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SOLVENT EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) WITH N-HYDROXY-N,N'-DIPHENYLBENZAMIDINE AND THIOCYANATE AND COBALT(II) WITH N-HYDROXY-N,N'-DIPHENYLBENZAMIDINE

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Gebray Asgedom

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Solvent Extraction and Spectrophotometric Determination of Iron (III)
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Cobalt (II) with N-hydroxy-N,N'-diphenylbenzamidine

by

Gebray Asgedom
Chemistry Department
Faculty of Science

Approved by:

Dr. B.S. Chandravanshi
Advisor

B.S. Chandravanshi

Dr. J. David Smith
Examiner

David Smith

Dr. Theodros Solomon
Examiner

Theodros Solomon

Dr. Nigussie Retta
Examiner

Nigussie Retta

Dr. M. Socher
Examiner

M. Socher

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A B S T R A C T

Solvent Extraction and Spectrophotometric Determination of Iron(III) with N-Hydroxy-N,N'-diphenylbenzamidine and Thiocyanate and Cobalt(II) with N-Hydroxy-N,N'-diphenylbenzamidine

by

Gebra Asgedom

Advisor: Dr. B.S. Chandravanshi

N-Hydroxy-N,N'-diphenylbenzamidine, HDPBA, a bidentate chelating agent was found to react with iron(III) in the presence of thiocyanate to give an orange-red mixed ligand complex which is quantitatively extractable into toluene from 0.1 - 0.6 M hydrochloric acid solution allowing spectrophotometric determination of the metal ion. The colored system has a wavelength of maximum absorption at 465 nm with a molar absorption coefficient of $10,000 \text{ l mol}^{-1} \text{ cm}^{-1}$. The composition of the Fe(III)-SCN-HDPBA complex has been determined by spectrophotometric methods and was found to be 1:2:2 ($\text{Fe}^{3+}:\text{SCN}^-:\text{HDPBA}$). The effects of foreign ions and of several other experimental variables have been studied to establish the optimum conditions for extraction and determination of iron(III). On the basis of these studies, a simple, precise, sensitive and very selective method has been proposed for the determination of iron. This method has been applied successfully for the

determination of iron in blood and steel samples.

Cobalt(II) was found to react with N-hydroxy-N,N'-diphenylbenzamidino to form a yellow-brown complex. The complex was found to be quantitatively extractable into toluene from the aqueous phase at pH 7.5 - 9.5. The spectra of the cobalt(II) complex exhibited absorption maxima in the visible region at 405 nm with molar absorptivity of $7000 \text{ l mol}^{-1} \text{ cm}^{-1}$. The composition of the complex has been found to be 1:3 (Co(II):HDPBA). The effects of foreign ions and of other experimental variables has been evaluated and the method has been found to be rapid, precise, selective and moderately sensitive. The method has been applied for the determination of cobalt in Vitamin B₁₂.

1. INTRODUCTION

The increasing awareness of the important role of trace amounts of inorganic compounds in chemical, physical, and biological systems has greatly stimulated the refinement and extension of chemical analysis in which the substance to be determined is treated with an auxiliary substance being added (the reagent). The properties and the amount of reaction product formed are then considered in order to draw conclusions as to the qualitative and quantitative composition of the sample being analyzed.

The analytical requirements imposed by the complex composition of the substances has led to rapid advances in analytical chemistry mainly in the field of new analytical methods based on instrumental techniques. However, the chemical reaction of a suitable reagent with the substance to be determined still remains the true basis of numerous methods of detection, separation and determination. In this respect organic reagents play a predominant role and find wide application in spectrophotometric methods, titrimetry, spot tests and last but not least in separation methods (precipitation, masking, solvent extraction and ion-exchangers) and pre-concentration procedures.

The tests for and determinations of substances with

organic reagents can often be performed with higher sensitivity and selectivity. The separations are also more effective if organic reagents are employed. Organic reagents are attractive for the simple reason that a large number of them are known and therefore, a better choice can be made. Therefore the scope and number of their applications in analytical practice continues to increase.

The reactions of organic reagents with inorganic ions in solution can yield products of various properties, for example they can exhibit a change in color, luminescence, solubility, and volatility. The reaction products may be complex compounds, or new organic substances (formed due to the oxidation-reduction or catalytic action of inorganic ions), or other forms of the reagent (acid-base indicators). Besides these reaction types the organic reagent in solution can be adsorbed on a precipitate of an inorganic substance, the adsorption being accompanied by a color change of the reagent. The formation of a product which is insoluble in a given solvent can be employed for the gravimetric determination, separation or precipitation titration of an ion. If the reaction product is volatile, the organic reagent can be used for an analytical separation based on distillation, or sublimation or gas chromatography. If the reaction product is less soluble in water than in an organic solvent immiscible with water, the reaction can be used for solvent extraction to be followed by spectrophotometric determination.

In many reactions of organic reagents a conspicuous

color or fluorescence is developed, or conversely, a colored component in solution is decolorized during the reaction or its fluorescence is quenched. Such reactions can be applied for end point indication in acid-base, oxidation-reduction or complexometric titrations and spectrophotometric or fluorometric determinations.

1.1 Spectrophotometry

Spectrophotometric methods are based on the measurement of the absorbance for monochromatic light passing through the solution containing the substance being determined. provided that the thickness of the absorbing layer, l , and the absorption coefficient, ϵ (measure of extent of interaction between the molecule of a substance and radiation), of the substance being determined at a given wavelength are known and the absorbance, A , is measured it is possible to use Beer's law in order to determine the unknown concentration, C .

$$C = \frac{A}{\epsilon l} \quad (1)$$

Spectrophotometric methods are commonly used for the determination of inorganic substances with organic reagents. The reliability of the method depends on the nature of the organic reagent used. Organic reagents used in spectrophotometric method should be sufficiently stable and resistant to aerial oxidation or to photometric decomposition. The same should hold for the reaction

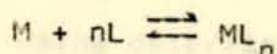
products. Moreover, in the absorption spectrum of a product there must be a characteristic intense absorption band, at sufficient distance from that of the reagent or of substance being determined: $\lambda_{(\text{product})_{\text{max}}} - \lambda_{(\text{reagent})_{\text{max}}} \geq 100 \text{ nm}$. The reagents for which $\lambda_{(\text{product})_{\text{max}}} \sim \lambda_{(\text{reagent})_{\text{max}}}$ are less suited for spectrophotometry and are applicable only when the absorption coefficients differ by a factor of at least 2.

