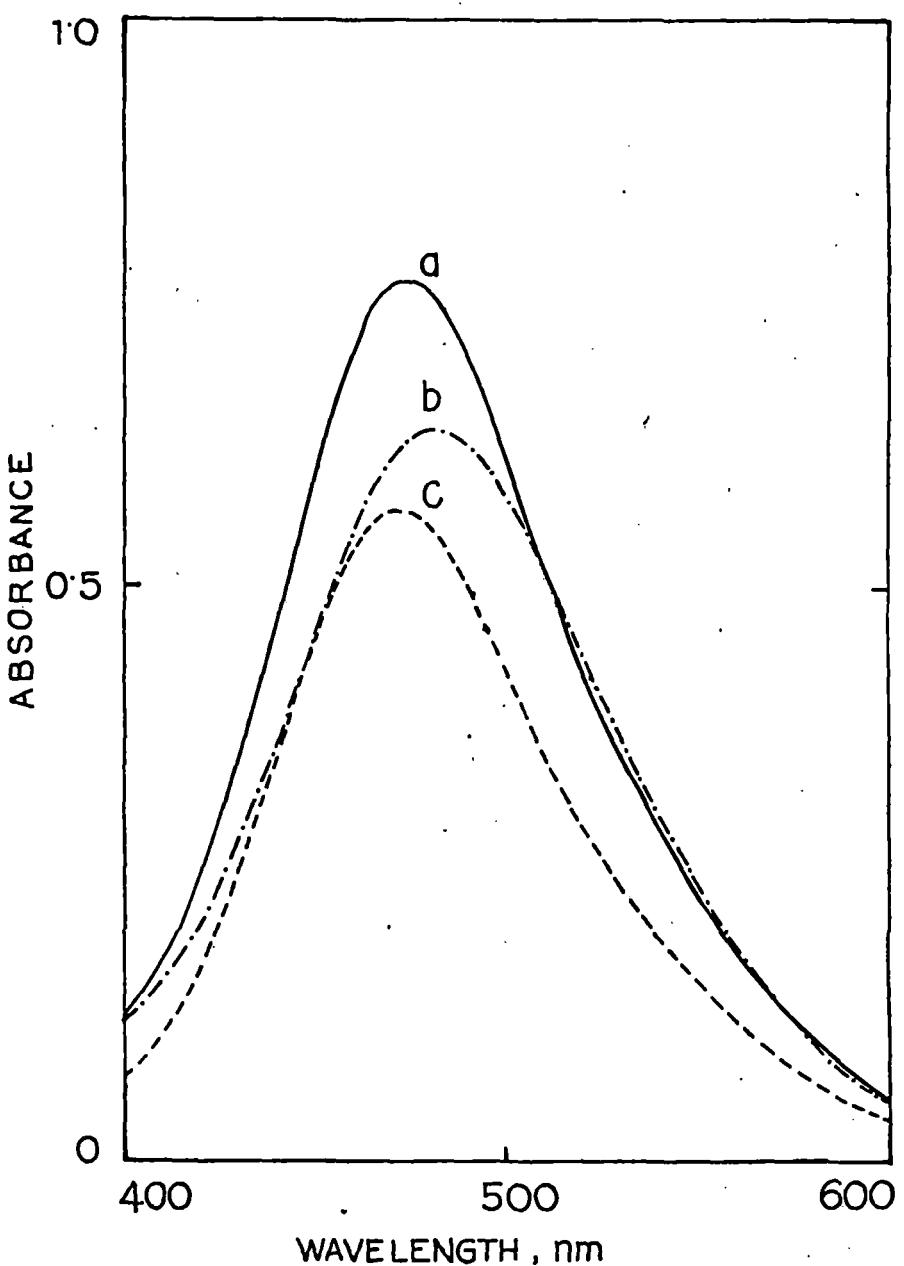


FIG. 1. SPECTRAL CURVES OF IRON (II) THIOCYNATE  
CTA (1.2 ppm Fe) IN BENZENE (a), ETHYLACETATE (b)  
AND CHLOROFORM (c).

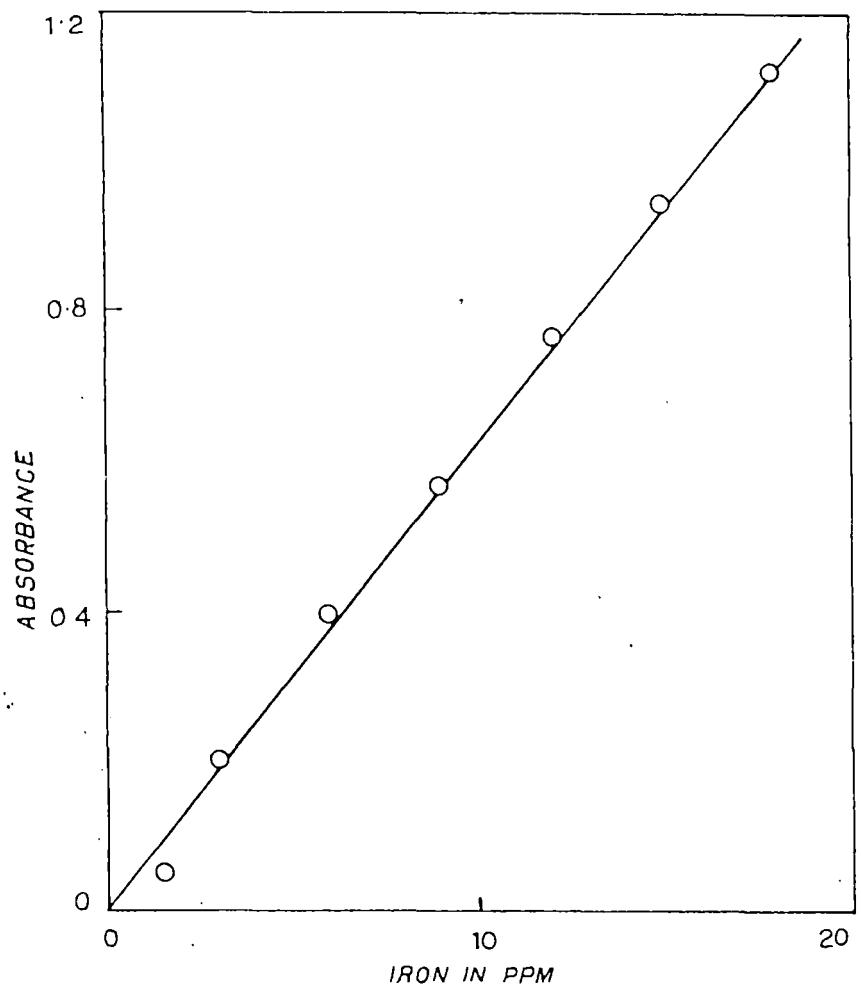


Fig- 3. BEER'S LAW(Fe(II)-SCN-CTAB System )

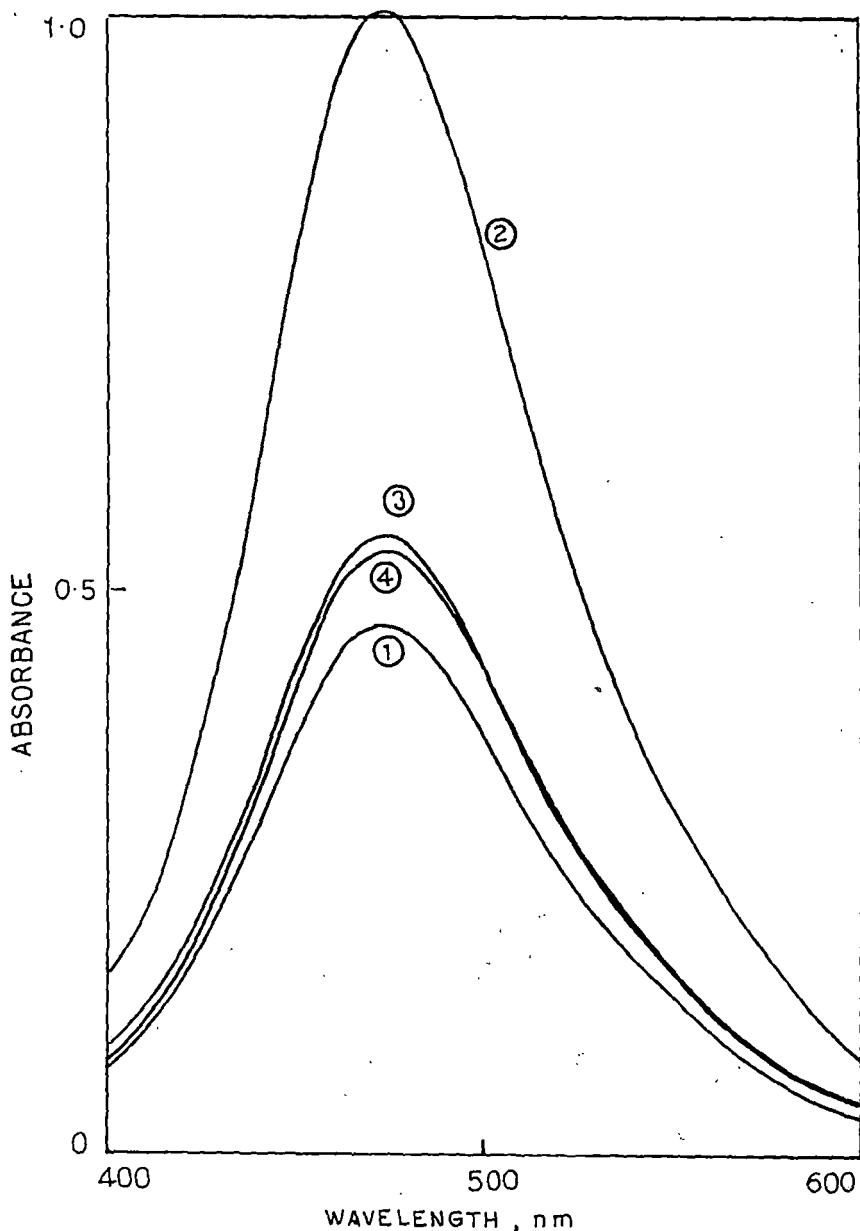


Fig-2 : SPECTRAL CURVES OF IRON-SCN-CTAB COMPLEXES  
IN BENZENE

(1) Fe(II) without borate (2) Fe(II) with borate  
(3) Fe(III)without borate (4) Fe(III)with borate.

Table 1 : Beer's law data

Iron(II) taken in $\mu\text{g}$	Absorbance at 475 nm
1.5	0.050
3.0	0.205
6.0	0.402
9.0	0.570
12.0	0.772
15.0	0.950
18.0	1.102

Table 2 : Effect of thiocyanate concentration

The aqueous phase (10 ml) contains 9  $\mu\text{g}$  of Fe(II), 0.1 ml of 0.1 M CTAB and 0.5 ml of 0.025 M borate. Extraction pH-1.0

Thiocyanate concentration M	Amount added ml	Absorbance at 475 nm
0.2	0.1	0.205
0.2	0.2	0.502
0.2	0.4	0.570
0.2	0.6	0.575
0.2	0.8	0.572
0.2	1.0	0.580

Table 3 : Effect of CTAB concentration

The aqueous phase (10 ml) contains 9  $\mu\text{g}$  of Fe(II), 0.5 ml of 0.2 M  $\text{NH}_4\text{SCN}$  and 0.5 ml of 0.025 M sodium tetraborate. Extraction pH-1.0

CTAB concentration M	Amount added ml	Absorbance at 475 nm
0.05	0.05	0.502
	0.10	0.580
0.1	0.05	0.568
	0.1	0.570
0.2 <del>(0.4)</del>	0.1	0.565
0.4	0.1	0.572
0.5	0.1	0.575

Table 4 : Effect of the presence of sodium tetraborate

The aqueous phase (10 ml) contains 9  $\mu\text{g}$  of Fe(II), 0.5 ml of 0.2 M  $\text{NH}_4\text{SCN}$  and 0.1 ml of 0.1 M CTAB. Extraction pH-1.0

Borate concentration M	Amount added ml	Absorbance at 475 nm
0.025	0.05	0.450
0.025	0.1	0.505
0.025	0.2	0.580
0.025	0.3	0.565

contd...

Table 4 contd ...

0.025	0.4	0.560
0.025	0.5	0.570
0.025	0.6	0.565
0.025	0.8	0.580
0.025	1.0	0.570
0.025	1.2	0.550
0.025	1.4	0.520
0.025	1.6	0.425
0.025	1.8	0.400
0.025	2.0	0.305

Table 5 : Effect of extracting solvents \*

Solvent	$\lambda_{\text{max}}$ nm	Molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$	Sandell's sensitivity $\mu\text{g}/\text{cm}^2$
Benzene	475	$3.59 \times 10^4$	0.0015
Ethyl acetate	480	$2.99 \times 10^4$	0.0018
Chloroform	470	$2.66 \times 10^4$	0.0021
Carbon tetrachloride	NE	NE	NE
Butyl alcohol	NE	NE	NE

\* NE = Complex not extractable

Table 6 : Variation of absorption with time

Time in min after extraction	Absorbance at 475 nm
5	0.575
10	0.570
20	0.570
40	0.575
60	0.570
90	0.565
120	0.570

Table 7 : Effect of diverse ions on the determination of Iron

Iron(II) taken - 9  $\mu$ g; Extraction pH-1.0 (unless otherwise mentioned).

Diverse ion added	Amount tolerated mg	Iron(II) found $\mu$ g	Error %
Aluminium(III)	6.0	9.0	0
Barium(II)	5.5	9.2	2.2
Beryllium(II)	6.0	9.1	1.1
Calcium(II)	6.0	9.0	0
Strontium(II)	5.5	9.0	0
Cerium(III)	5.5	8.0	2.2
Cadmium(II)	6.0	8.8	2.2

contd ...

Table 7 contd ...

Chromium(IV)	4.0	9.1	1.1
Lanthanum(III)	6.0	9.1	1.1
Lead(II)	5.5	9.2	2.2
Magnesium(II)	6.0	9.0	0
Nickel(II)	6.0	9.2	2.2
Rhodium(III)	6.0	9.1	1.1
Bismuth(III)	3.5	8.8	2.2
Thallium(I)	5.5	9.0	0
Thorium(IV)	6.0	9.1	1.1
Uranium(VI)	5.0	9.2	2.2
Zirconium(IV)	6.0	9.2	2.2
Silver(I)	3.5	8.8	2.2
Cobalt(II)	3.0	9.2	2.2
Manganese	3.5	9.0	0
Molybdenum(VI)	2.0	9.2	2.2
Platinum(IV)	1.0	9.2	2.2
Vanadium(V)*	1.0	9.2	2.2
Copper(II)	Nil	-	-
Zinc(II)	Nil	-	-
Mercury(II)	Nil	-	-
Tin(II)	Nil	-	-
Palladium	0.5	8	10
Citrate	6.0	9.0	0

Contd ...

Table 7 contd ...

Tartrate	6.0	9.0	0
Acetate	6.0	9.1	1.1
Phthalate	6.0	9.1	1.1
Phosphate	6.0	9.1	1.1
Nitrate	5.0	9.0	0
EDTA*	6.0	8.8	2.2
Fluoride*	4.0	9.1	1.1
Oxalate*	4.0	9.0	0
Iodide	Nil	-	-
Nitrite	Nil	-	-
Ascorbate	Nil	-	-
Thiourea	1.5	8.8	2.2

\* Extraction carried out from 3 M HCl medium

Table 8 : Reproducibility of iron recovery

Iron taken μg	Iron found μg			Mean μg	Std devia- tion %
3	3.1	3.0	2.9	2.96	0.10
	2.8	3.0	3.0		
6	6.2	6.0	5.9	5.95	0.15
	6.0	5.8	5.8		
9	9.0	9.2	8.9	9.05	0.12
	9.2	9.0	9.0		
12	11.8	12.0	12.2	12.0	0.17
	12.2	12.0	11.8		

Table 9 : Sensitivities of some other existing methods -  
A comparison

Reagents	Sandell's sensitivity $\mu\text{g}/\text{cm}^2$	$\lambda_{\text{max}}$	Ref.
1. $\alpha$ -(N-benzylamino) salicyl phosphonic acid and $\alpha$ -(N-chlorobenzylamino) salicyl phosphonic acid	0.0110	(450 nm)	148
2. 1,10-phenanthroline and tetraphenyl borate	0.0048	(500 nm)	149
3. 3-Hydroxy-2-methyl-1-4, napthaquinone monoxime	0.0046	(470 nm)	119
4. N-hydroxy-N-m-tolyl-N-(3,4 dimethyl) phenyl benzimidine	0.0048	(460 - 470 nm)	150
5. Acenaphthenequinone dioxime	0.008	(460 nm)	143
6. N-hydroxy-N-P-chlorophenyl-N-O-chlorophenyl benzimidine hydrochloride and thiocyanate	0.004	(480 nm)	151
7. 3-aldehydosalicylidene cyano acetyl hydrazene	0.043	(370 nm)	111
8. Ethylenediaminetetramethylene phosphoric acid	0.009	(255 nm)	103
9. 2-Hydroxy-3,5 dimethyl acetophenone	0.056	(550 nm)	152
10. Music acid	0.016	-	101
11. N-Quinolyl-N'-phenyl thiourea	0.0042	(425 nm)	102
12. Present method	0.0015	(475 nm)	146

Table 10 : Determination of Iron (9  $\mu\text{g}$ ) in various mixtures with 200  $\mu\text{g}$ . of each ion added

Ions added	Iron found ( $\mu\text{g}$ )		
1. Co(II), Ni(II), Mn(II)	9.1,	9.1,	9.2
2. Ni(II), Mn(II), Cr(III)	9.0,	9.2,	9.0
3. Mn(II), Cr(III), Bi(III)	9.3,	9.1,	9.0
4. Cr(III), Bi(III), Pb(II)	8.9,	9.1,	9.1
5. Al(III), Cd(II), Th(IV)	9.0,	9.1,	9.1

Table 11 : Determination of iron in standard samples

Sample	Composition	Iron found %	Mean %	Error %
24b Portland cement	CaO - 62.9			
	MgO - 2.56	1.750		
	Fe <sub>2</sub> O <sub>3</sub> - 2.44	1.672	1.729	1.34
	Al <sub>2</sub> O <sub>3</sub> - 6.22	1.766		
	SiO <sub>2</sub> - 20.4			
9h Dolomite	CaCO <sub>3</sub> - 55.2	.140		
	MgCO <sub>3</sub> - 43.1	.150	.151	3.42
	SiO <sub>2</sub> - 0.88	.165		
	Fe <sub>2</sub> O <sub>3</sub> - 0.21			

Section 4 : Extraction and Spectrophotometric determination  
of Cobalt

INTRODUCTION

Cobalt forms a variety of mixed complexes with the ligands  $\text{NH}_3$ , Py,  $\text{H}_2\text{O}$ , halides,  $\text{SCN}^-$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$  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  $= \text{C}' \overset{\text{NO}}{\underset{\text{OH}}{\text{—}}} \text{C}' =$  group. Cobalt(II) was extracted<sup>153</sup> 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 first. The red complex of cobalt with sodium 4-nitroso-2-hydroxynaphthalene-3,6-disulphonate<sup>154</sup> has been investigated. The complex is stable in acid solution. The metal:ligand ratio was found to be 1:3.

Cobalt forms coloured complex with 1-nitroso-2-naphthol<sup>155</sup> at pH 3.5-8.0 which can be extracted into carbontetra-chloride. 2-nitroso-1-naphthol<sup>156</sup> 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<sup>151</sup> determined cobalt at 550 nm after oxidation to Co<sup>+3</sup> with alk H<sub>2</sub>O<sub>2</sub> as its 1:2 complex with 1,6-hexanediamine tetra acetic acid at pH 9.5.

Nakashima et al<sup>158</sup> 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 chloroform. The metal:ligand ratio was found to be 1:3. The absorbance was measured at 410 nm.

Two water soluble complexes of cobalt with 2-/di(2-Pyridyl) methylidenehydrazino<sub>7</sub> quinoline at pH 2-12 and in 0.1-6 M HClO<sub>4</sub> has been investigated by R.B.Singh et al<sup>159</sup>. The ion-association complex of cobalt with NaOCN and 2,3,5-triphenyl tetrazolium chloride<sup>160</sup> was studied at pH 5.8. The complex was extractable into propylene carbonate and absorbs maximum at 631 nm.

Gimenez et al<sup>161</sup> developed a method based on the formation of a 1:1 complex of cobalt(II) with 2-Pyridine carboxaldehyde 2-Pyridylhydrazone. The absorbance was

measured at 350-90 nm after 15 min. Cobalt(II) forms a greenish yellow complex with 3-(o-acetophenyl)-1-methyl triazene-N-oxide<sup>162</sup> in 50% EtOH-H<sub>2</sub>O at pH 6.8-10.0. The complex was extractable into chloroform and the absorbance of the complex was measured at 460 nm.

Spectrophotometric determinations of cobalt with 1-phenyl-3-thiobenzoylthiocarbamide<sup>163</sup>, 2-(5-bromo-2-Pyridylazo)-5-diethylaminol<sup>164</sup> 1,3-cyclohexanedione dithiosemicarbazone monohydrochloride<sup>165</sup>, 1-(2-Pyridylazo)-4-benzylresorcinol<sup>166</sup>, 5-chloro-7-iodo-8 quinolinol<sup>167</sup>, 2-(2-thiazolylazo)-4-methyl-5-(sulfo methylamino) benzoic acid<sup>168</sup>, 2'-hydroxy-4-methoxy-5'-methyl chalcone oxime<sup>169</sup>, 2-(2-(3,5 dibromopyridyl) azo) 7-5-dimethyl amino benzoic acid<sup>170</sup>, morpholine-4-carbodithioate<sup>171</sup>, 2,2'-dipyridyl-2-benzothiazolyl hydrazone<sup>172</sup>, 2,4-dihydroxyacetophenone thiosemicarbazone<sup>173</sup>, thiocyanate and brilliant green<sup>174</sup>, 2-(2-benzothiazolylazo)-5-dimethylamino benzoic acid<sup>175</sup>, 5-methoxy-2-nitrosophenol<sup>176</sup>, Isonitrosothio camphore<sup>177</sup>,  $\beta$ -mercaptopropanoic acid anilide<sup>178</sup>, Pot. Propyl xanthate<sup>179</sup>, Isophthal dihydroxamic acid<sup>180</sup>, 2-(3'-sulfobenzoyl) pyridine benzoyl hydrazone<sup>181</sup>, 1,2,3-indanetrionetrioxime<sup>182</sup>, thiocyanate and benzyltrimethyl ammonium chloride<sup>183</sup>, Erichrome Azurol B - v, 4'bipyridyl and cetyltrimethyl ammonium bromide<sup>184</sup>, 5,5 dimethyl-1,2,3-cyclohexane trione 1,2 dioxime-3-thiosemicarbazone<sup>185</sup>, 3-hydroxy-2-methyl-1-4-napthoquinone 4-oxime<sup>186</sup>, and

2-hydroxy-1-naphthaldehyde guanyl hydrazone<sup>187</sup> have been suggested by various workers.

Zhang, Guang and Han Quan<sup>188</sup> developed a spectrophotometric method for the determination of cobalt by using 4-(2-thiazolylazo)-1,3 diamino benzene. The complex is stable in a medium of 0.3-3.5 M perchloric acid. The metal :ligand ratio was found to be 1:3. The absorbance of the complex was measured at 582 nm. A Greenish-yellow coloured complex of cobalt with 2'-hydroxy acetophenone thiosemicarbazone has been investigated by Murthy et al<sup>189</sup> in acetate buffer (pH 5.0-7.5). The absorbance of the complex was measured at 360 nm.

Dawson Martin V and Lyle Samuel J<sup>190</sup> used dithizone as a reagent for the spectrophotometric determination of cobalt. The complex was extractable into carbon tetrachloride and shows its maximum absorbance at 550 nm.

It has been found that Cobalt forms a blue complex with thiocyanane and cetyl trimethyl ammonium bromide (CTAB). This ion pair is readily extractable into chloroform, which is the basis of our present investigation.

## EXPERIMENTAL

### Apparatus and Reagents :

Spectral curves and absorbance measurements were carried out with a Shimadzu PR1 model recording spectrophotometer, provided with 1 cm optically matched quartz cells.

pH values were measured with an ECL 5651 digital pH meter. Separatory funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of cobalt(II) was prepared by dissolving 7.433 gms of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 500 ml of distilled water and was standarised by using a complexometric method with xlenol orange as indicator<sup>191</sup>. Solutions of lower concentrations were prepared by appropriate dilution.

Solutions of ammonium thiocyanate (0.2 M), cetyltrimethyl ammonium bromide (CTAB) (0.1 M) were prepared in distilled water. Acetic acid-sodium acetate buffer was used to adjust the pH of the aqueous phase.

Standard solutions of diverse ions were prepared from nitrates, chlorides, sulphate (in case of cations) and from sodium-potassium or ammonium salts (in case of anions) of the species concerned to study interferences.

Determination of cobalt :

To an aliquot containing upto 300  $\mu\text{g}$  of cobalt, 2 ml of 0.2 M ammonium thiocyanate and 0.4 ml of 0.1 M cetyltrimethyl ammoniumbromide (CTAB) solutions were added. The total volume of the aqueous phase was made upto 10 ml with acetate buffer and distilled water so that the pH of the solution was maintained at  $3.5 \pm 0.5$ . The resulting mixture was then shaken for 30 sec with 10 ml chloroform. The blue organic layer was separated and poured over anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the chloroform extract was then measured at 625 nm against pure solvent.

A standard calibration curve was prepared and the amount of cobalt, present in unknown solution, was evaluated therefrom. To test the interference, the respective foreign ion was added to the aqueous solution before addition of the reagents.

## RESULTS AND DISCUSSION

Absorption spectra :

The absorption spectrum of Co(II)-SCN-CTAB complex in chloroform, taken against pure solvent as a reference, has

been shown in fig.1. The blue cobalt complex shows absorption maxima at 625 nm with a shoulder at around 585 nm. The reagent blank does not absorb in the aforesaid wavelength region. The pattern of the absorption spectrum of the complex, extracted through the entire range i.e., from 4 m HCl medium to pH 8.0 remains unchanged. This indicates the existence of a single variety of the complex species in the system.

Beer's law and calibration curve :

Different amounts of cobalt(II) were taken and extracted following the general procedure at pH  $3.5 \pm 0.5$  and the absorbances were measured against the pure solvent in order to observe the adherence of the coloured system to Beer's law (table 1). The absorbances of the blue complex in chloroform show a linear response upto 30 ppm of cobalt (Fig.2.). In each case the aqueous phase after extraction was clear and colourless. Furthermore the aqueous phase, as tested by an independent method, was void of cobalt.

The molar absorptivity of the complex based on cobalt content, was calculated to be  $1.92 \times 10^3 \text{ l mol}^{-1} \text{cm}^{-1}$  and Sandell's sensitivity was  $0.031 \mu\text{g/cm}^2$  at 625 nm.

Effect of thiocyanate concentration :

Keeping the other factors constant, the amount of aqueous ammonium thiocyanate was varied to study the effect of thiocyanate concentration on absorbance. It was found that 1 ml of 0.2 M ammonium thiocyanate along with 0.2 ml of 0.1 M CTAB was sufficient to extract 135  $\mu\text{g}$  of cobalt in a single operation. Higher concentration of CTAB did not bring about any significant change in the maximum value of the absorbance. Table 2 shows the effect of thiocyanate on absorbance of the cobalt(II) complex.

Effect of CTAB concentration :

It was observed that, 0.2 ml of 0.1 M CTAB was sufficient for quantitative extraction of 135  $\mu\text{g}$  of cobalt. Increased concentration however did not bring about any significant change in the absorbance value of the organic extract. Experimental results are tabulated in table 3.

Effect of acidity :

Effect of acidity on the system was examined in terms of absorbance of the Co(II)-SCN-CTAB complex in the organic phase. A steady and maximum absorbance was obtained when the extractions were carried out from 4 M HCl medium to

pH 8.0. In each case, after extraction, the aqueous phase was clear and colourless. Complete and quantitative extraction of cobalt occurred from this entire range. Above or below this range the extraction was found to be incomplete. At 0.1 M sodium hydroxide medium, cobalt(II) showed no colour reaction with the reagent. Extractions were carried out at pH  $3.5 \pm 0.5$  for our investigations, unless otherwise mentioned.

Choice of solvents : Apart from chloroform, some other solvents were tested as extracting solvents, but those showed no special advantage over chloroform.

Stability of colour : The reaction between cobalt(II) thiocyanate and CTAB was instantaneous. Time is not a critical factor in the determinations of cobalt(II). The absorbance of the chloroform extract containing Co(II)-SCN-CTAB complex were measured at different intervals of time. The colour of the complex in chloroform was found to stable for at least 96 hrs as seen from table 4.

Interference : In order to study the effects of diverse ions on the extraction behaviour, cobalt was determined

according to the recommended procedure in presence of the respective foreign ion. Extraction pH was set at 3.5 with acetate buffer unless otherwise mentioned. An ion was considered to interfere if the recovery of cobalt differed by more than  $\pm$  3% from the actual amount taken. Cobalt(II) (135  $\mu$ g) could be determined without interference in presence of Be(II), Tl(II), Al(III), Th(IV), Cl(VI), Pt(IV), Rh(III), La(III), Ca(II), Ba(II), Sr(II), Mn(II), Cr(III), Bi(III), Pb(II), V(V), Ni(II), Ag(I), Zr(IV), Mg(II), Ce(III), Sn(II), Mo(IV) and Pd(II). Interference due to iron(III) was avoided by using ammoniumhydrogenfluoride as the masking agent. Cadmium could be tolerated if the extraction was carried out from 3M HCl medium. In presence of copper (II) the chloroform extract became hazy and absorbance of the organic layer could not be measured. All attempts failed to remove this interference. Zinc(II) and mercury(II) must be absent as cobalt(II) showed no colour reaction with the reagents in presence of them.

Among the anions tested the system tolerated the followings : thiosulphate, ascorbate, iodide, fluoride, borate, phosphate, acetate, phthalate, tartrate, sulphate, citrate and oxalate. Extraction should be carried out from 3 M HCl medium to avoid the interference due to EDTA. Results are shown in table 5.

Precision and accuracy : The proposed method has been tested by analyzing solutions containing a known amount of cobalt. The results for the determination of cobalt(II) is presented in table 6. Thus the method is fairly precise and reproducible. The total operation time for each run requires 10-15 minutes. The method is compared to some other existing methods as seen from table 7.

Application:Analysis of synthetic mixtures : The method has been applied to a number of synthetic mixtures in absence of real samples and the results are shown in table 8.

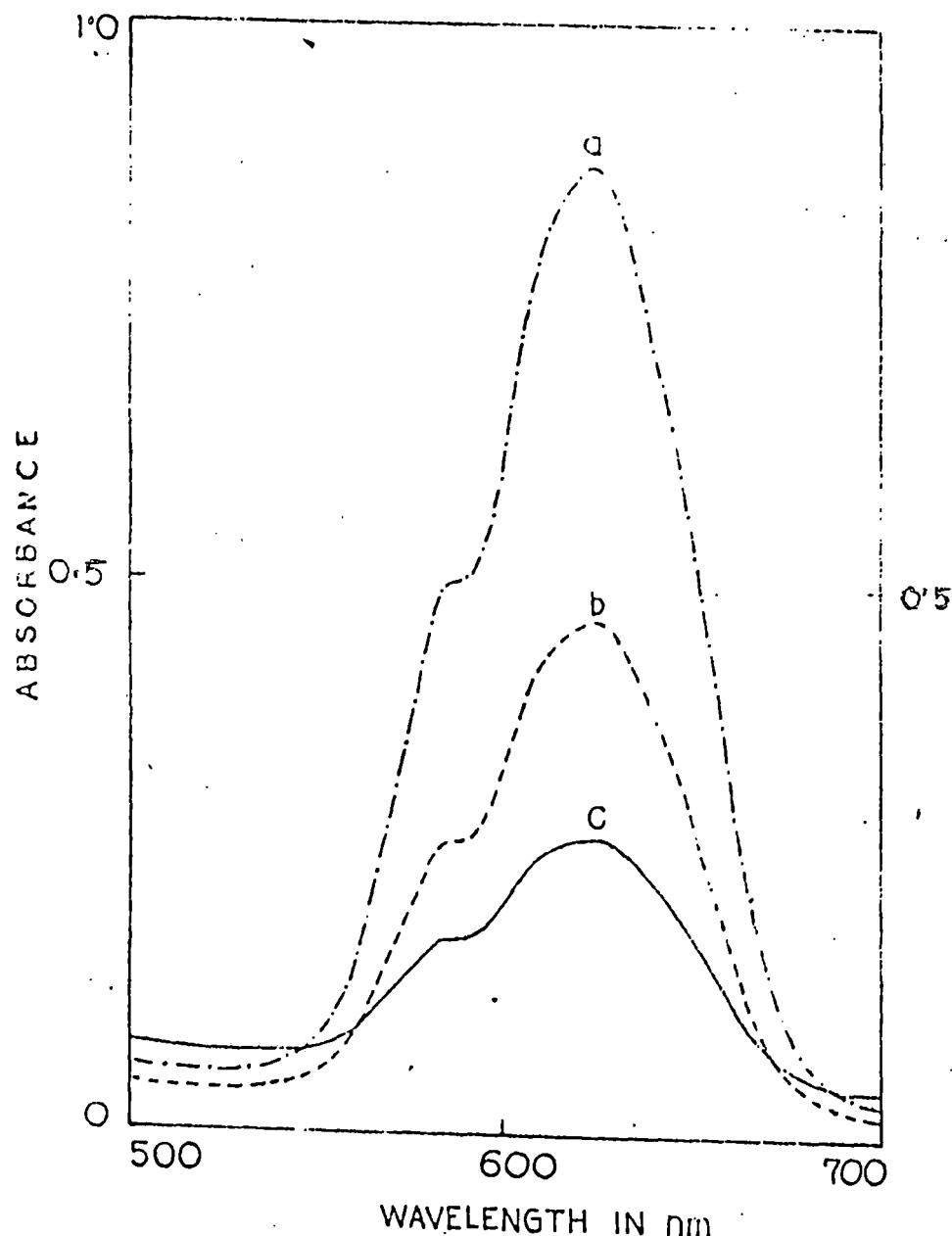


FIG-1 : ABSORPTION SPECTRUM OF  $\text{Co}(\text{II})\text{-SCN-CTA}$  COMPLEX  
a - 27 ppm Co, b - 13.5 ppm Co, c - 6.75 ppm Co.

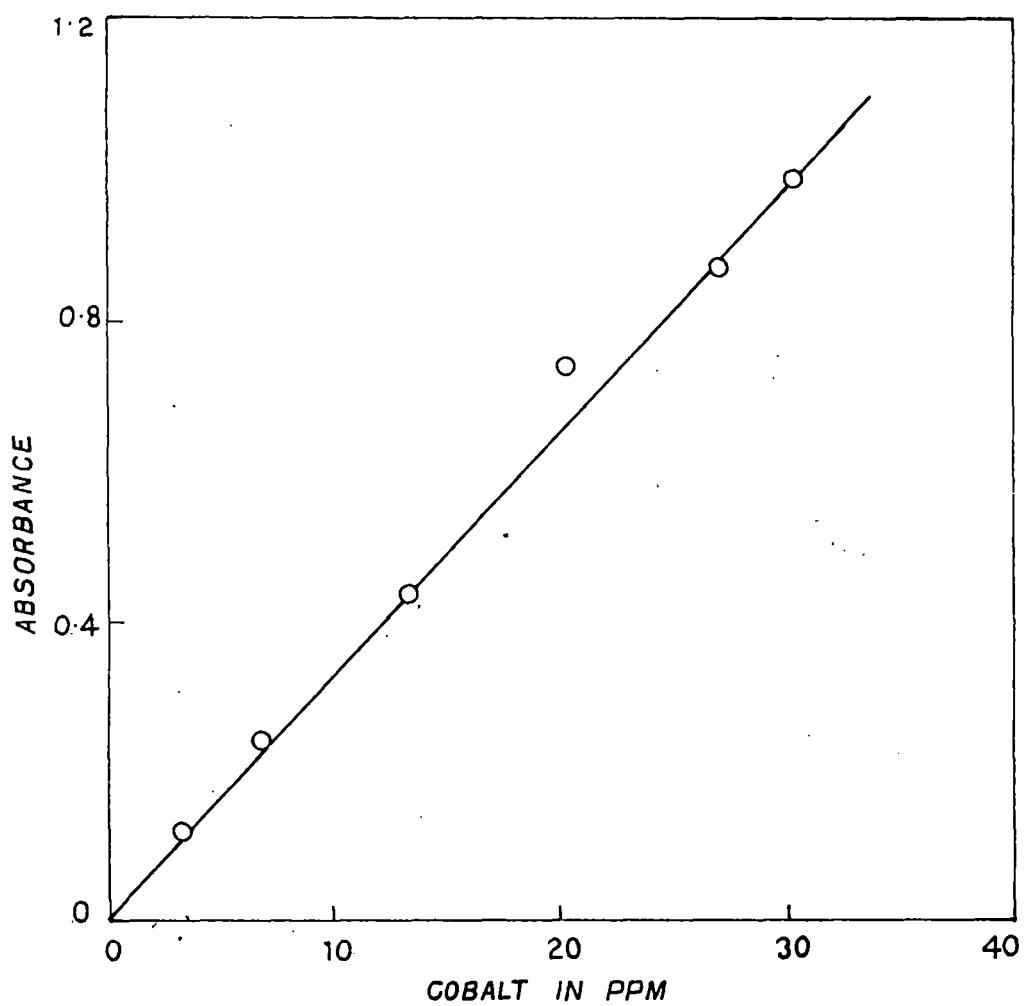


Fig - 2. BEER'S LAW (Co(II)-SCN-CTAB System )

Table 1 : Adherence to Beer's law

Cobalt(II) in ppm	Absorbance at 625 nm
3.37	0.122
66.75	0.240
13.50	0.442
20.25	0.740
27.00	0.875
30.37	0.990

Table 2 : Effect of thiocyanate concentration

The aqueous phase (10 ml) contains 135  $\mu\text{g}$  of cobalt(II) and 0.2 ml of 0.1 M CTAB. Extraction pH - 3.5  $\pm$  0.5

Aqueous thiocyanate concentration in M	Amount added (ml)	Absorbance at 625 nm
0.2	0.1	-
0.2	0.2	0.160
0.2	0.3	0.305
0.2	0.4	0.340
0.2	0.5	0.440
0.2	0.6	0.445
0.2	0.8	0.442
0.2	1.0	0.442
0.2	1.5	0.440

Table 3 : Effect of CTAB concentration

The aqueous phase (10 ml) contains 135  $\mu\text{g}$  of cobalt(II) and 1 ml of 0.2 M  $\text{NH}_4\text{SCN}$ . Extraction pH - 3.5  $\pm$  0.5

CTAB concentration (M)	Amount added (ml)	Absorbance at 625 nm
0.1	0.05	0.350
0.1	0.10	0.440
0.1	0.15	0.442
0.1	0.20	0.445
0.1	0.25	0.442
0.1	0.30	0.442
0.1	0.40	0.440
0.1	0.50	0.442

Table 4 : Variation of absorption with time  
(cobalt taken 135  $\mu\text{g}$ )

Time in hours after extraction	Absorbance at 625 nm
0.5	0.442
1	0.442
2	0.440
6	0.442
12	0.442
24	0.442
48	0.440
96	0.442

Table 5 : Effect of diverse ions on determination 135  $\mu\text{g}$  of cobalt

Extraction pH set at  $3.5 \pm 0.5$  unless otherwise mentioned

Ion added	Amount tolerated	Cobalt found $\mu\text{g}$	Error (%)
Be(II)	9.0	134.0	0.74
Tl(I)	7.5	137.5	1.8
Al(III)	8.5	136.0	0.74
Th(IV)	6.5	136.0	0.74
U(VI)	7.0	133.0	1.5
Pt(IV)	6.0	137.0	1.5
Rh(III)	6.0	136.0	0.74
La(III)	7.0	135.0	0
Ca(II)	10.0	136.5	1.1
Ba(II)	10.0	137.0	1.5
Sr(II)	10.0	137.0	1.5
Mn(II)	6.0	133.0	1.5
Cr(III)	7.0	135.0	0
Bi(III)	6.0	138.0	2.2
Pb(II)	7.5	136.0	0.74
V(V)	6.0	138.0	2.2
Ni(II)	6.0	137.0	1.5
Ag(I)	5.0	133.0	1.5
Zr(IV)	8.0	134.0	0.74
Mg(II)	7.0	135.0	0

contd ...

Table 5 contd. . .

Ce(III)	6.0	135.0	0
Sn(II)	6.0	132.0	2.2
Mo(IV)	2.5	137.0	1.5
Fe(III) <sup>a</sup>	7.0	137.0	1.5
Pd(II)	0.7	138.5	2.6
Cd(II) <sup>b</sup>	3.5	137.0	1.5
Cu(II)	nil	-	-
Zn(II)	nil	-	-
Hg(II)	nil	-	-
Thiosulphate	14.0	132.0	2.2
Iodide	15.0	137.0	2.2
Floride	15.0	136.0	0.74
Borate	14.0	136.5	1.1
Phosphate	14.0	132.5	1.8
Acetate	15.0	135.0	0
Phthalate	15.0	134.0	0.74
Tartarate	12.0	132.0	2.2
Ascorbate	12.0	132.0	2.2
Sulphate	15.0	135.0	0
Citrate	5.0	134.0	0.74
EDTA <sup>b</sup>	6.0	132.0	2.2

a : in presence of  $\text{NH}_4\text{HF}_2$ ; b : Extraction from 3 M HCl medium

Table 6 : Reproducibility of cobalt recovery

Cobalt taken $\mu\text{g}$	Cobalt found $\mu\text{g}$	Mean $\mu\text{g}$	Std. deviation %
67.5	65.8, 67.0, 67.2	67.15	1.2
	68.0, 69.0, 66.0		
135	136.5, 135.0, 132.5	134.5	1.6
	134.0, 136.0, 133.0		
270	275.0, 270.8, 268.0	271.38	2.4
	270.0, 273.0, 271.5		

Table 7 : Comparison

Reagent	Absorp- tion maxima (nm)	molar -absorp- tivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$	Ref.
Propylene carbonate	320	$1.15 \times 10^4$	192
	620	$1.8 \times 10^3$	
Triphenyltetrazolium cation	620	$3.2 \times 10^3$	193
Antipyrinium ion	625	$1.9 \times 10^3$	194
2-(P-iodophenyl)-3-(P-nitro phenyl)-5-phenyltetrazolium cation	620	$0.7 \times 10^3$	195
N-thioglycolyl-N-phenyl hydroxylamine	475	$7.64 \times 10^3$	196
1,3-cyclohexadione dithiosemicarbazone hydrochloride	600	$1.2 \times 10^4$	165
Potassium propyl xanthate	480	-	179
	620	-	
3-(2-Pyridyl)-5, 6-diphenyl -1,2,4-triazine	500	$4.1 \times 10^3$	197
Present method	625	$1.92 \times 10^3$	198

Table 8 : Determination of cobalt ( $135 \mu\text{g}$ ) in various mixtures with  $500 \mu\text{g}$  of each ion added

Ions added	Cobalt found ( $\mu\text{g}$ )
1. $\text{Fe}^{+3}$ , $\text{Ni}^{+2}$ , $\text{Mn}^{+2}$	132.5
2. $\text{Fe}^{+3}$ , $\text{Pb}^{+2}$ , $\text{Cr}^{+3}$	135.0
3. $\text{Ni}^{+2}$ , $\text{Bi}^{+3}$ , $\text{Sn}^{+2}$	136.0
4. $\text{Fe}^{+3}$ , $\text{Ni}^{+2}$ , $\text{Zr}^{+4}$	136.5
5. $\text{Ni}^{+2}$ , $\text{Mo}^{+6}$ , $\text{Bi}^{+3}$	133.5 <sup>b</sup>
6. $\text{Pd}^{+2}$ , $\text{Pt}^{+4}$ , $\text{Rh}^{+3}$	133.0

Section 5 : Extraction and Spectrophotometric Determination  
of Palladium

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<sup>199</sup>, in the detection and estimation of the metal.