1.2 Spectrophotometric Determination of Metal Ions (1-6)

Spectrophotometric determination of metal ions is usually based on the formation of metal complexes. The formation of a stable metal complex required the presence of acidic or basic analytical functional group in the molecule of the reagent (ligand), preferably in those positions which allow the formation of a five or six membered chelate ring. Colored metal complexes are formed , only when the organic reagent has Π -electron chromophoric groups in the molecule, the cyclo group should also form a part of the Π -electron system and no insulating group is permitted between the acid group and the conjugated system of the molecule.

Completeness of Complexation Reaction. Both the accuracy and precision of a photometric determination depend on the completeness of a given reaction. As the reaction solution usually contains components competing in the

reaction, it is necessary to consider the conditional stability constant for the general complexation equilibrium



in which the determination is based

$$B'_{ML_n} = \frac{(ML_n)}{C'_M (C'_L)^n} \quad (2)$$

where B'_{ML_n} is the conditional stability constant and C'_M and C'_L are respectively the total concentration of the metal and the ligand unconsumed in the formation of the complex ML_n .

If a reaction is considered as complete when 99% of the metal being determined is transformed into the particular complex ML_n , it follows that

$$\frac{(ML_n)}{C'_M} = B'_{ML_n} (C'_L)^n \geq 10^2 \quad (3)$$

The ligand is usually an anionic species of a weak acid H_fL and so its concentration is pH dependent.

The expression in equation 3 can be used for the calculation of the necessary minimum excess of the reagent, or for estimation of the pH range over which B'_{ML_n} attains the required value.

Selectivity. If adequate selectivity in the photometric

determination of a given substance is to be achieved, it is necessary to choose a suitable wavelength at which to make the measurements. The absorption coefficient of the substance being determined should be high and those of the other substances present be negligible. Selectivity can be increased by pH adjustment or by masking. The masking reagent (and the complex formed) should be colorless and not form any complexes with the metal being determined or react with the colorimetric reagent.

Selectivity can often be increased by extraction of the reaction product. Thus it is possible to separate the component to be determined from other interfering substances.

In the determination of a metal ion M in presence of another metal N, if both form colored complexes ML_n (B'_{ML_n}) and NL_n (B'_{NL_n}) with similar absorption spectra, correct results for ML_n are obtained if the condition in equation 3 is fulfilled. At the same time the following expression must hold for the ratio of absorbance values of the two complexes, provided that the colorimetric reagent itself does not absorb at the wavelength used:

$$\frac{A_{ML_n}}{A_{NL_n}} = \frac{\epsilon_{ML_n} ML_n}{\epsilon_{NL_n} NL_n} = \frac{\epsilon_{ML_n} B'_{ML_n} C_M [1 + B_{NL_n} (C_L')^n]}{\epsilon_{NL_n} B'_{NL_n} C_N [1 + B'_{ML_n} (C_L')^n]} \cdot 10^2 \quad (4)$$

where C_M and C_N are the total concentrations of M and N, respectively. If the concentrations of M and N are the

same and the absorption coefficients of the two complexes are equal, the concentration of the complex NL_n must be negligible if an accurate result is to be obtained for M:

$$\frac{[NL_n]}{C_N} = B'_{NL_n} (C'_L)^n \leq 10^{-2} \quad (5)$$

Combination of equations 3 and 5 gives

$$\frac{B'_{ML_n}}{B'_{NL_n}} \geq 10^4 \quad (6)$$

Thus the values of the conditional stability constants of the complexes ML_n must differ at least by four orders of magnitude.

If the absorption maxima of the two complexes, ML_n and NL_n , are at different wavelengths, it is possible to determine both metal ions, M and N, simultaneously.

The simultaneous spectrophotometric determination of two solutes in solution can be achieved if there is no reaction between the two solutes. Since absorbances are additive, we can write

$$A_{\lambda_1} = A_1(\lambda_1) + A_2(\lambda_1) \quad (7)$$

$$A_{\lambda_2} = A_1(\lambda_2) + A_2(\lambda_2) \quad (8)$$

where A_{λ_1} and A_{λ_2} are the measured absorbances at the two wavelengths λ_1 and λ_2 , and the subscript 1 and 2 refer to two different substances, and the subscripts λ_1 and λ_2 refer to the two different wavelengths. The wavelengths are selected to coincide with the absorption maxima of the two solutes, i.e. the absorption spectra of the two solutes should not overlap appreciably, so that substance 1 absorbs strongly at λ_1 and weakly at wavelength λ_2 , and substance 2 absorbs strongly at λ_2 and weakly at λ_1 . Now according to Beer's law $A = \epsilon Cl$, where ϵ is the molar absorption coefficient at any particular wavelength, C is the molar concentration, and l is the thickness (length) of the absorbing solution expressed in cm. If l is 1 cm:

$$A_{\lambda_1} = \epsilon_1(\lambda_1) \cdot C_1 + \epsilon_2(\lambda_1) \cdot C_2 \quad (9)$$

$$A_{\lambda_2} = \epsilon_1(\lambda_2) \cdot C_1 + \epsilon_2(\lambda_2) \cdot C_2 \quad (10)$$

the solutions of these simultaneous equations are

$$C_1 = \frac{\epsilon_2(\lambda_2) \cdot A_{\lambda_1} - \epsilon_2(\lambda_1) \cdot A_{\lambda_2}}{\epsilon_1(\lambda_1) \cdot \epsilon_2(\lambda_2) - \epsilon_1(\lambda_2) \cdot \epsilon_2(\lambda_1)} \quad (11)$$

$$C_2 = \frac{\epsilon_1(\lambda_1) \cdot A_{\lambda_2} - \epsilon_1(\lambda_2) \cdot A_{\lambda_1}}{\epsilon_1(\lambda_1) \cdot \epsilon_2(\lambda_2) - \epsilon_1(\lambda_2) \cdot \epsilon_2(\lambda_1)} \quad (12)$$

The values of the molar absorption coefficients ϵ_1 and ϵ_2 can be deduced from measurements of the abso-

rbances of pure solutions of substances 1 and 2. Therefore, by measuring the absorbance of the mixture at λ_1 and λ_2 the concentrations of the two components can be calculated.