Palladium(II) forms complex with sodiumdiethyldithiocarbonate<sup>200</sup> at pH 11. The complex is extractable into carbontetrachloride and absorbs maximum at 305 nm. Benzoylmethyl glyoxime<sup>201</sup> is also a good reagent for palladium(II).

Another important reagent for the determination of palladium is 2-nitroso-1-naphthol<sup>202</sup>. Palladium was extracted pH 1.5-3.5 into toluene in the presence of EDTA and measured at 370 or 550 nm. 1-(2-pyridylazo)-2-naphthol<sup>203</sup> forms a green chelate with Palladium(II) which can be

extracted into chloroform at pH 2-5. The absorbance was measured at 678 nm.

Palladium(II) was determined<sup>204</sup> in thiocyanate complex with thiourea at pH 5-5.5. The complex absorbs maximum at 350 nm. 1-Benzyl-3-indazolone<sup>205</sup> forms yellow 1:3 (metal : ligand) complex with Palladium(II), at pH-6, extractable into chloroform and the absorbance was measured at 400 nm. Nath Deblina and Sing A.K<sup>206</sup> devised a spectrophotometric method for the determination of palladium with substituted pyrimidine thiols and 4-amino-2,6-dimercapto-1,3,5-triazine.

Spectrophotometric method for the determination of palladium(II) with thiocaprolactum<sup>207</sup> in aqueous solution containing Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup> have been investigated. The complexes were extractable into chloroform and absorb maximum at 400 nm. Beaupre P.W et al<sup>208</sup> used 2,2'-diquinolyl ketone 2-Pyridyl for the determination of palladium. The complex was extractable into chloroform at pH 2 and the absorbance of the organic phase was measured at 624 nm.

Procedures based on the formation of palladium(II) complexes with 2-Pyridine carboxaldehyde-2-Pyridyl hydrazone<sup>209</sup>; sodium 7-(4-amino-1,2,4-triazole-3-ylazo)-1-naphthol-4-sulfonate<sup>210</sup>, 2,2' dipyridyl-2-quinolyl hydrazone<sup>211</sup>, 3-bromo-2-hydroxy-5-methyl acetophenone hydrazone<sup>242</sup>; N,N-dimethyl-N-(4-phenyl-2-thiazolyl) thiourea<sup>213</sup>;

2-furaldehyde-2-Pyridyl-hydrazone<sup>214</sup>; 1-pyrrolidine carbodithioate<sup>215</sup>; 3,5 dichloro-2-hydroxy acetophenone oxime<sup>216</sup>; 2-methyl-1,4-naphthoquinone thiosemicarbazone<sup>217</sup>; Pyridine, substituted pyridines and thiocyanate<sup>218</sup>; 2-thiopyrogallol and  $\beta$ -mercaptoresorcinol<sup>219</sup>; Eriochrome azurol B and cetyltrimethyl ammonium bromide<sup>220</sup>; 2-hydroxy-1-acetonaphthone oxime<sup>221</sup>; 2-2'-bipyridyl  $\langle$ ketone $\rangle$ -2-pyridyl hydrazone<sup>222</sup>; benzyl dimethylphenyl ammonium chloride<sup>223</sup>; thiazole-2-carboxaldehyde-2-quinolyl hydrazone<sup>224</sup>; salicyl fluorone and cetyl trimethyl ammonium bromide<sup>225</sup>, xanthates<sup>226</sup>; have been suggested by various workers.

A sensitive spectrophotometric method for the determination of palladium has been described by Jayanana Yathiranjan H.S et al<sup>227</sup> by using phenothiazine (Pz) and promazene (PM). The molar absorptivities were  $3.542 \times 10^3$  and  $9.213 \times 10^3$   $1 \text{ mol}^{-1} \text{cm}^{-1}$  for Pz and PM respectively. According to Shravah Kamini et al<sup>208</sup> Palladium(II) forms two coloured complexes, a green complex at low pH and brown complex at higher pH with phenanthraquinone monothiosemicarbazone. Both the complexes were soluble in DMF with maximum absorbance at 590 and 540 nm respectively.

At pH 3.4 Palladium forms a 1:1 complex with mesotetra-kis(4-acetoxyphenyl) porphyrin in the presence of sodium dodecyl sulphate which can be used for the determination<sup>229</sup>

at 443 nm. According to Lorenzo, E et al<sup>230</sup> palladium could be determined with picoline amidoxime. The absorbance was measured at 370 nm with molar absorptivity of  $4.9 \times 10^3 \text{ l mol}^{-1}\text{cm}^{-1}$ .

A method of photometric determination of palladium was presented by Sarkar Purabi et al<sup>231</sup> who used P-nitrodimethyl-aniline to get a brown coloured complex of palladium. The molar absorptivity of the 1:2 (metal:ligand) complex was found to be  $7.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}\text{cm}^{-1}$ . In slightly acid medium palladium(II) forms a red complex with 2-Pyridyl ketone 2-Pyridyl hydrazone<sup>232</sup> and was determined spectrophotometrically. The complex shows its absorption maximum at 545 nm.  $\alpha, \beta, \gamma, \delta$ -tetra-(4-dimethyl aminophenyl) porphine reacts with palladium in presence of sodium dodecyl benzene sulphonate and ascorbic acid to form a coloured complex, which can be used for the spectrophotometric determination of palladium<sup>233</sup>. Thokdar et al<sup>234</sup> used pyridine bases and iodide to obtain complexes of palladium, that can be used for the determination of palladium. The molar absorptivities of the complexes were found to be  $1.6-1.9 \times 10^4 \text{ l mol}^{-1}\text{cm}^{-1}$ .

In our laboratory it has been noted that palladium forms ion-association complex with iodide in presence of

cetyltrimethyl ammonium bromide<sup>235</sup>. The resulting reddish-brown coloured complex is extractable into chloroform under optimum conditions. This property of the palladium complex suggested that further study of the system might lead to the development of a simple spectrophotometric method for palladium determination which is presented here.

## EXPERIMENTAL

Apparatus and Reagents : A Shimadzu PR1 model

Spectrophotometer equipped with matched quartz cells of 10 mm optical path length was used for the absorbance measurements. An ECL 5651 digital pH meter was used to measure the acidity of the aqueous solutions. Separatory funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of palladium(II) was prepared by dissolving 1 gm palladium chloride (Johnson & Matthey) in HCl (1 ml) and diluted to 250 ml with distilled water. This was then standarised with dimethylglyoxime<sup>236</sup>. Appropriate dilution was made from this stock solution as needed.

All chemicals and solvents used were of analytical grade. Chloroform, benzene, ethylacetate, carbon-tetrachloride were distilled before used.

Solutions of potassium iodide (0.1 M) and cetyltrimethylammonium bromide (CTAB) (0.1 M) were prepared in distilled water.

Buffer solutions of different pH were prepared by standard procedures.

Potassium chloride - hydrochloric acid (pH 1-2)

Potassium hydrogen phthalate- hydrochloric acid (pH 2-4)

Potassium hydrogen phthalate - sodium hydroxide (pH 4.5 -

5.9) Potassium dihydrogen phosphate - sodium hydroxide

(pH 6-8) borax-hydrochloric acid (pH 9.5-10.8).

Standard solutions of diverse ions were prepared from their corresponding salts to study interferences.

Determination of Palladium : An aliquot containing upto 50  $\mu\text{g}$  of Pd(II) was treated with KI (0.5 ml), CTAB (0.1 ml) and volume to 10 ml. The mixture was equilibrated (30 sec) with chloroform (10 ml) and the separated organic layer was dried over anhydrous sodium sulphate. Finally the absorbance of the chloroform extract was measured at 340 nm against pure solvent. Palladium was computed from a calibration curve. To test the interference, the respective foreign ion was added to the aqueous solution before addition of the reagents.

#### RESULTS AND DISCUSSION

With aqueous potassium iodide, palladium(II) gives a reddish-brown colouration due to the formation of  $\text{PdI}_4^{2-}$ . This complex anion, as such, is not extractable into

chloroform. On addition of CTAB to this coloured solution, an ion-association complex, probably of the type  $\text{[PdI}_4\text{]}^{2-}$   $\text{[CTA]}_2^+$  is formed, which is extractable into chloroform.

Absorption Spectra : The absorption spectra of the Pd(II)-I-CTAB complex in chloroform is shown in fig.1. The complex exhibits absorption maxima at 340 nm with a broad band of comparatively lower intensity around 440 nm. The reagent blank itself shows insignificant absorbance in the aforesaid wavelength region. Wavelength of 340 nm was selected for all analytical measurements.

The pattern of the absorption spectra of the complex remains unchanged when the extractions were carried out from pH 1 to 12. This indicates the presence of single variety of complex species in the system.

Beer's law and calibration curve : The absorbances of different amounts of palladium(II), extracted as in the general procedure at pH 6.0, were noted against pure solvent at 340 nm. The absorbances show a linear response up to 5 ppm of palladium. In each case the remaining aqueous phase after a single extraction, was clear and colourless.

Furthermore, the aqueous phase was free from palladium. Table 1 shows the results (Fig.2.).

Effect of potassium iodide concentration : The variation of absorbance has been studied with different concentration of iodide keeping the CTAB concentration constant. It has been found that 0.5 ml of 0.1 M KI along with 0.1 ml of 0.1 M CTAB is sufficient to extract up to 50  $\mu\text{g}$  of palladium in a single operation. Higher concentration of KI however did not bring about any significant change in the maximum value of absorbance. The results are shown in table 2.

Effect of cetyltrimethyl ammonium bromide (CTAB) concentration : The effect of the CTAB concentration on absorbance has also been examined by varying the amount of CTAB, maintaining the other variables constant. It has been found that 0.1 ml of 0.1 M CTAB was sufficient to extract upto 50  $\mu\text{g}$  of palladium in a single operation. Higher concentration had no effect on absorbance value. Experimental results are shown in table 3.

Effect of pH : The effect of pH on the system was investigated in terms of absorbance of the Pd(II)-I-CTAB complex

in the organic phase over the pH range 1-12. Anions of the buffer had no effect on the colour development. The complex exhibits constant and maximum absorbance in the pH range 2-10.

In a second consecutive operation within the above pH range the organic extract showed no absorption. This indicates quantitative extraction of palladium in a single extraction. From 1 M HCl medium the extraction resulted incomplete recovery of the metal. When the extraction pH was greater than 10, absorbance of the organic extract was found to decrease.

The pattern of the absorption spectra of the complex extracted throughout the entire range (pH 1-10) remains unchanged, indicating the formation of a single variety of the complex species in all cases. For our practical purpose pH - 6.0 was selected.

Choice of solvent : Apart from chloroform, other solvents like carbontetrachloride, benzene, and ethylacetate were tested as the extracting solvents but these offered no special advantages over chloroform which was used as the extracting solvent in the present investigation.

Stability of colour : The rapid development of the maximum absorbance and its constancy with time indicate that time is not a critical factor in palladium determination. The absorbance of the palladium complex in chloroform was measured at elapsed interval of time. The results are summarized in table 4.

Interference : To test the effects of diverse ions on the extraction behaviour, palladium(II) was extracted and determined according to the recommended procedure in presence of the respective foreign ions. Extraction pH was set at 6.0 with  $\text{KH}_2\text{PO}_4$ -NaOH buffer. An ion was considered to interfere if the recovery of palladium differed by more than  $\pm 3\%$  from the actual amount taken. Palladium(II) (41.75  $\mu\text{g}$ ) could be determined without interference in presence of the following ions :

Al(III), Ca(II), Ba(II), Sr(II), Be(II), Bi(III), Cd(II), Ce(III), Cr(III), Co(II), Cu(II), Fe(III), V(V), La(III), Pb(II), Mg(II), Mn(II), Ni(II), Rh(III), Zn(II), Th(IV), U(VI), Mo(VI), and Zr(IV). Mercury(II) and platinum(IV) interfered. In presence of silver the organic extract becomes turbid due to some yellow precipitate.

Among the anions tested the followings are tolerable : EDTA, fluoride, ascorbate, citrate, tartarate, phosphate,

borate, phthalate. Thiocyanate interfered. In presence of thiosulphate palladium is not extracted. The results are shown in Table 5.

Precision and accuracy : The precision and accuracy of the method were tested by analysing solutions containing a known amount of palladium following the recommended procedure. The results are shown in table 6. The process is very simple and rapid requiring hardly 10-15 min for each run.

Application to the analysis of synthetic mixtures : The applicability of the proposed method was tested by analysing some synthetic mixtures. The composition of the mixtures with percentage recovery of palladium are shown in table 7. The results show that the recovery of palladium was satisfactory. Average of three determination was taken in each case.

The sensitivity of the method has also been compared to those of some other existing methods as seen from Table 8.

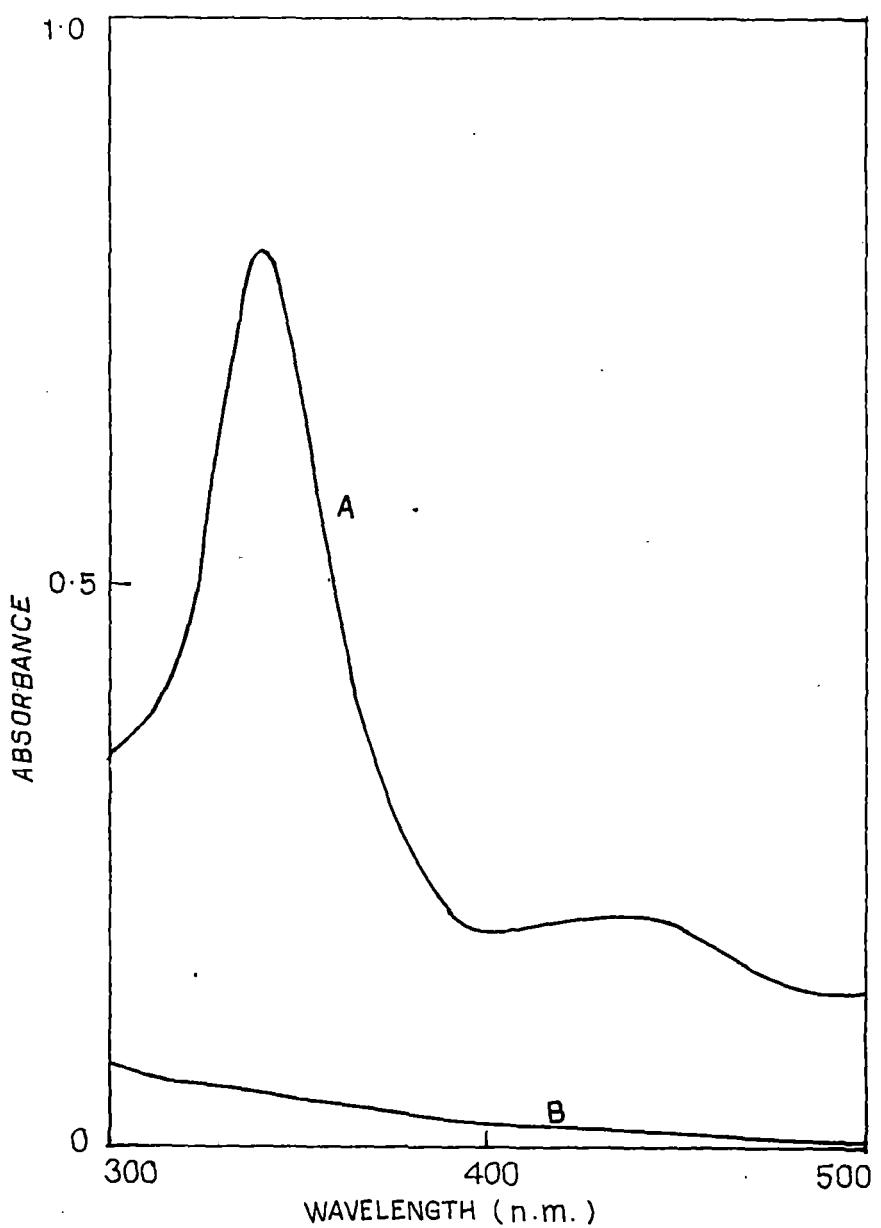


Fig-1. ABSORBANCE SPECTRA OF (A) Pd(II)-I-CTAB COMPLEX (4.17 ppm Pd) and (B) REAGENT BLANK .

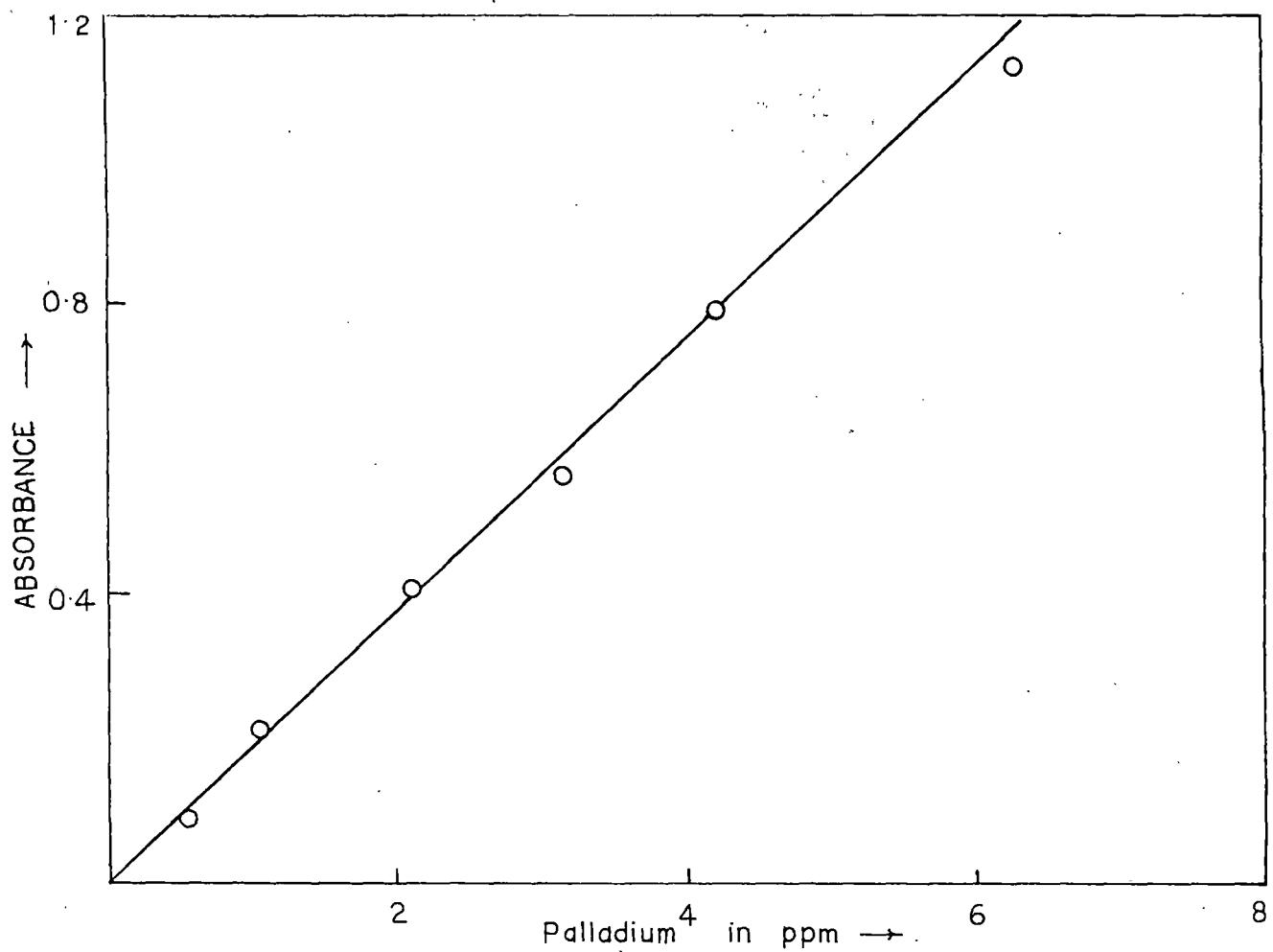


Fig 2. BEER'S LAW ( Pd-I- CTAB System )

Table 1 : Adherence to Beer's law

Palladium taken in $\mu\text{g}$	Absorbance at 340 nm
5.22	0.090
10.44	0.215
20.87	0.410
31.31	0.570
41.75	0.799
62.62	1.135

Table 2 : Effect of 0.1 M Potassium iodide concentration

The aqueous phase (10 ml) contains 41.75  $\mu\text{g}$  of Pd(II) and 0.1 ml of 0.1 M CTAB. Extraction pH-6.0

Amount of KI added in ml	Absorbance at 340 nm
0.1	0.560
0.2	0.770
0.3	0.795
0.4	0.790
0.5	0.795
0.6	0.800
0.8	0.795
1.0	0.790

Table 3 : Effect of CTAB concentration

The aqueous phase contains 41.75  $\mu\text{g}$  of palladium and 0.5 ml of 0.1 M KI. Extraction pH-6.0

CTAB concentration in M	Amount added in ml	Absorbance at 340 nm
0.05	0.05	0.550
0.05	0.1	0.780
0.1	0.05	0.790
0.1	0.1	0.795
0.2	0.05	0.790
0.2	0.1	0.795
0.3	0.1	0.805

Table 4 : Variation of absorbance with time

Pd(II) taken 41.75  $\mu\text{g}$

Time in hr after extraction	Absorbance at 340 nm
0.25	0.799
0.5	0.790
1.0	0.800
6.0	0.795
12.0	0.799
24.0	0.795

Table 5 : Effect of diverse ions in the determination of palladium(II)

Palladium(II) taken 41.75  $\mu\text{g}$ . Extraction pH 6.0

Ion added	Amount tolerated (mg)	Palladium found ( $\mu\text{g}$ )	Error %
Al(III)	9.0	42.0	0.6
Ca(II)	9.0	42.5	1.8
Ba(II)	10.0	40.8	2.2
Sr(II)	10.0	41.5	0.6
Be(II)	9.0	40.8	2.2
Bi(III)	8.5	42.5	1.8
Cd(II)	8.0	40.5	2.9
Ce(III)	8.0	40.8	2.2
Cr(III)	8.0	41.0	1.8
Co(II)	8.0	41.0	1.8
Cu(II)	8.0	40.5	2.9
Fe(III)	9.0	40.8	2.2
V(V)	8.0	41.5	0.6
La(III)	8.0	41.5	0.6
Pb(II)	9.0	41.0	1.8
Mg(II)	9.0	41.5	0.6
Mn(II)	9.0	41.2	1.3
Ni(II)	10.0	41.2	1.3
Rh(III)	6.0	40.8	2.2
Zn(II)	8.0	41.0	1.8

Contd...

Table 5 contd ...

Th(IV)	3.5	42.5	1.8
U(VI)	4.0	42.5	1.8
Mo(VI)	3.0	42.8	2.5
Zr(IV)	4.0	40.2	3.7
Hg(II)	nil	-	-
Pt(IV)	nil	-	-
Ag(I)	nil	-	-
EDTA	18.0	40.5	2.9
fluoride	20.0	41.2	0.6
ascorbate	20.0	41.2	1.3
citrate	20.0	41.0	1.8
tartarate	20.0	42.0	0.6
phosphate	25.0	42.2	1.0
borate	25.0	40.8	2.2
phthalate	25.0	40.5	2.9
thiocyanate	nil	-	-
thiosulphate	nil	-	-

Table 6 : Reproducibility of palladium recovery

Palladium taken ( $\mu$ g)	Palladium found ( $\mu$ g)	Mean ( $\mu$ g)	Std. devia- tion %
10.44	9.2, 9.2, 10.0 10.5, 9.5, 9.0	9.56	0.57
20.87	20.0, 21.5, 21.0 22.0, 19.8, 19.8	20.68	0.94
41.75	41.5, 40.5, 41.8 39.8, <del>40.5</del> , 42.3	41.0	0.95

Table 7 : Determination of palladium (41.75  $\mu$ g) in various mixtures

Composition with amount taken ( $\mu$ g)	Recovery of palladium %
Cr (200), Rh(200), Fe(200)	101
Rh (200), Fe(200), Ni(200)	101
Fe (200), Ni(200), Co(200)	99
Cr (200), Co(200), Al (200)	98

Table 8 : Sensitivities of some other existing methods - A comparison

Reagent	$\lambda_{\text{max}}$ nm	molar absorptivity $1 \text{ mol}^{-1}\text{cm}^{-1}$	Sensi- tivity $\mu\text{g}/\text{cm}^2$	Ref.
2-thiobarbituric acid	374 in water	$1.0 \times 10^4$	0.0106	237
	386 in ETOH	$7.5 \times 10^3$	0.0146	
3-bromo-2-hydroxy-5-methyl acetophenone hydrazone	400	$4.5 \times 10^3$	0.0235	212
2,2-di pyridyl-2-quinolyl hydrazone	570	$14 \times 10^3$	0.0076	211
Xanthates	-	$(1.76-1.9) \times 10^2$	0.5-0.65	226
N-naphthyl-N'-pyridyl thiourea	390	$3.4 \times 10^4$	0.0096	238
Phenanthrazinone-mono thiosemi-carbazone	590	-	0.025	228
	540	-	0.0083	
n-butyl xanthate	385	$1.319 \times 10^4$	0.008	239
2-Mercapto acetamide	320	$3.2 \times 10^4$	0.016	240
2-hydroxy-3,5-dimethyl acetophenone oxime	400	$1.08 \times 10^3$	0.10	241
Potassium iodide and substituted pyridines	354-360	$(1.5-1.9) \times 10^4$	0.1-0.018	234
Present method	340	$2.038 \times 10^4$	0.0052	235

Section 6 : Extraction and Spectrophotometric Determination of Platinum

INTRODUCTION

The principal methods for the liquid-liquid extraction of platinum involved the utilisation of different organic reagents such as theonyltrifluoroacetone, dithizone, dithiocarbamates, tributylphosphate, dithiophosphoric acid, thiosemicarbazide, high molecular weight amines etc. In most of the cases the organic phases after extraction have been utilised for the colourimetric determination of the metal. Some of the recent methods are cited here.

Khopkar S.M<sup>242</sup> utilized Molecular and ionassociation compounds for the spectrophotometric determination of platinum from 5 M HCl medium into mesityloxide. In presence of iodide or thiocyanate platinum gets extracted into tributylphosphate<sup>243</sup>. 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<sup>+2</sup> acted as catalyst. This 1:1 (metal:ligand) complex can be used for the determination<sup>244</sup> of the metal. The absorbance was measured at 504 nm. Bhandari C.S et al<sup>245</sup> suggested a method for the determination of platinum(IV) using 1,3 diamino-8-methoxy phenothiazine. The reagent forms an intense yellow complex at pH 0.8-4.5. The absorbance was read at 460 nm. Another method is based on the formation of a greenish-brown 1:1 complex with mepazine hydrochloride<sup>246</sup> in the HCl-NaOAc (pH 2-4). The complex absorbs maximum at 514 nm. Gowda H.Sanke and Padmaji K.A<sup>247</sup> determined platinum(IV) spectrophotometrically by reaction with chloropromazine hydrochloride in 5 (M) H<sub>3</sub>PO<sub>4</sub> solution containing CuSO<sub>4</sub> as a catalyst. Beaupre P.W et al<sup>248</sup> utilized 2-Pyridyl-2-thienyl-Z-keroxime for the determination of Platinum(II) spectrophotometrically. The 1:2 (metal:ligand) complex was extractable into chloroform and the absorbance of the organic phase was measured at 473 nm. Platinum forms a 1:2 (metal:ligand) complex with 4-5-benzyl-1-P-chlorophenyl-5-phenyl-2,4 dithiobiuret in 4 M HCl medium. The complex was extractable into chloroform and the absorbance of the organic extract was read at 407 nm for determination platinum<sup>249</sup>. Some other methods involve the utilization of promazine hydrochloride<sup>250</sup>, thiazolylazo compounds<sup>251</sup>, N-phenyl-N'-(2-Pyridyl)thiourea<sup>252</sup>,

P-dimethylaminobenzylidene rhodamine<sup>253</sup>, methyl green<sup>254</sup>, propionyl promazine phosphate<sup>255</sup>, O-mercuто acetanilide<sup>256</sup>, 2-furan carbothioic acid hydrazide<sup>257</sup>, methopromazine<sup>258</sup>, crystal violet<sup>259</sup>, phenanthrenequinone monothiosemicarbazone<sup>260</sup>, 2-oximino-1-indanone<sup>261</sup>, substituted pyrimidine-2-thiol<sup>262</sup>, phenothiazine derivatives<sup>263</sup>, 4,4'-bis(dimethylamino) thienbenzophenone<sup>264</sup>, phenanthraquinoneximate<sup>265</sup>, and  $\text{N}^4\text{-}(5\text{-chloro-2-pyridyl})$  azo -1,3 diaminobenzene<sup>266</sup> for the spectrophotometric determination of platinum.

Chang Wenbao<sup>267</sup> et al found that platinum(II) gives a colour reaction with 4,4'-bis (diethylamino) thienbenzophenone, which could provide a method for its determination spectrophotometrically. A mixed ligand complex of platinum has been investigated by Thokdar T.K<sup>268</sup> et al using Pyridine,  $\alpha$ -Picoline,  $\beta$ -picoline,  $\gamma$ -picoline or 2,4,6 collidine in presence of iodide for the spectrophotometric determination of platinum(IV). The complexes were extractable into chloroform.

In 0.64 M HCl (or  $\text{H}_2\text{SO}_4$ ) medium Platinum(II) reacts with 4-(3,5 dibromo-2-Pyridylazo)-2-methyl-1,5-diamino benzene<sup>269</sup> forming a 1:1 (metal:ligand) complex. The absorbance of the complex was read at 616 nm for determination of platinum. An ion-association complex containing bromoplatenate and nile blue B was studied by Geokehyan N.O<sup>270</sup> et al. Extraction was carried out from aq  $\text{H}_2\text{SO}_4$

solution (pH 1-3). Paria P.K<sup>271</sup> et al studied the use of isonitrosothiocamphor as a reagent for the spectrophotometric determination of platinum(IV). The greenish chelate was extractable into chloroform and the absorbance of the chloroform extract was measured at 369 nm.

In our laboratory it has been noted that platinum forms an ion-association complex with cetyltrimethyl ammonium bromide (CTAB) in presence of potassium iodide. The greenish complex is extractable into ethylacetate. This property of the platinum complex suggested that further studies of the system might lead to the development of a simple spectrophotometric method for the determination of platinum which is described here.

## EXPERIMENTAL

### Apparatus and Reagents :

Spectral curves and analytical measurements were made with a Shimadzu PR1 model spectrophotometer equipped with matched quartz cells of 10 mm optical path length. An ECL 5651 digital pH meter was used to measure the acidity of the aqueous phase. Separatory funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of platinum(IV) was prepared by dissolving 1 gm chloroplatinic acid (Johnson & Matthey) in 100 ml distilled water followed by its standarization<sup>273</sup>. Solution of lower concentration of the metal was prepared by appropriate dilution of the stock.

All the chemicals and solvents used were of analytical grade. Ethylacetate, benzene, chloroform, 1,2 dichloroethane, carbontetrachloride were distilled before used.

Solutions of 0.05 M potassium iodide and 0.1 M cetyltrimethylammonium bromide were prepared in distilled water.

Standard solutions of diverse ions were prepared from their corresponding salts to study interferences.

Determination of platinum :

An aliquot containing 30  $\mu\text{g}$  of Pt(IV) was transferred to a 50 ml separatory funnel. To this were added 0.1 ml of 0.05 M potassium iodide and 0.1 ml of 0.1 M CTAB solution followed by adequate amount of hydrochloric acid and water to make the aqueous volume up to 10 ml and 0.5 M with respect to hydrochloric acid. It was then equilibrated with 10 ml ethylacetate for 30 sec. After phase separation the organic layer was poured over anhydrous sodiumsulphate to remove any associated water droplets. Finally the absorbance of the ethylacetate extract was measured at 290 and 360 nm against a reagent blank prepared under identical conditions. Amount of platinum was computed from a 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

When potassium iodide is added to a neutral or slightly acidic solution containing platinum(IV), a reddish-brown colouration due to the formation of  $\text{PtI}_6^{2-}$  is formed. This complex anion is not extractable into ethylacetate. On addition an aqueous solution of cetyl-trimethylammonium bromide (CTAB) to this coloured solution,

an ion-association complex probably of the type  $\text{[PtI}_6\text{]}_2^{+}$  is formed. This is extractable into ethylacetate.

Absorption spectra : The absorption spectrum of the platinum -I-CTAB complex extracted into ethylacetate is shown in fig.1. The complex shows absorption maximum at 290 and 360 nm. The reagent blank absorbs strongly at 250 nm and it becomes insignificant beyond 290 nm. Wavelength of 290 or 360 nm may be selected for analytical measurements.

Beer's law and calibration curve :

Different amounts of platinum(IV) extracted as in the general procedure from 0.5 M HCl medium and the corresponding absorbances were noted against a blank at 290 and 360 nm. The absorbances show a linear response up to 3 ppm of platinum(IV). In each case the remaining aqueous phase, after a single extraction was clear and colourless. Furthermore the aqueous phase, as tested by an independent method, was void of platinum. The results are shown in table 1 and Fig.2. The molar absorptivities of the complex (based on platinum content), were found to be  $5.36 \times 10^4$  and  $3.08 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1}$  and sensitivities 0.0036 and

0.0063  $\mu\text{g}/\text{cm}^2$  at 290 and 360 nm respectively.

Effect of potassium iodide concentration :

The effect of iodide concentration on absorbance has been tested when the other variables remain fixed. It has been found that 0.1 ml of 0.05 M KI along with 0.1 ml of 0.1 M CTAB is sufficient to extract 30  $\mu\text{g}$  of platinum in a single operation. Higher concentration of KI did not bring about any significant change in the maximum value of absorbance. Table 2 shows the effect of KI concentration on absorbance of the Pt(IV) complex.

Effect of CTAB concentration :

As regards the reagent, 0.1 ml of 0.1 M CTAB was quite adequate for quantitative extraction of 30  $\mu\text{g}$  of platinum. Below 0.05 ml of 0.05 M CTAB, the organic extract was found to give low absorbance values. Increased concentration had no effect on the maximum value of absorbance. The results are shown in the table 3. Order of adding the reagents had no effect on colour development.

Effect of acidity :

The effect of acidity on the extractability of Pt(IV) into ethylacetate was examined in terms of absorbance of the complex. The complex exhibits constant and maximum absorbance when the extractions were carried out from 0.1 - 1 M hydrochloric acid medium. In a second consecutive operation within this acidity range, the organic extract virtually showed no absorption. This indicated a quantitative extraction of platinum in a single operation. Below 0.1 M HCl concentration, the absorbance value was found to decrease. However concentration above 1 M HCl should be avoided because the reagent blank develops strong colouration with considerable absorption in the aforesaid wavelength region. For our practical purpose the aqueous phase was maintained at 0.5 M HCl with respect to HCl.

Effect of solvents :

Apart from ethylacetate other solvents like benzene, chloroform, 1,2-dichloroethane and carbontetrachloride were tested as the extracting solvents but those offered no special advantage over ethylacetate. The complex however is not extracted into carbontetrachloride.

Stability of colour :

The rapid development of the maximum colour and its absorbance with time indicate that time is not a critical factor in platinum determination. The absorbance of the ethylacetate extract was measured at different intervals of time. The colour of the ethylacetate extract was found to be stable for 24 hrs and the results are shown in table 4.

Interference :

In order to study the effects of diverse ions on the extraction behaviour, Pt(IV) was extracted and determined according to the general procedure in presence of the desired foreign ion. The tolerance limit was set at that amount of foreign species for which platinum could be recovered within  $\pm 3\%$  error. Platinum(IV) (30  $\mu\text{g}$ ) could easily be determined without interference in presence of the following ions Co(II), Ni(II), Cu(II), Pd(II), Fe(III), Cd(II), Zn(II), Mo(VI), V(V), Mn(II), U(VI), Zr(IV), Rh(III), Pb(II), Al(III), Ca(II), Ba(II), Sr(II), Be(II), Bi(III), Ca(III), Cr(III), La(III) and Mg(II). The system develops no colour in presence of mercury(II) and thorium(IV). In presence of silver, formation of some yellowish precipitate hampers the procedure.

Amongst the anions tested the following did not interfere in the estimation of platinum; borate, phosphate, tartarate, citrate, fluoride, phthalate, ascorbate, oxalate and EDTA. In presence of nitrate high results are obtained. However thiosulphate, thiocyanate and thiourea must be absent as these inhibit the colour development. The results are summarised in the table 5.

Precision and accuracy :

The precision and accuracy of the proposed method were tested by analysing solutions containing a known amount of platinum following the recommended procedure. The results are shown in table 6. The process is very simple and rapid requiring only 10-15 min for each run.

Application : Analysis of Synthetic mixtures :

The applicability of the proposed method was tested by analysing some synthetic mixtures. The composition of the mixtures with percentage recovery of platinum are shown in table 7. The results show that the recovery of platinum was highly satisfactory. Average of three determination was taken in each case.

The method has been compared to some other existing methods (Table 8).

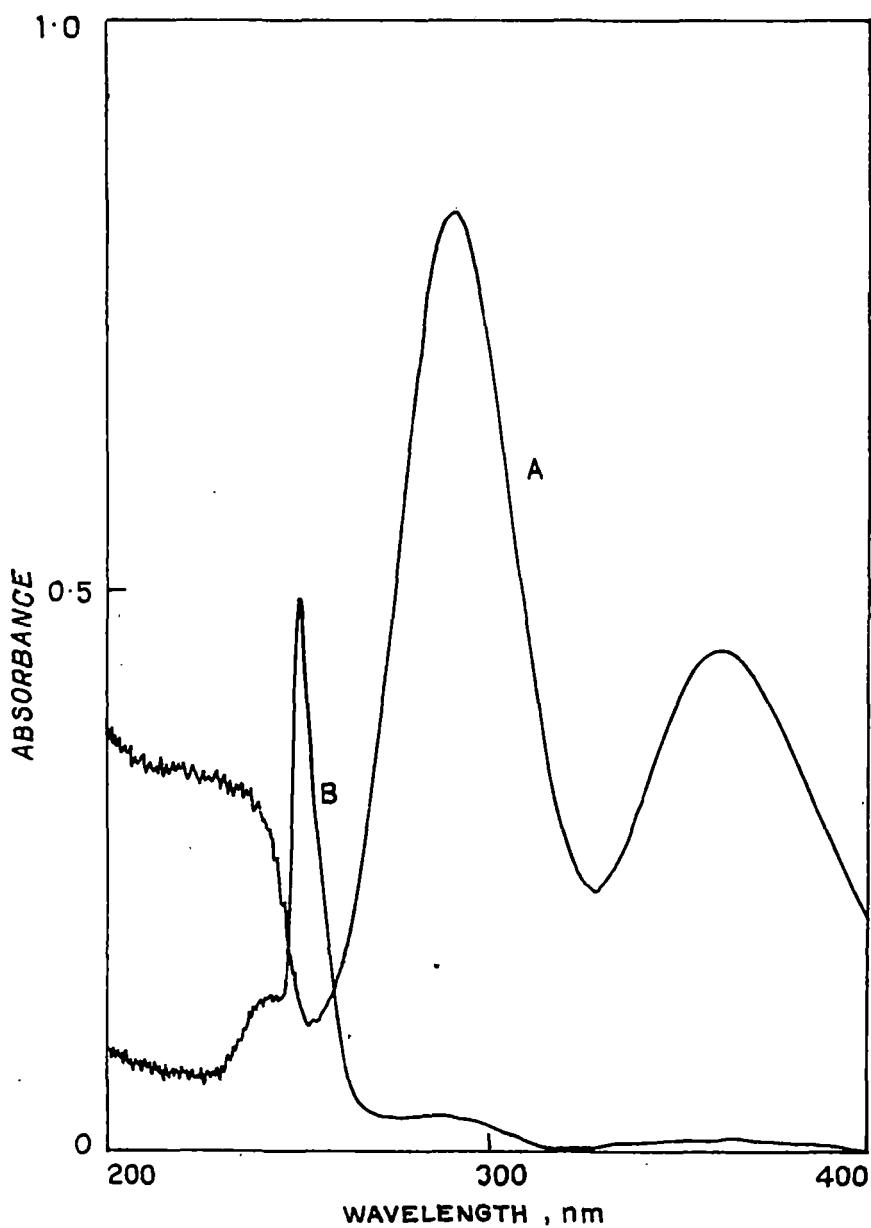


Fig-1: ABSORBANCE SPECTRA OF (A) Pt(IV)-CTAB COMPLEX (3 ppm Pt) AND (B) REAGENT BLANK

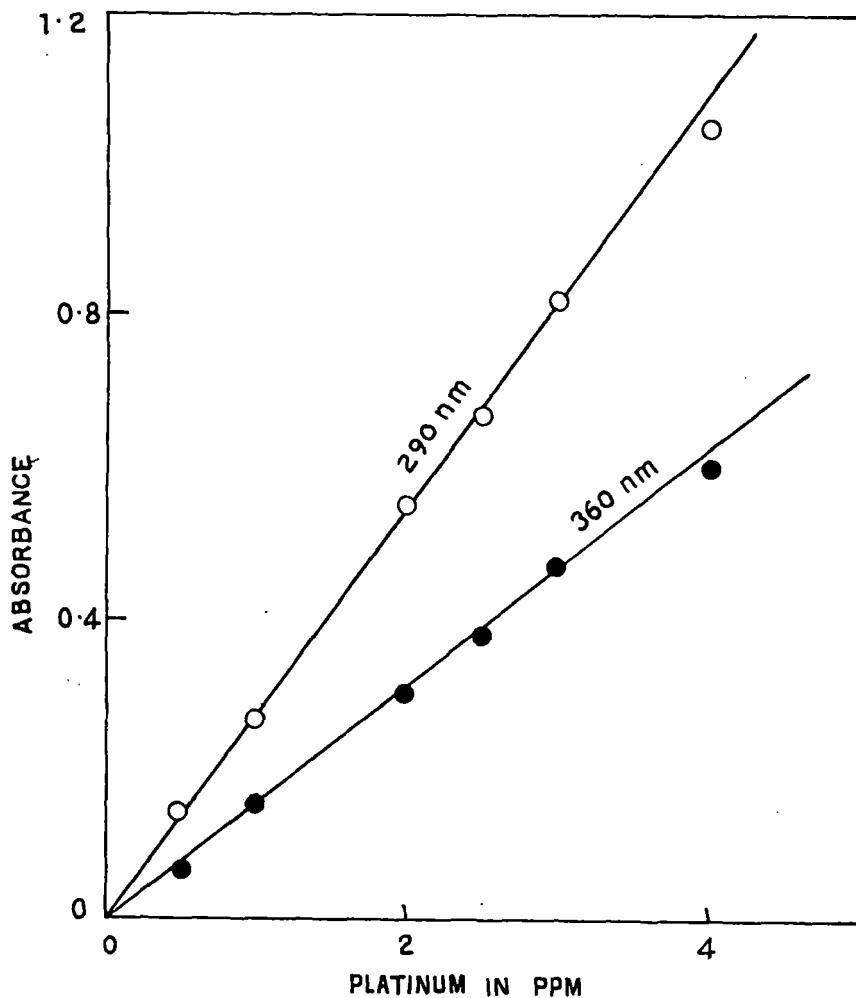


Fig - 2 : BEER'S LAW ( Pt - CTAB system )

Table 1 : Adherence to Beer's law

Platinum(IV) ( $\mu\text{g}$ )	Absorbance at 290 nm	Absorbance at 360 nm
5	0.140	0.600
10	0.260	0.150
20	0.552	0.300
25	0.670	0.380
30	0.824	0.473

Table 2 : Effects of KI concentration

The aqueous phase (10 ml) contains 30  $\mu\text{g}$  of Pt(IV) and 0.1 ml of 0.1 M CTAB. Extraction - 0.5 M HCl medium

KI concentration (M)	Amount added (ml)	Absorbance at 290 nm	Absorbance at 360 nm
0.025	0.05	0.550	0.060
0.025	0.1	0.705	0.204
0.05	0.1	0.824	0.473
0.1	0.1	0.825	0.473
0.15	0.1	0.824	0.472
0.20	0.1	0.824	0.472
0.25	0.1	0.824	0.472

Table 3 : Effect of CTAB concentration

The aqueous phase (10 ml) contains (30  $\mu$ g) Pt(IV) and 0.1 ml of 0.5 KI. Extraction - 0.5 M HCl medium

CTAB concentration (M)	Amount added (ml)	Absorbance at	
		290 nm	360 nm
0.025	0.05	0.550	0.060
0.025	0.10	0.750	0.250
0.05	0.05	0.825	0.470
0.05	0.1	0.824	0.470
0.1	0.1	0.824	0.472
0.15	0.1	0.822	0.472
0.20	0.1	0.824	0.470

Table 4 : Variation of absorbance with time

Time in hr after extraction		Absorbance at	
		290 nm	360 nm
0.25		0.824	0.473
0.50		0.824	0.473
1.0		0.824	0.473
2.0		0.820	0.471
6.0		0.822	0.470
12.0		0.820	0.470
24.0		0.820	0.470

Table 5 : Effect of diverse ions

Pt(IV) taken 30  $\mu\text{g}$ ; Extraction from 0.5 M HCl medium  
 Absorbance measured at 290 nm

Ion added	Amount tolerated (mg)	Platinum found ( $\mu\text{g}$ )	Error (%)
Co(II)	3.0	29.2	2.65
Ni(II)	3.5	29.5	1.66
Cu(II)	2.5	29.2	2.66
Pd(II)	3.0	30.8	2.66
Fe(III)	3.5	30.5	1.66
Cd(II)	3.5	29.6	1.33
Zn(II)	3.0	29.6	1.33
Mo(VI)	3.5	30.0	0
V(V)	4.0	30.0	0
Mn(II)	4.0	29.4	2.0
U(VI)	3.5	29.6	1.33
Zr(IV)	4.0	29.5	1.66
Rh(III)	3.0	29.5	1.66
Pb(II)	5.0	30.3	1.0
Al(III)	5.5	30.1	0.33
Ca(II)	6.5	30.0	0
Ba(II)	6.5	29.8	0.66
Sr(II)	6.5	29.8	0.66
Be(II)	5.0	30.1	0.33
Bi(III)	2.5	29.4	2.0

contd ...

Table 5 contd ...

Ce(III)	3.5	29.5	1.66
Cr(III)	4.0	29.5	1.66
La(III)	5.0	29.6	1.33
Mg(II)	6.0	29.8	0.66
Hg(II)	nil	-	-
Th(IV)	nil	-	-
Ag(I)	nil	-	-
Borate	5.0	29.5	1.66
Phosphate	6.0	30.2	0.66
Tartarate	6.5	30.0	0
Citrate	7.0	29.6	1.33
Floride	7.0	30.4	1.33
Phthalate	6.0	30.0	0
Ascorbate	6.0	29.4	2.0
Oxalate	6.5	29.6	1.33
EDTA	5.5	29.4	2.0
Nitrate	nil	-	-
thiosulphate	nil	-	-
thiocyanate	nil	-	-
thiourea	nil	-	-

Table 6 : Reproducibility of platinum recovery  
Absorbance measured at 290 nm

Platinum taken ( $\mu\text{g}$ )	Platinum found ( $\mu\text{g}$ )	Mean ( $\mu\text{g}$ )	Std. deviation (3)
5	5.0, 4.5, 4.8	4.98	0.43
	5.5 5.5, 4.6		
15	15.0, 14.6, 14.5	14.96	0.48
	15.6, 15.5, 14.6		
30	29.6, 29.5, 29.0	29.25	0.42
	29.5, 29.5, 28.5		

Table 7 : Determination of platinum ( $30 \mu\text{g}$ ) in various mixtures. Absorbance measured at 290 nm

Comparison with amount taken ( $\mu\text{g}$ )	Recovery of platinum (%)
1. Pd (100), Rh (100), Fe (100)	101
2. Rh (100), Fe (100), Co (100)	99
3. Fe (100), Co (100), Ni (100)	98
4. Rh (100), Mo (100), V (100)	98

Table 8 : Comparison

Reagent	Absorp- tion maxima (nm)	Molar absorptivity $1 \text{ mol}^{-1} \text{cm}^{-1}$	Sandell 's sensi- tivity $\mu\text{g}/\text{cm}^2$	Ref.
1,3 Cyclohexanedione bis thiosemicarbazone	375	$1.0 \times 10^4$	0.0195	274
1-Pyridyl-4-4, 6 tri- methyl-1-H, 4H-Pyri- midine-2 thiol	430	$5 \times 10^3$	.039	262
Phenanthraquinone monoximate	425	$1.755 \times 10^4$	.011	265
Propionyl promazine phosphate	512-516	$5.95 \times 10^3$	.032	255
O-Marcptoace to acetanilide	593	$9.56 \times 10^3$	0.019	256
2-Furan carbothioic acid hydrazide	710	33860	.0057	257
1,3-diamino-8-methoxy phenothiazine	460	$11.20 \times 10^3$	0.0246	245
Promethazine hydrochloride	406	$1.001 \times 10^4$	$0.195 \text{ mg}/\text{cm}^2$	250
Chloropromazine hydrochloride	400	$1.886 \times 10^4$	$9.8 \text{ mg}/\text{cm}^2$	247
Present method	290	$5.36 \times 10^4$	0.0036	272
	360	$3.08 \times 10^4$	0.0063	

Section 7 : Extraction and Spectrophotometric Determination  
of molybdenum

INTRODUCTION

Use of thiocyanate complexation as a method for chemical separation has been known since long. Bock<sup>275</sup> intensively studied the distribution of metal thiocyanates into ethyl ether at various ammonium thiocyanate concentration. It has been observed that Mo(V) is extracted well over a wide range of thiocyanate concentration. Some of the well known methods for the determination of molybdenum involves the utilization of acetyl acetone<sup>276</sup>, 8-quinolinol<sup>277</sup>, toluenedithiol<sup>278</sup> and tricetylamine<sup>279</sup>. Dhara and Khopkar<sup>280</sup> extracted Mo(VI) with 20% tri-n-butyl phosphate into chloroform from 6 M HCl/4M LiCl.

Traces of molybdenum in minerals is determined spectrophotometrically<sup>281</sup> as the 1:1:1 (Mo:bromopyrogallol red:cetyl pyridinium) complex in 0.1-0.3 M HCl medium in presence of small amount of EtOH and ascorbic acid. The maximum absorbance of the complex is at 630 nm.

Tananai Ko and Gorenshstein<sup>282</sup> have determined molybdenum(VI) spectrophotometrically with 1,10-phenanthroline and bromopyrogallol red. The complex absorbs maximum at 610 nm.

Nytko et al<sup>283</sup> method for the spectrophotometric determination of molybdenum is based on reduction of molybdenum with hydrazine sulphate in HCl medium to Mo(IV) and reaction of the latter with NH<sub>4</sub>SCN and lobeline, and extraction of the ternary complex into chloroform. The absorbance of the organic phase was measured at 465 nm. Another spectrophotometric method for the determination of molybdenum involves the utilization of N-hydroxy-N-p-tolyl-N-(3,4 dimethyl phenyl) benzylamidine<sup>284</sup> in the presence of thiocyanate. The red orange complex shows a sharp maximum at 470 nm.

The following reagents have been suggested by different workers for the photometric determination of molybdenum : pyrogallol red and cetyltrimethyl ammonium bromide<sup>285</sup>,  $\beta$ -diketones<sup>286</sup>, amidine and thiocyanate<sup>287</sup>, salicylfluorone and cetyl trimethyl ammonium bromide<sup>288</sup>, thiocyanate and amidopyridine<sup>289</sup>, 1,4-dihydroxy phthalimide dithiosemicarbazone, 8-hydroxy-5-quinoline sulfonic acid and trioctylammonium chloride<sup>290</sup>, promethazine hydrochloride and thiocyanate<sup>292</sup>, thiocyanate and amides<sup>293</sup>, 4,5-dibromophenyl fluorone and cetyltrimethyl ammonium bromide<sup>294</sup>, 1,5-diphenyl carbazone<sup>295</sup>, thiocyanate and

acetone thiosemicarbazone<sup>296</sup>, 2,3,4-trihydroxy-2-azo-(p-aminobenzene sulfonamide)-5-ethyl-1,3,4-thioadiazole<sup>297</sup>, thiocyanate and adogen<sup>298</sup>, potassium thiocyanate and benzyl trimethyl ammonium chloride<sup>299</sup>, 2-benzylidenimino benzo hydroxamic acid and 2-salicylideneimino benzo hydroxamic acid<sup>300</sup>, 2,4-dithiobiuret<sup>301</sup>, benzyl trimethyl ammonium chloride<sup>302</sup>, malachite green and O-chloromandelic acid<sup>303</sup>, 3-hydroxy flavone<sup>304</sup>, benzyltrimethyl phenyl ammonium chloride<sup>305</sup>, p-aminophenyl fluorone and cetyltrimethylammonium bromide<sup>306</sup> and 4,6-di-tert-butyl-3-methoxy catechol and malachite green<sup>307</sup>.

Rao S. Brahmaji<sup>308</sup> suggested a colour reaction between salicylaldoxime and sodium molybdate in the presence of isoniazid in acetic acid for the determination of molybdenum(VI) spectrophotometrically. The complex has an absorption maximum at 430 nm.

Tarek et al<sup>309</sup> determined molybdenum spectrophotometrically in some alloys and steels using quinalizarin and cetylpyridinium chloride. The absorbance of the complex was measured at 580 nm. Martinez<sup>310</sup> et al determined molybdenum in vegetal tissues, soils and pharmaceutical compounds with mandelohydroxamic acid and methyl trioctyl ammonium cation. The absorbance of the yellow complex was measured at 375 nm.

In the present investigation it has been noted that molybdenum(VI) forms an ion-association complex with thiocyanate and cetyltrimethyl ammonium bromide (CTAB). Extraction of this complex into benzene may yet be another approach, in addition to the earlier ones, for micro determination of molybdenum, which we present here.

## EXPERIMENTAL

Apparatus and Reagents : A Shimadzu PR1 model recording spectrophotometer with matched quartz cells of 10 mm optical path length was used for the absorbance measurements. All the pH measurements were carried out with an ECL 5651 digital pH meter. Separatory funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of molybdenum(VI) was prepared by dissolving 0.9472 gm of ammonium molybdate in 250 ml of distilled water. This was standarised gravimetrically with 8-hydroxyquinoline<sup>311</sup>. Test solutions were prepared by appropriate dilution of the stock. All the chemicals and solvents used were of analytical grade. Benzene, chloroform, ethylacetate, carbontetrachloride, 1,2-dichloroethane were distilled before used. Solutions of ammonium thiocyanate (3M), cetyltrimethylammonium bromide (CTAB) (.1M) and thiourea (2M) were prepared in distilled water.

Standard solutions of diverse ions were prepared as before, to study interferences.

Determination of molybdenum : To a sample solution of molybdenum ( $40 \mu\text{g}$ ) were added aqueous solutions of thiourea

(4 ml), ammonium thiocyanate (2 ml) and CTAB (1 ml), followed by addition of hydrochloric acid to make the volume of the aqueous phase to 10 ml and 2M with respect to HCl. The mixture was then equilibrated (30 sec) with benzene (10 ml). The separated organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. Finally the absorbance of the benzene extract was read at 330 nm and 460 nm against a blank. The amount of molybdenum was computed from a calibration curve. To test the interferences the respective foreign ion was added individually to the system before addition of the reagents.

### RESULTS AND DISCUSSION

In acid solution and in the presence of thiourea, thiocyanate gives an orange yellow colour with molybdenum(VI). The coloration is due to the formation of a thiocyanate complex of quinquevalent molybdenum, which by itself is not extractable into benzene. Cetyl trimethyl ammonium bromide (CTAB) interacts with the thiocyanate complex of molybdenum, which is presumably  $\text{Mo}(\text{SCN})_6^{2-}$ , yielding the ion-pair,  $\text{[CTA]}^+ \text{[Mo}(\text{SCN})_6^{2-}]$ . This is extractable into benzene.

Absorption spectra : The spectrum of the Mo-SCN-CTAB complex in benzene taken against reagent blank as the reference has

been shown in fig.1. The complex, as evident from the spectrum exhibits absorption maxima at 330 and 460 nm. The reagent blank shows insignificant absorbance in this region.

The pattern of the absorption spectra of the complex remains unchanged when extracted from 0.5 M HCl to 5 M HCl medium. This indicates the formation of a single variety of the complex species in all cases.

#### Beer's law and calibration curves :

The absorbance of the orange-yellow Mo-SCN-CTAB complex shows a linear response up to 10 ppm of molybdenum when measured at 330 nm and 460 nm. Different amounts of molybdenum were taken and extracted following the general procedure at 2 M HCl medium. The results have been presented in table 1 and Fig.2. The aqueous phase after extraction was clear and colourless. The molar absorptivities of the complex works out to be  $2.21 \times 10^4$  (330 nm) and  $1.97 \times 10^4$  (460 nm)  $1 \text{ mol}^{-1} \text{ cm}^{-1}$  with Sandell's sensitivities of 0.0043 (330 nm) and 0.0048 (460 nm)  $\mu\text{g}/\text{cm}^2$ .

Effect of thiocyanate concentration : The extent of absorbance of the Mo-complex has been examined with different

amount of thiocyanate keeping all other variables constant. It was found that 0.5 ml of 3 M ammonium thiocyanate along with 1 ml of .1 M CTAB and 4 ml of 2 M thiourea is sufficient to extract 40  $\mu\text{g}$  of molybdenum in a single operation. For our practical purpose 2 ml of 3 M  $\text{NH}_4\text{SCN}$  was used. Increased concentration of thiocyanate did not bring about any significant change in the maximum value of absorbance. Concentration below the optimum mark should be avoided. The results are shown in table 2.

#### Effect of Cetyltrimethylammonium bromide concentration :

The effect of the CTAB concentration on absorbance has also been studied by varying the CTAB concentration maintaining the other variables constant. It has been found that .5 ml of  $2.3 \times 10^{-3}$  M CTAB was sufficient to extract 40  $\mu\text{g}$  of molybdenum. For our practical purpose, however, a higher concentration i.e. 1 ml of 0.1 M CTAB was used as higher concentration had no effect on absorbance value. Experimental results are shown in table 3.

#### Effect of the presence of thiourea :

Presence of thiourea in the reaction mixture played a role in reducing molybdenum(VI) to molybdenum(V)<sup>304</sup> and

also enhance the rate of formation and stability of the coloured complex. Concentration of aqueous thiourea below 2 M (.5 ml) causes lower absorbance value. Higher concentration had no effect on absorbance. The results are tabulated in table 4.

Effect of acidity :

Effect of acidity on the system has been investigated in terms of absorbance of the Mo-complex in the organic phase. Maximum absorbance was obtained when the extractions were carried out from 0.5 M HCl medium to 5 M HCl. In each case the remaining aqueous phase after extractions was clear and colourless. Complete and quantitative extraction of molybdenum occurred from this entire range. If the acidity is less than 0.5 M, absorbance of the organic extract is less than the maximum value. At higher acidities the values were found to decrease. Extractions were carried out at 2 M HCl medium for our investigation.

Choice of solvent :

Apart from benzene, some other solvents like chloroform, carbontetrachloride, ethylacetate or 1,2-dichloroethane were

tested as extracting solvents, but these offered no special advantages over benzene. However the spectral curves of the molybdenum complex in various water-immisible solvents are identical in nature indicating the formation of similar type of complex in all cases.

#### Stability of colour :

The absorbance and its constancy with time indicate that the system is stable for at least 6 hr. The absorbances of the Mo-complex in benzene was measured at elapsed intervals of time as indicated in table 5.

#### Interference :

To test the effects of diverse ions molybdenum was extracted according to the recommended procedure in presence of the desired foreign ion. The tolerance limit was set at that amount of foreign species for which the recovery of molybdenum within  $\pm$  3% error could be achieved. Molybdenum (40  $\mu$ g) could be determined without interference in presence of the following ions : Zn(II), Cd(II), Pb(II), Ca(II), Ba(II), Sr(II), Au(III), Bi(III), V(V), Mn(II), Ni(II), Co(II), Rh(III), Pt(IV), Be(II), Cr(III), U(VI), Ce(III), Th(IV), Zr(IV), Mg(II), Al(III), La(III), Hg(II), Cu(II),

Fe(III), Pd(II), W(VI). In presence of W(VI) the absorbance was measured at 460 nm. Sn(II) interfered.

Amongst the anions tested the followings did not interfere in the estimation of molybdenum : fluoride, iodide, bromide, borate, phosphate, phthalate, acetate, arsenate, oxalate, citrate, tartarate, thiosulphate, EDTA. Nitrite forms immulsion in the process and must be absent. The results are shown in table 6.

#### Precision and accuracy :

The precision and accuracy of the method were tested by analysing solutions containing a known amount of molybdenum following the recommended procedure. The results are shown in table 7. The proposed method has been compared to some other existing methods in respect of molar absorptivity and sensitivity as mentioned in table 8. The process is very simple and rapid requiring only 10-15 min for each run.

#### Application to the analysis of synthetic mixture :

The applicability of the proposed method was tested by analysing some synthetic mixtures. The composition of mixtures with percentage of recovery of molybdenum was satisfactory. Average of three determination was taken in each case. The results are shown in table 9.

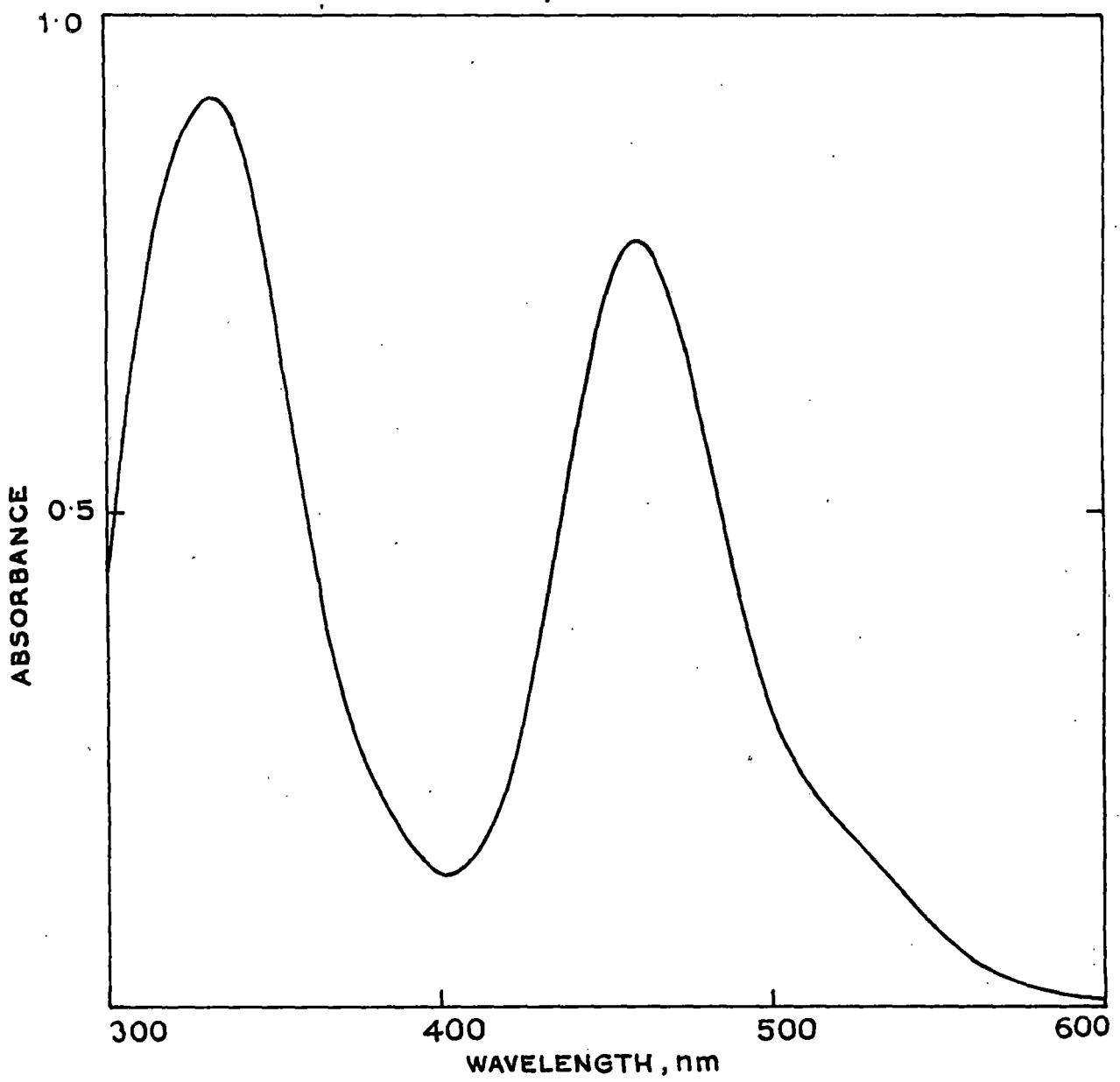


FIG-1: ABSORBANCE SPECTRUM OF Mo-SCN-CTAB COMPLEX (4 ppm Mo)

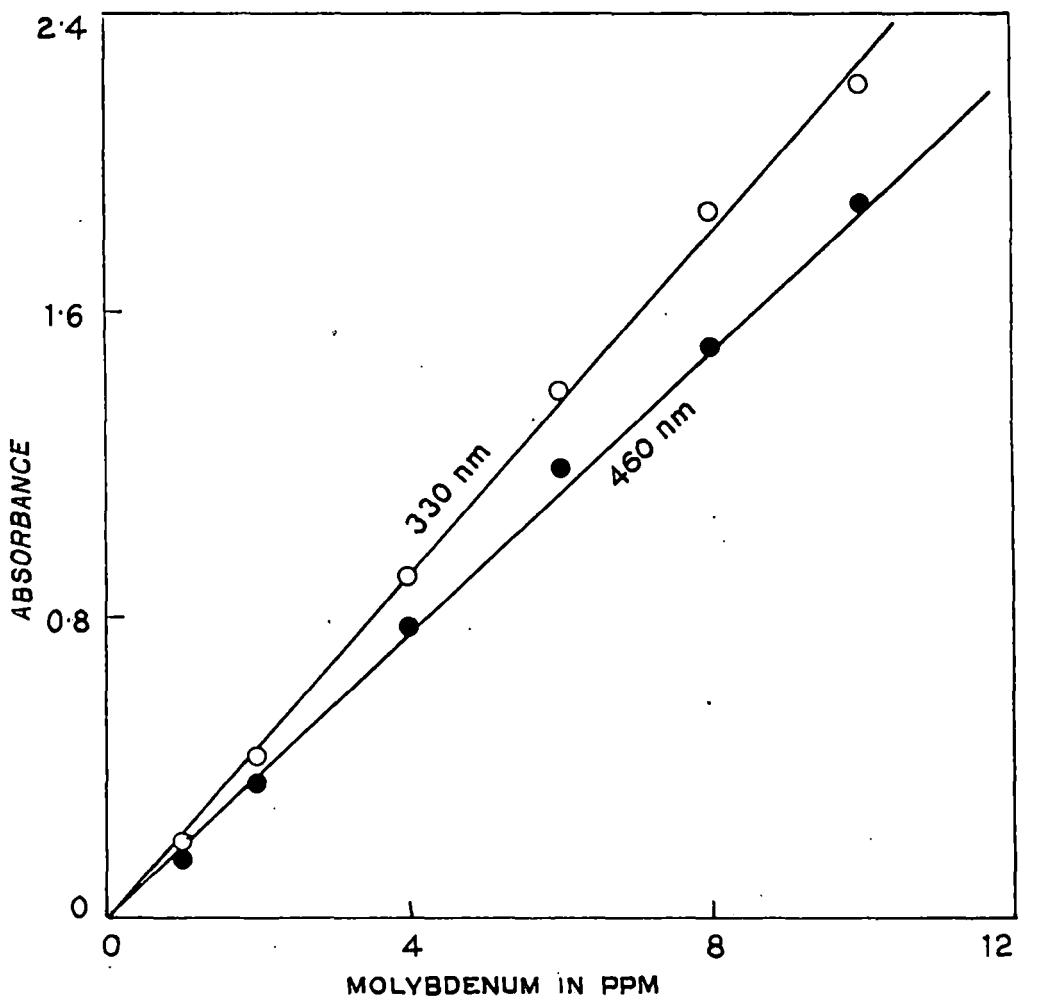


Fig- 2 : BEER'S LAW ( Mo - SCN - CTAB system )

Table 1 : Adherence to Beer's law

Molybdenum taken in μg	Absorbance at 330 nm	Absorbance at 460 nm
10	0.200	0.198
20	0.432	0.350
40	0.910	0.788
60	1.420	1.200
80	1.800	1.520
100	2.210	1.910

Table 2 : Effect of thiocyanate concentration

The aqueous phase (10 ml) contains 40 μg of molybdenum, 1 ml of 0.1 M CTAB and 4 ml of 2 M thiourea. Extraction from 2 M HCl medium.

Aqueousthiocyanate concentration (M)	Amount added (ml)	Absorbance at 330 nm	Absorbance at 460 nm
0.40	0.5	0.560	0.440
0.80	0.5	0.780	0.580
1.2	0.5	0.780	0.540
1.6	0.5	0.842	0.662
2.0	0.5	0.902	0.810
2.4	0.5	0.905	0.788
2.8	0.5	0.910	0.788
3.6	0.5	0.905	0.780
4.0	0.5	0.900	0.782

Table 3 : Effect of CTAB concentration

The aqueous phase (10 ml) contains 40 $\mu$ g of molybdenum along with 2 ml of 3 M thiocyanate and 4 ml of 2 M thiourea. Extraction from 2 M HCl medium

CTAB concentration (M)	Amount added (ml)	Absorbance at 360 nm	Absorbance at 460 nm
5.2 $\times 10^{-4}$	0.5	0.22	0.18
7.8 $\times 10^{-4}$	0.5	0.32	0.26
1.04 $\times 10^{-3}$	0.5	0.42	0.36
1.3 $\times 10^{-3}$	0.5	0.60	0.52
1.6 $\times 10^{-3}$	0.5	0.66	0.58
1.82 $\times 10^{-3}$	0.5	0.82	0.700
2.1 $\times 10^{-3}$	0.5	0.84	0.720
2.3 $\times 10^{-3}$	0.5	0.90	0.768
2.6 $\times 10^{-3}$	0.5	0.90	0.780
2.6 $\times 10^{-2}$	0.5	0.910	0.780
2.6 $\times 10^{-1}$	0.5	0.905	0.785

Table 4 : Effect of thiourea concentration

The aqueous phase (10 ml) contains 40 $\mu\text{g}$  of molybdenum, 2 ml of 3 M  $\text{NH}_4\text{SCN}$  and 1 ml of 0.1 M CTAB. Extraction from 2 M HCl medium

Thiourea concentration (M)	Amount added (ml)	Absorbance at 330 nm	Absorbance at 460 nm
0.002	0.5	0.540	0.200
0.02	0.5	0.780	0.640
0.2	0.5	0.88	0.710
2.0	0.5	0.905	0.780
2.0	1.0	0.900	0.785
2.0	1.0	0.900	0.785
2.0	2.0	0.905	0.780
2.0	4.0	0.900	0.785

Table 5 : Variation of absorbance with time  
(Mo taken 40 $\mu\text{g}$ )

Time in hr. after extraction	Absorbance at 330 nm	Absorbance at 460 nm
0.25	0.905	0.780
0.5	0.905	0.785
1.0	0.905	0.780
2.0	0.900	0.780
6.0	0.902	0.782

Table 6 : Effect of diverse ions in the determination of molybdenum (40  $\mu\text{g}$ ). Extraction at 2 M HCl medium. Absorbance measured at 330 nm

Ion added	Amount tolerated (mg)	molybdenum found ( $\mu\text{g}$ )	Error %
Zn(II)	5.5	40.8	2
Cd(II)	4.0	39.0	2.5
Pb(II)	6.5	40.0	0
Ca(II)	6.0	40.5	1.2
Ba(II)	6.0	40.5	1.2
Sr(III)	6.5	40.5	0
Au(III)	3.5	41.2	3
Bi(III)	3.0	41.0	2.5
V(V)	2.5	41.2	3
Mn(II)	3.5	40.5	1.2
Ni(II)	4.0	40.0	0
Co(II)	4.0	41.2	3
Rh(III)	3.5	40.5	1.2
Pt(IV)	1.5	41.0	2.5
Be(II)	4.5	40.0	0
Cr(III)	5.0	40.5	1.2
U(VI)	3.5	40.7	1.7
Ce(III)	3.5	40.5	1.2
Th(IV)	4.0	40.5	1.2
Zr(IV)	4.0	39.6	1.0
Mg(II)	6.0	39.6	1.0

contd...

Table 6 contd ...

Al (III)	4.5	40.2	0.5
La(III)	6.0	40.2	0.5
Hg(II)	1.5	39.0	2.5
Cu(II)	1.5	39.2	2.0
Fe(III)	1.5	40.5	1.2
Pd(II)	1.5	41.2	3.0
W*(VI)	2.0	41.2	3.0
Sn(II)	nil	-	-
Fluoride	10.0	40.0	0
Iodide	10.0	40.5	1.2
Bromide	10.0	40.2	0.5
Borate	8.0	41.0	2.5
Phosphate	8.0	40.5	1.2
Phthalate	9.0	40.2	0.5
Acetate	12.0	40.2	0.5
Arsenate	8.0	39.0	2.5
Oxalate	7.0	39.0	2.5
Citrate	8.0	40.0	0
Tartarate	8.0	40.0	0
Thiosulphate	6.0	39.0	2.5
EDTA	6.0	41.2	3.0
Nitrite	nil	-	-

\* absorbance measured at 460 nm.

Table 7 : Reproducibility of molybdenum recovery, Absorbance measured at 330 nm

Molybdenum taken ( $\mu\text{g}$ )	Molybdenum found ( $\mu\text{g}$ )	Mean ( $\mu\text{g}$ )	Std. deviation (%)
20	19.0, 19.0, 21.5	20.5	1.26
	20.5, 22.0, 21.0		
40	40.6, 42.2, 40.5	41.23	0.88
	41.0, 42.5, 40.6		
60	61.5, 62.0, 60.0	61.25	0.81
	60.5, 62.0, 61.5		

Table 8 : Determination of molybdenum (40  $\mu\text{g}$ ) in various mixtures

Composition with amounts taken ( $\mu\text{g}$ )	Recovery of molybdenum (%)
1. Mo(VI) 40, Cu(II) 50, Cr(III) 50	102
2. Mo(VI) 40, V(V) 50, W(VI) 50	101*
3. Mo(VI) 40, Mn(II) 50, Fe(III) 50	102
4. Mo(VI) 40, W(VI) 50, Cr(III) 50, Cu(II) 50	98*
5. Mo(VI) 40, Fe(III) 50, Cr(III) 50, W(VI) 50	98

\*absorbance measured at 460 nm

Table 9 : Comparison to some other existing methods for the spectrophotometric determination of molybdenum

Reagent	Molar absorbtivity $1 \text{ mol}^{-1} \times 10^4$	Sensitivity $\mu\text{g/cm}^2$	Ref.
1. Benzyltriethyl ammonium chloride	1.8	.0053	302
2. Benzyl dimethyl phenyl ammonium chloride	2.83	0.0034	305
3. N-hydroxy-N-phenyl-N'-P-tolyl benzene-o-chloro benzamide hydrochloride	3.36	0.0285	312
4. $\beta$ -Mercapto propanoic acid anilide	2.06	0.047	313
5. N-phenyl-N'-P-tolyl-m-tolumidine hydrochloride	1.73	-	314
6. P-mercaptop resorcyclic acid	1.94	.0049	315
7. 4-Hydroxy cumarinthiol	1.2	0.0081	316
8. Present method	2.21	0.0043	
	1.97	0.0048	

Section 8 : Extraction and Spectrophotometric Determination  
of Vanadium

INTRODUCTION

Vanadium thiocyanate complexes have been studied in aqueous solution<sup>317-319</sup>. Spectrophotometric method for vanadium depends on the absorption properties of the blue vanadyl ion<sup>320-323</sup> and on vanadyl thiocyanate in aqueous solutions<sup>321</sup> and in acetone-water solutions<sup>322</sup>. Baird<sup>323</sup> noted that vanadium formed a pyridine thiocyanate complex under different conditions. Utilizing this property Ayres<sup>324</sup> developed a spectrophotometric method for vanadium. Sinde, V.M and Khopkar S.M<sup>325</sup> studies an ion-association complex of vanadium which was extracted from 6 M HCl into mesityl oxide.

Vanadium could be extracted at pH 3.5 with 0.1 M 8-hydroxyquinoline<sup>326</sup> into chloroform. The absorbance of the complex was measured at 550 nm.

Mathur S.P et al<sup>327</sup> investigated vanadium(V) complexes of N-allyl-N'-(P-benzoyl glycine) thiourea. The complexes were extractable into isoamyl alcohol from 7-9.5 and 10-11.5 M HCl solution respectively. The absorbance were measured at 360 and 380 nm. N-hydroxy-N,N'-diphenyl cinnamidine has been proposed for the spectrophotometric determination of vanadium(V) by Deb, Nauk, Kanti and Mishra Rajindre K<sup>328</sup>. The 1:2 (metal:ligand) complex was extractable into chloroform from 1.0-9.5 M aq AcOH solution. Verizade, N.A; and Ragimova, Z.B<sup>329</sup> found that (V)II reacts with SCN<sup>-</sup> and diphenyl guanidine(I) to form ternary complex with a V-SCN-I ratio of 1:2:2 at 0.42-2.8 or 1.8-2.7 M HCl or H<sub>2</sub>SO<sub>4</sub> medium respectively. The maximum absorbance occurred at 340 nm.

Verdizade, N.A and Ragimova Z.B<sup>330</sup> determined vanadium(VI) by extracting the yellow 1:2:3 (V-SCN-diantipyrimethane) complex into chloroform. Patel K.S. et al<sup>331</sup> used N-hydroxy-N-P-chlorophenyl-N'-(2-methyl-5-chlorophenyl)-P-toluamidine hydrochloride and some phenol for the spectrophotometric determination of vanadium(V). Pyridine-2-acetaldehyde salicyloylhydrazone<sup>332</sup> has been proposed as an analytical reagent for the spectrophotometric determination of vanadium. The yellow complex absorbs maximum at 415 nm in chloroform. A highly sensitive method for the spectrophotometric determination of trace amounts of vanadium(V) was described by

Abbasi, Shahid Abbas and Ahmad Jameel<sup>333</sup>. Vanadium(V) was extracted from 4-8 M HCl solution as a violet complex with N-p-methoxyphenyl-2-furohydroxamic acid into chloroform. The extract showed maximum absorbance at 545 nm. Dila Alexandra and Caramtan Maria<sup>334</sup> described a photometric method for the determination of vanadium by using the reaction of molybdoavanado phosphoric acid with malachite green. The complex was extractable into nitrobenzene at pH 8 and absorbs maximum at 630 nm.

The solvent extraction behaviour of the ternary complex formed by V(V) with N-anthraniol hydroxamic acid and thiocyanate was investigated at pH 0.95 by Bag S.P et al<sup>335</sup>. Paul K and Gupta V.K<sup>336</sup> proposed another spectrophotometric method for the determination of vanadium(V) with N-m-chlorophenyl-2-thionylhydroxamic acid in presence of thiocyanate. The blue coloured complex was extractable into chloroform having absorption maximum at 580 nm.

Procedures based on the formation of vanadium complexes with 2,7-diamino fluorene<sup>237</sup>, 5-(2-hydroxyphenylazo)-6-amino-2-marcapto-4-pyrimidinol<sup>338</sup>, 2-(3,5 dibromo-2-pyridylazo)-5-dimethylaminophenol<sup>339</sup>, erichrome cyanine R and cetyl trimethyl ammonium bromide<sup>340</sup>, isophthal dihydroxamic acid<sup>341</sup>, chlorosulfophenols<sup>342</sup>, 4-(2-pyridylazo) resorcinol and tetrazolium chloride<sup>343</sup>, 2-(5-bromo-2-pyridylazo)-5-(N-propyl-N-sulphopropyl amino) phenol<sup>344</sup>,

2-(5-bromo-2-pyridylazo)-5-(diethylaminophenol) and cetyl pyridinium bromide<sup>345</sup>, O-aminobenzohydroxamic acid<sup>346</sup>, 2-acetyl pyridine thiosemicarbazone<sup>347</sup>, thiocyanate and diphenylguanidine<sup>348</sup>, phenyl fluorone<sup>349</sup>, tannic acid<sup>350</sup>, substituted hydroxamic acids<sup>351</sup>, and N-hydroxy-N-phenyl-N-P-phenatylbenzamidine<sup>352</sup> have been proposed by various workers.

Zhao Mingren<sup>353</sup> et al studied the miceller solubilization of vanadium complex with 4-(2-pyridylazo) resorcinol and crystal violet in the presence of surfactant at pH 1.6-3.8. The complex has maximum absorbance at 545 nm. The extraction of the mixed ligand complex of vanadium(V): isophthalidihydroxamic acid into tolune solutions of Adogen 464 has been proposed by Salinas F et al<sup>354</sup>. Vanadium(V) was determined spectrophotometrically by using methoxy propazine<sup>355</sup> in 1-3 M phosphoric acid. The absorbance of the violet species was measured at 565 nm. The method finds its applicable for the determination of vanadium in vanadium steels and minerals. Another method for the spectrophotometric determination of vanadium has been proposed by Xu Qiheng and Yang, Hui<sup>356</sup> by using 9-O-chlorophenyl-1,6,7-trihydroxyfluorone (OCPF) and cetyltrimethyl ammonium bromide pH 4.0. The complex absorbs maximum at 560 nm. The V(IV)-OCPF ratio was found to be 1:2.

A method of spectrophotometric determination of vanadium(II) in presence of 35 common cations by means of di-2-pyridyl ketone-2-pyridylhydrazone (DPPH) was presented by Kavlentis E<sup>357</sup>. The V(II)-DPPH complex has  $\lambda_{\text{max}}$  at 545 nm with molar absorptivity  $14,000 \text{ l mol}^{-1} \text{cm}^{-1}$ . Martinez et al<sup>358</sup> studied a mixed ligand complex of vanadium(V) with mandelo hydroxamic acid and oxalate. The complex was extractable into Aldogen 464-toluene solution.

(3) In our present investigation it has been found that Vanadium(III) forms complex with thiocyanate in presence of cetyltrimethyl ammonium bromide (CTAB) and the resulting complex is extractable into ethyl acetate under optimum conditions. The systems conforms to Beer's law. This property of the vanadium complex suggested yet another approach to the development of a spectrophotometric method for determination of the metal which is described here.

## EXPERIMENTAL

### Apparatus and Reagents :

Spectral curves and analytical measurements were made with a Shimadzu PR1 model recording spectrophotometer. Stoppered quartz cells of 10 mm optical path length were used. An ECl 5651 digital pH meter was used to measure the acidity of the aqueous solutions. Separatory funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of vanadium(IV) was prepared by dissolving 1.75 gm vanadyl sulphate dihydrate in 250 ml distilled water. The solution was standarised by EDTA titration<sup>359</sup>. Standard vanadium(III) solution was prepared by reducing an aliquot of the stock vanadium(IV) solution by Zn in HCl. Appropriate dilution was made as needed.

All chemicals used were of analytical grade. Benzene, chloroform, ethylacetate, carbontetrachloride and 1,2-dichloroethane were distilled before use.

Solutions of ammonium thiocyanate (2.5 M), cetyltrimethylammonium bromide (CTAB) (0.007 M) were prepared in distilled water. Hydrochloric acid-potassium chloride buffer was used to adjust the pH of the aqueous solution.

Standard solutions of diverse ions were prepared from their chlorides, nitrates or sulphates (in case of cations) and from sodium, potassium or ammonium salts (in case of anions) to study interferences.

#### Determination of Vanadium :

To an aliquot containing up to 70  $\mu\text{g}$  of vanadium(III) were added 5 ml of ammonium thiocyanate and 2 ml of CTAB followed by addition of buffer (pH-2) to give a total volume of 10 ml of the aqueous solution. The mixture was then equilibrated (30 sec) with ethylacetate (10 ml) and the separated organic layer was dried over anhydrous sodium sulphate and finally its absorbance was measured at 305 nm against a blank. Amount of vanadium was computed from a calibration curve. To test the interference, the respective foreign ion was added to the aqueous solution before addition of the reagents.

#### RESULT AND DISCUSSION

#### Absorption spectra :

The absorption spectrum of the vanadium(III)-SCN-CTAB complex as extracted above into ethyl acetate is shown in

Fig.1. The complex shows, absorbance maxima at 250 nm, 305 and 400 nm. The reagent blank itself exhibits absorption maximum at 240 nm and the absorption becomes insignificant beyond 300 nm. All measurements were carried at 305 nm due to higher absorbance. The pattern of the absorption spectrum of the complex remains unchanged when the extractions were carried out from 1 M HCl medium to pH-3. This indicates the presence of single variety of complex species in the system.

It has been noted that vanadium(IV) in the aforesaid conditions does not form with the reagents, any complex to be extractable into ethylacetate.

Beer's law and calibration curve :

The absorbance of different amounts of vanadium(III) extracted as in the procedure were noted against reagent blank. The absorbance of vanadium(III)-SCN-CTAB complex in ethylacetate shows a linear response over a concentration of 15 ppm of vanadium. The results are shown in table 1 and calibration curve in Fig.2. In each case the remaining aqueous phase after a single extraction was clear and colourless. Furthermore the aqueous phase, as tested by an independent method, was void of vanadium.

The molar absorptivity and Sandell's sensitivity were evaluated to be  $7.87 \times 10^3 \text{ l mol}^{-1} \text{cm}^{-1}$  and  $0.0065 \mu\text{g/cm}^2$  respectively at 305 nm.

#### Effect of thiocyanate concentration :

The effect of thiocyanate concentrations has been studied by varying the amount of ammonium thiocyanate (2.5 M) keeping the other variables constant. It was found that 5 ml of 2.5 M ammonium thiocyanate along with 2 ml of 0.007 M cetyltrimethyl ammonium bromide solution was sufficient to extract  $70 \mu\text{g}$  of vanadium in a single operation. Increased amount of thiocyanate did not bring about any significant change in the maximum value of the absorbance. Table 2 shows the effect of thiocyanate concentration on absorbance of the vanadium(III) complex.

#### Effect of cetyltrimethylammonium bromide (CTAB) concentration :

As regards the reagent, 2 ml of 0.007 M CTAB along with 5 ml of 2.5 M thiocyanate was quite adequate for quantitative extraction of  $70 \mu\text{g}$  of vanadium. Below 1.4 ml of 0.007 M CTAB the absorbance of the ethyl acetate extract was found to give low absorbance values. Increased

concentration however could not produce any significant change in the maximum colour intensity. The results are given in table 3.

The mole-ratio method indicated a 1:3 (V:CTAB) stoichiometry in the green V(III)-SCN-CTAB complex. However, the molar ratio of vanadium to thiocyanate in the complex could not be determined as the amount of thiocyanate required would be large excess (1:4000).

#### Effect of acidity :

The effect of acidity on the extractability of vanadium (III)-SCN-CTAB complex into ethylacetate was examined in terms of absorbance. Maximum absorbance was obtained when the extraction were carried out from 1 M HCl medium to pH-3. In a second consecutive operation within this acidity range the organic extract virtually showed no absorbance. This indicated a quantitative extraction of vanadium in a single operation. At higher pH the system showed no colour development. On the other hand when the acidity of the aqueous phase was made to exceed 1 M with respect to hydrochloric acid, the reagent blank develops strong colouration with considerable absorption at the aforesaid wavelength region. Thus for our practical purpose extractions were carried out at pH-2.0 where the

reagent blank absorbs minimum. The results are shown in tables 4 & 5. Extraction of vanadium(III) as a function of acidity has been shown in Fig.3.