1.3 Photometric Sensitivity and Limit of Determination

The sensitivity of a quantitative photometric method is now usually defined as the slope dA/dC of the calibration curve $C=f(A)$ at the origin (7), where C is the concentration of the substance to be determined and A is the absorbance of the solution.

The initial linear portion of the calibration curve can be expressed as

$$C = (A - A_0) \left(\frac{dA}{dC} \right)^{-1} \quad (13)$$

where A_0 is the absorbance of the blank. The steeper the slope of the calibration line, the higher is the sensitivity of the determination it is thus proportional to the absorption coefficient of the species which is measured and to the path-length through the cuvette. The sensitivity of a photometric determination can thus be increased if the wavelength is chosen in the region of a high absorption maximum and if a long enough cuvette is taken for the measurement.

The lowest concentration (or amount) of a given substance which can be determined by employing a specified procedure is called the limit of determination (C_{min}).

This is usually expressed as the lowest weight amount (e.g. μg) or as the lowest molar concentration, M , or in any other convenient way, e.g. as μgml^{-1} , percentage, ppm, which shows a statistically significant difference from zero or the average value of the blank. Kaiser defines (8) the limit of determination by the following equation:

$$C_{\min} = (\Lambda_{\min} - \Lambda_0) \left(\frac{d\Lambda}{dC} \right)^{-1} = 3S_0 \left(\frac{d\Lambda}{dC} \right)^{-1} = \frac{3S_0}{\epsilon l} \quad (14)$$

where S_0 is the standard deviation of the blank determination.

Sandell defines (3) the limit of determination (called sensitivity) as the weight in μg per 1 ml of solution, which corresponds to an absorbance $\Lambda = 0.001$ measured in a cuvette of cross-sectional area 1 cm^2 and $l = 1 \text{ cm}$. Its dimensions are $\mu\text{g} \cdot \text{cm}^{-2}$. This definition of the limit of determination, C_s , is given by:

$$C_s = \frac{M}{\epsilon} \quad (\mu\text{g/ml}) \quad (15)$$

where M is the molar mass of the substance to be determined.

The disadvantage of this mode of expressing the limit of determination is that the spread of the blank determinations is not taken into account.

1.4 Precision of Photometric Determination

In 1939 Ringbom (9) introduced a method of plotting

spectrophotometric data in which percent transmittance, T (or percent absorbance, A) is plotted against the logarithm of concentration, C. When these functions are plotted a sigmoid or S-shaped curve is obtained. Ringbom has shown that the accuracy is greatest when the value of

$$\frac{\Delta C/C}{\Delta T} = \frac{2.303}{\Delta T / \Delta \log C} \quad (16)$$

reaches a minimum, i.e. at the point of the steepest slope ($\frac{\Delta C/C}{\Delta T}$ is the relative analysis error and $\frac{\Delta T}{\Delta \log C}$ is the slope of the curve).

A useful application of the Ringbom's plot is for the determination of concentration limits within which the analysis error is minimum. The concentration range can be evaluated by constructing a tangent to the steepest portion of the curve. The slope is then translated to points of tangency to the curve one on the lower and one on the upper limits of the curve. These points define concentration limits within which the relative analysis error is minimum.

1.5 Spectrophotometric Methods for Determination of Composition of Complexes

There are several methods (6,10,11) for determining the composition of metal complexes. Of these the most commonly used methods for investigating comp-

lexes in solutions are the continuous variations (12), the mole ratio (13) and the absorptiometric method (6).

Continuous Variations Method. One of the most generally applicable and widely used method for elucidating the formula of a complex is the method of continuous variations. Suppose that a metal ion M and a ligand X react to form a complex MX_n . A series of solutions is prepared in which the sum of molar concentrations of M and X is the same while their mole fractions vary between 0 and 1. Representing the molar concentrations of the metal ion and the ligand by C_M and C_X respectively, one gets

$$C_M + C_X = C \quad (17)$$

A quantity f is defined in such a way that, in any of the series of solutions

$$C_X = fC \quad (18)$$

$$\text{and } C_M = (1-f)C \quad (19)$$

In any mixture of M and X,

$$(M) = (1-f)C - (MX_n) \quad (20)$$

$$(X) = fC - n(MX_n) \quad (21)$$

Obviously, the concentration of the complex will change as f is varied. It will be zero when f is either zero or unity and will have maximum value at some interme-

diate point. If the absorbance is measured at a wavelength, where the complex absorbs but M and X do not absorb the value of f at the point of maximum absorbance will correspond to maximum concentration of MX_n .

This in turn, will be the value of f at the point where

$$\frac{d(MX_n)}{df} = 0, \text{ since}$$

$$[MX_n] = \frac{\{(1-f)C - (MX_n)\} \{fC - n(MX_n)\}^n}{K} \quad (22)$$

where K is the dissociation constant of the complex.