#### Effect of solvents :

Apart from ethyl acetate, some other solvents like chloroform, benzene or 1,2-dichloroethane were tested as extracting solvents but none of these offered any special advantages over ethyl acetate. The vanadium complex was not extractable in carbon tetrachloride.

#### Stability of colour :

The absorbance of the V(III)-SCN-CTAB complex in ethylacetate was measured at elapsed intervals of time and was found to be stable for at least 6 hr. The result are tabulated in table 6.

#### Interference :

To test the effect of diverse ions on the extraction behaviour, vanadium(III) was extracted according to the recommended procedure in presence of the desired foreign

ion. Extraction pH was set at 2.0 with KCl-HCl buffer. An ion was considered to interfere if the recovery of vanadium differed by more than  $\pm$  3% from the actual amount taken. Vanadium ( $70\mu\text{g}$ ) could be determined without interference in presence of the following ions : Ni(II), Fe(II), Mg(II), Mn(II), Mo(IV), Pb(II), Cr(VI), Sn(II), Zr(IV), Ca(II), Ba(II), Sr(II), Cd(II), Co(II). The absorbance of the organic extract was measured at 305 nm to avoid the interference due to the following ions Th(IV), Be(II), La(III), Pd(II), Au(III), Ce(III) and Al(III). Copper(II), Mercury(II), zinc(II), uranium(VI) and silver(I) interfered.

Among the anions tested the followings were tolerable, phosphate, tartarate, ascorbate, fluoride, acetate, bromide, phthalate, citrate, oxalate, iodide, arsenate and thiosulphate. The system tolerated borate and EDTA provided the absorbance were measured at 400 nm. Nitrite interferred. The results are shown in table 7.

#### Reproducibility :

The precision and accuracy of the method were tested by analysing solutions containing a known amount of vanadium following the recommended procedure. The results are shown in table 8. The method is simple and rapid

requiring only 10-15 min for each run. The method has been compared to some other existing method as seen from table 9.

Application : Analysis of synthetic mixtures :

In absence of real samples the applicability of the method was tested by analysing some synthetic mixtures comprising V(III), Ni(II), Fe(II), Mn(II), Mo(IV), and Co(II). The composition of the mixtures with the percentage recovery of vanadium are given in table 10. The results shows that the recovery of vanadium from the synthetic mixtures are satisfactory.

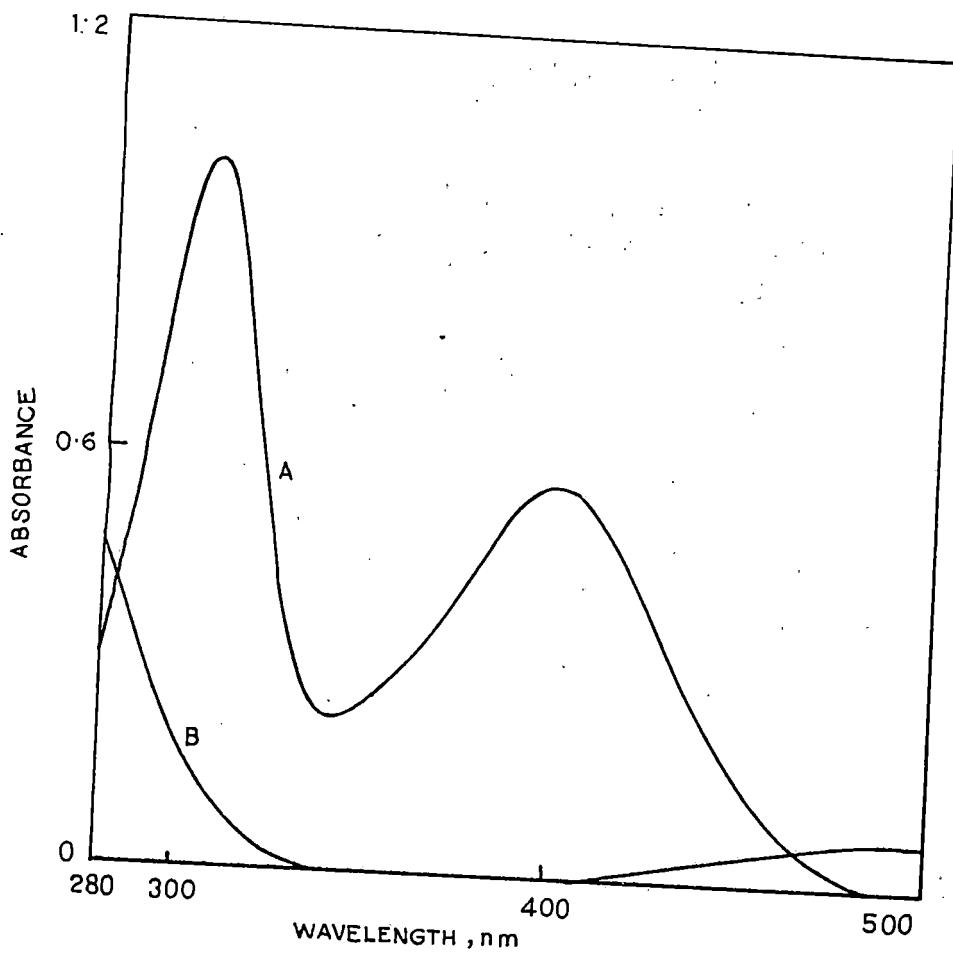


Fig - 1: Absorbance spectra of (A) V(III)- SCN- CTAB Complex  
(7 ppm V) and (B) Reagent blank.

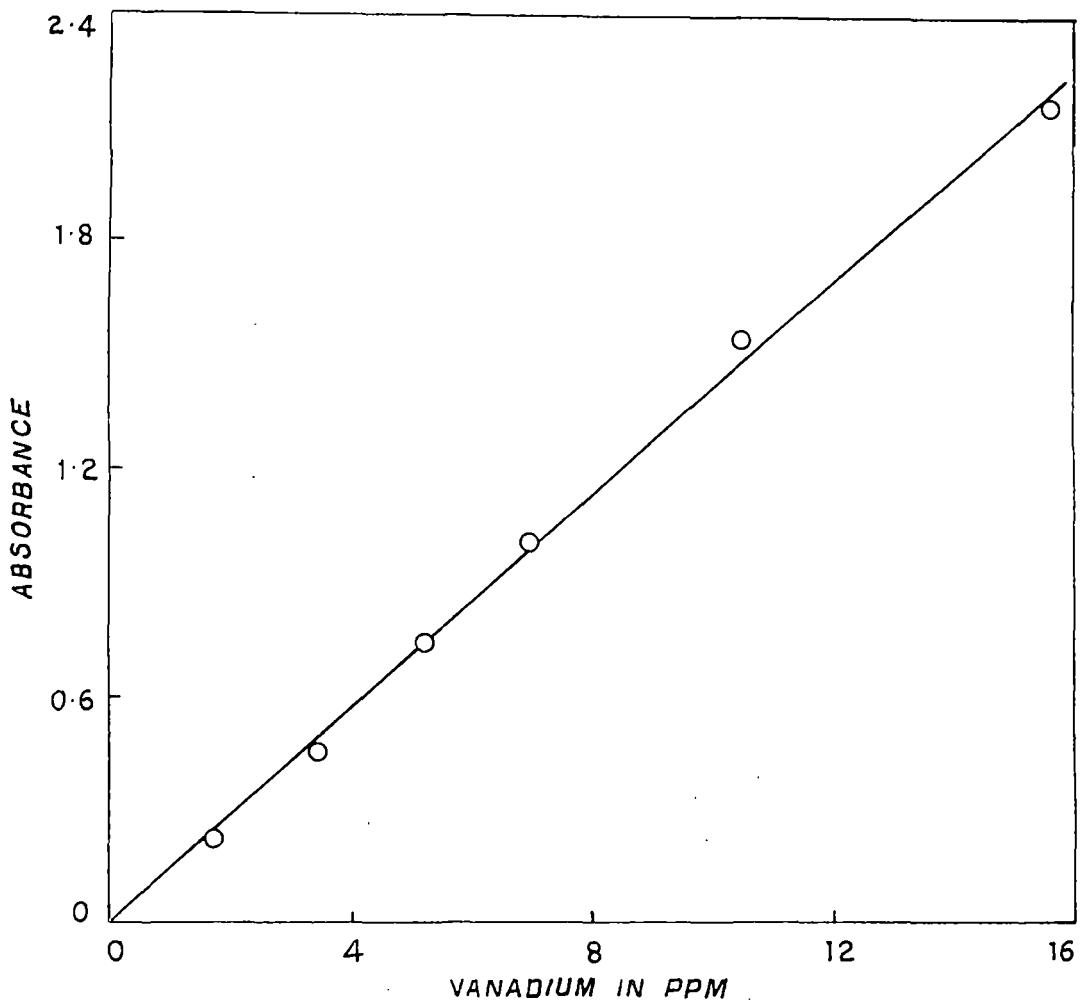


Fig-2. BEER'S LAW (V(III) - SCN - CTAB System .

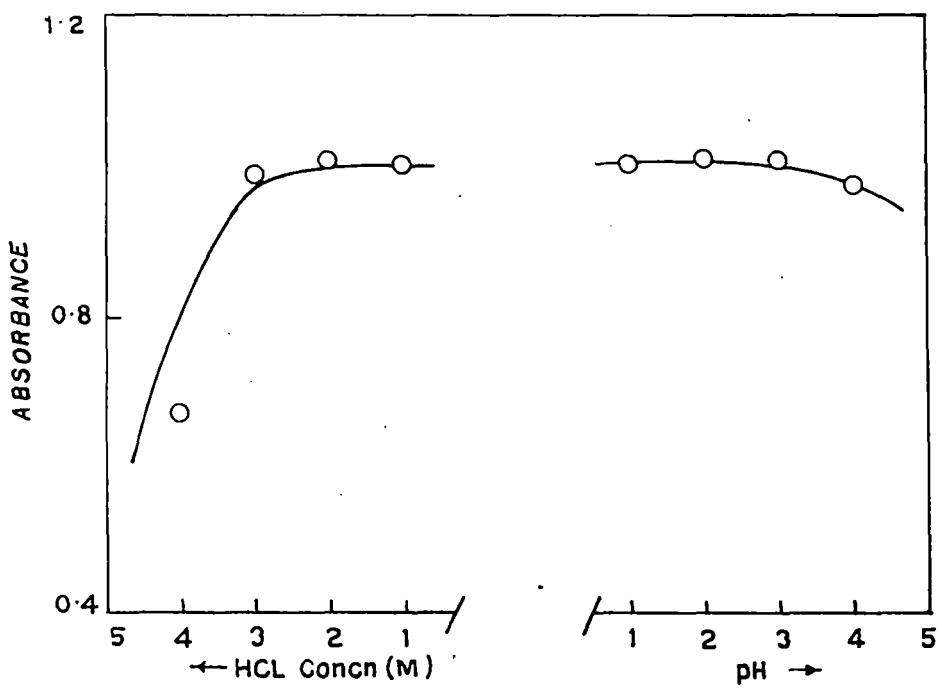


Fig- 3. ABSORBANCE AS A FUNCTION OF ACIDITY Vanadium taken 70  $\mu$ g.

Table 1 : Adherence to Beer's law

Vanadium(III) in ppm	Absorbance at 305 nm
1.75	0.220
3.5	0.462
5.25	0.745
7.0	1.006
10.5	1.540
15.75	2.160

Table 2 : Effect of variation of ammonium thiocyanate concentration (2.5 M) on absorbance of the organic extract

The aqueous phase contains 70  $\mu\text{g}$  of vanadium along with 2 ml of 0.007 M CTAB. Extraction pH-2.0

NH <sub>4</sub> SCN added (2.5 M) in ml	Absorbance at 305 nm
0.5	0.625
1.0	0.760
1.5	0.852
2.0	0.882
2.5	0.960
3.0	1.006
3.5	1.004
4.0	1.006
4.5	1.002
5.0	1.004
5.5	1.006
6.0	1.004

Table 3 : Effect of CTAB concentration

The aqueous phase (10 ml) contains 70 $\mu$ g of vanadium along with 5 ml of 2.5 M thiocyanate. Extraction pH-2.0

Amount of CTAB (0.007 M) added in ml	Absorbance at 305 nm
0.1	0.40
0.2	0.40
0.6	0.70
1.0	0.86
1.4	0.98
1.8	1.006
2.4	1.004
3.0	1.002
5.0	1.006

Table 4 : Effect of acidity on absorbance

The aqueous phase (10 ml) contains 70 $\mu$ g of V(III), 5 ml of 2.5 M  $\text{NH}_4\text{SCN}$  and 2 ml of 0.007 M CTAB

pH	Absorbance at 305 nm
1.0	1.006
2.0	1.002
3.0	1.005
4.0	0.980
5.0	-
6.0	-

Table 5 : Effect of acid concentration on absorbance

The aqueous phase (10 ml) contains 70 $\mu$ g of V(III), 5 ml of 2.5 M  $\text{NH}_4\text{SCN}$  and 2 ml of 0.007 M CTAB

HCl concentration in M	Absorbance at 305 nm
1.0	1.006
2.0	1.002
3.0	0.980
4.0	0.660
5.0	-
6.0	-

Table 6 : Variation of absorbance of with time  
(V taken 70  $\mu$ g)

Time in hr after extraction	Absorbance at 305 nm
0.25	1.006
0.50	1.006
2.0	1.005
6.0	1.004
12.0	1.000

Table 7 : Effect of diverse ions

Ion added	Amount tolerated (mg)	Vanadium found ( $\mu$ g)	Error (%)
Ni(II)	7.0	71.0	1.4
Fe(II)	6.0	72.0	2.8
Mg(II)	8.0	70.2	0.0
Mn(II)	8.0	71.0	1.4
Mo(IV)	6.0	72.0	2.8
Pb(II)	6.0	69.5	0.7
Sn(II)	5.0	69.0	1.4
Zr(IV)	7.0	71.0	1.4
Ca(II)	8.0	70.5	0.7
Ba(II)	8.0	71.0	1.4
Sr(II)	8.0	70.0	0.0
Cd(II)	6.0	69.0	1.4

contd ...

Table 7 contd ...

Co(II)	7.0	70.5	0.7
Cr(VI)	0.6	71.5	2.1
Th(IV)	6.0	70.5	0.7
Be(II)	7.0	70.0	0.0
La(III)	7.0	70.0	0.0
Pd(II)	5.0	72.0	2.8
Au(III)	1.0	71.0	1.4
Ce(III)	5.0	70.0	0.0
Al(III)	8.0	70.0	0.0
Phosphate	15.0	70.0	0.0
Tartarate	15.0	71.0	1.4
Ascorbate	15.0	70.5	0.7
Fluoride	15.0	70.5	0.7
Acetate	15.0	69.5	0.7
Bromide	15.0	70.0	0.0
Phthalate	15.0	70.0	0.0
Citrate	15.0	70.0	0.0
Oxalate	15.0	69.0	1.4
Iodide	15.0	69.5	0.7
Arsenate	15.0	69.0	1.4
Thiosulphate	15.0	71.0	1.4
Nitrite	nil	-	-

Table 8 : Reproducibility of vanadium recovery

Vanadium taken in $\mu\text{g}$	Vanadium found $(\mu\text{g})$	Mean $\mu\text{g}$	Std. deviation %
35	35.5,    35.2,    34.8	35.13	0.63
	34.0,    35.8,    35.5		
70	70.5,    70.6,    69.0	69.65	0.81
	68.8,    69.0,    70.0		
105	102.8,    105.5,    104.0	104.88	1.54
	106.0,    107.0,    104.0		

Table 9 : Comparison

Reagents	$\lambda_{\text{max}}$ (nm)	Molar absorptivity $1 \text{ mol}^{-1} \text{cm}^{-1}$	Sandell's sensitivity $\mu\text{g}/\text{cm}^2$	Ref.
1. N-Hydroxy-N-phenyl N -P-chlorophenyl -o-chlorobenzene- namidine Hydro- chloride and thiocyanate	620	$4.71 \times 10^3$	0.018	360
2. O-Dianisidine	440	$3.01 \times 10^3$	0.0015	361
3. N-Hydroxy-N-N -diarylbenzamidine and P-Hydroxy benzaldehyde	590	$7.90 \times 10^3$	-	362
4. D-Dimethylsulpha- mido-10- <u>3</u> -(4- methane sulphonyl pipirazino) propyl phenothiazine Methane sulphonate	513	$9.26 \times 10^3$	0.0056	363
5. N-m-chlorophenyl -R-theno-Hydroxamic acid and thiocyanate	580	$7.00 \times 10^3$	0.0073	336
6. Pyridine and thiocyanate	740	$2.80 \times 10^3$	0.4	364
7. Present method	305	$7.87 \times 10^3$	0.0065	

Table 10 : Determination of vanadium (70  $\mu\text{g}$ ) in various mixtures

Composition with amounts taken in $\mu\text{g}$	Recovery of vanadium %
1. V(III) 70, Ni(II) 100, Fe(II) 100, Mn(II) 100	98
2. V(III) 70, Fe(II) 100, Mn(II) 100, Mo(IV) 100	98
3. V(III) 70, Fe(II) 100, Ni(II) 100, Co(II) 100	101
4. V(III) 70, Mn(II) 100, Mo(IV) 100, Co(II) 100	100

Section 9 : Extraction and Spectrophotometric Determination  
of Gold

#### INTRODUCTION

The classical iodide system is known since long back, for the purpose of developing methods of separations for a variety of elements. Gold(III) was extracted into ethyl ether from 6.9M HI by S.Kitahara<sup>365</sup>. Rangnekar A.V and Khopkar S.M<sup>366</sup> determined gold(III) at pH 4.0 in presence of 10 M lithium chloride as salting out agent, with 0.015 M theonyltrifluoroacetone into xylene as an orange-red complex the absorption of which was measured at 440 nm. The reagents,  $\text{Fe}(\text{Phenanthroline})_3^{2+}$ <sup>367</sup>, tetraphenyl arsonium chloride<sup>368</sup>, Rhodamine B<sup>369</sup> or mesityl oxide<sup>370,371</sup> have also been used in spectrophotometric methods for determination of gold. Different worker utilized different organic reagents for the determination of gold from time to time.

Jenik Josef<sup>372</sup> proposed a spectrophotometric method for the determination of gold using O-anisidine. The reagent reacts with  $\text{AuCl}_4^-$  in weakly acidic medium to give a red complex. KF-HF buffered solution was used to suppress the formation of colloid. The complex was extractable into EtOAc and the absorbance was measured at 490 nm.

Gold was determined by extraction of its complex with 2-pyridyl-2-thienyl-Z-ketoxime<sup>373</sup> from pH 3.1-3.4 in presence of  $\text{KClO}_4$  into dichloroethane. The absorbance of the organic layer was measured at 447 nm. Gowda H. Sauke and Thimaiah K.N.<sup>374</sup> used fluphenazine hydrochloride and promazine hydrochloride for the determination of gold(III) spectrophotometrically.

Matouska E et al<sup>375</sup> determined gold spectrophotometrically with bromopyrogallol red at pH 5.4-6.0. The metal:ligand ratio was found to be 1:2. The effect of cationic surfactants on the reaction was studied. Traces of gold was determined in copper sulfide ores and industrial concentration by extraction of  $\beta$ -acriflavine chloro aurate<sup>376</sup> from 0.1 M HCl into 1,2-dichloroethane. The absorbance was read at 490 nm.

Matouskova E et al<sup>377</sup> studied the formation of ion association of  $\text{AuCl}_4^-$  with carbethoxypentadecyl trimethyl ammonium bromide, which was utilized for the

determination of gold(III). The absorbance of the ion-<sup>-</sup><sub>A</sub> association complex was measured at 332 nm at pH 0.1-1.0. 5-p-dimethylaminocinnamylidine-1-phenyl-2-thiobarbituric acid<sup>378</sup> produces a blue complex with gold(III) in dil HCl medium. The complex was extracted into chloroform and the absorbance was measured at 622 nm. Other reagents for the micro determination of gold include, thiazolylazo derivatives<sup>379</sup>, chromopyrazole<sup>380</sup>, antipyrine dyes<sup>381</sup>, 4,4' tetraethyl diamino benzophenone<sup>382</sup>, 2-(P-methoxy phenyl)-5,7-diphenyl-1,3,4-thiadiazolo / 3,2,4 7 -pyridinium chloride<sup>383</sup>, propericiazine<sup>384</sup>, potassium iodide and butylrhodamine B<sup>385</sup>, trifluoroethyl xanthate<sup>386</sup>, Rhodamine B and thiocyanate<sup>387</sup>, acetylpyridine semicarbazone<sup>388</sup>, 1-(2',4',6'-trichlorophenyl)-4,4,6-trimethyl-(1H, 4H)-2-Pyrimidinethiol and tri-iso-octylamine<sup>389</sup>, amides and amidines<sup>390</sup>.

Simonova L.N et al<sup>391</sup> determined gold spectrophotometrically at 356 nm as Au(III) naphthyl-bismuthiol complex following extraction into butanone. Zhang Xianjuan and Tan, Shili<sup>392</sup> found that in  $H_2SO_4-Na_4$  medium containing arabic gum,  $AuBr_4^-$  reacts with victoria blue B to form a ion association. The complex shows its maxima at 570 nm with molar absorptivity  $1.5 \times 10^5$   $1\ mol^{-1}cm^{-1}$ .

A sensitive method for the determination of gold have been proposed by Zhou, Huiwen and Chai Yanying<sup>393</sup>. They

observed that gold reacts with methyl green to form a purple complex in  $H_2SO_4$  medium in the presence of NaBr. The complex was extracted with cyclohexane + butane (1:1). The absorbance of the extract was measured at 596 nm. Other methods involve the utilization of various amidines<sup>394</sup>.

In the present investigation we noted that gold(III) forms an yellow ion-association complex with cetyltrimethyl ammonium bromide (CTAB) in presence of potassium iodide and is extractable into chloroform. Based on this a simple spectrophotometric method for the determination of gold is reported.

## EXPERIMENTAL

### Apparatus and Reagents :

Absorbance measurements were carried out with a Shimadzu PR1 model recording spectrophotometer, provided with matched quartz cells of 10 mm optical path length. pH values were measured with an ECL 5651 digital pH meter.

A stock solution of Au(III) was prepared by dissolving 1 gm gold chloride (Johnson and Matthey) in 100 ml distilled water. This was then standardised gravimetrically<sup>395</sup>. Solutions of lower concentration of the metal was prepared by appropriate dilution of the stock.

All the chemicals and solvents used were of analytical grade. Chloroform, benzene, ethylacetate, 1,2-dichloroethane and carbontetrachloride were distilled before use.

Solutions of potassium iodide (0.03 M), cetyltrimethylammonium bromide (CTAB) (0.025 M) were prepared in distilled water.

Buffer solutions of different pH values were prepared by standard procedures :

KCl-HCl (pH 1-2) Potassium hydrogen phthalate - HCl (pH 2-4), Potassium hydrogen phthalate - sodium hydroxide

(pH 4.5-5.9), Potassium dihydrogen phosphate - sodium hydroxide (pH 6-8), borax-hydrochloric acid (pH 9.5-10.8). Standard solutions of diverse ions were prepared from chlorides, nitrates or sulphates (in case of cations) and from sodium, potassium or ammonium salts<sup>m</sup> (in case of anions) of the species concerned to study interferences.

Determination of gold :

To an liquor containing Au(III) (70  $\mu\text{g}$ ) were added potassium iodide (1 ml 0.33 M) and cetyltrimethyl ammonium bromide (0.1 ml, 0.025 M). Acidity of the aqueous phase was adjusted to pH 7.0 with  $\text{KH}_2\text{PO}_4$  - NaOH buffer and water as necessary to give a total volume of 10 ml. The resulting mixture was transferred to a 50 ml separating funnel and equilibrated with chloroform (10 ml) for 30 sec. After phase separation the organic extract was dried over anhydrous sodium sulphate. Finally the absorbance of the chloroform extract was measured at 290 and 360 nm against a blank prepared in a similar manner. Amount of gold was computed from a calibration curve. To test the interference by other ions, the respective ion was added to the system individually before addition of the reagents.

## RESULTS AND DISCUSSION

When potassium iodide was added to a nutral or slightly acidic solution of gold(III), a yellow colouration due to the formation of  $\text{[AuI}_4\text{]}^-$  was formed. This complex anion was not extractable into chloroform. On addition of an aqueous solution of CTAB to this coloured solution, an ion-association complex, probably of the type  $\text{[AuI}_4\text{]}^- \text{[CTA]}^+$  was formed. This was extractable into chloroform.

Absorption spectra :

The absorption spectrum of Au(III)-I-CTAB complex taken against a blank is shown in Fig.1. The yellow complex exhibits absorption maxima at 290 and 360 nm. The reagent blank itself shows absorption maximum at 250 nm which becomes insignificant beyond 290 nm. Hence all absorption measurements were made at 290 or 360 nm.

The pattern of the absorption spectrum of the complex remains unchanged when the extractions were carried out from pH 1 to 9. This indicates the presence of a single variety of complex species in the system.

Beer's law and calibration curve :

The absorbances of different amounts of Au(III) extracted as in the general procedure at pH 7.0 were noted against the reagent blank. The absorbances showed a linear response up to 15 ppm of gold as seen from table 1 and Fig.2. In each case the remaining aqueous phase after a single extraction was clear and colourless. Furthermore the aqueous phase as tested by an independent method was void of gold.

Effect of potassium iodide concentration :

The extraction behaviour of gold(III) has been studied by varying the iodide concentration in terms of absorbance, keeping rest of the other variables constant. It has been found that 1 ml of 0.03 M aqueous potassium iodide along with 0.1 ml of 0.025 M CTAB is sufficient to extract  $70\mu\text{g}$  of gold. The results are presented in table 2.

Effect of CTAB concentration :

The effect of CTAB concentration of absorbance has also been examined with the variation of CTAB concentration, when the other variables remain constant. It has been found

that 0.1 ml of 0.025 M CTAB is sufficient to extract 70% of gold(III) in a single operation. Increasing concentration of CTAB did not bring about any significant change in the maximum value of absorbance as seen from table 3.

#### Effect of pH :

The liquid-liquid extraction behaviour of the Au(III)-I-CTAB system was investigated over the pH range 0-10. Anions of the buffers had no effect. The complex after extraction, exhibits constant and maximum absorbance in the pH range 0-9.

In a second consecutive operation the organic extract virtually showed no absorption. This indicates a quantitative extraction of Au(III) in a single operation. When the pH value was greater than 9 the absorbance value was found to decrease. From 1 M HCl medium the complex exhibits lower absorbance value. pH 7.0 was selected for all the analytical experiments. Absorbance of the Au(III) complex as a function of pH has been shown in Fig.3.

#### Effect of solvents :

Apart from chloroform some other solvents like benzene, 1,2-dichloroethane, ethylacetate, carbontetrachloride were

tested as the extracting solvents but these offered no special advantages over chloroform. The complex is not extractable into carbontetrachloride. In the present investigation chloroform has been used as the extracting solvents. The results are presented in table 4.

#### Stability of colour :

The rapid development of the maximum colour and its constancy with time indicate that time is not critical factor in gold(III) determination. The absorbance of the Au(III)-I-CTA complex in chloroform measured at different intervals of time are shown in table 5.

#### Interference :

To test the effect of diverse ions on the extraction behaviour, Au(III) was extracted and determined according to the recommended procedure in presence of the desired foreign ion. Extraction pH was set at 7.0 with  $\text{KH}_2\text{PO}_4$  - NaOH buffer. An ion was considered to interfere if the recovery of gold differed by more than  $\pm 3\%$  from the actual amount taken. Gold(III) ( $70 \mu\text{g}$ ) could be determined without interference in presence of the following ions : Cr(III), V(V), Mo(VI), Hg(II), Rh(III), Al(III), Cu(II), Ni(II),

Mg(II), Pt(IV), Pd(II), Zn(II), Cd(II), Pb(II), Zr(IV), Ca(II), Ba(II), Sr(II), Th(IV), La(III), Fe(III), Co(II), Mn(II), Ag(I) and Bi(III). Uranium(VI) interfered.

Among the anions tested the followings did not interfere; borate, phosphate, tartarate, citrate, fluoride, bromide, phthalate, oxalate, acetate, nitrite, ascorbate and EDTA.

Thiocyanate, thiosulphate, thiourea and arsenate interfered. The results are summarised in table 6.

#### Precision and accuracy :

The precision and accuracy of the method were tested by analysing solutions containing a known amount of gold following the recommended procedure. The results are shown in table 7. The process is very simple and rapid requiring only 10-15 minutes for each run.

#### Application - Analysis of synthetic mixtures :

The applicability of the method was tested by analysing some synthetic mixtures. The composition of the mixtures

with percentage recovery of gold are shown in table 8. The results show that the recovery of gold was highly satisfactory. Average of three determinations was taken in each case.

The method has been compared to some other existing methods as seen from Table 9.

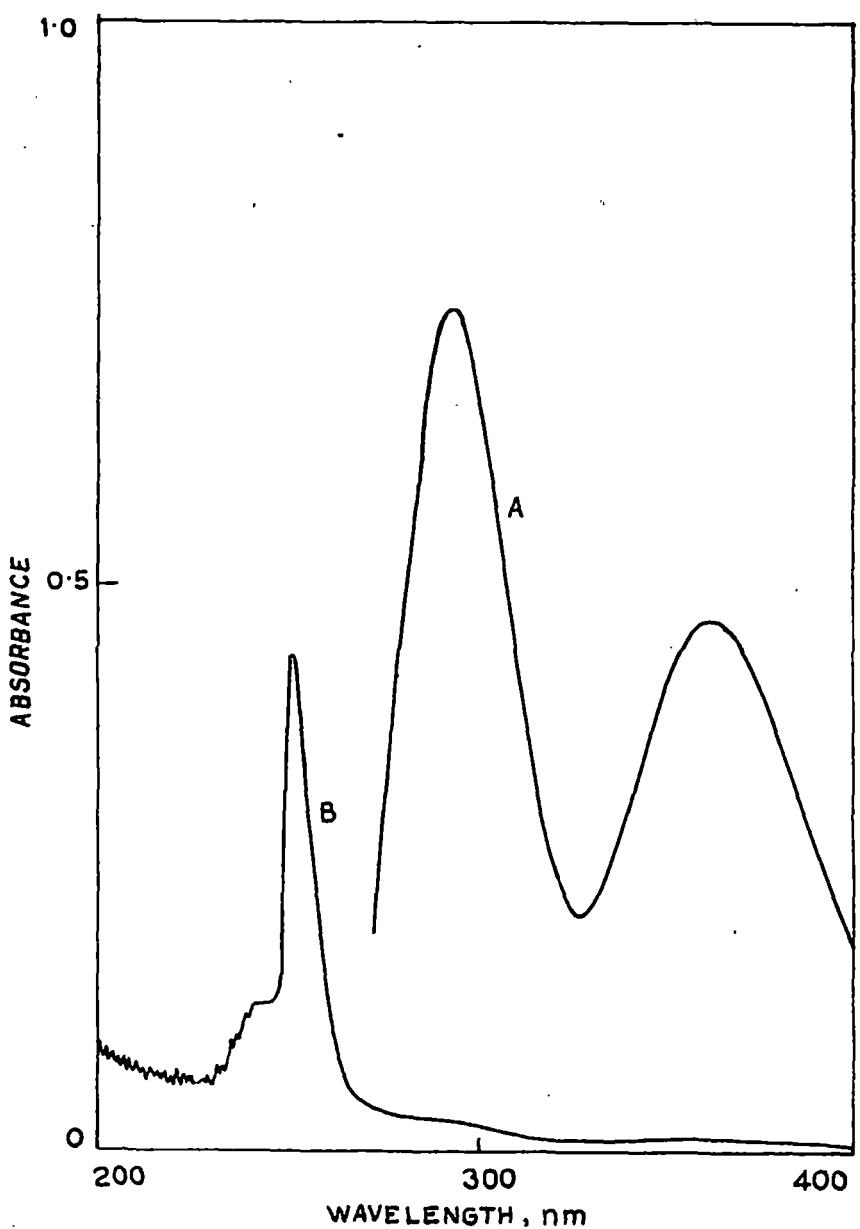


Fig-1. ABSORBANCE SPECTRA OF (A) Au(III)- CTAB COMPLEX(7 ppm Au) AND (B) REAGENT BLANK .

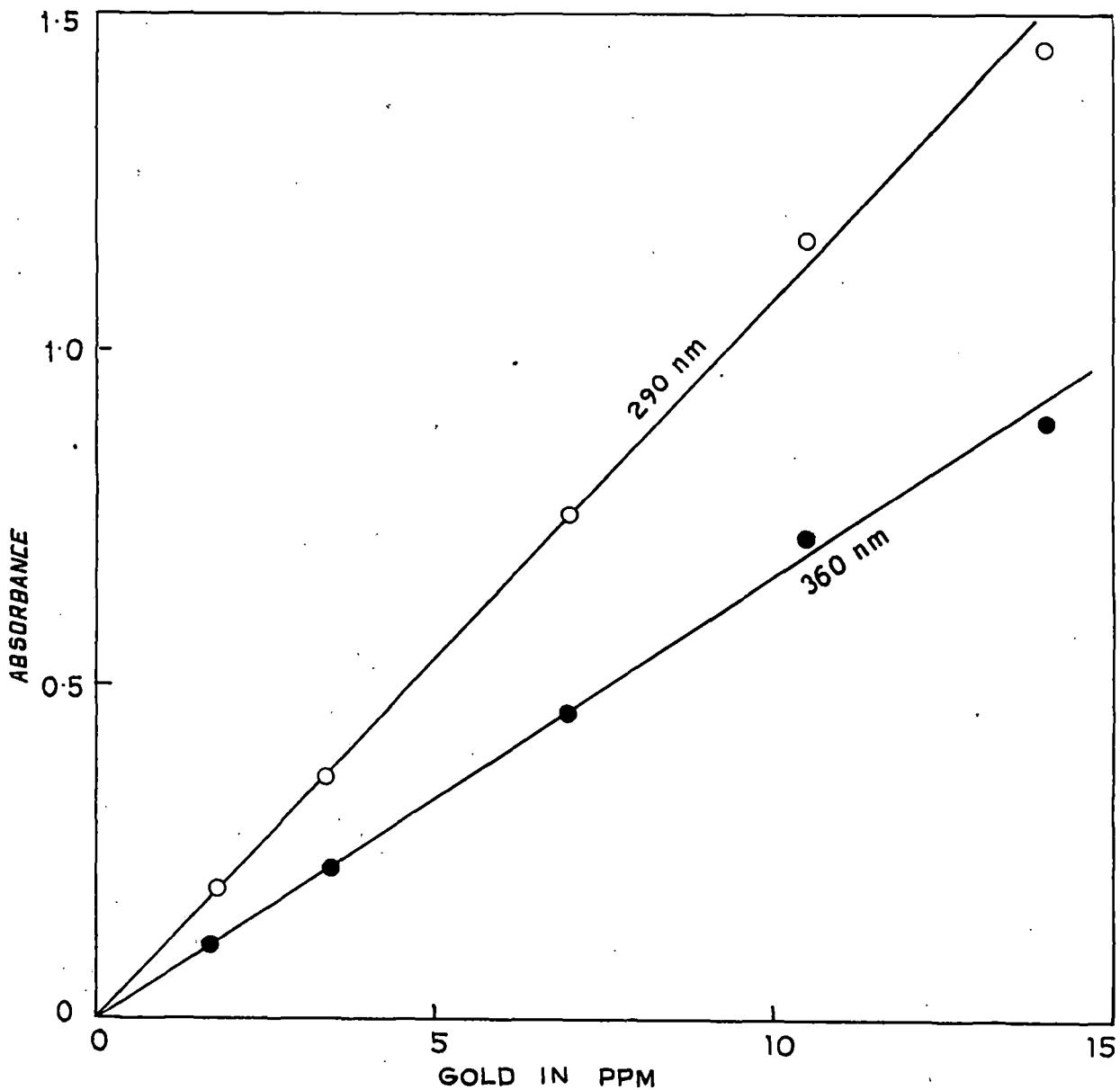


Fig - 2 : BEER'S LAW (Au(III)-I- CTAB System )

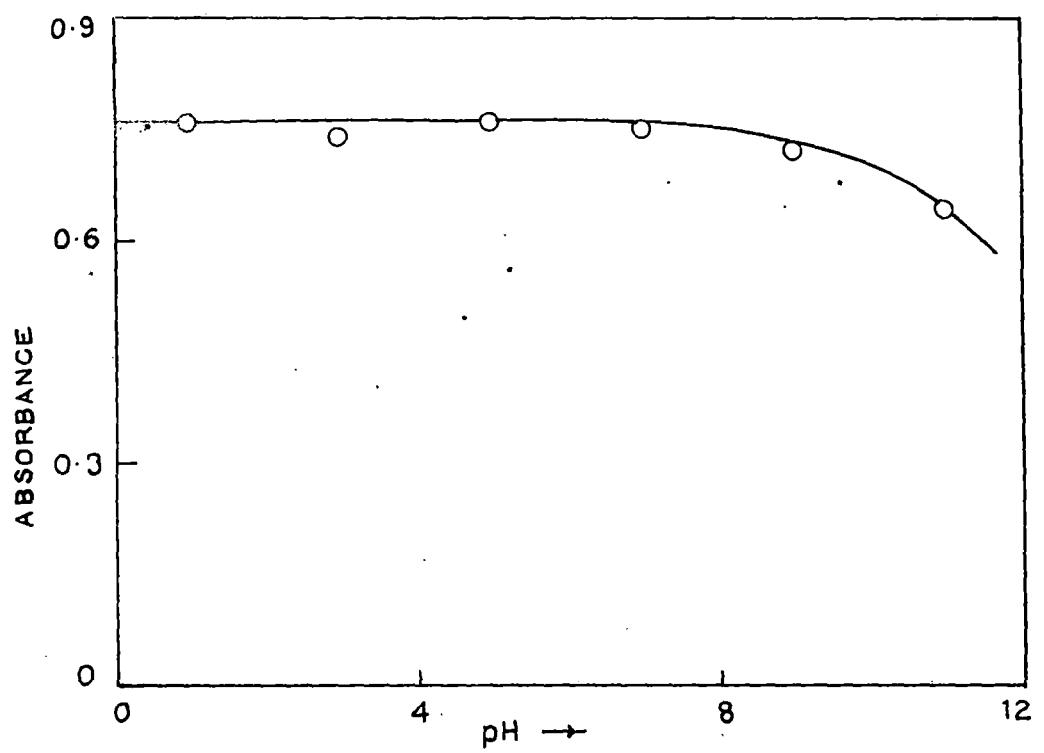


Fig-3: ABSORBANCE AS A FUNCTION OF pH(Gold taken 70  $\mu\text{g}$ )

Table 1 : Adherence to Beer's law

Gold in ppm	Absorbance	
	290 nm	360 nm
1.75	0.195	0.105
3.5	0.360	0.220
7.0	0.760	0.458
10.5	1.170	0.720
14.0	1.45	0.890

Table 2 : Effect of potassium iodide concentration

The aqueous phase (10 ml) contains 70 $\mu$ g gold(III) and 1 ml of 0.025 M CTAB. Extraction pH - 7.0

Aqueous KI concentration in M	Amount added (ml)	Absorbance	
		290 nm	360 nm
0.03	0.05	-	-
0.03	0.1	0.400	-
0.03	0.2	0.550	0.250
0.03	0.3	0.620	0.352
0.03	0.4	0.700	0.400
0.03	0.5	0.762	0.458
0.03	0.6	0.762	0.460
0.03	0.8	0.764	0.455
0.03	1.0	0.762	0.458

Table 3 : Effect of CTAB concentration

The aqueous phase (10 ml) contains 70 $\mu$ g Au(III) and 1 ml 0.03 M KI. Extraction pH-7.0

CTAB concentration (M)	Amount added (ml)	Absorbance at 290 nm	Absorbance at 360 nm
0.012	0.05	-	-
0.012	0.1	0.480	-
0.025	0.05	0.700	0.380
0.025	0.1	0.764	0.458
0.05	0.05	0.760	0.460
0.05	0.1	0.762	0.455
0.1	0.05	0.762	0.458
0.1	0.1	0.764	0.456

Table 4 : Effect of solvents

The aqueous phase (10 ml) contains 70  $\mu\text{g}$  Au(III) along with 1 ml of 0.03 M KI and 0.1 ml of 0.025 M CTAB.  
Extraction pH - 7.0

Solvent	Absorp- tion maxima (nm)	Molar absorpti- vity 1 mol <sup>-1</sup> cm <sup>-1</sup> ( $\times 10^4$ )	Sandell 's sensiti- vity $\mu\text{g}/\text{cm}^2$
Chloroform	290	2.14	0.009
	360	1.29	0.015
Benzene	298	1.97	0.010
	365	1.32	0.014
Ethyl acetate	290	2.08	0.009
	360	1.13	0.017
1,2-dichloroethane	295	1.77	0.011
	365	1.07	0.018
Carbon tetrachloride	NE	NE	NE

NE : Complex is not extractable.

Table 5 : Variation of absorbance with time

Time in hours after extraction	Absorbance at 290 nm	Absorbance at 360 nm
0.25	0.762	0.458
0.5	0.762	0.458
1.0	0.760	0.456
2.0	0.762	0.458
6.0	0.762	0.456
12.0	0.760	0.456
24.0	0.760	0.456

Table 6 : Effect of diverse ions

Au(III) taken 70  $\mu\text{g}$ . Extraction pH 7.0  
(Absorbance measured at 290 nm)

Ions added	Amounts tolerated (mg)	Gold found ( $\mu\text{g}$ )	Error (%)
Cr(III)	7.5	68.5	2.14
V(V)	7.0	72.0	2.8
Mo(VI)	6.5	71.5	2.2
Hg(II)	6.0	70.0	0
Rh(III)	8.0	71.0	1.4
Al(III)	8.8	69.5	0.71
Cu(II)	6.5	68.2	1.0
Ni(II)	7.5	68.5	2.1
Mg(II)	8.0	69.8	0.3
Pt(IV)	6.0	69.5	0.7
Pd(II)	7.0	71.8	2.5
Zn(II)	7.5	68.5	2.1
Cd(II)	7.0	71.0	1.4
Pb(II)	8.0	70.0	0
Zr(IV)	8.0	70.0	0
Ca(II)	9.0	71.0	1.4
Ba(II)	9.0	71.0	1.4
Sr(II)	9.0	70.0	0
Th(IV)	7.0	70.5	0.7

contd...

Table 6 contd ...

La(III)	8.0	69.5	0.7
Fe(III)	3.0	71.8	2.5
Co(II)	3.5	71.0	1.4
Mn(II)	4.0	70.0	0
Ag(I)	4.0	68.0	2.8
Bi(III)	4.0	68.4	2.2
U(VI)	nil	-	-
Borate	14.0	69.5	0.7
Phosphate	15.0	69.0	1.4
Tartarate	15.0	70.0	0
Citrate	16.0	69.8	0.3
Fluoride	15.0	70.4	0.6
Bromide	15.0	70.4	0.6
Phthalate	15.0	70.0	0
Oxalate	14.0	69.5	1.0
Acetate	15.0	70.0	0
Nitrite	15.0	70.0	0
Ascorbate	1.5	68.0	2.8
EDTA	1.5	68.0	2.8
Thiocyanate	nil	-	-
Thiosulphate	nil	-	-
Thiourea	nil	-	-
Arsenate	nil	-	-

Table 7 : Reproducibility of gold recovery  
(Absorbance measured at 290 nm)

Gold taken μg	Gold found (μg)	Mean (μg)	Std. devia- tion (%)
35	35.5, 36.0,	35.5	
	35.0, 34.0,	35.5	35.25 0.62
70	68.5, 70.0,	70.0	
	71.0, 69.0,	68.5	69.5 1.00
105	105, 107,	105	
	107, 106.5,	106.5	106.16 0.96

Table 8 : Analysis of synthetic mixtures  
(Absorbance measured at 290 nm)

Composition with amounts taken in μg	Recovery of gold (%) (Average of three determination)
Au(III) 70, Ag(I) 100, Cu(II) 100, Zn(II) 100	98
Au(III) 70, Fe(III) 100, Co(II) 100, Ni(II) 100	98
Au(III) 70, Pd(II) 100, Pt(IV) 100, Rh(III) 100	101

Table 9 : Comparison

Reagent	$\lambda_{\text{max}}$ (nm)	Molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$	Sandell's Ref. sensitivity $\mu\text{g}/\text{cm}^2$
Methiomeprazine hydrochloride	630	$1.3 \times 10^4$	- 396
Trifluoroethylxanthate	452	$1.09 \times 10^3$	0.018 386
2-Hydroxy-1-naphthaldehyde -4-phenyl-3-thiosemicarbazone	446	$2.08 \times 10^3$	- 397
Acetylpyridine thiosemicarbazone	460	$1.5 \times 10^4$	0.0156 388
1-(2',4',6'-trichloro-phenyl)-4,4,6-trimethyl-(1H,4H)-2-pyrimidinethiol	480	$4.6 \times 10^3$	- 389
2-Pyridyl-2-thieryl-2-ketoxime	477	$2.34 \times 10^4$	- 373
Fluphenazine hydrochloride and	500	$1.334 \times 10^4$	X - 374
Promazine hydrochloride	516	$2.415 \times 10^4$	X -
Amidines	390-395	$(3.15-3.60) \times 10^3$	- 394
Present method	290	$2.14 \times 10^4$	0.009 398
	360	$1.29 \times 10^4$	0.015

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CHAPTER III

4-Nitrosoresorcinol as an Analytical Reagent

### General Discussion

4-Nitrosoresorcinol is a light yellow crystalline solid. Although it is unstable in solid state, its ethanolic solution is stable for weeks.

The colour of the reagent varies markedly with the pH of the solution : below pH 2.5 the colour is pale greenish-yellow, and this increases in intensity and finally becomes orange at about pH 5.6. An increase in the pH above 7.0 results in a slow decrease in intensity of colour.

A programme has been undertaken to develop methods for the spectrophotometric determinations of cobalt, palladium and copper with the reagent.

Section 1 : Extraction and Spectrophotometric Determination  
of Cobalt

EXPERIMENTAL

Apparatus and reagents :

Spectral curves and absorbance measurements were carried out with a Shimadzu PR1 model recording spectrophotometer, equipped with matched quartz cells of 10 mm optical path length.

pH values were measured with an ECL 5651 digital pH meter. Separatory funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of cobalt(II) was prepared by dissolving 5.1 gm cobalt nitrate in 250 ml distilled water and was standarised by using a complexometric method with xylene orange as indicator<sup>8</sup>. Solutions of lower concentrations were prepared by appropriate dilution.

All the chemicals used were of analytical grade. Chloroform (E. Merck), Pyridine (BDH),  $\alpha$ -Picoline (Riedel),  $\beta$ -Picoline (BDH),  $\gamma$ -Picoline (Fluka) and 2,4,6 collidine (BDH) were distilled before use.

4-Nitrosoresorcinol was prepared<sup>9</sup> by mixing a solution of 33 gm of resorcinol in 90 ml of absolute alcohol with a solution of 24 gm of potassium hydroxide in a little absolute alcohol and treating in a freezing mixture with 39 gm of freshly prepared isoamyl nitrite. The solution was cooled for 3-4 hrs in ice. The separated potassium salt was washed with alcohol and ether. 50 gm of the salt was shaken with water to form a thin paste and then acidified with careful cooling with 100 gm of 25% sulphuric acid in which pieces of ice were floating. The light yellow crystalline solid, which was formed was filtered off and recrystallized from dilute alcohol. The reagent in solid state is unstable but its alcoholic solution is stable.

1% ethanolic solution of 4-nitrosoresorcinol was used for our routine work.

Buffer solutions of different pH were prepared by standard procedures. Sodium acetate - acetic acid buffer was used for our practical purpose.

Stock solutions of diverse ions were prepared from their nitrates, chlorides or sulphates in dilute acid or water. Sodium or ammonium salts were used in case of anions.

Determination of cobalt :

An aliquot containing upto 200 $\mu$ g of cobalt(II) was mixed with 0.1 ml of 1% ethanolic solution of 4-nitrosoresorcinol following by the addition of 0.2 ml of Pyridine/ $\alpha$ -Picoline/ $\beta$ -Picoline/ $\gamma$ -Picoline or 2,4,6 collidine. Buffer solution (pH-6) was then added and volume of the aqueous phase was made up to 10 ml. The solution was then equilibrated with 10 ml of chloroform in a separating funnel for 30 sec. The two layers were allowed to settle. 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 395 nm against a cobalt free reagent blank. Amount of cobalt was determined from a previously prepared calibration curve. To test the effect of diverse ions, the respective foreign ion was added to the system before addition of the reagents.

## RESULTS AND DISCUSSION

Absorption spectra :

The spectral curves of cobalt(II) complexes in chloroform are shown in fig.1. The complexes absorbs maximum at 395 nm. The reagent blank absorbs insignificantly in this region. Wave length of 395 nm was

chosen for analytical measurements.

Calibration curve :

Different amount of cobalt were extracted following the general procedure. The absorbance measured showed a linear response over a concentration of 30 ppm of cobalt in all cases. The aqueous phases after each extraction were clear and colourless. The results are shown in table 1 and Fig.2.

Molar absorptivities of the complexes (on the basis of cobalt content) and Sandell's sensitivities were evaluated as shown in table 2.

Effect of 4-nitrosoresorcinol concentration :

The extraction behaviour of cobalt(II) complex have been examined by varying the 4-nitrosoresorcinol concentration maintaining the other variables constant. It has been found that 0.1 ml of 1% ethanolic solution of 4-nitrosoresorcinol along with 0.2 ml of Pyridine/substituted pyridines is sufficient to extract 177 $\mu$ g of cobalt in a single operation. Addition of excess reagent caused a high blank absorbance and was avoided.

Effect of pyridine bases concentration :

The extraction behaviour of cobalt(II) complexes in terms of absorbance have also been studied with different amounts of pyridine/ $\alpha$ -picoline/ $\beta$ -picoline/ $\gamma$ -picoline or 2,4,6 collidine keeping the 4-nitrosoresorcinol concentration fixed. To extract 177 $\mu$ g of cobalt(II) 0.2 ml of the respective pyridine bases has been found to be adequate.

Effect of pH :

Extractability of cobalt(II) into chloroform was investigated in terms of absorbance of the mixed ligand complexes in the pH range 1-12. Maximum absorbance was obtained in the pH region 4-7 in all cases. In a second consecutive operation, the organic extract virtually showed no absorbance. In this pH range complete and quantitative extraction of the metal was achieved within 30 sec in a single extraction. Absorbance as a function of pH is shown in Fig.3.

Choice of solvent :

Apart from chloroform some other solvents were tested as extracting solvents but those offered no special advantages over chloroform.

Stability of colour :

The reaction between cobalt(II)-4-nitrosoresorcinol and pyridine bases were instantaneous. Time is not a critical factor in the determination of the metal. The absorbance of the chloroform extract were measured at different intervals of time. The colour of the cobalt complex was stable for at least 24 hours. The results are tabulated in table 3.

Interference :

In order to study the effect of diverse ions on the extraction behaviour, a definite amount of cobalt(II), was extracted and determined according to the general procedure in presence of the respective foreign ions. In practice all the bases i.e. pyridine,  $\alpha$ -picoline,  $\beta$ -picoline,  $\gamma$ -picoline or 2,4,6 collidine showed similar behaviour in extracting cobalt. In the present investigation -picoline was used as the auxiliary ligand to study interferences. An ion was considered to interfere if the recovery of cobalt (II) differed by more than  $\pm 3\%$  from the actual amount taken. Average of three determination was taken.

177 $\mu$ g of cobalt could be determined without interference of the following ions : Cu(II), Cd(II), Hg(II),

Zn(II), Ni(II), Pt(IV), Rh(IV), La(III), Mn(II), Ca(II), Ba(II), Sr(II), Be(II), Zn(IV), Al(III), Th(IV), Pb(II), Cr(II), U(VI), Mo(VI) and V(V). Interference due to iron (III) was avoided using ammonium bifluoride as the masking agent.

Among the anions tested the following did not interfere in the cobalt determination : thiocyanate, thiosulphate, EDTA, borate, phosphate, tartarate, citrate, fluoride, bromide, iodide, ascorbate and phthalate. The results are shown in table 4.

Precision and accuracy :

Using  $\beta$ -picoline the precision and accuracy of the method were tested by analysing solutions containing a known amount of cobalt(II) following the recommended procedure. The results are shown in table 5. The proposed method is fairly precise and reproducible. The proposed method has also been compared with some other existing methods (Table 6).

Application: Analysis of synthetic mixtures :

In absence of real samples the proposed method (using  $\beta$ -picoline) was applied to the analysis of various synthetic mixtures containing 177 $\mu$ g of cobalt. The results are shown in table 7.

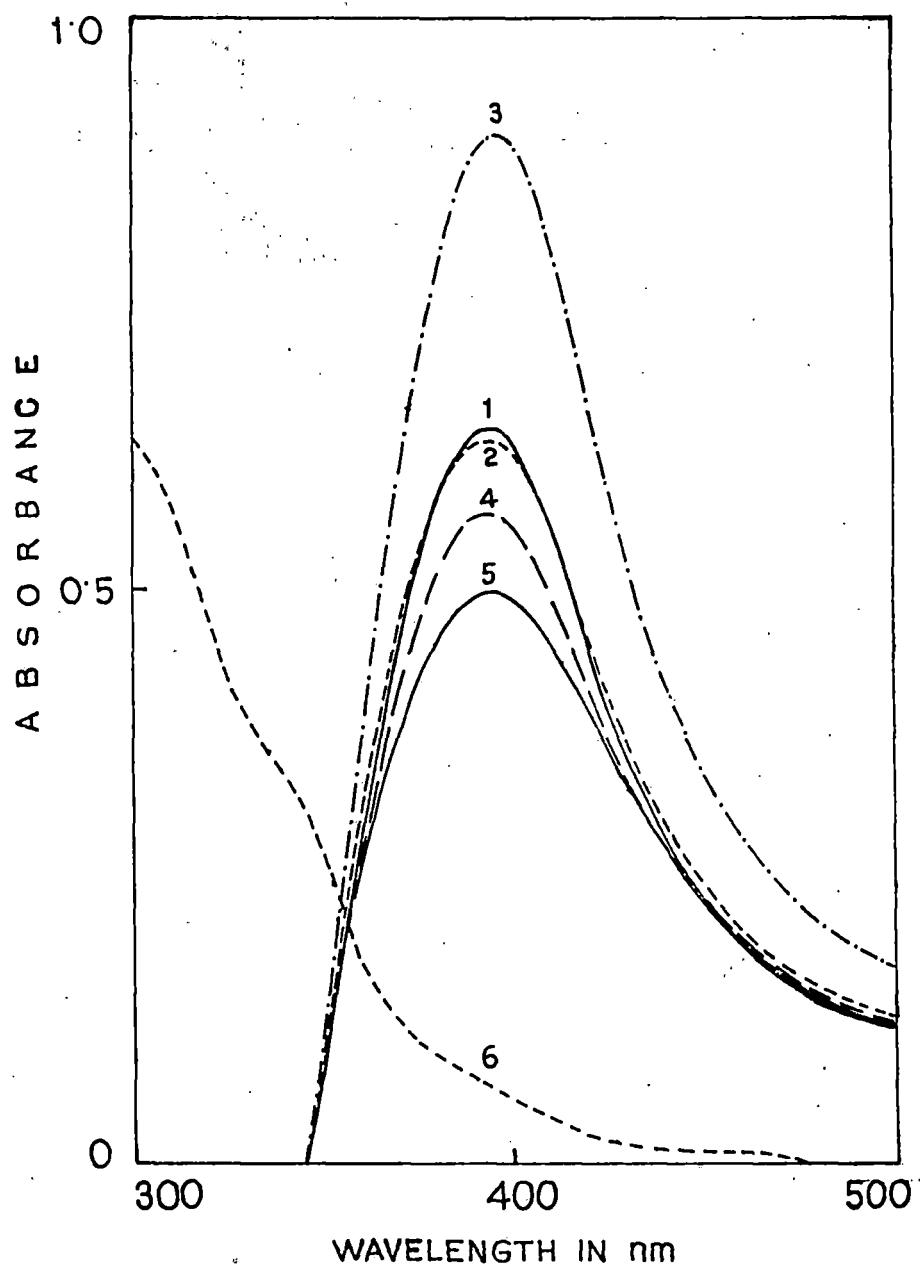


Fig. 1. ABSORPTION SPECTRA OF COBALT COMPLEXES  
(17.7 ppm Co) AND REAGENT BLANK

- (1) 4-NITRORESORCINOL-PYRIDINE
- (2) 4-NITRORESORCINOL- $\alpha$ -PICOLINE
- (3) 4-NITRORESORCINOL- $\beta$ -PICOLINE
- (4) 4-NITRORESORCINOL- $\gamma$ -PICOLINE
- (5) 4-NITRORESORCINOL-2,4,6-COLLIDINE
- (6) 4-NITRORESORCINOL-PYRIDINE BLANK

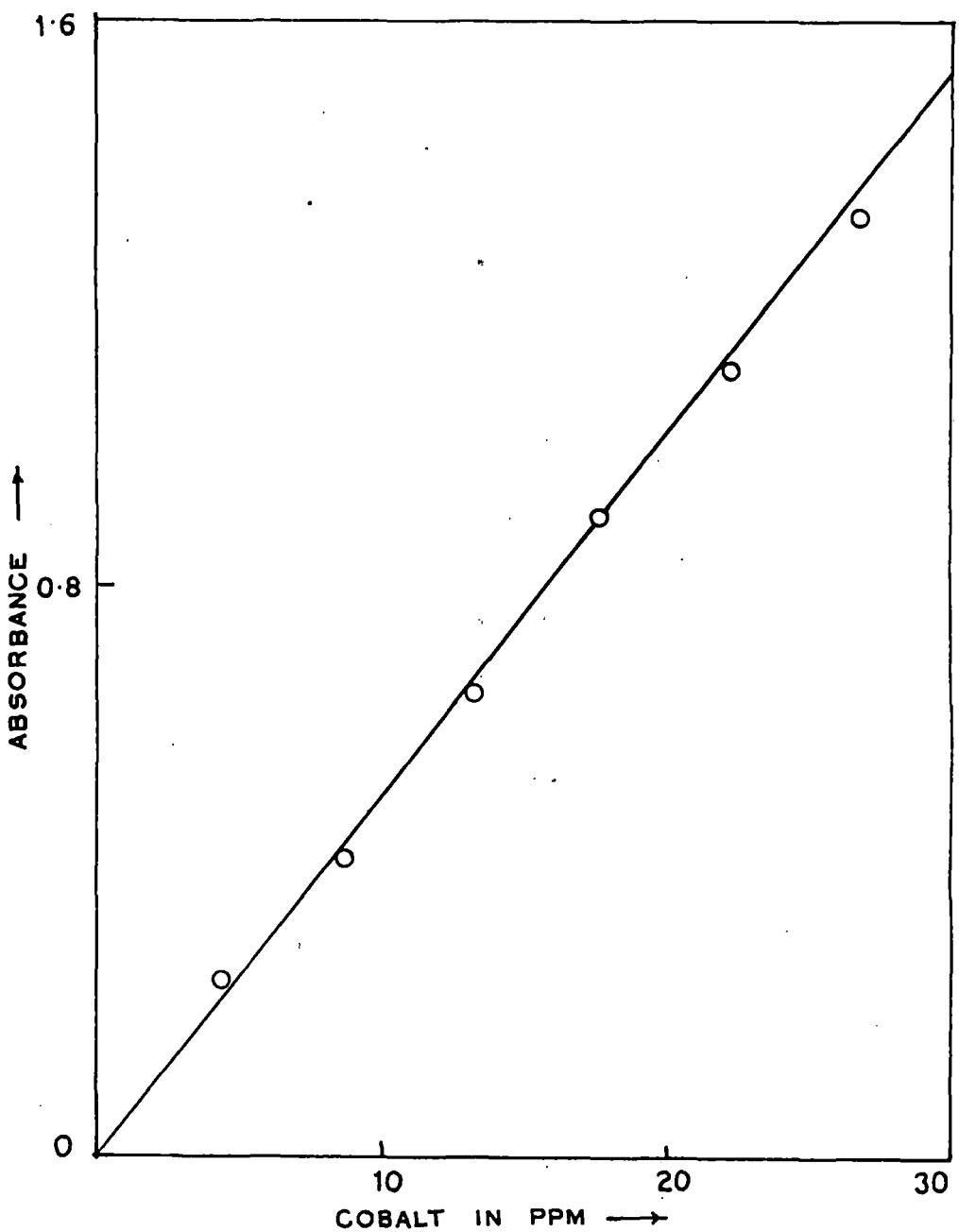


Fig-2 : BEER'S LAW (with  $\beta$ -picoline )

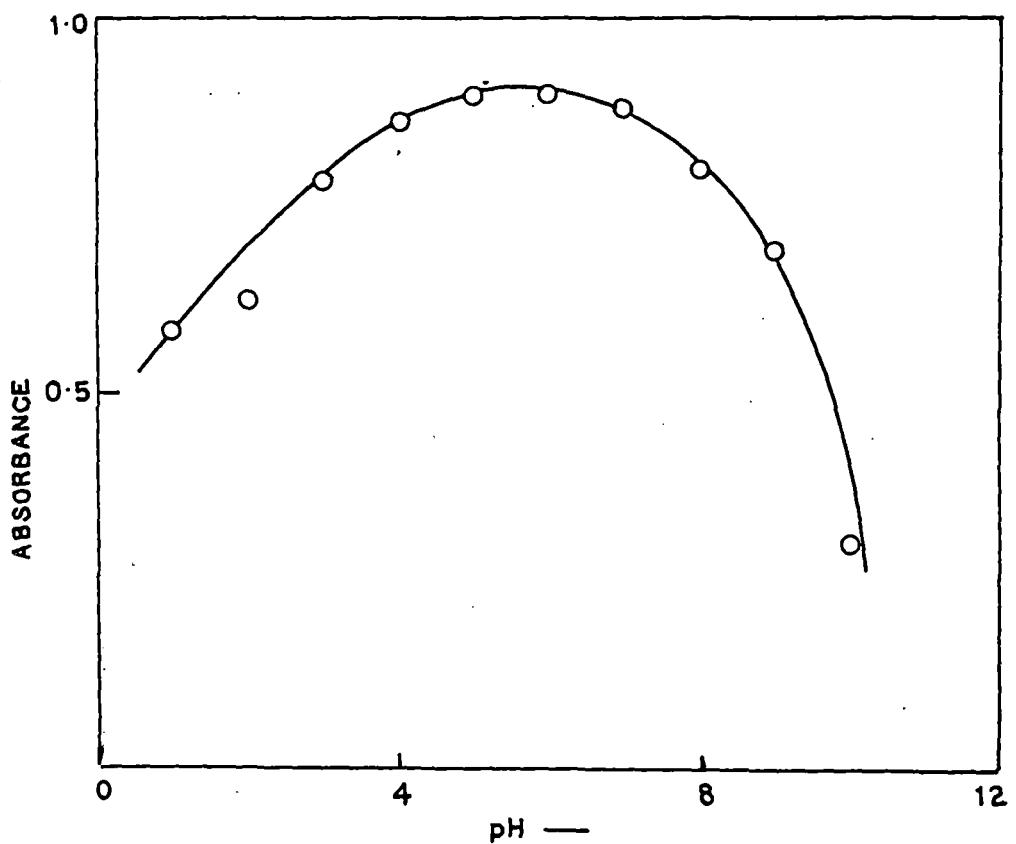


Fig-3 - Absorbance as a function of pH. Co taken 177  $\mu\text{g}$ .

Table 1 : Beer's law data  
(with  $\beta$ -picoline)

Cobalt in ppm	Absorbance at 395 nm
4.42	0.250
8.45	0.422
13.27	0.650
17.70	0.898
22.12	1.110
26.55	1.330

Table 2 : Details of Extractive Methods

Parameter	Base employed				
	Pyridine	$\alpha$ -Picoline	$\beta$ -Picoline	$\gamma$ -picoline	2,4,6-collidine
pH	4-7	4-7	4-7	4-7	4-7
$\lambda_{max}$	395	395	395	395	395
Molar absorptivities ( $1 \text{ mol}^{-1} \text{cm}^{-1}$ )	$2.12 \times 10^3$	$2.09 \times 10^3$	$2.99 \times 10^3$	$1.89 \times 10^3$	$1.65 \times 10^3$
Sandell's sensitivity $\mu\text{g}/\text{cm}^2$	0.027	0.028	0.019	0.031	0.035

Table 3 : Variation of absorbance with time (with  
β-picoline) Co taken - 177 μg

Time in hours after extraction	Absorbance at 395 nm
0.25	0.898
0.50	0.898
2.0	0.896
6.0	0.896
12.0	0.895
24.0	0.895

Table 4 : Effect of diverse ions (using  $\beta$ -picoline)  
(Cobalt taken 177  $\mu$ g)

Ion added	Amount tolerated (mg)	Cobalt found ( $\mu$ g)	Error %
Cu(II)	5.1	181.0	2.2
Cd(II)	4.9	177.5	0.3
Hg(II)	5.0	175.0	1.1
Zn(II)	6.0	177.0	0.0
Ni(II)	5.3	177.0	0.0
Pd(II)	5.0	180.0	1.7
Pt(IV)	3.9	179.0	1.1
Rh(III)	3.2	177.5	0.3
La(III)	2.0	174.0	1.7
Mn(II)	5.2	176.0	0.5
Ca(II)	6.0	176.6	0.2
Ba(II)	5.9	178.0	0.5
Sr(II)	5.7	177.0	0.0
Be(II)	5.1	175.4	0.9
Zr(IV)	0.1	173.0	2.2
Al(III)	0.2	173.5	2.2
Th(IV)	0.4	173.5	1.9
Pb(II)	0.5	174.0	1.7
Cr(III)	0.3	174.0	1.7
U(VI)	0.2	173.5	1.9

contd ...

Table 4 contd ...

Mo(VI)	20.0	181.0	2.0
Fe(III)*	1.5	180.0	1.7
V(V)	20.0	180.0	1.7
Thiocyanate	15.0	179.0	1.1
Thiosulphate	7.0	176.0	0.5
EDTA	0.1	173.0	2.2
Borate	20.0	179.0	1.1
Phosphate	0.1	173.0	2.2
Tartarate	20.0	177.0	0.0
Citrate	0.5	176.6	0.2
Fluoride	20.0	177.6	0.0
Bromide	20.0	177.5	0.3
Iodide	11.0	178.5	0.8
Ascorbate	20.0	178.0	0.5
Phthalate	20.0	177.5	0.3

\* In presence of  $\text{NH}_4\text{HF}_2$

Table 5 : Reproducibility of cobalt recovery  
(using  $\beta$ -Picoline)

Cobalt taken $\mu\text{g}$	Cobalt found ( $\mu\text{g}$ )	Mean $\mu\text{g}$	Std. deviation
	87.5,    87.0,    89.2		
88.5		88.45	1.13
	90.0,    88.0,    89.0		
	175.5,    176.0,    179.4		
177.0		177.06	1.49
	177.5,    178.0,    176.0		
	263.5,    264.0,    266.5		
265.5		265.0	1.45
	265.0,    267.0,    264.0		

Table 6 : Comparison

Reagent	$\lambda_{\text{max}}$ (nm)	molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$	Sensitivity $\mu\text{g/cm}^2$	Ref.
1,6-Hexanediamine -N,N,N',N'-tetra acetic acid	550	137	0.4301	1
NaOCN and 2,3,5 triphenyl tetra- zolium chloride	631	$1.08 \times 10^3$	-	2
Triphenyl tetra- zolium cation and tetrathiocyanate cobaltate	620	$3.2 \times 10^3$	-	3
5-Methoxy-2-nitro- sophenol	540	$5.5 \times 10^5$	0.0107	4
Potassium propyl xanthate	480	-	0.09	5
	620	-	0.14	
2-Thio ortic acid and $\text{Et}_3\text{N}$	-	$1.158 \times 10^3$	0.051	6
Tetrathiocyanato cobaltate(II) and neotetrazolium chloride	-	-	0.02	7
Present method	395	$2.99 \times 10^3$	0.019	

Table 7 : Determination of cobalt ( $177 \mu\text{g}$ ) in various mixtures with 500 g of each ion added.  
(Auxiliary ligand used  $\beta$ -Picoline)

Ion added	Cobalt found $\mu\text{g}$
1. $\text{Cu}^{+2}$ , $\text{Ni}^{+2}$ , $\text{Fe}^{+3}$ *	175.5
2. $\text{Mn}^{+2}$ , $\text{Cu}^{+2}$ , $\text{Fe}^{+3}$ *	174.5
3. $\text{Cr}^{+3}$ , $\text{Mn}^{+2}$ , $\text{Zn}^{+2}$	176.5
4. $\text{Cu}^{+2}$ , $\text{Cd}^{+2}$ , $\text{Pb}^{+2}$	180.5
5. $\text{Cu}^{+2}$ , $\text{Cd}^{+2}$ , $\text{Mg}^{+2}$	178.5

\*Plus  $\text{NH}_4\text{HF}_2$  (2 mg).

Section 2 : Extraction and Spectrophotometric Determination  
of Palladium

EXPERIMENTAL

Apparatus and Reagents :

Spectral curves and absorbance measurements were carried out with a Shimadzu PR-1 model recording spectrophotometer, provided with optically matched quartz cells of 10 mm path length. pH values were measured with an ECL 5651 digital pH meter. Separatory funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of palladium(II) was prepared by dissolving 1 gm palladium chloride (Johnson & Mathey) in 1 ml of HCl and diluted to 250 ml with distilled water followed by standarisation with dimethylglyoxime<sup>21</sup>. Working solution (210.5  $\mu$ g Pd/ml) was prepared by dilution. Solutions of lower concentrations were prepared by appropriate dilution.

All the chemicals used were of analytical grade. Chloroform (E. Merck), Pyridine (BDH),  $\alpha$ -Picoline (Riedel),  $\beta$ -Picoline (BDH),  $\gamma$ -Picoline (Fluka) and 2,4,6 collidine (BDH) were distilled before use.

4-Nitrosoresorcinol was prepared as described earlier. 1% Ethanolic solution of the reagent was used for our investigation.

Buffer solutions of different pH were prepared by standard procedures. Standard solutions of diverse ions were prepared from their corresponding salts to study interferences.

#### Determination of palladium :

An aliquot containing upto 100  $\mu$ g of palladium was mixed with 0.2 ml of 1% ethanolic solution of 4-nitroso-resorcinol followed by addition of 0.5 ml of pyridine/ $\alpha$ -Picoline/ $\beta$ -Picoline/ $\gamma$ -Picoline or 2,4,6 collidine. The pH of the solution was adjusted to 2.0 with KCl-HCl buffer. The volume of the aqueous phase was maintained at 10 ml. The solution was then equilibrated with 10 ml of chloroform in a separating funnel for 1 min. The two layers were allowed to settle. The separated organic layer was shaken with anhydrous sodium sulphate to remove

any moisture. Finally the absorbance of the organic extract was measured at the corresponding absorption maxima (Table 2) against a palladium free reagent blank. The amount of palladium(II) was determined from a previously prepared calibration curve.

#### RESULTS AND DISCUSSION

##### Absorption spectra :

The spectra of the mixed-ligand complexes were scanned in the wave-length region 300-600 nm against the corresponding reagent blanks. The Pd(II)-complexes showed absorption maxima at 395-400 nm. As the reagent blanks showed some absorbances in the aforesaid wave-length region, all the analytical measurements were carried out against the respective blanks. Fig.1 shows the spectra of Pd(II)-4-nitrosoresorcinol- $\beta$ -picoline and the corresponding blank. The pattern of the spectra of other Pd-complexes extracted in presence of pyridine and other substituted pyridine bases remains the same.

##### Calibration curve :

Different amounts of palladium have been extracted following the general procedure at pH-2 and the absorbance

were measured. The system conforms to Beer's law in each case. In each case the aqueous phase after extraction was clear and colourless. Furthermore the aqueous phase as tested by an independent method was void of palladium. The results are shown in table 1 and Fig.2.

The molar absorptivities of the complexes and Sandell's sensitivities (on the basis of palladium content) are calculated as seen from table 2.

#### Effect of 4-nitrosoresorcinol concentration :

The extent of absorbance has been examined with different amount of 4-nitrosoresorcinol, keeping all other variables constant. It has been found that 0.2 ml of 1% ethanolic solution of 4-nitrosoresorcinol along with 0.5 ml of pyridine/ $\alpha$ -picoline/ $\beta$ -picoline/ $\gamma$ -picoline or 2,4,6-collidine is sufficient to extract upto 100 $\mu$ g of Pd(II) in a single operation. The higher concentration of reagent had no adverse effects on the absorbance but was avoided.

#### Effect of Pyridine bases concentration :

The extraction behaviour of palladium(II) in terms of absorbance has also been studied with different amounts of

pyridine,  $\alpha$ -picoline,  $\beta$ -picoline,  $\gamma$ -picoline, and 2,4,6-collidine maintaining rest of the variables fixed. It was observed that 0.5 ml of pyridine,  $\alpha$ -picoline,  $\beta$ -picoline,  $\gamma$ -picoline or 2,4,6-collidine along with 0.2 ml (1%) of ethanolic solution of 4-nitrosoresorcinol is sufficient to extract upto 100  $\mu\text{g}$  of Palladium(II).

#### Effect of acidity :

The extraction of palladium complexes was investigated in terms of absorbance in the pH range 0-11. A steady and maximum absorbance was obtained when the extractions were carried out in the pH range 1-8. When the extraction was repeated with the same aqueous phase, the organic extract virtually showed no absorbance. The aqueous phase, after extraction, was also tested for palladium by an independent method. This indicated a complete and quantitative extraction of palladium in this pH range. Extraction of palladium as a function of acidity has been shown in Fig.3.

Apart from chloroform some other solvents were tested as extracting solvents but those offered no special advantages over chloroform.

Stability of colour :

The reaction between palladium(II) 4-nitrosoresorcinol and pyridine bases were instantaneous. The absorbance of the chloroform extracts were stable for at least 6 hours as seen from Table 3.

Interference :

In order to study the effect of diverse ions on the extraction behaviour, palladium was determined according to the recommended procedure (using  $\gamma$ -Picoline) in presence of the respective foreign ion. Extraction pH was set at 2 with KCl-HCl buffer. Deviation of not more than  $\pm$  3% from the recovery of palladium was taken as the standard tolerance limit. In practice all the pyridine bases i.e., pyridine/ $\alpha$ -picoline/ $\beta$ -picoline/ $\gamma$ -picoline or 2,4,6-collidine showed similar behaviour. Palladium(II) (84.2  $\mu$ g).could be determined without interference in presence of the followings : Ni(II), Cd(II), Hg(II), Zn(II), V(V), Pt(IV), Rh(IV), Mn(II), Be(II), Mo(VI), Zr(IV), U(VI), La(III), Al(III), Tl(I), Pb(II) and Cr(III). Fe(III) and Cu(II) could be tolerated in presence of ammoniumbifluoride and citrate respectively. High results were obtained in presence of cobalt(II).

Among the anions tested, the system tolerated the followings : borate, phosphate, bromide, iodide, phthalate, acetate, tartarate, citrate, fluoride, ascorbate, oxalate, EDTA, chloride, nitrate and sulphate. Thiocyanate and thiosulphate interfere seriously. The results are presented in table 4.

Precision and accuracy :

With  $\sqrt{-}$ -Picoline the precision and accuracy of the proposed method were tested by analysing solutions containing a known amount of palladium(II) following the recommended procedure (Table 5). The proposed method is fairly precise reproducible. The total operation for each run requires hardly 10-15 min. The method has been compared to some other existing methods (Table 6).

Application: Analysis of synthetic mixtures :

In absence of real samples the method has been applied to a number of synthetic mixture to estimate palladium (Table 7).

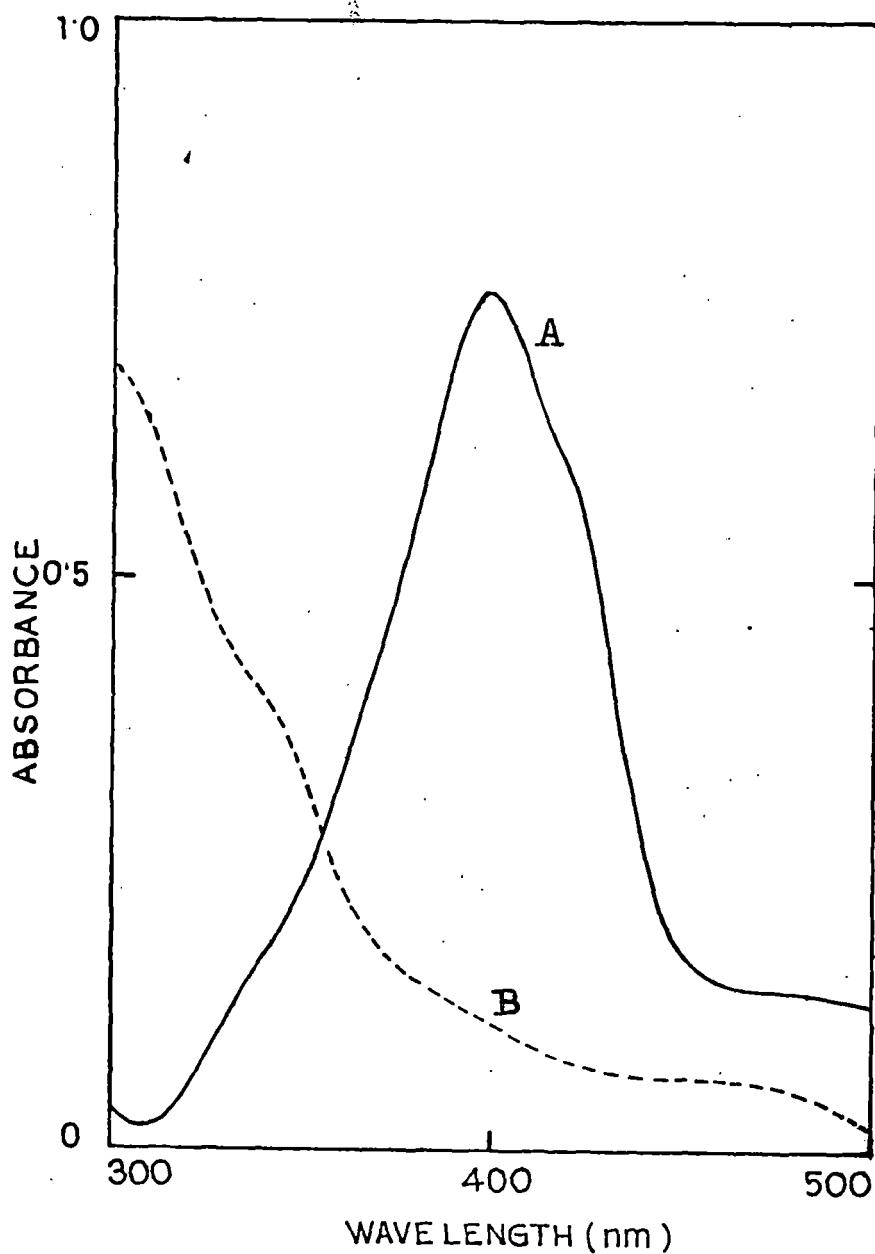


Fig.1. Absorbanc spectra of (A) Pd(II)-4-nitroresorcinol-2-picoline complex (4.2 ppm Pd) and (B) Reagent blank.

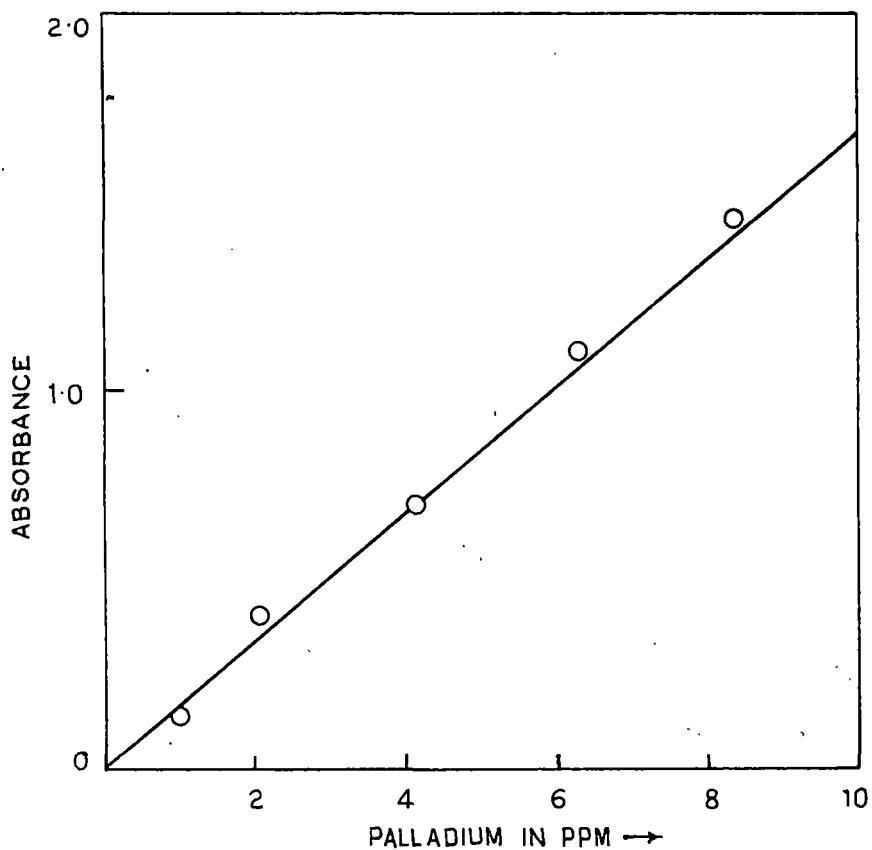


Fig-2. BEER'S LAW (with  $\delta$ - picoline )

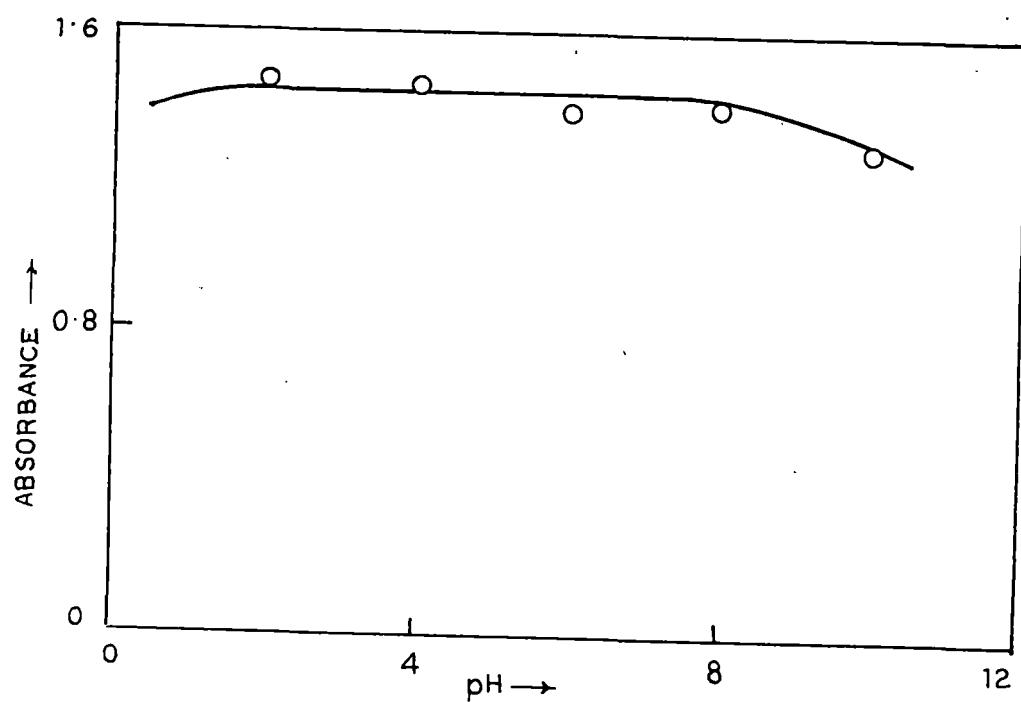


Fig-3: ABSORBANCE AS A FUNCTION OF pH. Pd taken 84.2  $\mu\text{g}$   
(with  $\delta$ -picoline ).

Table 1 : Beer's law data  
(with  $\gamma$ -picoline)

Palladium in ppm	Absorbance at 395 nm
1.05	0.148
2.1	0.400
4.2	0.690
6.3	1.110
8.4	1.486

Table 2 : Details of Extractive Methods

Parameter	Base employed				
	Pyridine	$\alpha$ -Picoline	$\beta$ -picoline	$\gamma$ -picoline	2,4,6-collidine
$\lambda_{max}$	395	400	395	395	400, 410*
Molar absorptivity ( $1 \text{ mol}^{-1} \text{cm}^{-1}$ )	$3.28 \times 10^4$	$2.68 \times 10^4$	$3.44 \times 10^4$	$3.52 \times 10^4$	$3.47 \times 10^4$
Sandell's sensitivity ( $\mu\text{g}/\text{cm}^2$ )	0.0032	0.0039	0.0030	0.0029	0.0031

\*shoulder

Table 3 : Variation of absorbance with time  
(Palladium taken 84.2  $\mu$ g, base  
used -  $\gamma$ -Picoline)

Time in hours after extraction	Absorbance at 395 nm
0.25	1.486
0.5	1.486
2.0	1.480
4.0	1.482
6.0	1.480

Table 4 : Effect of diversions on determination of 84.2  $\mu\text{g}$  of palladium (using  $\gamma$ -Picoline). Extraction pH-2.0

Ion added	Amount tolerated (mg)	Palladium found $\mu\text{g}$	Error %
Ni(II)	4.5	83.5	0.8
Cd(II)	4.5	83.0	1.4
Hg(II)	4.0	84.0	0.2
Zn(II)	5.0	85.5	1.5
V(V)	5.0	83.6	0.7
Pt(IV)	3.0	86.0	2.1
Rh(II)	2.5	86.0	2.1
Mn(II)	4.5	82.5	2.7
Be(II)	5.0	82.5	2.7
Mo(VI)	3.0	83.0	1.4
Zr(IV)	2.0	85.5	1.5
U(VI)	2.0	86.0	2.1
La(III)	2.5	84.0	0.2
Al(III)	2.5	84.5	0.3
Tl(I)	2.0	85.6	1.6
Pb(II)	2.5	85.0	1.0
Cr(III)	2.5	84.6	0.5
Fe(III) <sup>1</sup>	1.0	86.0	2.1
Cu(II) <sup>2</sup>	1.0	86.0	2.8
Co(II)	nil	-	-

contd ...

Table 4 contd ...