It can be shown that

$$K \frac{d(MX_n)}{df} = \left\{ fC - n(MX_n) \right\}^n \cdot \left\{ C - n \frac{d(MX_n)}{df} \right\} + \left\{ (1-f)C - (MX_n) \right\} \cdot \left\{ C - n \frac{d(MX_n)}{df} \right\} \cdot n \left\{ fC - n(MX_n) \right\}^{n-1} \quad (23)$$

on putting, $\frac{d(MX_n)}{df} = 0$, this equation reduces to

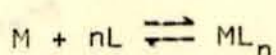
$$n = \frac{f}{1-f} \quad (24)$$

Accordingly, the absorbance of the solutions is plotted against, f, the mole fraction of the ligand in the solution and then n is calculated from the abscissa of the maximum of the curve.

Mole Ratio Method. Another convenient and popular method for the investigation of the composition of the

complexes in solution is the mole ratio method. The principle of this method is that a series of solutions is prepared in which the concentration of one component (usually C_M) is kept constant and that of the other varied. The absorbance of the solution is measured at a suitable wavelength and plotted against the ratio of the variable and constant concentrations. If only one stable complex absorbs at the wavelength studied, then the absorbance increase approximately linearly with the mole ratio and then becomes constant. The abscissa of the point of intersection of the two tangents gives the number of ligand molecules in the complex, if it was the ligand concentration that was varied.

Absorptiometric Method. The complex formation equilibrium between metal M and ligand L can be represented by



The formation constant is given by

$$K = \frac{[ML_n]}{[M][L]^n} \quad (25)$$

or

$$\log \frac{[ML_n]}{[M]} = \log k + n \log [L] \quad (26)$$

Since

$$[M] = C_M - [ML_n]$$

equation 26 can be written as

$$\log \frac{[ML_n]}{C_M - [ML_n]} = \log k + n \log [L] \quad (27)$$

where C_M is the total concentration of metal ion.

If only one stable complex is formed, which has selective light absorption, then from Beer's law $(ML_n) = A/\epsilon$ and $C_M = \frac{A_{\max}}{\epsilon}$ (for $l = 1$ cm) where A is the equilibrium absorbance and $A_{\max}$ is the maximum absorbance with an excess of the ligand. Equation 27 can thus be written as

$$\log \frac{A}{A_{\max} - A} = \log k + n \log [L] \quad (28)$$

Thus, the slope of the curve obtained by plotting $\log \frac{A}{A_{\max} - A}$ against $\log [L]$ gives the number of ligands n , in the complex.

1.6 Electronic Spectra of Transition Metal Complexes (1, 14, 15)

The spectral characteristics of transition metal complexes arise from several types of electronic transitions. The type of electronic transition involved depends on the chromophoric group present in the complex compounds. Chromophoric groups of interest in analytical chemistry can be classified into

the following three groups:

- a. d-electron chromophores
- b. d-II chromophores
- c. II-electron chromophores

d-Electron Chromophores. This type is characterized by a metal ion with an unfilled d-level and combined with particular donor atoms. This chromophoric group is found in complex compounds of transition metals and can be generally denoted as MX_n where M is the central ion and X is the donor atom. The absorption bands assigned to these chromophoric groups are due to transitions substantially localized on the d-level ion; they can be described as d-d transitions. Since for the d-electron chromophores these transitions occur between states with the same parity quantum number, these transitions are Laporteforbidden. They are allowed by a vibronic interaction and the molar absorption coefficients are $1-200 \text{ l mol}^{-1}\text{cm}^{-1}$. Thus they are not useful for quantitative analysis.

d-II Chromophores. This type of chromophore is represented by a configuration consisting of a d-element and the II-electron system of the ligand molecule. Its presence is shown by intense absorption bands which are assigned either to the electron transition from ligand to metal ($L \rightarrow M$ transitions) or vice versa ($M \rightarrow L$ transitions). As in these transitions the electron is

transferred from one component of the complex to the other, these transitions are called charge-transfer transitions.

- a. M $\rightarrow$ L Transitions. As this transition is characterized by the transfer of a d-electron from the central field of the metal ion, the metal must be in the lower of the readily available oxidation state. On the other hand, there must be a possibility of accepting this electron in an unfilled orbital of the ligand. Such ligands are found among organic compounds with a double bond or a chain of conjugated bonds attached to the donor atom. If this chromophoric group has a centre of symmetry, the molar absorption coefficient is about $10^2 \text{ l mol}^{-1} \text{ cm}^{-1}$, where as for chromophoric groups which possess no centre of symmetry it is $10^3 - 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$.
- b. L $\rightarrow$ M Transitions. This type of charge-transfer transition, i.e., the transition involving the transfer of an electron from the ligand to the metal, is found with complexes where the d-shell metal can be reduced easily to a lower oxidation state by accepting one electron. At the same time, the ligand molecule must have a π -electron system to which an acidic group is attached: this group interacts with the metal ion and provides non-bonding electrons free for transfer to the metal ion.

II-Electron Chromophores. The chromophores are systems with a single or several double bonds. They can undergo $\Pi \rightarrow \Pi^*$ and $n \rightarrow \Pi^*$ transitions. Complexation with a metal ion is similar to protonation of the molecule and will result in a change in the wavelength and intensity of absorption bands. These changes are slight in most cases.

Sensitivity is one of the obvious demands in application of analytical methods. In order to comply with this requirement for reactions which involve a change of color, the molecule of the complex formed or the organic reagent itself must contain chromophoric groups which are characterized by transitions with molar absorption coefficients in the range $10^3 - 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$. Such chromophoric groups are found among d-II and II chromophores. The complexes with d-II chromophores are restricted in use to transition elements, in particular those which can exist in two oxidation states differing by one electron.

The reagents with II-electron groups are most frequently employed in analytical applications. The main reason can be found in the intensity of transitions (with molar absorption coefficients up to $10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$) which characterize these chromophoric groups. A further reason is that the color change can also take place when complexes with non-transition elements are formed.

1.7 Solvent Extraction (1,16-21)

Solvent extraction is a versatile, useful, and popular separation technique. Because of its ease, simplicity, speed, and wide scope, solvent extraction enjoys a favored position among the separation techniques.