Borate	8.5	84.5	0.5
Phosphate	8.0	85.5	1.5
Bromide	10.0	84.2	0.0
Iodide	10.0	84.0	0.2
Phthalate	10.0	84.6	0.5
Acetate	10.0	84.0	0.2
Tartarate	10.0	85.2	1.2
Citrate	10.0	84.6	0.5
Fluoride	10.0	84.6	0.5
Ascorbate	10.0	83.6	0.70
Oxalate	10.0	84.8	0.70
EDTA	2.0	83.4	1.0
Chloride	10.0	84.6	0.5
Nitrate	10.0	85.6	1.6
Sulphate	10.0	84.2	0.0

1. in presence of  $\text{NH}_4\text{HF}_2$
2. in presence of citrate

Table 5 : Reproducibility of palladium recovery

Palladium taken / $\mu$ g	Palladium found / $\mu$ g	Mean / $\mu$ g	Std deviation %
21.05	20.5, 20.5, 20.0	20.21	0.46
	19.5, 20.0, 20.8		
42.1	43.5, 41.5, 42.0	42.21	0.78
	42.8, 42.0, <del>41.5</del>		
84.2	83.5, 83.0, 83.0	83.50	0.63
	84.0, 84.5, 83.0		

Table 6 : Comparison

Reagent	$\lambda_{\text{max}}$ (nm)	molar absorptivity $1 \text{ mol}^{-1} \text{cm}^{-1}$	Sensi- tivity $\mu\text{g}/\text{cm}^2$	Ref.
1. 2-thiobarbutric acid	374 in water	$1.0 \times 10^4$	0.0106	X
	386 in EtOH	$7.5 \times 10^3$	0.0141	X X X 10
2. 3-bromo-2-hydroxy-5-methyl acetophenone hydrazone	400	$4.5 \times 10^3$	0.0235	11
3. 2,2 dipyridyl-2-quinolyl hydrazone	570	$14.00 \times 10^3$	0.0076	12
4. Xanthates	-	$(1.76-1.9) \times 10^2$	0.5-0.65	13
5. N-Naphthyl-N-pyridyl thiourea	390	$3.4 \times 10^4$	0.0096	14
6. Phenanthraquinone monothiosemicarbazone	590	-	0.025	X
	540	-	0.0083	X X 15
7. n-Butylxanthate	385	$1.32 \times 10^4$	0.008	16
8. N-Mercapto acetamide	320	$1.85 \times 10^4$	0.016	17

contd ...

Table 6 contd ...

9.	2-Hydroxy 3,5-dimethyl acetophenone oxime	400	$1.08 \times 10^3$	0.10	18
10.	Potassium iodide and substituted pyridines	354-360	$(1.6-1.9) \times 10^4$	0.1-0.018	19
11.	Present method	395-400	$(2.6-3.5) \times 10^4$	0.003-0.004	20

Table 7 : Estimation of palladium ( $84.2\mu\text{g}$ ) in various synthetic mixtures with  $200\mu\text{g}$  of each ion added (average of three determinations)

Ions added	Palladium found ( $\mu\text{g}$ )
1. Pd, Pt, Rh, Ni	84.0
2. Pd, Pt, Ni, Mn	83.5
3. Pd, Rh, Ni, Mn	84.6
4. Pd, Fe, V, Mo <sup>1</sup>	86.0
5. Pd, Cu, V, Mo <sup>2</sup>	86.5()

1 in presence of  $\text{NH}_4\text{HF}_2$ 

2 in presence of citrate.

Section 3 : Extraction and Spectrophotometric Determination  
of Copper

INTRODUCTION

Numerous methods 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  $\beta$ -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<sup>22</sup> was investigated at pH 8.5. The absorbance of the complex was measured at 560 nm in butyl acetate. Other well known

method involves the utilization of neo-cuproin<sup>23</sup> and biscyclohexanone oxalyl dihydrazone<sup>24</sup> 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<sup>25</sup>.

Hy, Tse-Te and Kao, Fa-Kuei<sup>26</sup> used 2-z-(5-bromo-2-pyridyl) azoz-5-(diethylamino) phenol for the spectrophotometric determination of copper. The 1:1 (metal:ligand) complex was extracted into chloroform and the absorbance was measured at 550 nm. Gonzalez et al<sup>27</sup> determined copper (II) spectrophotometrically at 680 nm as its 1:2 (metal:ligand) complex with mucic acid at pH 10.0.

Reddy T et al<sup>28</sup> 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 mono ethyl ester of n-butyl-amino-o-hydroxy benzyl phosphonic acid<sup>29</sup>. 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-ylidine)

diaminoethane<sup>30</sup>, 6-(2-quinolylazo)-3,4 dimethylphenol<sup>31</sup>, di-2-Pyridylglyoxal-2-quinolylhydrazone<sup>32</sup>, 1-phenyl-3 thio benzyoylthio carbamide<sup>33</sup>, ammonium (2-amino-3-hydroxy-4-pyridylazo) benzene-4-arsonate<sup>34</sup>, citric acid or EDTA<sup>35</sup>, biacetylmonoquinolyl hydrazone<sup>36</sup>, 2,2'-dipyridyl-2-pyridyl hydrazone<sup>37</sup>, m-xylene diamine-N,N,N',N'-tetracetic acid<sup>38</sup>, 3,5-dibromo salicyl aldehyde-4-phenyl-3-thiosemicarbazone<sup>39</sup>, 4-methyl tetrahydrobenzofurano (6,7-6) coumarin<sup>40</sup>, ethylene diamine tetramethylene phosphonic acid<sup>41</sup>, 2-(2-furanyl methylene hydrazine carbothioamide) and 2-(diphenylmethylen) hydrazine carbothioamide<sup>42</sup> N-(o-carboxyphenyl)-N'-(P-sulfophenyl)-c-phenyl formazin<sup>43</sup>, 2-methyl-1,3-cyclohexanedione bis (4-phenyl-3-thiosemicarbazone)<sup>44</sup>, Isonitrosothiocamphor<sup>45</sup> have been investigated for the spectrophotometric determination of copper.

Xia, Daopei and Lin, Qingxiong<sup>46</sup> determined copper(I) spectrophotometrically by using 2-(5 bromo-2-Pyridylazo)-5-(diethylamino) phenol and sodium luryl sulphate. The complex exhibits maximum absorbance at 545 nm in the pH range 4.0-7.0. Copper(II) was determined spectrophotometrically by using 2-( -pyridyl)-thioquinalidinamide<sup>47</sup>. The blue-violet chelate was formed over a wide pH range (0.5-6.5). The metal-ligand ratio was found to be 1:3.

Shrivastava, Madhulika and Pandey G.S<sup>48</sup> determined copper spectrophotometrically by using 2-thioortic acid.

The 1:1 complex shows its absorption maximum at 410 nm over the pH range 11.3-11.8. Copper(II) was extracted at pH 4.5 with 3-methoxy salicyl aldoxime<sup>49</sup> into chloroform and was spectrophotometrically determined. The complex absorbs maximum at 360 nm.

Evtimova, B<sup>50</sup> determined copper(II) with chrome azurols and cationic surfactants. An ion-association complex of copper(II) with alizarin complexon and allogen<sup>51</sup> has been studied spectrophotometrically. The complex was extractable into toluene. Another ion-association system for copper involves the utilization of benzyltrimethylammonium chloride in presence of thiocyanate<sup>52</sup>. The complex was extractable into 1,2 dichloroethane and shows its maximum absorbance at 470 nm.

Thokdar T.K<sup>53</sup> et al determined copper(II) by using mixed ligand complex formulation with pyridine,  $\alpha$ -Picoline,  $\beta$ -Picoline,  $\gamma$ -Picoline or 2,4,6-collidine in presence of bromide/iodide.

Copper was determined spectrophotometrically after absorption of its tetrahydrofarfuryl xanthate<sup>54</sup> on micro-crystalline naphthalene at pH 4.0-10.0. The complex absorbs maximum at 430 nm. Xu, Manyi<sup>55</sup> et al determined copper(II) spectrophotometrically by using  $\alpha, \beta, \gamma, \delta$  tetra (4-Pyridyl)-Porphyrin. The 1:1 complex absorbs maximum at 418 nm.

## EXPERIMENTAL

### Apparatus and Reagents :

A Shimadzu PR1 model recording spectrophotometer with matched quartz cells of 10 mm optical path length was used for the absorbance measurements. All the pH measurements were carried out with ECL 5651 digital pH meter. Separating funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of Copper(II) was prepared from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in distilled water containing few drops of sulphuric acid and was standarised<sup>21</sup>. Test solutions were prepared by appropriate dilution of the stock.

All the chemicals used were of analytical grade. Chloroform (E.Merck), Pyridine (B.D.H),  $\alpha$ -Picoline (Riedel)  $\beta$ -Picoline (BDH)  $\gamma$ -Picoline (Fluka) and 2,4,6-collidine (BDH) were distilled before use.

4-Nitrosoresorcinol was prepared in the laboratory as before and its ethanolic solution (1%) was used. Buffer solution of different pH were prepared by standard procedures. Standard solution of diverse ions were prepared from their corresponding salts to study interference.

Determination of copper :

An aliquot containing upto 100  $\mu\text{g}$  of Cu(II) was mixed with 1% ethanolic solution (0.2 ml) of 4-nitroresorcinol followed by addition of pyridine/ $\alpha$ -picoline/ $\beta$ -picoline/ $\gamma$ -picoline or 2,4,6-collidine (0.5 ml). Buffer solution (pH-2) was then added and volume of the aqueous phase was made upto 10 ml. The solution was then equilibrated with chloroform (10 ml) in a separating funnel. 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 the corresponding absorption maxima against a copper free reagent blank and the amount of copper 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 spectra of the mixed ligand complexes were recorded in the wave length region 300-600 nm against the corresponding blanks. The copper complexes showed absorption maxima

at 365-375 nm. The reagent blank absorbs insignificantly in the aforesaid wavelength region. The absorption spectra of Cu(II)-4 nitroresorcinol- $\gamma$ -picoline complex and the reagent blank are cited in Fig.1. The pattern of the spectra of other Cu-complexes are similar in nature.

#### Beer's law :

Different amounts of Copper(II) were extracted as described in the general procedure. In all the cases Beer's law was found to be valid over the concentration of 10 ppm of Copper. The results are shown in table 1 and Fig.2. The molar absorptivities of the complexes (on the basis of copper content) and Sandell's sensitivities were evaluated as seen from table 2.

#### Effect of Reagent Concentration :

While studying the extraction behaviour of copper in terms of absorbance by varying the amount of 4-nitroresorcinol and the pyridine bases, the optimum concentration of the reagents have been ascertained. It has been found that 0.2 ml of 1% ethanolic solution of 4-nitroresorcinol along with pyridine/ $\alpha$ -Picoline/ $\beta$ -Picoline/ $\gamma$ Picoline or 2,4,6-collidine (0.5 ml) was sufficient to extract upto 100 Mg

of copper quantitatively. Use of excess pyridine bases resulted incomplete recovery of copper. In presence of higher concentration of 4-nitrosoresorcinol, the absorbance of the blank goes high.

#### Effect of acidity :

The optimum pH for extraction of copper was ascertained by extracting the mixed-ligand complexes in the pH range 1-11. In all cases maximum absorbance was attained at pH 1.5-2.5. In a second consecutive operation within this pH range, the organic extract virtually showed no absorbance. This indicated quantitative extraction of copper in this condition. Absorbance as a function of pH has been shown in Fig.3.

#### Stability of colour :

Absorbance of the chloroform extract obtained after the recommended procedure was measured at different intervals of time. In each case the chloroform extracts showed a steady absorbance for at least 24 hrs. So it was convenient to measure the absorbance of the organic extract within 24 hrs after the extraction. Experimental results are shown in the table 3.

Choice of solvents :

Apart from chloroform some other solvent were tested as extracting solvent but those offered no special advantages over chloroform.

Effect of diverse ions :

In order to study the effect of diverse ions on the extraction behaviour, copper(II) was extracted and determined according to the general procedure in presence of the desired foreign ions. Average of three determinations was taken in each case. Deviation of not more than  $\pm 3\%$  from the recovery of copper was taken as the standard tolerance limit for the respective foreign ion. In practice all pyridine bases i.e. Pyridine/ $\alpha$ -Picoline/ $\beta$ -Picoline/ $\gamma$ -Picoline or 2,4,6-collidine showed similar behaviour regarding interferences.

Copper(II) ( $48 \mu\text{g}$ ) could be determined without interference in presence of Ni(II), V(V), Pt(IV), Rh(III), Ca(II), Zn(II), Mo(IV), U(VI), La(III), Al(III), Th(IV), Be(II), Mn(II), Ba(II), and Sr(II). High results are obtained in presence of cobalt and palladium. Mercury interferes seriously. Presence of iron and zirconium showed low recovery of copper.

Among the anions tested the followings did not interfere in the determination of copper : borate, phosphate, bromide, phthalate, iodide and acetate. Thiocyanate, thiosulphate, EDTA, oxalate, tartarate, citrate, fluoride, ascorbate interfered. The results are shown in table 4.

Precision and accuracy :

Using  $\gamma$ -picoline the precision and accuracy of the proposed method were tested by analysing solutions containing a known amount of Copper(II) following the recommended procedure. The results are shown in table 5. The method is fairly precise and reproducible. The total operation for each run requires hardly 10-15 min. The proposed method has also been compared with some other existing method as seen from table 6.

Analysis of synthetic mixtures :

In absence of real samples the method has been applied to a number of synthetic mixtures to estimate copper and the results are shown in table 7.

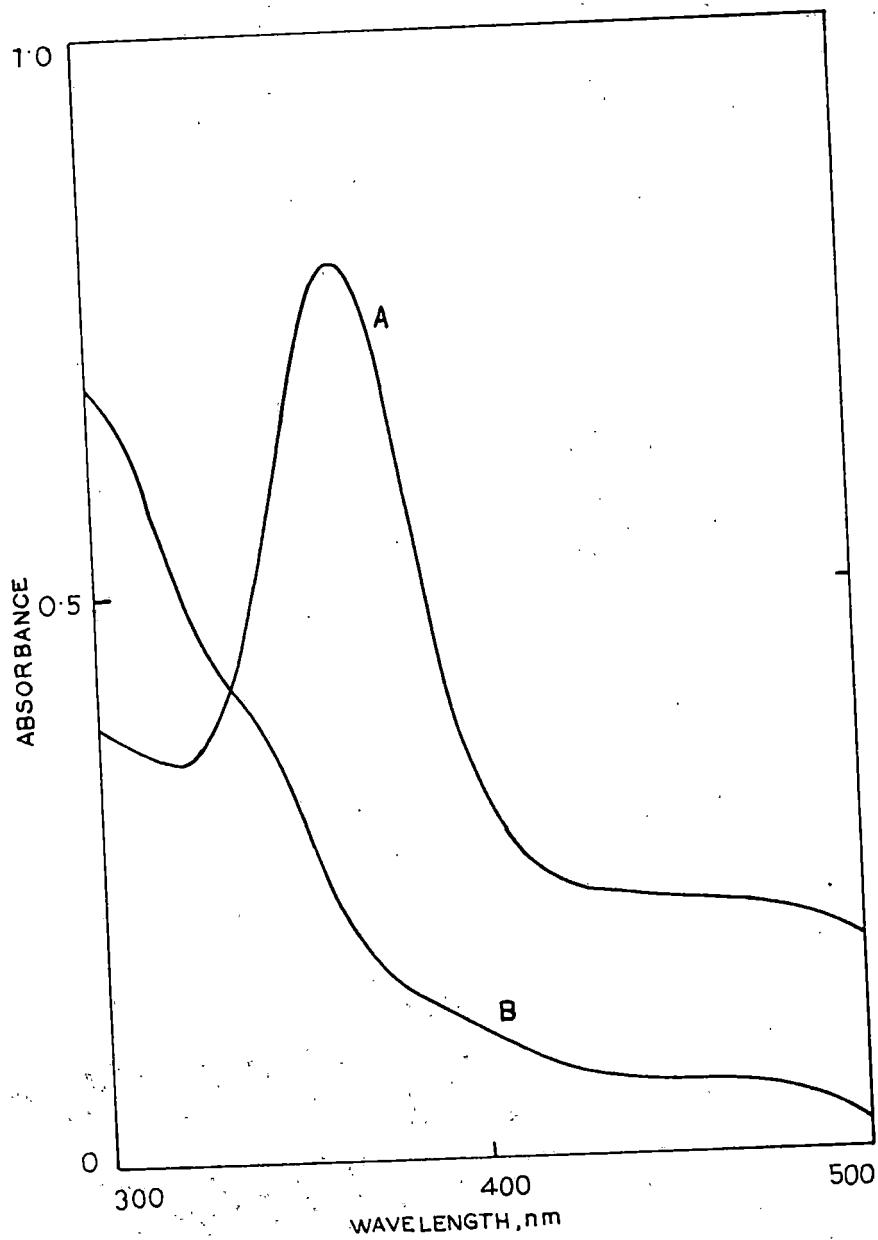


Fig. 1. Absorbance spectra of (A) Cu(II)-4-Nitrosoresorcinol-4-picoline complex (4.8 ppm Cu) and (B) Reagent blank.

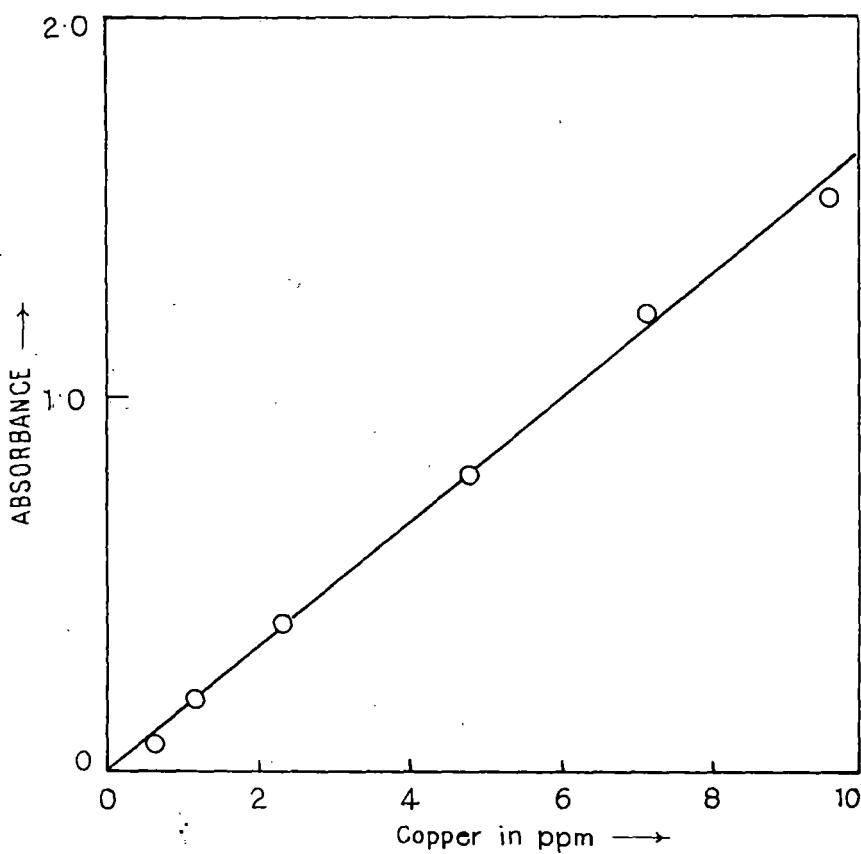


Fig 2: BEER'S LAW (WITH *S*-PICOLINE )

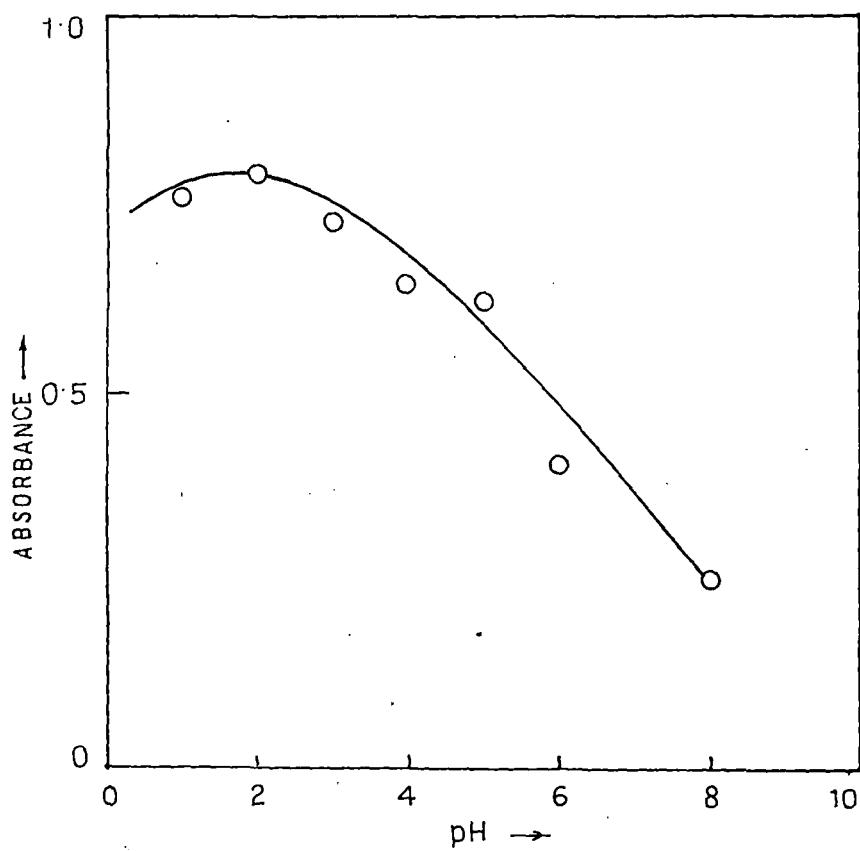


Fig- 3: ABSORBANCE AS A FUNCTION OF pH (Cu taken 48  $\mu\text{g}$ )

Table 1 : Beer's law data  
(with  $\gamma$ -Picoline)

Copper in ppm	Absorbance at 370 nm
0.6	0.080
1.2	0.190
2.4	0.405
4.8	0.800
7.2	1.205
9.6	1.520

Table 2 : Details of extractive methods

Parameters	Base employed				
	Pyridine	$\alpha$ -Picoline	$\beta$ -Picoline	$\gamma$ -Picoline	2,4,6-collidine
Extraction pH	1.5 - 2.5	1.5 - 2.5	1.5 - 2.5	1.5 - 2.5	1.5 - 2.5
$\lambda_{max}$ (nm)	365	375	370	370	365
Molar absorptivity ( $1 \text{ mol}^{-1} \text{cm}^{-1}$ )	$0.71 \times 10^4$	$0.45 \times 10^4$	$0.89 \times 10^4$	$1.06 \times 10^4$	$0.21 \times 10^4$
Sandell's sensitivity $\mu\text{g}/\text{cm}^2$	0.009	0.014	0.007	0.006	0.030

Table 3 : Variation of absorbance with time (with  
 $\gamma$ -Picoline)  
(Copper(II) taken 48  $\mu$ g)

Time in hours	Absorbance at 370 nm
0.25	0.800
0.5	0.804
4	0.802
12	0.804
24	0.800

Table 4 : Effect of diverse ions

Copper(II) taken 48  $\mu$ g. Extraction pH-2. (using  $\gamma$ -picoline)

Ion added	Amount tolerated (mg)	Copper found ( $\mu$ g)	Error %
Ni(II)	3.5	49.0	2.1
V(V)	2.5	48.5	1.0
Pt(IV)	2.0	49.2	2.5
Rh(III)	2.0	46.5	3.1
Cu(II)	4.0	48.0	0

Contd ...

Table 4 contd . . .

Ba(II)	4.0	47.5	1.0
Sr(II)	4.0	47.5	1.0
Cd(II)	1.0	49.0	2.1
Zn(II)	1.5	47.2	1.6
Mo(VI)	1.5	49.2	2.5
U(VI)	1.5	49.0	2.1
La(III)	2.0	47.5	1.0
Al(III)	2.0	47.0	2.0
Th(IV)	2.5	47.5	2.0
Be(II)	2.5	48.5	1.0
Mn(II)	2.0	48.0	0
Co(II)	nil	-	-
Pd(II)	nil	-	-
borate	6.0	49.0	2.1
Phosphate	6.0	48.5	1.0
Bromide	6.0	48.8	1.6
Phthalate	6.0	49.0	2.1
Iodide	6.0	47.5	1.0
Acetate	6.0	47.8	0.4

Table 5 : Reproducibility of copper(II) recovery

Copper taken ( $\mu$ g)	Copper found ( $\mu$ g)	Mean ( $\mu$ g)	Std. deviation %
24.0	24.8, 25.6, 23.2	24.35	0.93
	24.0, 25.9, 25.5		
48.0	48.0, 47.0, 48.5	48.25	1.37
	50.0, 49.5, 46.5		
72.0	73.5, 72.8, 70.8	72.15	1.07
	71.0, 72.0, 72.8		

Table 6 : Comparison

Reagent	$\lambda_{\text{max}}$ nm	molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$	Sensi- tivity $\mu\text{g}/\text{cm}^2$	Ref.
2-Hydroxy acetophenone oxime	355	$3.4 \times 10^3$	0.018	28
Bis (4-hydroxy pent-2-ylidene) diamino ethane	540	$1.36 \times 10^3$	-	30
Tetraphenyl arsonium or tetraphenyl phosphonium thiocyanate cuprate	465	$2.8 \times 10^3$	-	56
1-P-chloroanilino-3-methyl cyclohexane-1-carboxylic acid	445	$1.45 \times 10^3$	0.0438	57
2-thio ortic acid	410	$1.17 \times 10^3$	0.0543	58
N-( $\alpha$ -Pyridyl)-2-thio-quinal dinamide	520	$5.2 \times 10^3$	-	59
3-Methoxy salicyl aldoxime	360	$7.1 \times 10^3$	-	60
3-Hydroxy-3-methyl-1-m-chlorophenyl triazine	415	$9.25 \times 10^2$	0.0686	61
Present method	370	$1.06 \times 10^4$	0.006	62

Table 7 : Determination of Copper (48 $\mu$ g) in various synthetic mixtures with 100 $\mu$ g of each ion added

Ion added	Copper found ( $\mu$ g)
1. Ni(II), V(V), Pt(IV)	48.6
2. Ni(II), Zn(II), Cd(II)	46.5
3. Mn(II), Zn(II), V(V)	49.5
4. V(V), Pt(IV), Zn(II)	48.0
5. Cd(II), Zn(II), Mo(VI)	48.0

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CHAPTER IV  
Ninhydrinoxime as an Analytical Reagent

Extraction and Spectrophotometric Determination of Cobalt

## INTRODUCTION

Various oximes have been reported<sup>11</sup> to determine cobalt spectrophotometrically. Ninhydrinoxime forms a yellowish brown complex with cobalt, which by itself is not extracted into organic solvents. In presence of pyridine, the complex is extractable into chloroform under optimum conditions. Taking advantage of this, a method has been devised to determine cobalt in micro quantities.

## EXPERIMENTAL

Apparatus and Reagents :

A Shimadzu PR1 model recording spectrophotometer equipped with matched quartz cells of 10 mm optical path length was used for the absorbance measurement. The pH measurements were carried out with an ECL 5651 pH meter. Separatory funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of cobalt(II) was prepared by dissolving 7.433 gm of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Analar) in 500 ml distilled water. This was standarised by complexometric titration using xylenol orange indicator<sup>10</sup>. Solutions of lower concentrations were prepared by appropriate dilution of the stock.

Buffer solutions of different pH were prepared by standard procedures : KCl-HCl (pH 1.0-2.0) K-H phthalate - HCl (pH 2.5-4.0), K-H phthalate - NaOH (pH 4.5-5.9) KH<sub>2</sub> phosphate-NaOH (pH 6.0-8.0), borax - HCl (pH 6.0-8.0), borax-NaOH (pH 9.5-10.8).

All other chemicals used were of analytical grade. Pyridine,  $\alpha$ -Picoline,  $\beta$ -Picoline,  $\gamma$ -Picoline, 2,4,6-collidine were distilled before used.

Benzene, chloroform, carbontetrachloride, 1,2-dichloroethane, ethylacetate were also distilled before used.

Synthesis of Ninhhydrin oxime :

Ninhhydrin (2 gm) was dissolved in minimum amount of pyridine. To this was added 100 ml ethanolic solution of hydroxylamine hydrochloride (2 gm) and the mixture was refluxed for 2 hr. The product was filtered and recrystallized from ethanol. Yield 80%. (Found C-57; H-4.2; N-6.8; Calculated for  $C_9H_7O_4N$  : C, 56; H, 3.6; N, 7.25).

0.5% ethanolic solution of the oxime was used in the present investigation.

Standard solutions of diverse ions were prepared from chlorides, nitrates or sulphates ( in case of cations) and from sodium potassium or ammonium salts (in case of anions) to study interferences.

General procedure :

To an aliquot containing upto 40  $\mu$ g of cobalt(II) was added 1 ml of 0.5% ethanolic solution of ninhydrin oxime followed by 0.2 ml of pyridine in a separatory funnel.

Buffer solution was then added to adjust the pH to 4. The mixture was then left for 1 min to ensure complete complexation. The volume of the aqueous phase was maintained at 10 ml. This was then equilibrated with 10 ml of chloroform for 30 sec. After phase separation the organic extract was poured over anhydrous sodium sulphate to remove any retained water droplets. Finally the absorbance of the chloroform extract was measured at 330 nm against a blank. Amount of cobalt was computed from a calibration curve.

To test the interferences, the respective diversions were added to the system prior to addition of the reagents.

#### RESULTS AND DISCUSSION

##### Absorption spectra :

The spectral curves of cobalt(II)-nihydrinoxime complex, extracted into chloroform in presence of pyridine was recorded against a blank as shown in fig.1. The complex exhibits absorption maximum at 330 nm. The reagent itself shows high absorbance below 300 nm. However the absorbance becomes insignificant beyond 320 nm onwards. Wavelength of 330 nm was selected for all absorbance measurements.

Beer's law and calibration curve :

Different amounts of cobalt(II) were taken and extracted as in the procedure at pH 4.0 and the corresponding absorbance was measured against the reagent blank in order to observe the adherence of the colour system to Beer's law (table 1). The absorbance shows a linear response over the concentration of 4 ppm of cobalt (Fig.2). In each case the remaining aqueous phase after a single extraction, was clear and colourless. Furthermore the aqueous phase as tested by an independent method was void of cobalt.

The molar absorptivity and Sandell's sensitivity were evaluated to be  $1.97 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  and  $0.003 \mu\text{g}/\text{cm}^2$  respectively at 330 nm.

Effect of ninhydrin oxide concentration :

The extent of absorbance has been examined with different amount of ninhydrin oxide keeping all other variables constant. It was found that 0.5 ml of 0.2% ethanolic solution of ninhydrin oxide along with 0.2 ml of pyridine was sufficient to extract 24  $\mu\text{g}$  of cobalt in a single operation. Increased concentration of ninhydrin oxide did not bring about any significant

change in the maximum value of the absorbance. However higher concentration was avoided as the absorption of the blank goes high. The results are shown in table 2.

The nature of the extracted species was indicated to be 1:3 (co:ninhydrinoxime) from mol ratio method.

#### Effect of pyridine concentration :

Keeping the other variable constant, the effect of pyridine has been examined in terms of absorbance. It was noted that 0.2 ml pyridine along with 0.5 ml of 0.5% ethanolic solution of ninhydrinoxime was sufficient to extract upto 40  $\mu\text{g}$  of cobalt in a single operation. Higher concentration of pyridine gives lower absorbance.

#### Effect of other pyridine bases :

Apart from pyridine, some other bases were tested as auxiliary ligands. Use of  $\beta$ -picoline or  $\gamma$ -picoline did not bring about any significant change in the maximum value of absorbance. In presence of  $\alpha$ -picoline or 2,4,6-collidine, the complex is not extractable into chloroform.

Effect of acidity :

The effect of acidity on the extractability of cobalt was examined in terms of absorbance of the complex. The complex exhibits constant and maximum absorbance when the extractions were carried out from pH 3-6. On each case the aqueous phase after extraction was free from cobalt as tested by an independent method. This indicated a quantitative extraction of the metal in the aforesaid acidity range in a single operation. The absorbance decreases above or below this pH range. The pattern of the absorption spectra of the complex extracted from pH 1-10 remains unchanged, indicating the formation of single complex species in all cases. The absorbance as a function of pH has been shown in Fig.3. For our practical purpose pH 4.0 was selected.

Effect of solvents :

Apart from chloroform, other solvents like, 1,2-dichloroethane, ethylacetate, benzene and carbontetrachloride were tested as extracting solvents. Use of ethylacetate and 1,2 dichloroethane offered no special advantages over chloroform while lower absorbance resulted in case of benzene. Carbontetrachloride did not extract the complex.

Stability of colour :

The absorbance of the chloroform extracts, containing 24  $\mu\text{g}$  of cobalt(II) extracted by the recommended procedure, was measured at the different intervals of time. The organic extract produced a steady absorbance for at least 24 hours at room temperature as seen from table 3.

Effect of diverse ions :

To test the effect of diverse ions cobalt was extracted according to the recommended procedure in presence of the desired foreign ions. Extraction pH was set at 4.0 with the buffer. An ion was considered to interfere if the recovery of cobalt differed by more than  $\pm 3\%$  from the actual amount taken. Cobalt(II) (24  $\mu\text{g}$ ) could be determined without interference in presence of the following ions : Fe(III), Ni(II), Pd(II), Pt(IV), Th(IV), Zn(II), Cd(II), Ca(II), Ba(II), Sr(II), U(VI), Sn(II), Cr(III), Hg(II), V(V), Mo(VI), Mn(II), Be(II), Bi(III), Cu(II) and La(III). Rhodium interfered.

Among the anions tested, the followings did not interfere : ascorbate, oxalate, tartarate, arsenate, bromide, iodide, fluoride, phosphate, citrate, thiocyanate, EDTA, thiosulphate, and thiourea. However nitrite interfered. The results are shown in table 4.

Precision and accuracy :

The proposed method has been tested by analysing solutions containing a known amount of cobalt (II). The experimental results for the determination of cobalt are shown in table 5. The process is very simple and rapid requiring only 10-15 min for each run. The method has been compared to some other existing methods as seen from table 6.

Application :

In absence of real samples the proposed method has been tested by analysing some synthetic mixtures. The composition of the mixtures with percentage of recovery of cobalt are given in table 7. The results show that recovery of cobalt was satisfactory. Average of three determination was taken in each case.

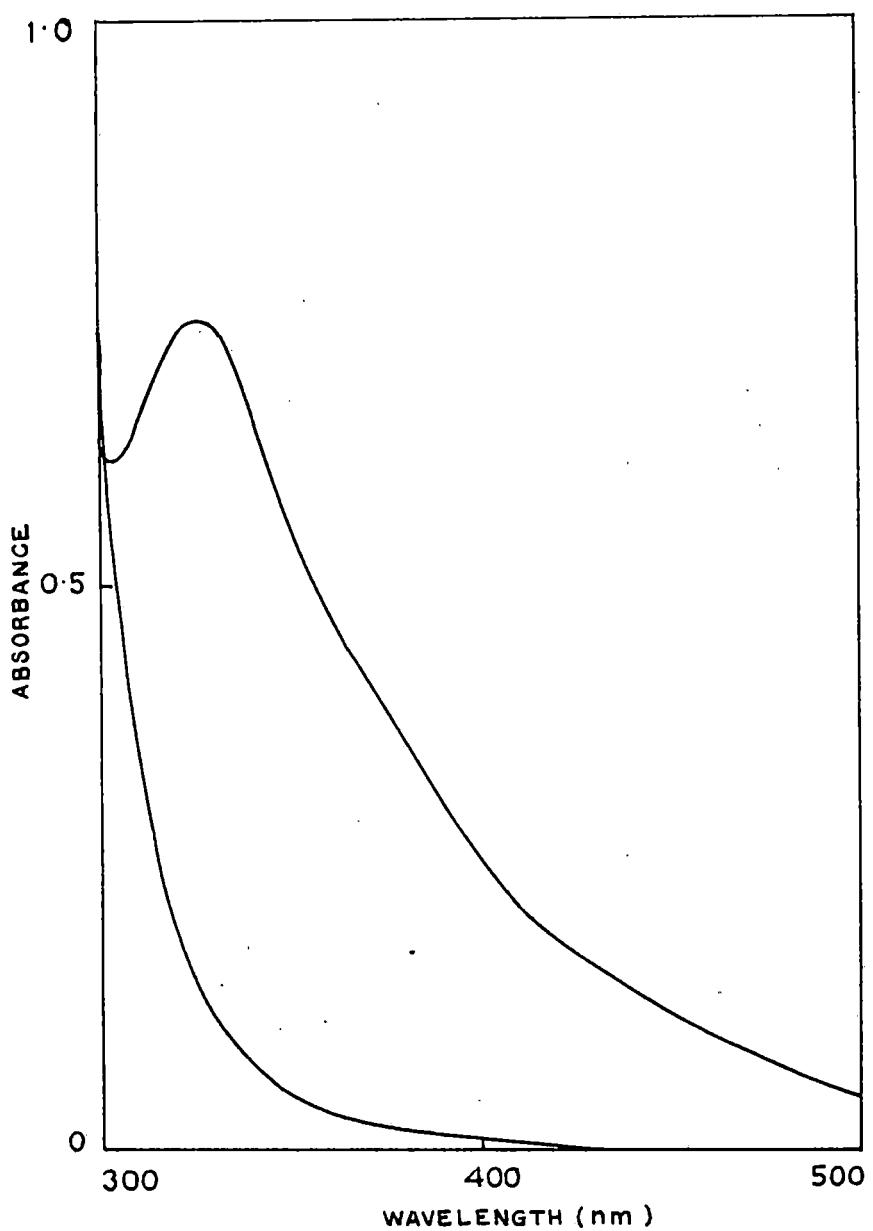


Fig-1. Absorbance spectra of (A) cobalt- Ninhydrinoxime - Pyridine complex (2.4 ppm Co) and (B) reagent blank .

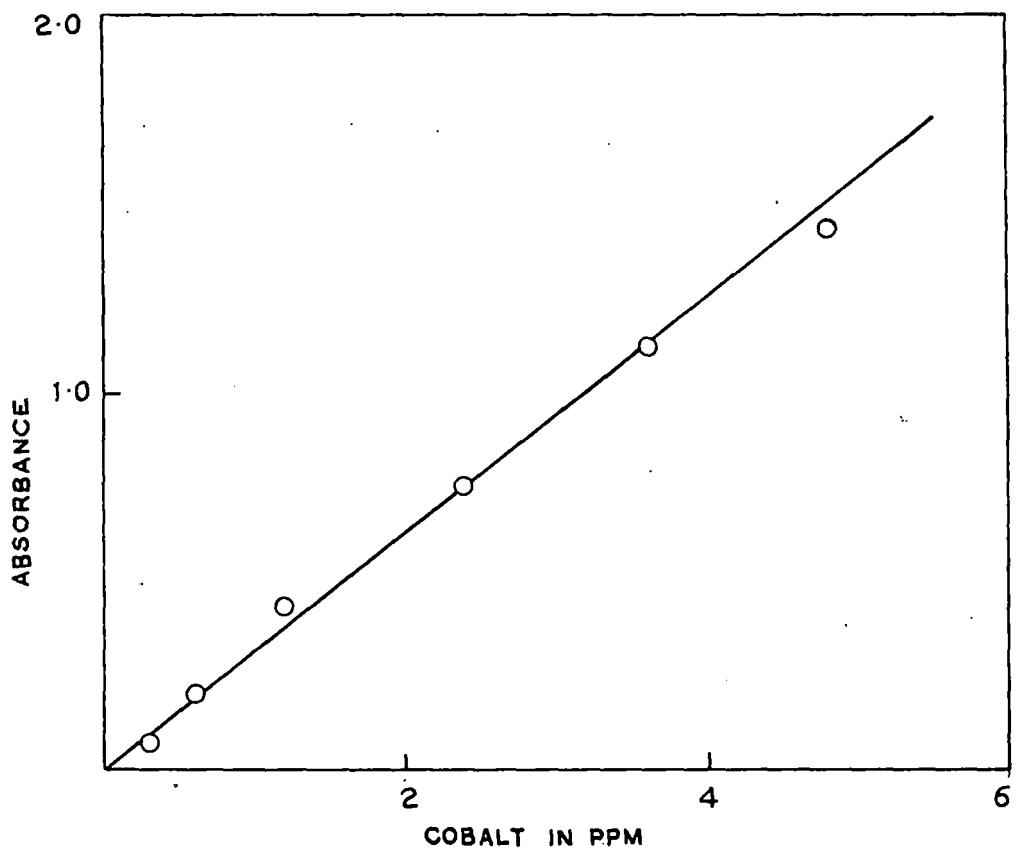


Fig-2: BEER'S LAW (Co-Ninhydrin system )

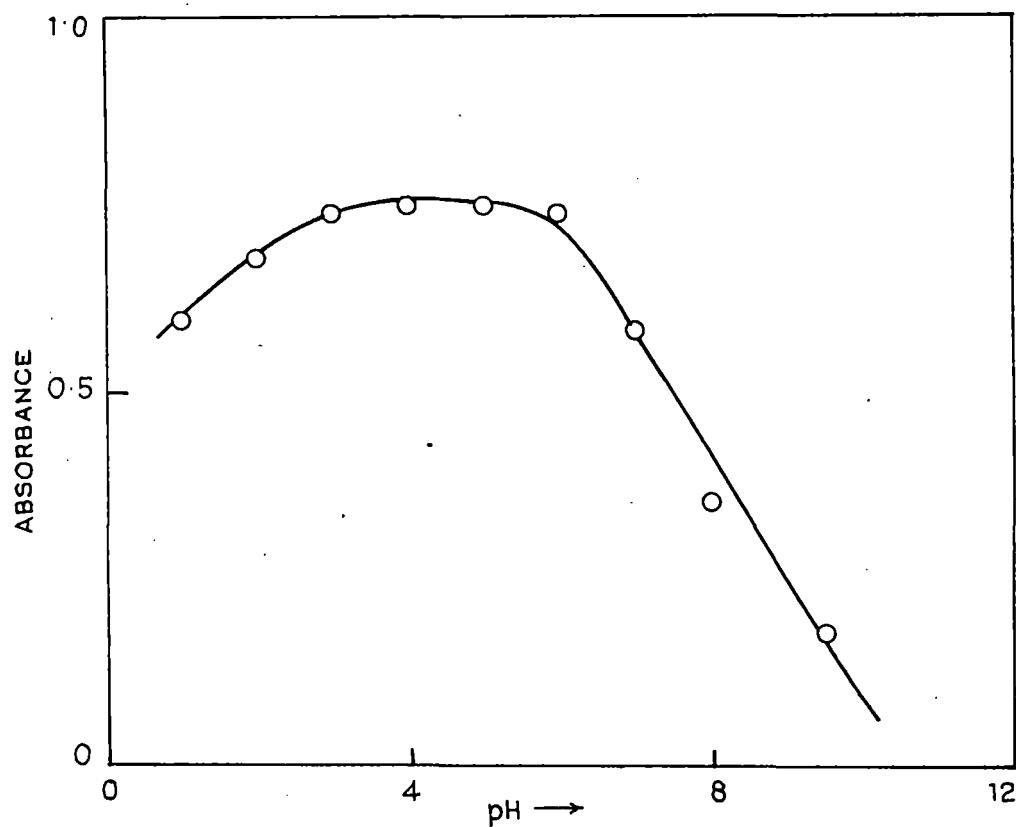


Fig- 3. Absorbance as a function of pH (Co taken 24  $\mu\text{g}$ )

Table 1 : Adherence to Beer's law. Extraction pH-4.0

Cobalt concentration in ppm	Absorbance at 330 nm
0.3	0.080
0.6	0.105
1.2	0.440
2.4	0.752
3.6	1.120
4.8	1.460

Table 2 : Effect of ninhydrin oxide concentration (0.20%)

The aqueous phase (10 ml) contains 24  $\mu\text{g}$  of cobalt (II) and 0.2 ml of pyridine. Extraction pH 4.0.

Amount added in ml	Absorbance (at) 330 nm
0.05	-
0.10	0.430
0.20	0.750
0.40	0.755
0.60	0.756
1.0	0.755

Table 3 : Variation of absorbance with time. Cobalt taken 24  $\mu\text{g}$ .

Time in hr after extraction	Absorbance at 330 nm
0.25	0.750
0.50	0.755
1.0	0.752
6.0	0.750
12.0	0.750
24.0	0.748

Table 4 : Effect of diverse ions on determination of cobalt (24  $\mu\text{g}$ ). Extraction pH 4.0.

Ion added	Amount tolerated, mg	Cobalt found $\mu\text{g}$	Error %
Fe(III)	5.0	24.5	2.0
Ni(II)	5.0	23.8	0.8
Pd(II)	4.5	23.5	2.0
Pt(IV)	4.5	24.0	0.0
Th(IV)	6.0	24.2	0.8
Zn(II)	5.5	24.2	0.8
Cd(II)	4.5	24.8	3.3
Ca(II)	6.0	24.5	2.0
Ba(II)	6.0	24.0	0.0
Sr(II)	6.0	24.0	0.0

contd ...

Table 4 contd ...

U(VI)	5.0	23.5	2.0
Sn(II)	5.0	24.2	0.8
Cr(III)	5.0	24.2	0.8
Hg(II)	4.0	23.5	2.0
V(V)	5.0	24.0	0.0
Mo(VI)	4.5	24.0	0.0
Mn(II)	5.0	24.5	2.0
Be(II)	0.60	23.4	2.5
Bi(II)	0.50	23.5	2.0
Cu(II)	0.50	24.0	2.5
La(III)	0.50	23.4	2.5
Rh(III)	Nil	-	-
Ascorbate	10.0	23.5	2.0
Oxalate	10.0	23.8	0.8
Arsenate	10.0	23.4	2.5
Bromide	10.0	24.2	0.8
Iodide	10.0	24.0	0.0
Fluoride	10.0	24.0	0.0
Phosphate	10.0	23.5	2.0
Citrate	10.0	23.5	2.0
Tartarate	10.0	24.5	2.0
Thiocyanate	10.0	24.6	2.5
EDTA	0.4	23.5	2.0
Thiosulphate	0.4	23.4	2.5
Thiourea	0.4	23.4	2.5
Nitrite	Nil	-	-

Table 5 : Reproducibility of cobalt(II) recovery

Cobalt taken ( $\mu\text{g}$ )	Cobalt found ( $\mu\text{g}$ )	Mean ( $\mu\text{g}$ )	Std deviation (%)
12.0	10.5, 12.0, 12.5	12.26	1.08
	12.8, 12.0, 13.8		
24.0	24.5, 23.5, 24.0	24.46	0.60
	25.0, 24.8, 25.0		
36.0	37.5, 36.5, 36.0	36.91	0.73
	38.0, 36.5, 37.0		

Table 6 : Comparison of some existing methods for the spectrophotometric determination of cobalt

Reagent	$\lambda_{\text{max}}$ (nm)	Molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1} \times 10^4$	Ref.
1. Acenaphthenequinone monoxime	400	1.18	1
2. Dimethyl glyoxime	435	1.08	2
3. Di-(2-Pyridylketoxime)	388	1.95	3
4. Dimedone dioxime	400	2.3	4
5. Nicotinamidoxime	540	0.59	5
6. Oxamidoxime	350	0.86	6
7. Phenanthrenequinone monoxime	470	1.75	7
8. Pyridil monoxime	408	1.7	8
9. Present method	330	1.97	9

Table 7 : Analysis of synthetic mixtures  
Extraction pH 4.0

Composition with amount taken ( $\mu$ g)	Recovery of cobalt(II) %
1. Co(II) 24, Fe(III) 100, Ni(II) 100, Cu(II) 100	98
2. Co(II) 24, Cr(III) 100, Mn(II) 100, Hg(II) 100	100
3. Co(II) 24, Pd(II) 100, Pt(IV) 100, Zn(II) 100	101
4. Co(II) 24, U(VI) 100, V(V) 100, Mo(VI) 100	98

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CHAPTER V

Diphenylthiocarbazide as an Analytical Reagent

Extraction and Spectrophotometric Determination of Copper

## INTRODUCTION

Diphenylthiocarbazide is obtained as prisms from warm alcohol. It melts at 150°C to form a dark green liquid. It is difficultly soluble in alcohol, benzene, acetone, ether, chloroform and acetic acid. The reagent gives coloured precipitates when added to solutions of salts of a number of the heavy metals<sup>12</sup>. Here a method has been proposed for the spectrophotometric determination of copper with diphenylthiocarbazide.

## EXPERIMENTAL

### Apparatus and reagents :

Spectral curves and absorbance measurements were made with a Shimadzu PR1 model recording spectrophotometer provided with matched quartz cells of 10 mm optical path length. Acidity of the aqueous solutions were measured with a ECL 5651 digital pH meter. Separatory funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of copper(II) was prepared by dissolving 1.9630 gm of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (BDH) in 250 ml distilled water followed by the standarisation as benzoin- $\alpha$ -oximate. Solutions of lower concentrains were prepared by appropriate dilution.

Diphenylthiocarbazide was prepared by mixing one part of carbondisulphide with two parts of phenylhydrazine and washing the white precipitate, so formed, few times with water by decantation and then dried. A 0.4% acetonnic solution of the reagent was used for the estimation of copper.

$\text{KH}_2\text{PO}_4$  - NaOH buffer was employed to adjust pH of the aqueous solution.

All the chemicals and solvents used were of analytical grade. Ethyl acetate, benzene, chloroform 1,2-dichloroethane, carbontetrachloride were distilled before used.

Standard solutions of diverse ions were prepared from their corresponding salts to study interferences.

Determination of copper :

To a suitable volume of sample solution containing 5 - 30 $\mu$ g of copper(II) was added 0.4% acetonnic solution (0.5 ml) of diphenylthiocarbazide followed by phosphate buffer (pH 6; 5 ml). Volume of the aqueous phase was then made upto 10 ml with distilled water and left for 1 min to ensure complete complexation. The solution was then equilibrated with ethylacetate (10 ml) for 1 min. The separated organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the organic extract was read at 540 nm against a copper free reagent blank and the amount of copper deduced from a calibration curve. To study the effects of diverse ions the respective foreign ions along with masking agents, if needed, were added to the aqueous sample solution before addition of the reagent.

## RESULTS AND DISCUSSION

Absorption spectrum :

The absorption spectrum of copper(II)-Diphenylthiocarbazide complex in ethylacetate taken against reagent blank as a reference has been shown in Fig.1. The brown copper complex shows absorption maximum at 540 nm. The reagent blank does not absorb in the aforesaid wavelength region. The pattern of the absorption spectrum of the complex remains unchanged when extracted from pH 4-8. This indicates the existence of a single variety of the complex species in the system.

Beer's law and calibration curve :

Different amounts of copper(II) were taken and   extracted as in the general procedure at pH 6.0 and the absorbance was measured against the reagent blank in order to observe the adherence of the colour system to Beer's law (table 1). It has been observed that the Beer's law is obeyed over 0.2 - 4 ppm of copper (Fig.2). In each case the aqueous phase after extraction was clear and colourless. Furthermore, the aqueous phase as tested by an independent method was found to be free from copper.

The molar absorptivity of the complex based on copper content was evaluated to be  $(4.87-5.20) \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1}$  with Sandell's sensitivity  $0.0013 \mu \text{ g/cm}^2$  at 540 nm.

Effect of Diphenylthiocarbazide concentration :

The effect of diphenylthiocarbazide concentration on absorbance has been examined keeping all other variables constant. It has been found that 0.5 ml of 0.4% acetonnic solution of the reagent is sufficient to extract 20 g of copper in a single operation. Amount of the organic reagent below 0.2 ml results low absorbance value. Higher concentration did not bring about any significant change on the maximum value of absorbance and was avoided. The results are shown in table 2.

Effect of pH :

Effect of pH on the system was examined in terms of absorbance of the copper-diphenylthiocarbazide complex in the organic phase. A steady and maximum absorbance was obtained when extractions were carried out from pH 4.8. In each case, after extraction the aqueous phase was clear and colourless. Complete and quantitative extraction of copper as a function of pH has been shown in fig.3.

Choice of solvents :

Apart from ethylacetate, some other common organic solvents were also tested as extracting solvents. Use of 1,2 dichloroethane offers no special advantages over ethylacetate. Benzene, carbontetrachloride or chloroform does not extract the complex.

Stability of colour :

The reaction between Copper(II) and diphenylthiocarbazide was instantaneous. Time is not a critical factor in the determination of copper(II). The absorbance of the ethylacetate extract containing copper(II)-diphenylthiocarbazide complex were measured at different intervals of time. The colour of the Copper(II) complex in ethylacetate was found to be stable for at least 24 hr as seen from table 3.

Interference :

In order to study the effect of diverse ions on the extraction behaviour, copper was determined according to the recommended procedure in presence of the respective foreign ions. Extraction pH was set at 6.0 with  $\text{KH}_2\text{PO}_4$ -NaOH

buffer. The tolerance limit was set as the amount of foreign ions required to cause a maximum  $\pm$  3% error in the estimation of copper. Copper(II) ( $20 \mu\text{g}$ ) could be determined without interference in presence of Ni(II), Mo(VI), Ca(II), Mn(II), Cr(III), La(III), Al(III), Ba(II), Sr(II), Mg(II), Co(II), U(VI), Be(II), Ag(III), Pt(IV), Rh(III), Th(IV), V(V), Cd(II) and Zn(II).

Interference due to Fe(III) and Sn(II) was eliminated using ammonium hydrogen fluoride as the masking agent. To avoid interference due to  $\text{Pd}^{+2}$ , copper was extracted in presence of ammonium thiocyanate. Potassium iodide masks Hg(II), Pb(II) and Bi(III).

Among the anion tested the system tolerated the followings : tartarate, citrate, oxalate, bromide, iodide, phosphate, acetate, thiocyanate, fluoride, phthalate, thiourea, ascorbate, EDTA and thiosulphate. However in presence of borate and nitrite high results are obtained. The results are presented in table 5.

#### Precision and accuracy :

The proposed method has been tested by analysing solutions containing a known amount of copper. The results for the determination of copper(II) is presented in

table 4. The method is fairly precise and reproducible. The total operation time for each run requires 10-15 minutes. The method is compared with some other existing methods with respect to molar absorptivity and Sandell's sensitivity as seen from table 6.

#### Application :

The metal has been estimated in sysnthetic mixtures and some standard samples following the general procedure.

##### a) Determination of copper in presence of As, Bi, Pb, Hg :

To a copper solution ( $20\mu$  g), were added 2 mg each of As(III), Bi(III), Pb(II), and Hg(II) followed by 10 mg of KI. Acidity of the aqueous solution was adjusted to pH 6 with phosphate buffer. Acetonic solution (0.5 ml, 0.4%) of diphenyl thiocarbazide was added to the system and the mixture was left for 1 min to ensure complete complexation. Copper was then determined according to the recommended procedure and was found to be  $19.8\mu$  g (average of four determination).

##### Determination of copper in presence of Fe, Co, Ni, Sn :

To a copper solution ( $20\mu$  g) were added 2 mg each of Fe(III), Co(II), Ni(II) and Sn(II). Ammoniumhydrogen-fluoride (10 mg) was then added to the system and pH was

adjusted as usual followed by addition of acetonic solution (0.5 ml, 0.4%) of diphenylthiocarbazide. Copper was then determined by the recommended procedure and was found to be  $19.5\mu\text{g}$  (average of four determination).

Determination of copper in presence of Pd, Pt, Rh :

To a sample solution containing copper ( $20\mu\text{g}$ ) were added 1 mg each of Pd(II), Pt(IV) and Rh(III) followed by addition of 5 mg each of KI and  $\text{NH}_4\text{SCN}$ . pH was adjusted to 6 with phosphate buffer. Copper was then estimated as usual and was found to be  $19.5\mu\text{g}$  (average of four determination).

Determination of copper in cupro-nickel alloy in presence of nickel :

The alloy sample (100 mg) was dissolved in a mixture of HCl and  $\text{HNO}_3$  (2:1). The solution was evaporated to dryness after addition of a few drops of conc  $\text{H}_2\text{SO}_4$ . The residue was dissolved in water and the resulting solution was diluted to 250 ml with distilled water in a volumetric flask. The solution was further diluted as needed. A 2 ml aliquot portions were taken in several of the determinations with 0.4% diphenylthiocarbazide (0.5 ml) being added in a separating funnel and pH was adjusted to 6 with phosphate buffer. The mixture was equilibrated with ethylacetate

(10 ml) and the absorbance of the organic extract was read at 540 nm. Copper was deduced from a calibration curve. Copper was found to be 69.2% (average of four determination) (certified 68.12% cu in cupro-nickel).

Determination of copper in white metal in presence of Pb, Sb, Sn, Bi, Ni, As :

The sample (1 gm) was dissolved in 6 M hydrochloric acid (10 ml) and digested on a hot plate. The clear solution was evaporated, cooled and diluted with distilled water. The solution was filtered to remove a major portion of lead, precipitated as lead chloride and washed few times with distilled water. The filtrate and washings were transferred quantitatively into a volumetric flask (100 ml) and the volume made up to the mark. A 2 ml aliquot portions were taken in several of the determinations followed by addition of 10 mg of KI and 5 mg  $\text{NH}_4\text{HF}_2$  along with acetonnic solution (0.5 ml, 0.4%) of diphenylthiocarbazide. pH was adjusted to 6 with phosphate buffer, copper was estimated by the recommended procedure and was found to be 0.13% (average four determinations) (certified : 0.12% cu in lead base white metal).

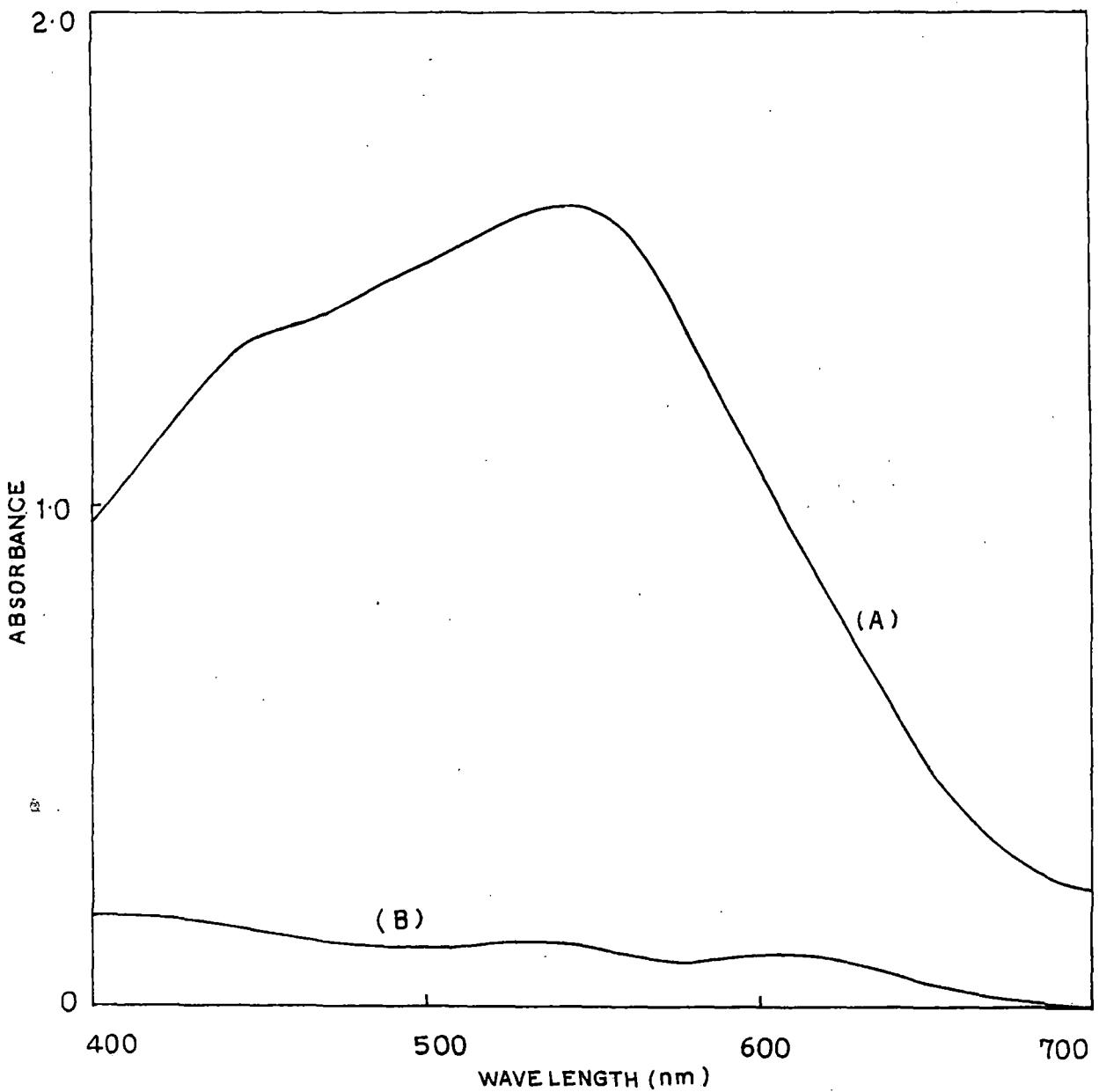


Fig-1: Absorbance spectra of (A) Copper-DPTC complex (2 ppm Cu)  
and (B) Reagent blank.

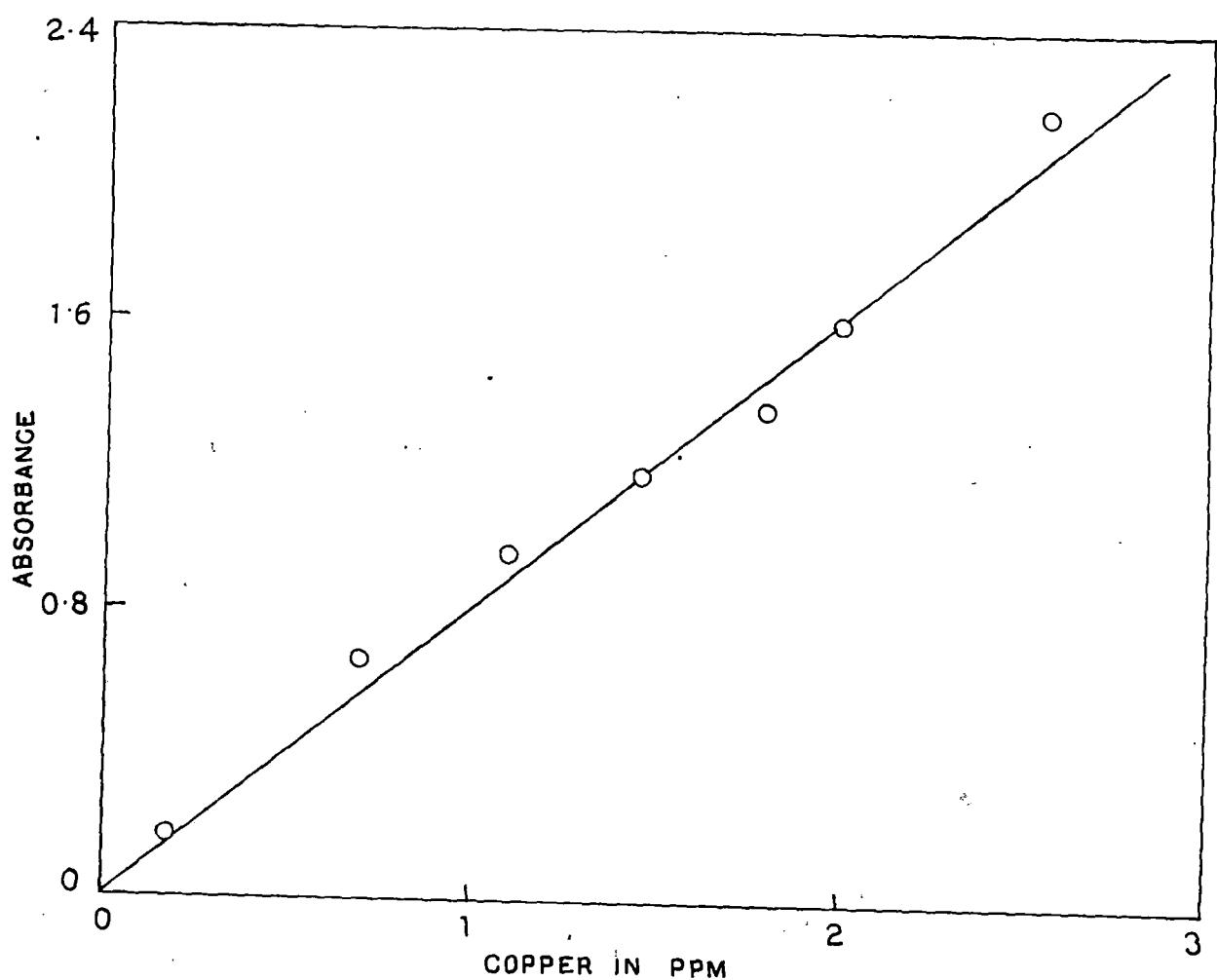


Fig-2: BEER'S LAW (Copper - DPTC system )

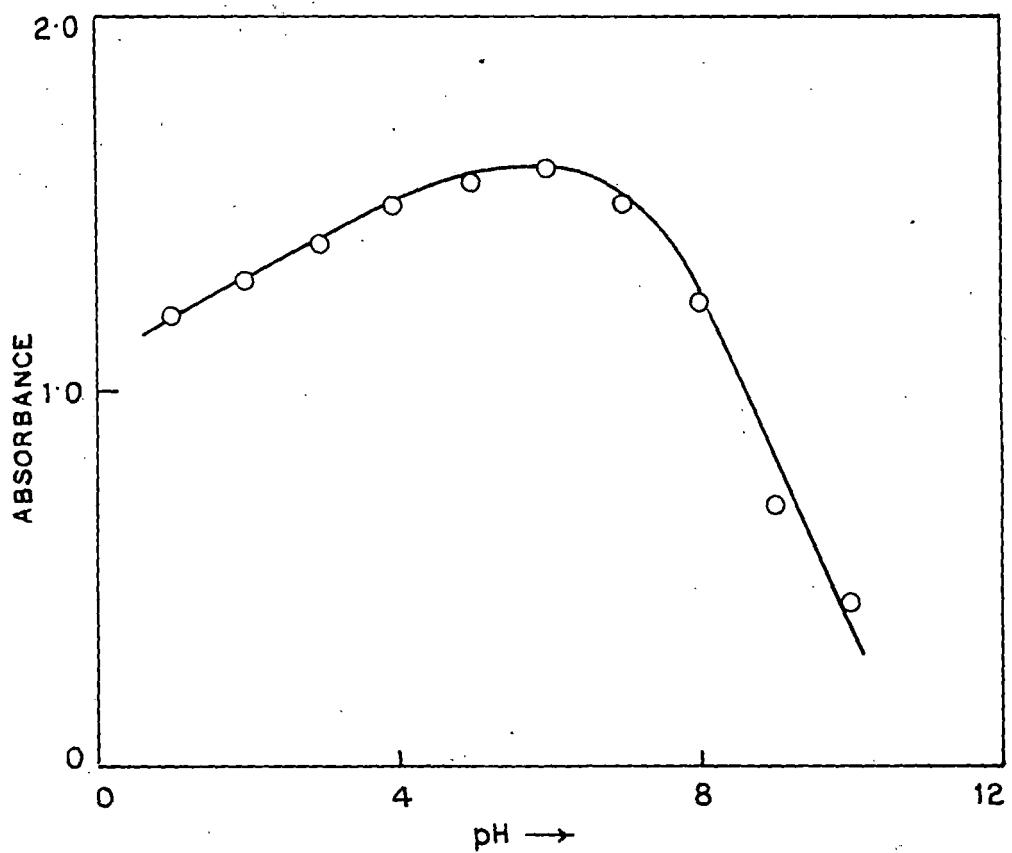


Fig - 3 : ABSORBANCE AS A FUNCTION OF pH(Cu taken 20 µg)

Table 1 : Adherence to Beer's law

Copper in $\mu$ g	Absorbance at 540 nm
1.81	0.180
7.20	0.670
10.90	0.960
14.45	1.180
18.18	1.360
20.00	1.600
25.45	2.180

Table 2 : Effect of diphenylthiocarbazide concentration

The aqueous phase (10 ml) contains 20  $\mu$  g of copper(II)  
Extraction pH - 6.0.

Diphenylthio- carbazide concentration in %	Amount added, (ml)	Absorbance at 540 nm
0.4	0.05	-
0.4	0.075	0.680
0.4	0.15	1.020
0.4	0.20	1.200
0.4	0.30	1.320
0.4	0.40	1.580
0.4	0.50	1.600
0.4	0.60	1.608
0.4	0.80	1.600
0.4	1.0	1.605

Table 3 : Variation of absorbance with time. Copper(II)  
taken 20 $\mu$  g

Time in hours after extractions	Absorbance at 540 nm
0.25	1.605
0.50	1.605
1.0	1.600
6.0	1.605
12.0	1.605
24.0	1.600

Table 4 : Reproducibility of copper recovery

Copper taken ( $\mu$ g)	Copper found ( $\mu$ g)	Mean ( $\mu$ g)	Std deviation (%)
14.45	15.5, 14.8, 14.4	14.46	0.72
	15.0, 13.5, 14.0		
20.0	20.5, 18.8, 19.0	20.05	0.97
	21.2, <u>20.8</u> , 20.0		
25.45	24.55, 24.80 25.60	25.36	0.80
	26.8, 25.40, 25.0		

Table 5 : Effect of diverse ions on determination 20 $\mu$ g of copper. Extraction pH set at 6.0

Ion added	Amount tolerated (mg)	Copper found ( $\mu$ g)	Error %
Fe(III)	4.0 <sup>a</sup>	20.5	2.5
Co(II)	3.5	20.2	1.0
Ni(II)	4.0	20.2	1.0
Pd(II)	2.5 <sup>b</sup>	20.5	3.0
Zn(II)	0.1	19.5	2.5
Mo(VI)	4.0	20.0	0.0
Pt(IV)	2.5 <sup>c</sup>	20.5	2.5
V(V)	0.1	19.8	1.0
Hg(II)	1.5 <sup>c</sup>	20.6	3.0
Ca(II)	4.0	20.2	1.0
Mn(II)	4.0	20.0	0.0
Cr(III)	4.0	20.2	1.0
La(III)	4.0	20.2	1.0
Al(III)	4.0	19.8	1.0
Be(II)	3.0	20.0	0.0
U(VI)	3.5	20.2	1.0
Ba(II)	4.0	20.0	0.0
Sr(II)	4.0	20.0	0.0
Rh(III)	2.5	20.2	1.0
Th(IV)	2.5	19.5	1.0
Pb(II)	1.5 <sup>c</sup>	20.6	3.0

contd ...

Table 5 contd ...

Cd(II)	0.1	20.5	2.5
Mg(II)	4.0	20.0	0.0
Sn(II)	2.5 <sup>a</sup>	19.4	3.0
As(III)	3.0	20.6	3.0
Bi(III)	1.5 <sup>c</sup>	20.5	2.5
Tartarate	9	20.2	1.0
Citrate	10	20.4	2.0
Oxalate	9	20.2	1.0
Bromide	10	20.4	2.0
Iodide	8	20.4	2.0
Phosphate	10	19.8	1.0
Acetate	12	20.0	0.0
Thiocyanate	8	20.2	1.0
Fluoride	10	19.8	1.0
Phthalate	10	20.0	0.0
Thiourea	10	20.0	0.0
Ascorbate	4	19.8	1.0
EDTA	4	19.8	1.0
Thiosulphate	4	19.5	2.5
Borate	Nil	-	-
Nitrite	Nil	-	-

a : in presence of  $\text{NH}_4\text{HF}_2$ 

b : in presence of thiocyanate

c : in presence of iodide

Table 6 : Comparison

Reagent	$\lambda_{\text{max}}$ nm	Molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$	Sandell's sensitivity $\mu\text{g}/\text{cm}^2$	Ref.
O-isopropyl-s-methyl dithiophosphate	420	$1.1 \times 10^4$	-	1
4-methyltetrahydrobenzofurano (6,7-b) cumarin	370	12700	0.0036	2
1-P-chloroanilino-3-methylcyclohexane	445	$1.45 \times 10^3$	0.0438	3
2-thigortic acid	410	$1.17 \times 10^3$	0.0543	4
N-( $\alpha$ -Pyridyl)-2-thio qualdinamide	520	$5.2 \times 10^3$	-	5
3-methoxysalicyl aldoxime	360	$7.1 \times 10^3$	-	6
3-Hydroxy-3-methyl-1-m-chlorophenyl triazene	415	$9.25 \times 10^2$	0.0686	7
Bis (4-hydroxypent-2-zlidene) diamino ethane	540	$1.36 \times 10^3$	-	8
Tetra phenyl arsonium or tetraphenyl phosphonium thiocyanate	465	$2.8 \times 10^3$	-	9
Tetrahydrofarfuryl-xanthale	430	$1.59 \times 10^3$	0.004	10
Present method	540	$5.04 \times 10^4$	.0013	11

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## **APPENDIX**

## List of Publications

1. Spectrophotometric Determination of Iron as Iron(II) Thiocyanate Cetyltrimethylammonium Bromide.  
Paria, P.K., Thokdar, T.K., Majumdar, S.K., J. Indian Chem Soc. 1989, 66, 465.
2. Extraction Photometric Determination of Microgram Amounts of Cobalt with Thiocyanate and Cetyltrimethylammonium Bromide.  
Paria, P.K., Thokdar, T.K., Majumdar, S.K., J. Indian Chem. Soc. 1990, 67, 787.
3. Extractive photometric Determination of Microgram Amounts of Palladium with Iodide and Cetyltrimethyl Ammonium Bromide.  
Thokdar, T.K., Paria, P.K., Majumdar, S.K., Indian Journal of Chemistry, 1989, 28A, 443.
4. Extraction and Spectrophotometric Determination of Platinum with Cetyltrimethylammonium Bromide in Presence of Iodide.  
Paria, P.K., Thokdar, T.K., Majumdar, S.K., Current Science, 1989, 58(2), 69.
5. Solvent Extraction and Spectrophotometric Determination of Molybdenum Using Cetyltrimethylammonium Bromide.  
Thokdar, T.K., Paria, P.K., Majumdar, S.K., J. Indian Chem. Soc. (In press).

6. Extraction and Spectrophotometric Determination of Vanadium with Cetyltrimethylammonium Bromide in Presence of Thiocyanate.

Thokdar, T.K., Paria, P.K., Majumdar, S.K., J. Indian Chem Soc. (In press).

7. Spectrophotometric Determination of Micro Quantities of Gold with Cetyltrimethylammonium Bromide in Presence of Iodide.

Paria, P.K., Thokdar, T.K., Majumdar, S.K., Current Science, 1989, 58(17), 964.

8. Extractive Spectrophotometric Determination of Cobalt with 4-nitrosoresorcinol in presence of Pyridine or Substituted Pyridines.

Sarkar, Miss Purabi, Thokdar, T.K., Sarkar, A., Paria, P.K., Majumdar, S.K., J. Indian Chem Soc. (Communicated for Publication).

9. Extractive photometric Determination of Palladium(II) with 4-Nitrosoresorcinol in presence of Pyridine & Some of Its Methyl Substituted Derivatives.

Sarkar, A., Thokdar, T.K., Paria, P.K., Majumdar, S.K., Indian Journal of Chemistry, 1988, 27A, 650.

10. Extraction and Spectrophotometric Determination of Copper with 4-Nitrosoresorcinol in Presence of Pyridine and Substituted Pyridine.

Sarkar, A., Thokdar, T.K., Paria, P.K., Majumdar, S.K., J. Indian Chem. Soc., 1988, 65, 742.

11. Extractive Spectrophotometric Determination of Cobalt(II)  
with Ninhydrinoxime in Presence of Pyridine.

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

12. Diphenylthiocarbazide as Analytical Reagent for  
Spectrophotometric Determination of Copper.

Paria, P.K., Thokdar, T.K., Majumdar, S.K., J. Indian  
Chem. Soc., 1990, 67, 263.

## Spectrophotometric Determination of Iron as Iron(II) Thiocyanate Cetyltrimethylammonium Bromide

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A spectrophotometric method of determination of iron is described. The red complex formed between iron(II), thiocyanate and cetyltrimethylammonium bromide is extractable into benzene. Addition of borate enhances the colour intensity. Absorbance, measured at 475 nm, shows a linear response upto 1.5 ppm of iron. Molar absorptivity of the complex and Sandell's sensitivity are determined and interferences studied. Iron has been determined in synthetic mixtures.

THIOCYANATE is extensively used for the colourimetric determination of iron, even though other reagents may give better results. The metal can be determined spectrophotometrically by using chrome azurol S and hexadecyltrimethylammonium chloride<sup>1</sup>.

Nagahiro *et al.*<sup>2</sup> determined iron(II) by extraction of its ion-association complex with 5,6-diphenyl-3-(4-phenyl-2-pyridyl)-1,2,4-triazine and tetraphenyl borate into molten naphthalene. Another highly sensitive and selective method for spectrophotometric determination<sup>3</sup> of iron(II) involves the use of bromopyrogallol red and pyrogallol red in presence of tetradecyltrimethylammonium bromide. Bayan<sup>4</sup> developed a method to determine trace amounts of iron(III) using benzyltriethylammonium chloride and thiocyanate in presence of ethyl methyl ketone. The complex is extractable into 1,2-dichloroethane. Numerous other reagents are found reported for spectrophotometric determination of iron. Here we present a highly sensitive method involving application of ammonium thiocyanate and cetyltrimethylammonium bromide(CTA).

In our present investigation it has been found that the above reagents form red complex with iron(II) as well as iron(III). Addition of small amounts of sodium tetraborate enhances the colour of the solution initially containing iron as iron(II). To a solution containing iron as iron(III), addition of borate does not bring about any change in color intensity. Extraction into benzene of the ion-pair formed between the thiocyanate complex of iron(II) and the quaternary ammonium ion from cetyltrimethylammonium bromide (CTA) and measurement of absorbance of the organic extract, forms the basis of the method.

### Experimental

Spectral measurements were made on a Shimadzu PR1 spectrophotometer, equipped with matched quartz cells of 10 mm optical path-length. An

ECL 5651 digital pH meter was used for pH measurements.

All chemicals and solvents used were of analytical grade. A stock solution of ferrous ammonium sulphate was prepared by dissolving it in distilled water and acidified with HCl (2–3 drops) and then standardised<sup>5</sup>.

Solutions of ammonium thiocyanate (0.2 M), cetyltrimethylammonium bromide (CTA) (0.1 M) and sodium tetraborate (0.025 M) were prepared in distilled water. KCl–HCl buffer was used to adjust pH of the aqueous solution.

Standard solutions of diverse ions were prepared from chlorides, nitrates or sulphates (in case of cations) and from sodium, potassium or ammonium salts (in case of anions) of the species concerned, to study interferences.

*Procedure:* To an aliquot of standard solution or sample containing upto 15 µg of iron(II), were added 0.2 M ammonium thiocyanate (0.5 ml), 0.1 M cetyltrimethylammonium bromide (0.1 ml) and 0.025 M sodium tetraborate solution (0.5 ml). KCl–HCl buffer (pH 1.0; 5 ml) and water as necessary were added to the above solution to give a total volume of 10 ml. The resulting mixture was equilibrated with benzene (10 ml) for 30 s. After phase separation, organic layer was poured over anhydrous sodium sulphate to remove any retained water. The absorbance of the organic extract was measured against a blank at 475 nm and the metal concentration computed from a calibration curve. To test the interference, the respective foreign ion was added to the aqueous solution before addition of the reagents.

### Results and Discussion

*Absorption spectra:* The iron complex (in benzene) exhibits absorption maxima at 475 nm. The reagent blank itself, shows insignificant absorbance in this wavelength region. The pattern

of the absorption spectrum of the complex, extracted throughout the entire range, i.e. from 4 M HCl medium to pH 1.0, remains unchanged. This indicates the presence of a single variety of the complex species in the system.

Spectral curves of benzene extracts obtained by applying the procedure to the solutions initially containing iron as iron(II) were identical in nature to those from iron(III) solutions.

*Beer's law and reagent concentrations :* The absorbance of the red complex in benzene shows a linear response upto 1.5 ppm of iron. The molar absorptivity of the complex, based on iron content, and the Sandell's sensitivity were calculated at 475 nm (Table 1).

With the variation of the reagent concentrations, it was found that 0.5 ml of 0.2 M ammonium thiocyanate along with 0.1 ml of 0.1 M cetyltrimethylammonium bromide and 0.5 ml of 0.025 M borate were sufficient to extract 9 µg of iron in a single operation. Increased concentration of the reagents, however, did not bring about any significant change in the  $\lambda_{\text{max}}$  value. Addition of borate raised the intensity of the colour when iron was present initially as iron(II). To a solution containing iron as iron(III), addition of borate had no effect.

*Addition of reagents :* Addition of reagents is important in the procedure. One must follow the sequence of adding the reagents as : thiocyanate, CTA, borate and buffer. No colour development was noted when borate was added before thiocyanate.

*Effect of acidity :* Effect of acidity on the system was examined in terms of absorbance of the complex in the organic phase. Maximum absorbance was obtained when the extractions were carried out from 4 M HCl medium to pH 1.0. In each case, the remaining aqueous phase, after a single operation, was clear and colourless. Furthermore, the aqueous phase, as tested by an independent method, was void of iron. Complete and quantitative extraction of iron occurred in the entire range. At higher acid concentrations, difficulty arises in separating the organic layer due to the formation of some emulsion. Beyond pH 1.0, iron showed no colour reaction with the reagents in the aqueous phase. The reagent blank absorbs minimum at pH 1.0, hence extractions were carried out at pH 1.0.

*Effects of solvents and stability :* Amongst the several solvents benzene, ethyl acetate, chloroform, carbon tetrachloride and butanol, and benzene were found to be suitable solvents for extraction of the iron complex (Table 1). The rapid development of the maximum absorbance and constancy of the absorbance with time indicate that time is not a critical factor in the determination. Spectral curves of the iron complex extracted into other water-immiscible liquids are identical in nature.

*Interference :* To test the effects of diverse ions on the extraction behaviour, iron(II) was extracted

TABLE 1—EFFECT OF SOLVENTS\*

Solvent	$\lambda_{\text{max}}$ nm	Molar absorptivity $\times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	Sandell's sensitivity $\mu\text{g cm}^{-2}$
Benzene	475	3.59	0.001 5
Ethyl acetate	480	2.99	0.001 8
Chloroform	470	2.66	0.002 1
Carbon tetrachloride	NE	NE	NE
Butanol	NE	NE	NE

\* NE = Complex not extractable.

and determined according to the recommended procedure in presence of the diverse ions. Extraction pH was set at 1.0, unless otherwise mentioned. An ion was considered to interfere if the recovery of iron differed by more than  $\pm 3\%$  from the actual amount taken. Iron(II) (9 µg) could be determined without interference in presence of 500-fold excess of Al<sup>III</sup>, Ba<sup>II</sup>, Be<sup>II</sup>, Ca<sup>II</sup>, Sr<sup>II</sup>, Ce<sup>III</sup>, Cd<sup>II</sup>, Cr<sup>III</sup>, La<sup>III</sup>, Pb<sup>II</sup>, Mg<sup>II</sup>, Ni<sup>II</sup>, Rh<sup>III</sup>, Bi<sup>III</sup>, Tl<sup>I</sup>, Th<sup>IV</sup>, U<sup>VI</sup>, Zr<sup>IV</sup> and Ag<sup>I</sup>; 250-fold excess of Co<sup>II</sup>, Mn<sup>II</sup> and Mo<sup>VI</sup>; and 50-fold excess of Pt<sup>IV</sup>. Upto 50-fold excess of V<sup>V</sup> could be tolerated provided the extraction be carried out from 3 M HCl medium. In presence of Cu<sup>II</sup>, the benzene extract became hazy and the absorbance of the organic layer could not be measured, and attempts to remove this interference failed. Zn<sup>II</sup>, Hg<sup>II</sup> and Sn<sup>II</sup> must be absent, as iron(II) showed no colour reaction with the reagents in presence of them. Presence of Pd<sup>II</sup> resulted low recovery of iron.

Among the anions tested, the presence of more than 500-fold excess of citrate, tartrate, acetate, phthalate, phosphate, nitrate had no effect. Extraction should be carried out from 3 M HCl medium to avoid the interference due to EDTA, fluoride and oxalate. The system, however, was found to be susceptible in presence of iodide, nitrite and ascorbate. In 3 M HCl medium 100-fold excess of thiourea could be tolerated.

*Precision and accuracy :* The proposed method was tested by analysing solutions containing a known amount of iron(II). The experimental results for the determination of 3–12 µg of iron(II) are shown in Table 2. The method is fairly precise and reproducible, requiring 10–15 min for each run.

TABLE 2—REPRODUCIBILITY OF IRON RECOVERY

$\text{Fe}^{II}$ taken $\mu\text{g}$	$\text{Fe}^{II}$ found $\mu\text{g}$	Mean $\mu\text{g}$	Std. Dev. %
3.0	3.1	2.96	0.10
	2.8		
6.0	6.2	5.95	0.15
	6.0		
9.0	9.0	9.05	0.12
	9.2		
12.0	11.8	12.00	0.17
	12.2		

TABLE 3—DETERMINATION OF IRON (9  $\mu$ g) IN VARIOUS MIXTURES WITH 200  $\mu$ g OF EACH ION ADDED

Sl. no.	Ions added	Fe found $\mu$ g
1.	Co <sup>II</sup> , Ni <sup>II</sup> , Mn <sup>II</sup>	9.1, 9.1, 9.2
2.	Ni <sup>III</sup> , Mn <sup>II</sup> , Cr <sup>III</sup>	9.0, 9.2, 9.0
3.	Mn <sup>II</sup> , Cr <sup>III</sup> , Bi <sup>III</sup>	9.3, 9.1, 9.0
4.	Cr <sup>III</sup> , Bi <sup>III</sup> , Pb <sup>II</sup>	8.9, 9.1, 9.1
5.	Al <sup>III</sup> , Cd <sup>II</sup> , Th <sup>IV</sup>	9.0, 9.1, 9.1

The method has been tested on a number of synthetic mixtures and the results are shown in Table 3.

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## Extraction Photometric Determination of Microgram Amounts of Cobalt with Thiocyanate and Cetyltrimethylammonium Bromide

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**T**HE thiocyanate complex of cobalt, which is not extractable into chloroform, readily forms extractable ion-pair with the quaternary ammonium ion derived from cetyltrimethylammonium bromide. Measurement of absorbance of this extract forms the basis of the present method for the estimation of  $\mu\text{g}$  amounts of cobalt.

### Experimental

Cobalt solution was prepared from  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and standardised. Solutions of 0.2 M ammonium thiocyanate and 0.1 M cetyltrimethylammonium bromide (CTAB) was prepared in distilled water. Acetate buffer was used for adjustment of pH of the aqueous solution. Acidity was measured with an ECL 5651 digital pH meter.

A Shimazu PR-1 spectrophotometer was used for absorbance measurement.

**Procedure:** To an aliquot of the cobalt(II) solution containing upto 300  $\mu\text{g}$  of cobalt, ammonium thiocyanate (2 ml) and CTAB solutions (0.4 ml) were added. The total volume of the aqueous phase was made upto 10 ml with acetate buffer and distilled water so that pH of the solution was maintained at  $3.5 \pm 0.5$ . The resulting mixture was then shaken (30 s) with chloroform (10 ml). The separated blue organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the chloroform extract was then measured at 625 nm against the reagent blank and the amount of cobalt estimated. To test the interference, foreign ions were added to the aqueous solution before addition of the reagents.

### Results and Discussion

The reaction between cobalt(II), thiocyanate and CTAB was instantaneous. 1 ml of ammonium

thiocyanate along with 0.2 ml of CTAB was insufficient to extract 135  $\mu\text{g}$  of cobalt in a single operation. Higher concentrations of the reagent, however, did not bring about any significant change in the maximum value of absorbance.

A steady and maximum absorbance was obtained when the extractions were carried out throughout the entire range, i.e. from 4 M HCl medium to pH 8.0. In each case the remaining aqueous phase, after a single extraction, was void of cobalt as tested by an independent method. At 0.1 M sodium hydroxide medium, cobalt(II) showed no colour reaction with the reagents.

The  $\text{Co}^{\text{II}}\text{-SCN-CTAB}$  complex in chloroform exhibited absorption maxima at 625 nm with a shoulder around 585 nm. The reagent blank does not absorb in the aforesaid wavelength region. The pattern of the absorption spectrum of the complex, extracted throughout the entire range (4 M HCl medium to pH 8.0) remained unchanged. This indicates the existence of a single variety of the complex species in the system. The absorbance of the chloroform extract remained virtually constant for at least 96 h.