Solvent extraction is the partition of one or more components between two liquids of limited miscibility. Such liquid-liquid partition is caused by the different solubilities of a given substance in the two phases. This method of partition of a given substance from one phase to the other is extremely useful for very rapid and clean separations of trace and major components of both organic and inorganic substances. A further advantage of extraction is that the extract, i.e., the solution of the separated substance in a given organic solvent usually has some properties on which the determination of the isolated constituent can be based: absorption of light, fluorescence, radioactivity and volatility can serve as examples. Thus the extract can be used directly for the determination of the isolated component by spectrophotometry, fluorimetry, gas chromatography, atomic absorption, radiochemical, or other suitable methods.

The fundamental parameters involved in solvent extraction are described briefly in the following sections

Distribution Constant. In analytical applications the

liquid-liquid partition equilibria, which are commonly called extraction equilibria, usually takes place between an aqueous phase (Phase I, subscript aq) and an organic solvent (Phase II, subscript org) which is immiscible with water. Such liquid-liquid extraction equilibria obey the Nernst's distribution law, according to which the ratio of the activities or (at constant ionic strength) the concentrations of a substance in the two phases, when it is distributed is constant at constant temperature. This constant is called the distribution constant and it is given by:

$$K_{D,A} = \frac{[A]_{org}}{[A]_{aq}} \quad (29)$$

where $[A]_{org}$ and $[A]_{aq}$ represent the equilibrium molar concentrations of the substance A in the organic and aqueous phase respectively.

Distribution Ratio. In liquid-liquid partition, a substance A can undergo in both phases various solvation, association, protonation, and complexation equilibria. Therefore, for analytical applications it is essential to define the partition of the substance irrespective of the particular forms which are encountered in the system. This can be done by expressing the equilibrium ratio of the total analytical concentrations of the substance A in the two phases:

$$D_A = \frac{C_{A,org}}{C_{A,aq}} \quad (30)$$

This quantity is called the distribution ratio.

Degree of Extraction. The completeness of transfer of substance A in any extractable form into the organic phase is given by the degree of extraction E, which is usually expressed in percent:

$$E_A = \frac{100 C_{A,org} V_{org}}{C_{A,org} V_{org} + C_{A,aq} V_{aq}} = \frac{100 D_A}{D_A + V_{aq}/V_{org}} \quad (31)$$

This is the fraction of the substance extracted from the aqueous phase (Volume V_{aq}) into the organic solvent (Volume V_{org}).

Extraction can be used either for separation or concentration.

Enrichment Factor. Extraction can be used as a concentration method in two ways, namely, for absolute and relative concentration. In absolute concentration procedures all extracted species remain in the same concentration ratios, but their concentrations are increased. A similar result could be achieved simply by boiling down the original solution. In relative concentration procedures the concentration ratios of the individual components in the extract differ from those in the original solution. The relative method is especially im-

rtant in trace analysis where a particular component has to be separated from the matrix either partially or completely. The degree of enrichment is expressed by the enrichment factor, $S_{A/B}$

$$\frac{(M_A)_{org}}{(M_B)_{org}} = S_{A/B} \frac{(M_A)_{aq}}{(M_B)_{aq}} \quad (32)$$

where subscript org refers to the extract and aq to the original aqueous solution. M_A and M_B refer to two metallic components.

Separation Factor. The efficiency of an extractive separation of two components (A and B) can be considered in terms of the separation factor α defined as

$$\alpha = \frac{D_A}{D_B} \quad (33)$$

Arbitrarily, the factor α is expressed so that $\alpha > 1$, i.e. $D_A > D_B$. The greater the difference of α from unity, the higher is the efficiency of separation.

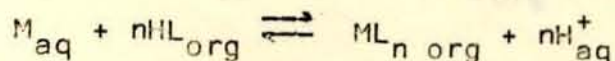
1.8 Solvent Extraction of Metal Chelates (1,16-21)

Organic reagents play an eminent role in extraction separations of metal ions, because they can react with metal ions to give products having the basic prerequisite for extractability. These are electrically neutral species and therefore they are more soluble in solvents of low relative permittivity than in

water.

If a metal ion is extracted from an aqueous solution into an organic non-polar solvent, the metal ion is transferred across the liquid-liquid boundary as an uncharged particle which can be either an electroneutral complex (or chelate) formed with the organic reagent or an ion association complex.

The extraction of a metal ion M with the extraction reagent HL, forming a chelate ML_n soluble in organic solvent is expressed by the equilibrium:



which is characterized by the extraction constant:

$$K_{ex} = \frac{[ML_n]_{org} [H^+]_{aq}^n}{[M]_{aq} [HL]_{org}^n} = \frac{K_{D,M} \beta_n}{(K_{D,L} \beta_{HL})^n} \quad (34)$$

As shown in equation 34, the value of the extraction constant depends on the stability constant β_n and the distribution constant $K_{D,M}$ of the chelate being extracted, and further, on the protonation constant β_{HL} and the distribution constant $K_{D,L}$ of the extracting reagent HL.

The equilibria involved in the extraction of metal chelates can be expressed by the following Scheme:

of the ionic strength when a common electrolyte is added. A change in the ionic strength affects the value of the relative permittivity and so the value of the extraction constant K_{ex} is influenced by these two changes.

For practical reasons the aqueous phase should contain a certain concentration of a salt, the formation of an emulsion is thus prevented, and the separation of the two phases is made easy.

There is no kinetics effect involved in the value of D_M , provided the distribution ratio has been determined for an equilibrium state. In practice, however, kinetic masking can be utilized if the rate of extraction of one species is much faster than that of another.

1.9 Occurrence and Analytical Chemistry of Iron and Cobalt (1,2,15,22)

Iron. Iron is the second most abundant metal in the Earth's crust after aluminum. It is rarely found in its elemental form but occurs widely in chemical compounds: the important ores and minerals are haematite (Fe_2O_3), magnetite (Fe_3O_4), goethite ($FeOOH$), limonite (hydrated iron oxide), siderite ($FeCO_3$) and pyrite (FeS_2). Natural water sometime contain considerable amount of iron. It is also found in plants and is an important constituent of blood and tissue of the animal body. In the body its compounds participate in oxygen transportation and mediation in electron transfer chains. In

every day life, in addition to its alloys, iron forms many useful compounds such as ferric ammonium citrate used as appetite stimulator and ferric pyrophosphate used to treat anaemia.

The oxidation state encountered in compounds of iron ranges from 0 to +6; however, the most common compounds are those of Fe(II) and Fe(III).

Iron(II) salts are usually pale green in aqueous solution; with alkalis pale green (white when pure) iron(II) hydroxide is precipitated; this darkens upon exposure to the air owing to oxidation. Potassium hexacyanoferrate(III) give a deep blue color or precipitate with iron(II) salts, but potassium thiocyanate give no coloration.

Iron(III) salts are normally yellow or violet in aqueous solution and give a reddish brown precipitate of hydrous iron(III) oxide with alkalis. Potassium hexacyanoferrate(II) gives a blue coloration or precipitate (prussian blue) with iron(III) salts and potassium hexacyanoferrate(III) gives a brown or green color. Potassium thiocyanate gives blood red coloration and this is an exceedingly delicate test for iron(III).

The gravimetric estimation of iron is usually carried out by precipitating the iron with ammonia as hydrous iron(III) oxide, igniting this precipitate to constant weight and weighing as Fe_2O_3 . Alternatively to increase the bulk of the precipitate, the iron can be precipitated

with 8-hydroxyquinoline or α -nitroso- β -naphthol and these ignited to Fe_2O_3 . Volumetric methods usually involve reduction of iron(III) to iron(II) and re-oxidation with dichromate, permanganate or cerium(IV). Alternatively iron(III) can be estimated iodometrically (Fe^{3+} liberates iodine from iodide ions) or by titration with a standard reducing agent such as titanium(III) solutions.

Rapid colorimetric methods for iron use either iron(III) with thiocyanate ions or iron(II) with 1,10-phenanthroline.

Cobalt. Cobalt is widely distributed in nature making about 0.001% of the igneous rocks of the earth's crust. It occurs in meteorites, stars, sea and fresh water, soils, plants and animals. Cobalt always occurs in nature in association with nickel and usually also with arsenic. The most important cobalt minerals are smeltite, CoAs_2 and cobaltite, CoAsS , but the main technical sources of cobalt are residues called "speisses" which are obtained in the smelting of arsenical ores of nickel, copper and lead. The chief outlet for cobalt metal is as an alloying element in the production of high speed steels "hard alloys" for cutting tools and in magnetic alloys. Cobalt alloys are also important because of their oxidation and corrosion resistance and, where elevated temperatures must be used, e.g. in gas turbines and jet engines, they are superior to many other alloys in

stress-to-rupture strength and creep properties. Vitallium containing 65% Co and 25% Cr is used as a dental and surgical alloy being unattacked by body fluids.

Cobalt is a vital trace element in animal nutrition. Small amounts of cobalt are invaluable in the treatment of pernicious anaemia. The discovery in 1926 of the antipernicious anaemia factor in liver led to the discovery in 1948 of vitamin B₁₂, which was very soon after shown to contain cobalt.

The principally occurring oxidation states of cobalt in aqueous solutions are +2 and +3.

Salts containing the aquocobalt(II) cation give no precipitate with hydrogen sulphide in acid solution, but precipitate black cobalt(II) sulphide in ammoniacal solution. With alkalis, the pink hexaaquocobalt(II) cation gives a pale blue precipitate of the hydroxide; with an excess of ammonia this precipitate dissolves and slowly gives a brown solution through oxidation. The addition of potassium nitrite to a neutral or acidic solution of Co(II) saturated with potassium chloride quickly results in the formation of a yellow precipitate of potassium hexanitrocobaltate(III). Concentrated ammonium thiocyanate solution gives a blue solution of the $(\text{Co}(\text{SCN})_4)^{2-}$ anion which can be precipitated by adding Hg^{2+} ions. Dithiooxamide (rubeanic acid), in alcoholic solution, added to ammoniacal cobalt solutions gives a brown precipitate; this reaction is used in

paper chromatography to distinguish cobalt from nickel (which gives a blue violet color).

Cobalt may be determined gravimetrically by a variety of methods. For the determination of cobalt in ferrous alloys, iron is first removed by precipitation either with zinc oxide suspension or with trisodium phosphate. The cobalt is then usually precipitated with α -nitroso- β -naphthol and the precipitate ignited to constant weight as Co_3O_4 . Other gravimetric procedures involve precipitation and weighing as $\text{Hg}(\text{Co}(\text{SCN})_4)$. A rapid method which can be completed in 30 minutes involves the precipitation of cobalt with pyridine in thiocyanate media and weighing as $(\text{Co}(\text{C}_5\text{H}_5\text{N})_4)(\text{SCN})_2$. Cobalt can also be determined gravimetrically by electrolysis. Platinum gauze electrodes are used in an electrolyte of cobalt(II) sulphate and ammonium sulphate. The cathode is washed with cold water, alcohol dried at 100°C and weighed. Volumetrically cobalt(II) salts may be estimated by potentiometric titration with standard potassium hexacyanoferrate(II) in the presence of high concentrations of ammonium citrate and ammonia solution.

Polarographic methods usually use the reduction of cobalt(III) amines. This method allows the determination of cobalt in a one thousand fold excess of nickel.

Colorimetric methods for estimating cobalt use the blue color developed by chloride ions or thiocyanate ions. When only small amounts of cobalt are present,

nitroso-R-salt, sodium-1-nitroso-2-hydroxynaphthalene-3, 6-disulphonate $C_{10}H_4OH \cdot NO(SO_3Na)_2$, must be used to give a red cobalt complex which is stable in nitric acid (a useful distinction from many other elements).