The absorbance of the blue complex in chloroform showed a linear response upto 30 ppm of cobalt. The molar absorptivity of the complex, based on cobalt content, was evaluated to be  $1.92 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  with the corresponding Sandell's sensitivity of 0.031  $\mu\text{g cm}^{-2}$  at 625 nm.

**Interference:** In order to study the effects of diverse ions on the extraction behaviour, cobalt was extracted and determined according to the recommended procedure in presence of the respective foreign ions. Extraction pH was set at 3.5 with acetate buffer, unless otherwise mentioned. An ion was considered to interfere if the recovery of cobalt differed by more than  $\pm 3\%$  from the actual amount taken. Cobalt(II) (135  $\mu\text{g}$ ) could be determined without interference in presence of 50–60 fold excess of  $\text{Be}^{\text{II}}$ ,  $\text{Tl}^{\text{I}}$ ,  $\text{Al}^{\text{III}}$ ,  $\text{Th}^{\text{IV}}$ ,  $\text{U}^{\text{VI}}$ ,  $\text{Pt}^{\text{IV}}$ ,  $\text{Rh}^{\text{III}}$ ,  $\text{La}^{\text{III}}$ ,  $\text{Ca}^{\text{II}}$ ,  $\text{Ba}^{\text{II}}$ ,  $\text{Sr}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Cr}^{\text{III}}$ ,  $\text{Bi}^{\text{III}}$ ,  $\text{Pb}^{\text{II}}$ ,  $\text{V}^{\text{V}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Ag}^{\text{I}}$ ,  $\text{Zr}^{\text{IV}}$ ,  $\text{Mg}^{\text{II}}$ ,  $\text{Ce}^{\text{III}}$ ,  $\text{Sn}^{\text{II}}$ . The system tolerated 20–25 fold excess of  $\text{Mo}^{\text{IV}}$  and  $\text{Fe}^{\text{III}}$  (more than 50-fold excess in presence of ammonium hydrogenfluoride), and 5–10 fold excess of  $\text{Pd}^{\text{II}}$ . A 30-fold excess of  $\text{Cd}^{\text{II}}$  did not interfere if the extraction be carried out from 3 M HCl medium. In presence of  $\text{Cu}^{\text{II}}$ , the chloroform extract became hazy and absorption of the organic layer could not be measured, and this interference could not be removed.  $\text{Zn}^{\text{II}}$  and  $\text{Hg}^{\text{II}}$  must be absent as  $\text{Co}^{\text{II}}$  showed no colour reaction in their presence.

Among the anions tested, a 100-fold excess of thiosulphate, iodide, fluoride, phosphate, acetate, phthalate, tartrate, ascorbate, sulphate, and a 30-fold excess of citrate and oxalate did not have any effect. Extraction should be carried out from 3 M HCl medium to avoid the interference due to EDTA.

The proposed method was tested by analysing

solutions containing a known amount of cobalt. The average of six determinations of 135  $\mu\text{g}$  Co was found to be 133  $\mu\text{g}$  with the relative mean deviation of  $\pm 1.3\%$ .

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## Extractive spectrophotometric determination of microgram amounts of palladium with iodide and cetyltrimethylammonium bromide

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The coloured complex formed between palladium(II), iodide and cetyltrimethylammonium bromide, is extractable into chloroform. Absorbance, measured at 340 nm, shows a linear response upto 5 ppm of palladium. Molar absorptivity of the complex, based on palladium content, is  $2.038 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  and Sandell's sensitivity is  $0.0052 \mu\text{g}/\text{cm}^2$ . The influence of foreign ions has been studied.

Iodide complexes of palladium, which can be extracted by organic solvents have been reported<sup>1-5</sup>. Presently it has been observed that tetraiodopalladate(II), obtained from the reaction between Pd(II) and KI in neutral or slightly acidic solution, forms with cetyltrimethylammonium bromide (CTAB) as ion-pair extractable into chloroform. This observation has led to the development of a sensitive method for the spectrophotometric microdetermination of palladium, which is being described in this note.

Absorbance measurements were made with a Shimadzu PR1 model spectrophotometer equipped with 10 mm matched quartz cells. An ECL digital pH meter was used to measure the acidity of the aqueous solution.

### Experimental

Stock solution of palladium(II) was prepared from  $\text{PdCl}_2$  (Johnson and Matthey) and standardised with dimethylglyoxime<sup>6</sup>. 0.1 M solution of cetyltrimethylammonium bromide (CTAB; SISCO) (0.1 M) and potassium iodide (BDH) solution (0.1 M) were prepared in conductivity water. Potassiumhydrogen phosphate - sodium hydroxide buffer was used to adjust the pH of the aqueous solution.

General procedure : An aliquot containing upto 50  $\mu\text{g}$  of Pd(II) was treated with KI (0.5 ml), CTAB (0.1 ml) and adequate amount of buffer (pH 6) to make the aqueous volume to 10 ml. The mixture was equilibrated with chloroform (10 ml) and the separated organic layer was dried over anhydrous sodium sulphate. Fi-

nally the absorbance of the chloroform extract was measured at 340 nm against pure solvent. Palladium was computed from a calibration curve.

### Results and discussion

With aqueous potassium iodide, palladium(II) gives a reddish-brown colouration due to the formation of  $[\text{PdI}_4]^{2-}$ . This complex anion, as such is not extractable into chloroform. On addition of CTAB to this coloured solution, an ion-association complex, probably of the type  $[\text{CTA}^+]_2 [\text{PdI}_4]^{2-}$  is formed, which is extractable into chloroform. The chloroform solution exhibits  $\lambda_{\max}$  at 340 nm with a broad band of comparatively lower intensity around 440 nm. The reagent blank shows insignificant absorbance in this region. Palladium could be quantitatively extracted in the pH range of 2-10. The pattern of the absorption spectra of the complex in this pH range remained unchanged, indicating the formation of only one complex species in all cases.

Use of other extracting solvents like carbon tetrachloride, benzene or ethyl acetate offered no special advantages over chloroform. The system conforms to Beer's law over 5 ppm of palladium. The molar absorptivity of the complex, based on palladium content, was found to be  $2.038 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  and Sandell's sensitivity  $0.0052 \mu\text{g Pd}/\text{cm}^2$  at 340 nm, which classifies the colour reaction as one of the most sensitive for palladium. CTAB (0.1 ml, 0.1 M) and KI (0.5 ml, 0.1 M) at the concentrations specified were sufficient to extract upto 50  $\mu\text{g}$  of palladium in a single operation.

Interference : To test the effects of diverse ions on the extraction behaviour, palladium(II) was extracted and determined according to the recommended procedure in the presence of the desired foreign ions at pH 6.0. An ion was considered to interfere if the recovery of palladium differed by more than  $\pm 3\%$  from the actual amount taken. Palladium(II) (41.75  $\mu\text{g}$ ) could be determined without interference in the presence of 200-fold excess of the following ions : Al(III), Ca(II), Ba(II), Sr(II), Be(II), Bi(III), Cd(II), Ce(III), Cr(III), Co(II), Cu(II), Fe(III), V(V), La(III), Pb(II), Mg(II), Mn(II), Ni(II), Rh(III), and Zn(II). Less than 50-fold excess of Th(IV), U(VI), Mo(VI) and Zr(IV) did not interfere in the determination of Pd(II). Mercury(II) and platinum(IV) interfered. In the presence of silver the organic extract becomes turbid due to some yellow precipitate.

Among the anions tested, 500-fold excess of the following are tolerable: EDTA, fluoride, ascorbate, citrate, tartrate, phosphate, borate and phthalate. Thiocyanate interfered. In the presence of thiosulphate, palladium could not be extracted.

The average of six determinations of  $41.75 \mu\text{g}$  of Pd(II) was  $41 \mu\text{g}$  with a relative mean deviation of 1.6%.

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## EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM WITH CETYLTIMETHYLAMMONIUM BROMIDE IN PRESENCE OF IODIDE

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LITERATURE reveals the extraction of platinum (IV)<sup>1</sup> into nitrobenzene as an ion-association complex with Fe(phenanthroline)<sub>3</sub><sup>2+</sup>. In presence of iodide or thiocyanate, platinum gets extracted into tributyl-phosphate<sup>2</sup>. In the process the metal has been separated from rhodium and iridium. In our laboratory it has been noted that platinum forms an ion-association complex with cetyltrimethylammonium bromide (CTA) in presence of potassium iodide. The green complex is extractable into ethyl acetate. This property of the platinum complex suggested that further studies of the system might lead to the development of a simple spectrophotometric method for the determination of platinum.

Spectral curves and analytical measurements were made with a Shimadzu PR1 model spectrophotometer equipped with stoppered quartz cells of 10 mm optical path length.

Chloroplatinic acid (Johnson & Matthey) (1 g) was dissolved in 100 ml of distilled water followed by its standardization<sup>3</sup>. Solution of lower concentration of the metal was prepared by appropriate dilution. Ethyl acetate and other solvents were distilled before use. Cetyltrimethylammonium bromide (0.1 M solution) and 0.05 M potassium iodide (BDH) were prepared in distilled water. All other reagents used for the purpose were of analytical grade. Standard solutions of diverse ions were prepared from their corresponding salts.

To an aliquot containing up to 30 µg of Pt(IV) were added 0.1 ml of 0.05 M potassium iodide and 0.1 ml of CTA (0.1 M) followed by adequate amount of hydrochloric acid and water to make the aqueous volume up to 10 ml and 0.5 M with respect to HCl. The mixture was then equilibrated with 10 ml of ethyl acetate for 30 sec. The separated organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. Finally the

absorbance of the ethyl acetate extract was measured at 290 or 360 nm against a blank prepared under identical conditions. Amount of platinum was computed from a calibration curve. To test the effects of diverse ions, the respective foreign ions were added to the system before addition of the reagents.

When potassium iodide is added to a neutral or slightly acidic solution containing platinum (IV), a reddish-brown coloration due to the formation of  $[PtI_6]^{2-}$  is formed. This complex anion is not extractable into acetate. On addition of an aqueous solution of CTA to this coloured solution, an ion-association complex, probably of the type,  $[CTA^+]_2 [PtI_6]^{2-}$  is formed. This is extractable into ethyl acetate.

The absorbance spectrum of the Pt(IV)-I<sup>-</sup>-CTA complex in ethyl acetate, taken against a blank, shows absorption maxima at 290 and 360 nm. The reagent blank exhibits absorption at 250 nm and the absorption becomes insignificant beyond 290 nm. Wavelength of 290 or 360 nm may be selected for all analytical measurements.

The effect of acidity on the extractability of Pt (IV) into ethyl acetate was examined in terms of absorbance of the complex. The complex exhibits constant and maximum absorbance when the extractions were carried out from 0.1 to 1 M hydrochloric acid medium. In a second consecutive operation within this acidity range, the organic extract virtually showed no absorption. This indicated a quantitative extraction of platinum in a single extraction.

Apart from ethyl acetate, other solvents like benzene, chloroform and 1,2-dichloroethane were tested as the extracting solvents, but those offered no special advantages over ethyl acetate. The complex, however, is not extracted into carbon tetrachloride.

The absorbance of the platinum complex in ethyl acetate shows a linear response up to 3 ppm of platinum when measured at 290 or 360 nm. The molar absorptivities of the complex, based on platinum content, were found to be  $5.36 \times 10^4$  and  $3.08 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  and sensitivities 0.0036 and 0.0063  $\mu\text{g}/\text{cm}^2$  at 290 and 360 nm, which classifies the colour reaction as one of the most sensitive for platinum. The colour is stable for at least 24 h.

With the variation of reagent concentrations, it

was noted that 0.1 ml of 0.05 M potassium iodide along with 0.1 ml of 0.1 M CTA was sufficient to extract up to 30 µg of platinum in a single extraction. Increased concentration of the reagents, however, did not bring about any significant change in the maximum value of absorbance. Order of adding the reagents had no effect on colour development.

To test the effects of diverse ions on the extraction behaviour, platinum (IV) was extracted and determined according to the recommended procedure in presence of the desired foreign ions. Extraction was carried out from 0.5 M hydrochloric acid medium. An ion was considered to interfere if the recovery of platinum differed by more than  $\pm 3\%$  from the actual amount taken. Platinum (IV) (30 µg) could easily be determined without interference in presence of 100–200 fold excess of the following ions: Co (II), Ni (II), Cu (II), Pd (II), Fe (III), Cd (II), Zn (II), Mo (VI), V (V), Mn (II), U (VI), Zr (IV), Rh (III), Pb (II), Al (III), Ca (II), Ba (II), Sr (II), Be (II), Bi (III), Ce (III), Cr (III), La (III) and Mg (II). The system develops no colour in presence of mercury (II) and thorium (IV). In presence of silver, formation of some yellowish precipitate hampers the procedure.

Amongst the anions tested 200-fold excess of the followings do not interfere: borate, phosphate, tartrate, citrate, fluoride, phthalate, ascorbate, oxalate and EDTA. In presence of nitrate, high results are obtained. However, thiosulphate, thiocyanate and thiourea must be absent as these inhibit the colour development.

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 of 30 µg of Pt (IV) was 29.25 µg with a relative mean deviation of 2.84%. The process is very simple and rapid requiring only 10–15 min for each run.

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We noted that gold(III) forms an yellow ion-association complex with cetyltrimethylammonium bromide (CTAB) in presence of potassium iodide and is extractable into chloroform. Based on this a simple spectrophotometric method for the determination of gold is reported.

A stock solution of Au(III) was prepared by dissolving gold chloride (Johnson and Matthey) in distilled water and standardizing<sup>8</sup>. Solution of lower concentration of the metal was prepared by appropriate dilution of the stock. Aqueous solutions of CTAB (0.025 M SISCO) and potassium iodide (0.03 M BDH) were used. KH<sub>2</sub>PO<sub>4</sub>-NaOH buffer was employed to adjust the pH of the aqueous solution. Standard solutions of diverse ions were prepared from their salts. Chloroform and other solvents were distilled before use. All other reagents used were of analytical grade.

Absorbance measurements were made with a Shimadzu PR1 model recording spectrophotometer. Stoppered quartz cells of 10 mm optical path length were used for all measurements. An ECL 5651 digital pH meter was used to measure the acidity of the aqueous solution.

To an aliquot containing Au(III) (70 µg) were added potassium iodide (1 ml) and CTAB (0.1 ml). The mixture was adjusted to pH 7.0 with buffer. The volume of the aqueous phase was made up to 10 ml. The mixture was then equilibrated (30 sec) with chloroform (10 ml). The separated organic layer was dried over anhydrous sodium sulphate. Finally the absorbance of the chloroform extract was measured at 290 or 360 nm against a blank prepared in a similar manner. The amount of gold was computed from a calibration curve. To test for interference by other ions, the ions were added to the system before addition of the reagents.

When potassium iodide was added to a neutral or slightly acidic solution containing gold(III), a yellow coloration due to the formation of [AuI<sub>4</sub>]<sup>-</sup> was formed. This complex anion was not extractable into chloroform. On addition of an aqueous solution of CTAB to the coloured solution, an ion-association complex, probably of the type [CTA]<sup>+</sup>[AuI<sub>4</sub>]<sup>-</sup>, was formed. This was extractable into chloroform. Other solvents like ethyl acetate, benzene and 1,2-dichloroethane were also tested as extracting solvents, but these offered no special advantages over chloroform (table 1). The complex was not extractable into carbon tetrachloride.

The reagent blank itself shows absorption maximum at 250 nm and the absorption becomes

#### SPECTROPHOTOMETRIC DETERMINATION OF MICRO QUANTITIES OF GOLD WITH CETYLTRIMETHYLAMMONIUM BROMIDE IN PRESENCE OF IODIDE

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THE reagents [Fe(phenanthroline)<sub>3</sub>]<sup>2+</sup><sup>1</sup>, tetraphenylarsonium chloride<sup>2</sup>, diethyl ether<sup>3</sup>, Rhodamine B<sup>4</sup>, mesityl oxide<sup>5,6</sup> or primaquine phosphate<sup>7</sup> have been used in spectrophotometric methods for determination of gold. In the present investigation

**Table 1** Absorption maxima and molar absorptivities of Au(III)-I-CTAB complex extracted into different solvents

Solvent	Absorption maxima (nm)	Molar absorptivity (l mol <sup>-1</sup> cm <sup>-1</sup> ) ( $\times 10^{-4}$ )	Sensitivity ( $\mu\text{g}/\text{cm}^2$ )
Chloroform	290	2.14	0.009
	360	1.29	0.015
Benzene	298	1.97	0.010
	365	1.32	0.014
Ethyl acetate	290	2.08	0.009
	360	1.13	0.017
1,2-Dichloroethane	295	1.77	0.011
	365	1.07	0.018
Carbon tetrachloride*	—	—	—

\*Complex not extractable.

insignificant beyond 290 nm. Hence all absorption measurements were made at 290 or 360 nm. The Au(III) complex showed constant and maximum absorbance when the extractions were carried out in the pH range 0–9, yielding quantitative recovery of gold in a single extraction.

The absorbance of the Au(III)-I-CTAB complex in chloroform showed a linear response up to 15 ppm of gold at 290 or 360 nm. The molar absorptivity of the complex on the basis of gold content worked out to be  $2.14 \times 10^4$  and  $1.29 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ , corresponding to Sandell's sensitivities 0.009 and  $0.015 \mu\text{g}/\text{cm}^2$ , at 290 and 360-nm respectively. This classifies the colour reaction (stable for 24 h) as one of the most sensitive for gold. Further, with variation of reagent concentration, it was noted that 1 ml of 0.03 M of KI with 0.1 ml of 0.025 M of CTAB was sufficient to extract 70  $\mu\text{g}$  of gold(III) in a single extraction. Increasing the concentration of the reagent did not bring about any significant change in the maximum value of absorbance.

The average of six determinations of 70  $\mu\text{g}$  of Au(III) was 69.5  $\mu\text{g}$ , with a relative mean deviation of 2.87%. The process is very simple and rapid, requiring only 10–15 min for each run.

In interference tests, an ion was considered to interfere if the recovery of gold differed by more than  $\pm 3\%$  from the actual amount. In the present method, gold(III) (70  $\mu\text{g}$ ) could be determined without interference in presence of 100-fold excess of Cr(III), V(V), Mo(VI), Hg(II), Rh(III), Al(III), Cu(II), Ni(II), Mg(II), Pt(IV), Pd(II), Zn(II), Cd(II), Pb(II), Zr(IV), Ca(II), Ba(II), Sr(II), Th(IV) and La(III). Fifty-fold excess of Fe(III), Co(II), Mn(II),

**Table 2** Analysis of synthetic mixtures

Composition with amounts taken in $\mu\text{g}$	Recovery of gold (%)
Au(III) 70, Ag(I) 100, Cu(II) 100, Zn(II) 100	98
Au(III) 70, Fe(III) 100, Co(II) 100, Ni(II) 100	98
Au(III) 70, Pd(II) 100, Pt(IV) 100, Rh(III) 100	101

Ag(I) and Bi(III) could be tolerated. U(VI) interfered. Among the anions tested, 200-fold excess of borate, phosphate, tartrate, citrate, fluoride, bromide, phthalate, oxalate, acetate and nitrite, and lower concentrations of ascorbate and EDTA did not interfere in the estimation of gold. Thiocyanate, thiosulphate, thiourea and arsenate interfered.

In the absence of real samples, the applicability of the method was tested by analysing some synthetic mixtures containing Au(III), Ag(I), Cu(II), Zn(II), Fe(III), Co(II), Ni(II), Pd(II), Pt(IV) and Rh(III). The compositions of the mixtures and percentage recovery of gold are given in table 2. The results show that recovery of gold was highly satisfactory. Average of three determinations was taken in each case.

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## Extractive Photometric Determination of Palladium(II) with 4-Nitrosoresorcinol in Presence of Pyridine & Some of Its Methyl Substituted Derivatives

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An extractive photometric method is proposed for the determination of Pd(II) using 4-nitrosoresorcinol and pyridine/substituted pyridines. The mixed-ligand complexes of palladium(II) with 4-nitrosoresorcinol and pyridine/its methyl derivatives are extractable into chloroform and obey Beer's law. The molar absorptivities of the complexes are  $(2.6-3.5) \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$  at  $\lambda_{\text{max}} 395-400 \text{ nm}$  and Sandell's sensitivities are 0.003-0.004  $\mu\text{g Pd(II)}/\text{cm}^2$ . The influence of foreign ions is studied.

The use of pyridine-thiocyanate for extractive-photometric determination of various metals is well established<sup>1-6</sup>. 4-Nitrosoresorcinol reacts with cobalt(II) and palladium(II) to form red complexes which are insoluble in chloroform. The reaction was used for detection and determination of the metals<sup>7,8</sup> in aqueous solution by colour comparison. In the present note we report the extractive photometric determination of Pd(II) with 4-nitrosoresorcinol in presence of pyridine and some of its methyl substituted derivatives like  $\alpha$ -picoline,  $\beta$ -picoline,  $\gamma$ -picoline and 2,4,6-collidine, extractable into chloroform under optimum conditions.

The absorbance measurements were made with a Shimadzu PR 1 spectrophotometer equipped with stoppered quartz cells of 10 mm path length. An ECL 5651 digital pH meter was used for pH measurements.

Palladium chloride (Johnson & Matthey) (1 g) was dissolved in hot conc. HCl (1 ml) and diluted to 250 ml with distilled water followed by standardisation with dimethylglyoxime<sup>9</sup>. A working solution (210.5  $\mu\text{g Pd/ml}$ ) was prepared by dilution. Chloroform (E Merck), pyridine (BDH),  $\alpha$ -picoline (Riedel),  $\beta$ -picoline,  $\gamma$ -picoline (BDH), (Fluka) and 2,4,6-collidine (BDH) were distilled before use.

4-Nitrosoresorcinol was prepared according to  $\gamma$ -picoline the known procedure<sup>10</sup>. The light yellow crystalline solid, which was formed, was filtered off and recrystallized from dilute ethanol. The reagent in the solid state is very unstable, but its ethanolic solution is stable.

### General procedure

An aliquot of sample solution was mixed with 0.2 ml of 1% ethanolic solution of 4-nitrosoresorcinol followed by addition of (0.5 ml, 100%) pyridine/ $\alpha$ -picoline/ $\beta$ -picoline/ $\gamma$ -picoline/2,4,6-collidine. The pH of the solution was adjusted to 2 with KCl-HCl buffer. The volume of the aqueous phase was maintained at 10 ml. The solution was then equilibrated with 10 ml of chloroform in a separating funnel for 1 min. The two layers were allowed to settle. The separated organic layer was shaken with anhydrous sodium sulphate to remove any moisture. Finally the absorbance of the organic extract was measured at the corresponding absorption maxima (Table 1) against a palladium-free reagent blank. The amount of palladium(II) was determined from a previously prepared calibration curve.

The extraction of palladium complexes was investigated in the pH range 0-11. Chloroform extracts showed maximum and steady absorbance when the extractions were carried out in the pH range 1-8. When the extraction was repeated with the same aqueous phase, the organic extract virtually showed no absorbance. The aqueous phase, after extraction, was also tested for palladium by an independent method. This indicated a complete and quantitative extraction of palladium in this pH range.

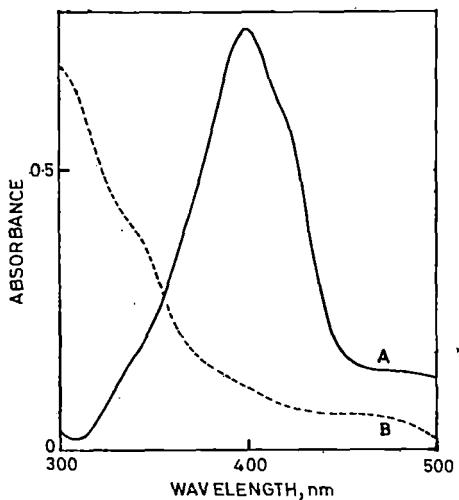
The spectra of the mixed-ligand complexes were scanned in the wave-length region 300-600 nm against the corresponding reagent blanks. The Pd(II)-complexes showed absorption maxima at 395-400 nm. As the reagent blanks showed some absorbances in the aforesaid wave-length region, all the analytical measurements were carried out against the respective reagent blanks. Figure 1 shows the spectrum of pd(II)-4-nitrosoresorcinol- $\gamma$ -picoline system and the corresponding reagent blank. The optimum concentration of the reagents for the purpose of quantitative extraction of the complexes was ascertained by extracting palladium(II) at various concentrations of 4-nitrosoresorcinol and pyridine bases. Extraction was found to be quantitative when 0.2 ml of 1% ethanolic solution of 4-nitrosoresorcinol and 0.5 ml of pyridine/ $\alpha$ -picoline/ $\beta$ -picoline/ $\gamma$ -picoline/2,4,6-collidine were used. Under these optimum conditions 84.2  $\mu\text{g}$  of Pd(II) was found to be quantitatively extracted. The higher concentrations of the reagents had no adverse effects on the extraction.

The quantitative extraction of palladium occurred in a single operation when the layers were shaken

Table 1—Details of Extractive Methods

Parameter	Base employed				
	Pyridine	$\alpha$ -picoline	$\beta$ -picoline	$\gamma$ -picoline	2,4,6-collidine
$\lambda_{\text{max}}$ (nm)	395	400	395	395	400,410*
Molar absorptivity ( $1 \text{ mol}^{-1} \text{ cm}^{-1}$ )	$3.28 \times 10^4$	$2.68 \times 10^4$	$3.44 \times 10^4$	$3.52 \times 10^4$	$3.47 \times 10^4$
Sandell's sensitivity ( $\mu\text{g}/\text{cm}^2$ )	0.0032	0.0039	0.0030	0.0029	0.0031

\*shoulder

Fig. 1—Absorbance spectra of (A) Pd(II)-4-nitrosoresorcinol- $\gamma$ -picoline complex (4.2 ppm Pd) and (B) reagent blank

for 1 min. Chloroform extracts, obtained after the recommended procedure, showed a steady absorbance for at least 12 hr.

In all the cases Beer's law was found to be valid over the concentration range 1-20 ppm of palladium. The corresponding molar absorptivities of the complexes (on the basis of palladium content) and respective Sandell's sensitivities were calculated and are presented in Table 1.

#### Effect of diverse ions

In order to study the effects of diverse ions on the extraction behaviour, palladium was extracted and determined according to the general procedure 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. In practice all the pyridine bases i.e., pyridine/ $\alpha$ -picoline/ $\beta$ -picoline/ $\gamma$ -picoline/2,4,6-collidine showed similar behaviour regarding interferences.

Palladium(II) (84.2  $\mu\text{g}$ ) can be determined without interference in presence of 50-60 fold excess of Ni(II), Cd(II), Hg(II), Zn(II), V(V), Pt(IV), Rh(III), Mn(II) and Be(II). The system tolerated 20-25-fold excess of Mo(VI), Zr(IV), U(VI), La(III), Al(III), Tl(I), Pb(II) and Cr(III). 10-fold excess of Fe(III) and Cu(II) could be tolerated in presence of ammonium bifluoride and citrate respectively. High results were obtained in presence of Co(III).

Among the anions tested, 100-fold excess of borate, phosphate, bromide, iodide, phthalate, acetate, tartrate, citrate, fluoride, ascorbate, oxalate did not interfere. 30-fold excess of EDTA did not have any effect. Thiocyanate and thiosulphate interfere seriously. More than 100-fold excess of chloride, nitrate and sulphate was found to be harmless.

With  $\gamma$ -picoline the precision and accuracy of the proposed method was tested by analyzing solutions containing a known amount of Pd(II) following the recommended procedure. The average of six determinations of 84.2  $\mu\text{g}$  Pd was found to be 83.4  $\mu\text{g}$  with the relative mean deviation of  $\pm 1\%$ .

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### Extraction and Spectrophotometric Determination of Copper with 4-Nitrosoresorcinol in Presence of Pyridine and Substituted Pyridines

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**E**XTRACTIVE-PHOTOMETRIC determination of various metals with pyridine bases-thiocyanate has been reported<sup>1-7</sup>. We have undertaken a systematic programme to study the extraction behaviour of copper(II) with 4-nitrosoresorcinol in presence of pyridine and some of its methyl-substituted derivatives. Based on these studies, a few rapid and sensitive methods for the extraction and spectrophotometric determination of copper(II) have been developed. The substituted-pyridines used are  $\alpha$ -picoline,  $\beta$ -picoline,  $\gamma$ -picoline and 2,4,6-collidine.

#### Experimental

A Shimadzu PR1 spectrophotometer was used for absorbance measurements. A ECL 5651 digital pH meter was used to measure the acidities of the aqueous solutions.

A stock solution of copper(II) was prepared from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and standardised<sup>8</sup> and solution of lower concentration made by appropriate dilution. Chloroform (E. Merck), pyridine (B.D.H.),  $\alpha$ -picoline (Riedel),  $\beta$ -picoline (B.D.H.),  $\gamma$ -picoline (Fluka) and 2,4,6-collidine (B.D.H.) were distilled before use. 4-Nitrosoresorcinol was prepared as reported<sup>9</sup> and its ethanolic solution (1%) was used. KCl-HCl buffer was used for pH adjustment.

**General procedure:** An aliquot containing upto 100  $\mu\text{g}$  of  $\text{Cu}^{II}$  was mixed with 1% ethanolic

solution (0.2 ml) of 4-nitrosoresorcinol followed by addition of pyridine/ $\alpha$ -picoline/ $\beta$ -picoline/ $\gamma$ -picoline/2,4,6-collidine (0.5 ml). Buffer solution (pH 2; 5 ml) was then added and volume of the aqueous phase was made upto 10 ml with distilled water. The solution was then equilibrated with chloroform (10 ml) in a separating funnel for 1 min. The separated organic layer was poured over anhydrous sodium sulphate to remove retained water droplets. Finally, the absorbance of the organic extract was measured at the corresponding absorption maxima against a copper-free reagent blank, and the amount of copper(II) determined. 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 optimum pH for extraction for copper was ascertained by extracting the mixed-ligand complexes in the pH range 1.0–11.0. In all the cases maximum absorbance was attained at pH 1.5–2.5. In a second consecutive operation within this pH range, the organic extract virtually showed no absorbance. This indicated that copper(II) was quantitatively extracted in this condition.

The spectra of the mixed-ligand complexes were recorded in the wavelength region 300–600 nm against the corresponding reagent blank. The copper complexes showed  $\lambda_{max}$  at 365–375 nm.

Different amounts of copper(II) were extracted as described in the general procedure. In all the cases, Beer's law was found to be valid over the concentration range 1–10 ppm of copper. The Ringbom's optimum concentration range for measurement was found to be 3–10 ppm of copper(II). The corresponding molar absorptivity of the complexes (on the basis of copper content) and the respective Sandell's sensitivity values are shown in Table 1.

The optimum concentration of the reagents for extraction of copper(II) has been ascertained. It has been found that 0.2 ml of 1% ethanolic solution of 4-nitrosoresorcinol along with pyridine/ $\alpha$ -picoline/

TABLE 1—DETAILS OF EXTRACTIVE METHODS

Parameter	Base employed				
	Pyridine	$\alpha$ -Picoline	$\beta$ -Picoline	$\gamma$ -Picoline	2,4,6-Collidine
pH	1.5–2.5	1.5–2.5	1.5–2.5	1.5–2.5	1.5–2.5
$\lambda_{max}$ (nm)	365	375	370	370	365
Molar absorptivity ( $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	$0.71 \times 10^4$	$0.45 \times 10^4$	$0.89 \times 10^4$	$1.06 \times 10^4$	$0.21 \times 10^4$
Sandell's sensitivity ( $\mu\text{g cm}^{-3}$ )	0.009	0.014	0.007	0.006	0.03

## NOTES

$\alpha$ -picoline/  $\gamma$ -picoline/2,4,6-collidine (0.5 ml) was sufficient to extract 100  $\mu\text{g}$  of copper(II) quantitatively. Higher concentration of the reagents had no adverse effect on the extraction but was avoided due to reagent economy. Moreover, in presence of higher concentration of the reagents, the absorbances of the reagent blanks become higher. Chloroform extracts showed a steady absorbance for at least 24 h.

Copper (II) was determined in presence of other diverse ions. Deviation of not more than  $\pm 3\%$  from the expected absorbance was taken as the standard tolerance limit. In practice, all the pyridine bases showed similar behaviour while studying interferences. Copper(II) (48  $\mu\text{g}$ ) could be determined without interference in presence of 50–60-fold excess of  $\text{Ni}^{II}$ ,  $\text{V}^V$ ,  $\text{Pt}^{IV}$ ,  $\text{Rh}^{III}$ ,  $\text{Ca}^{II}$ ,  $\text{Ba}^{II}$  and  $\text{Sr}^{II}$ . The systems tolerated 20–25-fold excess of  $\text{Cd}^{II}$ ,  $\text{Zn}^{II}$ ,  $\text{Mo}^{VI}$ ,  $\text{U}^{VI}$ ,  $\text{La}^{III}$ ,  $\text{Al}^{III}$ ,  $\text{Th}^{IV}$ ,  $\text{Be}^{II}$  and  $\text{Mn}^{II}$ . High results were obtained in presence of  $\text{Co}^{II}$  and  $\text{Pd}^{II}$ . Hg interfered seriously. Presence of  $\text{Fe}^{III}$  and  $\text{Zr}^{IV}$  showed low recovery of copper. Among the anions tested, 100-fold excess of borate, phosphate, bromide, phthalate, iodide, acetate did not interfere. Thiocyanate, thiosulphate, EDTA, oxalate, tartrate, citrate, fluoride and ascorbate interfered.

$\gamma$ -Picoline was found to be comparatively more 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 copper(II) following the recommended procedure. The average of six determinations containing 48  $\mu\text{g}$  of  $\text{Cu}^{II}$  gave a value of 48.25  $\mu\text{g}$ , which varies between 46.81 to 49.68 at 95% confidence limit. The standard deviation is 1.37  $\mu\text{g}$  and relative mean deviation 1.8%.

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### Extractive Spectrophotometric Determination of Cobalt(II) with Ninhydrinoxime in Presence of Pyridine

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THE most sensitive colourimetric methods for determination of cobalt are based on its reaction with compounds containing the grouping  $=\text{C}(\text{OH})-\text{C}(\text{OH})=$ . Various oximes have been reported<sup>1</sup> to determine cobalt spectrophotometrically. In pH 3–6 ninhydrinoxime forms a yellowish brown complex with cobalt, which by itself is not extracted into organic solvents. In presence of pyridine, the complex is extractable into chloroform. Measurement of absorbance of this extract shows a linear response with cobalt concentration. Taking advantage of this, a method has been devised to determine cobalt in micro quantities.

#### Experimental

Absorbance measurements were made with a Shimadzu PR1 spectrophotometer. A ECL 5651 pH-meter was used to measure the pH. A stock solution of cobalt(II) was prepared by dissolving  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (AnalaR) in distilled water. This was standardised by complexometrically using xylenol orange as indicator<sup>2</sup>. Pyridine, chloroform and other organic solvents were distilled before use. Potassium hydrogen phthalate–hydrochloric acid buffer was used to adjust the pH.

**Synthesis of ninhydrinoxime:** To a solution of ninhydrin (2 g) dissolved in pyridine (2 ml), was added ethanolic solution (100 ml) of hydroxylaminehydrochloride (2 g) and the mixture was refluxed for 2 h. The resulting solid was recrystallised from ethanol (80%) (Found : C, 57; H, 4.2; N, 6.8.  $\text{C}_9\text{H}_7\text{O}_4\text{N}$  calcd. for : C, 56; H, 3.6; N, 7.25%).

**General procedure :** To an aliquot containing upto 40  $\mu\text{g}$  of cobalt(II) was added 0.6% ethanolic solution (1 ml) of ninhydrinoxime followed by pyridine (0.2 ml). Buffer solution was then added to adjust the pH to 4. The mixture was left for 1 min and the volume of the aqueous phase was made upto 10 ml. This was then equilibrated with chloroform (10 ml) for 30 s. After phase separation, the organic extract was poured over anhydrous sodium sulphate to remove water droplets. Finally the absorbance of the chloroform extract was

measured at 330 nm. Amount of cobalt was computed from a previously prepared calibration curve. To test the interferences, the respective diverse ions were added to the system prior to the addition of the reagents.

#### Results and Discussion

The complex exhibits  $\lambda_{\text{max}}$  at 330 nm. The reagent itself shows high absorbance below 300 nm. However, the absorbance becomes insignificant beyond 320 nm. The complex exhibits constant and maximum absorbance when the extractions were carried out at pH 3–6. In each case, the aqueous phase after extraction was free from cobalt. The pattern of the absorption spectra of the complex extracted at pH 0–10 remains unchanged, indicating the formation of the single complex species in all cases. Apart from chloroform, other solvents like ethyl acetate, 1,2-dichloroethane, benzene and carbon tetrachloride were tested as extracting solvents. The use of ethyl acetate and 1,2-dichloroethane offered no special advantages over chloroform. Lower absorbance resulted in case of benzene. Carbon tetrachloride did not extract the complex. Apart from pyridine, some other bases were tested as auxiliary ligands. The use of  $\beta$ -picoline or  $\gamma$ -picoline did not bring about any significant change in the maximum value of absorption. In presence of  $\alpha$ -picoline or 2,4,6-collidine, the complex is not extractable into chloroform. The nature of the extracted species is 1 : 3 (M : L) (mole ratio method).

The system conforms to Beer's law. The absorbance of the cobalt complex in chloroform shows a linear response upto 4 ppm of cobalt at 330 nm and the molar absorptivity of the complex is  $1.97 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  with Sandell's sensitivity 0.003  $\mu\text{g cm}^{-2}$ .

Cobalt (24  $\mu\text{g}$ ) could be determined without interference in presence of 200-fold excess of the following ions :  $\text{Fe}^{\text{III}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Pd}^{\text{II}}$ ,  $\text{Pt}^{\text{IV}}$ ,  $\text{Th}^{\text{IV}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ ,  $\text{Ca}^{\text{II}}$ ,  $\text{Ba}^{\text{II}}$ ,  $\text{Sr}^{\text{II}}$ ,  $\text{U}^{\text{VI}}$ ,  $\text{Sn}^{\text{II}}$ ,  $\text{Cr}^{\text{III}}$ ,  $\text{Hg}^{\text{II}}$ ,  $\text{V}^{\text{V}}$ ,  $\text{Mo}^{\text{VI}}$  and  $\text{Mn}^{\text{II}}$ . The system tolerated less than 25-fold excess of  $\text{Be}^{\text{II}}$ ,  $\text{Bi}^{\text{III}}$ ,  $\text{Cu}^{\text{II}}$  and  $\text{La}^{\text{III}}$ .  $\text{Rh}^{\text{III}}$  interfered. The following anions did not interfere when present in 400-fold excess : ascorbate, oxalate, arsenate, bromide, iodide, fluoride, phosphate, citrate, tartrate and thiocyanate. Less than 50-fold excess of EDTA, thiosulphate and thiourea were permissible. Nitrite interferred.

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### Diphenylthiocarbazide as Analytical Reagent for Spectrophotometric Determination of Copper

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**DIPHENYLTHIOCARBAZIDE** can be used for the detection of a number of metals<sup>1</sup> since it forms characteristic coloured complexes. A method is presented for the extractive spectrophotometric determination of copper. The metal has been estimated in synthetic mixtures and standard samples.

#### Experimental

A Shimadzu PR-1 model spectrophotometer with optically matched quartz cells of 10 mm path length was used for absorbance measurements. Acidity of the aqueous solution was measured with a ECl 5651 pH meter.

Diphenylthiocarbazide was prepared<sup>1</sup> and a 0.4% acetonnic solution of the reagent was used. Stock solution of copper(II) was prepared by dissolving CuSO<sub>4</sub>.5H<sub>2</sub>O (B.D.H.) in distilled water followed by its standardisation as bezoin- $\alpha$ -oximate<sup>2</sup>. A working solution of copper was prepared by appropriate dilution. Ethyl acetate was distilled before use. KH<sub>2</sub>PO<sub>4</sub>-NaOH buffer was employed to adjust pH of the aqueous solution. All other chemicals used were of analytical grade.

**Determination of copper(II) :** To a suitable volume of sample solution containing 5–30 µg of copper(II) was added 0.4% acetonnic solution (0.5 ml) of diphenylthiocarbazide followed by phosphate buffer (pH 6; 5 ml). The aqueous phase was then diluted to 10 ml with distilled water and left for 1 min to ensure complete complexation. The solution was then equilibrated with ethyl acetate (10 ml) for 1 min. The separated organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the organic extract was read at 540 nm against the reagent blank and the amount of copper deduced from a calibration curve. To study the effects of diverse ions, the respective foreign ions along with the masking agents, if needed, were added to the aqueous sample solution before addition of the reagent.

#### Results and Discussion

The optimum conditions for extraction of copper have been established from critical evaluation of the pertinent factors.

The brown coloured complex of Cu-diphenylthiocarbazide shows a maximum absorption at 540 nm. Beer's law obeyed over 0.2–4 ppm of copper. The molar absorptivity was  $5.04 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  with Sandell's sensitivity 0.0013 µg Cu/cm<sup>2</sup> at 540 nm. Quantitative extraction of copper was achieved in the pH range 4–8.

**Interference :** Copper (20 µg) was determined in presence of known quantity of diverse ions. Interference due to Fe<sup>III</sup> and Sn<sup>II</sup> is eliminated by masking with ammoniumhydrogen fluoride. To avoid the interference due to Pd<sup>II+</sup>, copper was extracted in presence of ammonium thiocyanate. Potassium iodide masks Hg<sup>II</sup>, Pb<sup>II</sup> and Bi<sup>III</sup>. The tolerance limits for other ions (mg, in parenthesis) are as follows : Ni<sup>II</sup>, Mo<sup>VI</sup>, Ca<sup>II</sup>, Mn<sup>II</sup>, Cr<sup>III</sup>, La<sup>III</sup>, Al<sup>III</sup>, Ba<sup>II</sup>, Sr<sup>II</sup> and Mg<sup>II</sup> (all 4); Co<sup>II</sup>, and U<sup>VI</sup> (3.5); Be<sup>II</sup> and As<sup>III</sup> (3); Pt<sup>IV</sup>, Rh<sup>III</sup> and Th<sup>IV</sup> (2.5); V<sup>V</sup> and Cd<sup>II</sup> (0.1); Zn<sup>II</sup> (90.1). Among the anions tested, 500-fold excess of tartrate, citrate, oxalate, bromide, iodide, phosphate, acetate, thiocyanate, fluoride, phthalate and thiourea do not interfere. The system tolerated 200-fold excess of ascorbate, EDTA and thiosulphate. However in presence of borate and nitrite high results are obtained.

**Determination of copper in cupronickel alloys :** The alloy sample (100 mg) was dissolved in a mixture of HCl and HNO<sub>3</sub> (2 : 1). The solution was evaporated to dryness after adding a few drops of concentrated H<sub>2</sub>SO<sub>4</sub>. The residue was dissolved in water and the resulting solution was diluted to 250 ml with distilled water. The solution was further diluted as needed. A 2 ml aliquot was taken and copper determined by following the procedure outlined earlier. Copper was found to be 69.2% (average of four determinations ; certified : 68.12% Cu in cupronickel alloy).

**Determination of copper in white metal in presence of Pb, Sb, Sn, Bi, Ni, As :** The sample (1 g) was dissolved in 6 M HCl (10 ml) and digested on a hot-plate. The clear solution was evaporated, cooled and diluted with distilled water. The solution was filtered to remove a major portion of lead, precipitated as lead chloride. The filtrate was diluted to a known volume. A 2 ml portion was taken followed by addition of KI (10 mg) and NH<sub>4</sub>HF<sub>2</sub> (5 mg) along with acetonnic solution (0.5 ml, 0.4%) of diphenylthiocarbazide. Copper in white metal was estimated by the recommended procedure and was found to be 0.13% (average of four determinations ; certified : 0.12% Cu in lead base white metal).

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