1.10 Literature Survey

A large number of organic reagents are recommended for the separation, detection and determination of iron and cobalt.

Some of the common organic reagents that have been commended recently for spectrophotometric determination of iron are 2,4-dihydroxyacetophenonesemicarbazone (23), 2,2'-dipyridylketone-2-pyrimedylhydrazone (24), 2,2'-dipyridyl-2-benzothiazolyhydrazone (25) 4-(4-methyl-2-thiazolylazo) resorcinol (26), 1,2,4,6-tetraphenylpyridinium perchlorate (27), 2-acetylpyridinethiosemicarbazone (28), 2,6-bis[1-(2-methoxyethylimino) ethyl]-pyridine and sodium picrate (29), 2-(2-thienylmethyleneamino)-benzohydroxamic acid (30), 2-hydroxyimino-cyclohexanone thiosemicarbazone (31), 2-benzylidenimine benzohydroxamic acid (32), 2-(5-bromo-2-pyridylazo)5-dimethylaminophenol (33), 3-aldehydosalicylidencyanoacetylhydrazone (34). Chro azural S (35), 3-hydroxy-2-methyl-1,4-naphthaquinone monoxide (36), 2-(phenoxyacetyl)acetophenone (37), neoterazellium chloride (38), salicylaldehydethiosemicarbazone (39), N-phenylcinnamohydroxamic acid and azide (40), and 3-(4-sulphophenylazo)

chromothropic acid (41).

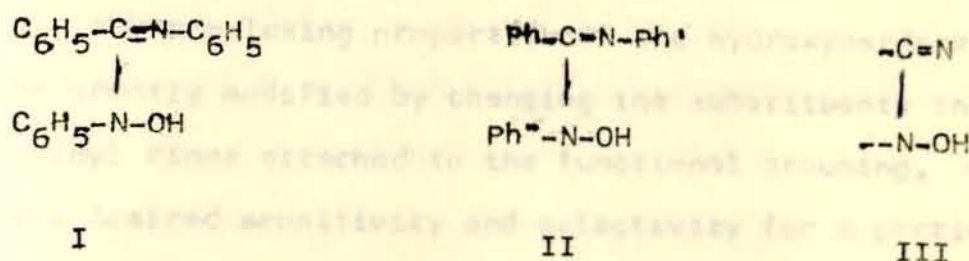
Recently recommended organic reagents for the spectrophotometric determination of cobalt are 2-nitroso-1-naphthol (42), 3-(o-acetophenyl)-1-methyltriazene N-oxide (43), biacetyl-monoxime-2-pyridylhydrazone (44), 8-mercaptoquinoline (45), isonitrosothiocamphor (46), potassium propylxanthate (47), 2,2'-dipyridylketone-2-picolyimine (48), 2,4-dibromo-5-(5-chloro-2-pyridylazo)toluene (49), pixolinamidoxime (50), 8-mercaptopropanoic acid anilide (51), cyclohexylthioglycolate (52), pyridine-2,6-dicarboxylic acid (53), triphenylsulphoniumchloride (54), 1,10-phenanthroline and eosin (55), thiocyanate (56), Benzyl-2-pyridylketone-2-pyridylhydrazone (57), pentane-2,4-dione (58), 4-formyl-3-methyl-1-phenyl-2-pyrazolin-5-one and pyridine (59), EDTA and t-butyl hydroperoxide (60), isonitrosobenzoylacetone (61).

The above literature survey reveals that, at the present time extensive use is made in analytical chemistry of organic reagents whose specific action makes it possible to determine a given metal ion in complex materials and further to provide simple, rapid and sensitive methods of determination.

In the present investigation N-hydroxy-N,N'-diphenylbenzamidine which has become a popular chelating agent in recent years, has been employed for the extraction and spectrophotometric determination of iron and cobalt. Hence its general properties and analytical applications are briefly reviewed.

1.11 N-Hydroxy-N,N'-Diarylbenzamidines as Analytical Reagents

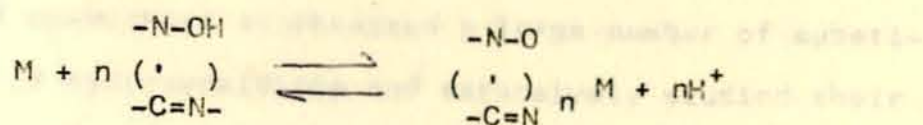
N-Hydroxy-N,N'-diphenylbenzamidine, I, and its analogues are typical monobasic and bidentate chelating agents. These compounds are represented by the general formula, II, having an analytical functional grouping III,



where Ph, Ph', Ph'' are phenyl or substituted phenyl groups. N-Hydroxy-N,N'-diarylbenzamidines were first synthesized by Ley (62) in 1901 and some of their properties were studied by Ley and Holzweissig (63). They are pale yellow crystalline solids. These compounds are stable toward heat, light and air and can be stored indefinitely without deterioration. They are insoluble in water but soluble in common organic solvents such as alcohol, acetone, chloroform, benzene and toluene.. Their solutions in organic solvents are light yellow and stable for several days if properly stored.

Hydroxyamidines react with metal ions to form five membered ring complexes. The metal chelates may be neutral or charged depending upon the co-ordination number and charge of the individual metal ion. The complexation

reaction of hydroxyamidines can be represented by the general complexation equilibrium



The charge of the metal ion has been omitted for simplicity.

The complexing properties of the hydroxyamidine can be greatly modified by changing the substituents in the phenyl rings attached to the functional grouping. Hence, the desired sensitivity and selectivity for a particular method of determination can be attained to a certain extent. This is a special feature of this group of organic reagents.

Some of the metal chelates of hydroxyamidines are water insoluble, thermally stable and directly weighable. Such metal chelates can be used for gravimetric determination of the metal ions. Most of the metal complexes of hydroxyamidines are intensely colored and highly stable. These reaction products can be used for simple spectrophotometric determination in aqueous system or for the simultaneous extraction and spectrophotometric determination of metal ions.

N-Hydroxy-N,N'-diphenylbenzamidine (HDPBA) was introduced as analytical reagent for the first time in 1974 by Satyanarayana and Mishra (64), for the extraction and spectrophotometric determination of vanadium(V). They

further extended the analytical application of HDPBA for the determination of other metal ions. Later on Mishra and co-workers synthesized a large number of substituted hydroxyamides and extensively studied their analytical potentialities. Several research papers have been published on the applications of hydroxyamides. N-Hydroxy-N,N'-diphenylbenzamide and its analogues are now widely used as reagents for the detection and determination of several metal ions in gravimetric analysis solvent extraction and spectrophotometry.

N-Hydroxy-N,N'-diphenylbenzamide has been applied for the extraction and spectrophotometric determination of iron(III) (65) and also for the spectrophotometric determination of iron(III) (66) in the aqueous phase. It was also employed for the gravimetric determination of nickel (67).

The analogues of HDPBA have been used for the gravimetric determination of copper (68-70) and molybdenum (71,72) and also for the spectrophotometric determination of manganese (73) in the aqueous phase. These reagents have also been used for the solvent extraction and spectrophotometric determination of vanadium (V) (74). The use of the analogues of HDPBA have been extended for synergic extraction and spectrophotometric determination of vanadium(V) in the presence of phenols (75,76), carboxylic acids (77,78) and aldehydes (79).

HDPBA was found to form mixed ligand complex with

azide in the determination of iron(III) (65) and cobalt(III) (80) and its analogues in the determination of vanadium (81,82) by solvent extraction and spectrophotometry. The derivatives of HDPBA have also been applied as reagents for the synergic extraction and spectrophotometric determination of iron(III) (83-87), vanadium (88,89) and molybdenum (90,91) by the formation of mixed ligand complexes with thiocyanate. Studies on the applicability of the N-hydroxy-N,N'-diarylbenzamidines has continued until very recently for the gravimetric, spectrophotometric and extraction - photometric determination of some metals ions.

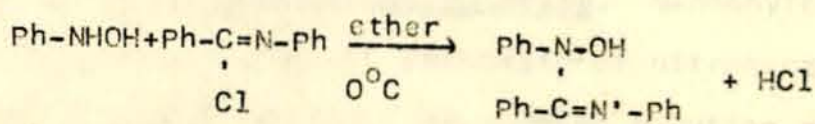
1.12 Aim of the Present Investigation

It is clear from the foregoing literature survey that hydroxyamidines have not been used for the extraction and spectrophotometric determination of Co(II) as a binary or mixed ligand complex with other adducts. Hence the parent compound, HDPBA has been applied in the present investigation for the extraction and spectrophotometric determination of cobalt(II). Although the derivatives of HDPBA were applied for the extraction and spectrophotometric determination of iron(III), the parent compound was not studied. Thus the extraction and determination of iron(III) with HDPBA and thiocyanate has also been studied under different conditions to improve the sensitivity and selectivity of the reported methods.

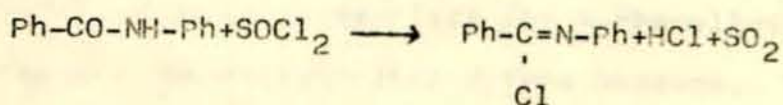
2. EXPERIMENTAL

2.1 Synthesis of N-Hydroxy-N,N'-Diphenylbenzimidine (HDPBA)

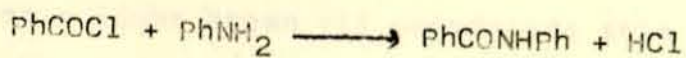
HDPBA was prepared by the condensation of N-phenylbenzimidoyl chloride with N-phenylhydroxylamine at 0°C in absolute ether medium (64). Thus the preparation of N-hydroxy-N,N'-diphenylbenzimidine required the synthesis of N-phenylbenzimidoyl chloride and N-phenylhydroxylamine.



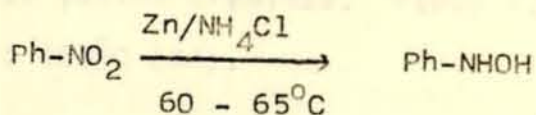
Preparation of N-Phenylbenzimidoyl Chloride. The synthesis of N-phenylbenzimidoyl chloride was made by chlorination of benzanilide using thionyl chloride as a chlorinating agent (92). A 20% excess of thionyl chloride (14.5 ml 0.20 mole) was mixed with benzanilide (33.0 g, 0.17 mole) and heated for 30 minutes at 110°C. The mixture was further heated under reflux at 150 - 160°C until the reaction mixture turned to a clear liquid. The excess thionylchloride was removed by distillation under partial vacuum. The imidoyl chloride was used as such for the synthesis of HDPBA.



Benzanilide which was used for the synthesis of N-phenylbenzimidoyl chloride was prepared by the addition of a slight excess of benzoyl chloride to aniline in 10% (w/v) of sodium hydroxide solution with stirring followed by crystallization in boiling benzene (93).



Preparation of N-Phenylhydroxylamine. N-phenylhydroxylamine was prepared by the reduction of nitrobenzene with zinc and ammonium chloride in aqueous solution at 60 - 65°C (94).



Nitrobenzene (50 g, 41.6 ml) was added with 800 ml of water to which 25 g of ammonium chloride was already added. To the mixture was added 60 g of zinc dust gradually with stirring during twenty five minutes, so that the temperature of the reaction mixture does not rise beyond 60 - 65°C due to the exothermicity of the reaction. The product was separated from the zinc oxide produced by suction. 150 g of sodium chloride was added to the solution to crystallize the N-phenylhydroxylamine. The product was recrystallized from benzene. Yield 61% melting point 80°C. The recrystallized product was immediately used for the preparation of HDPBA.

Preparation of N-Hydroxy-N,N'-Diphenylbenzimidine. N-phenylhydroxylamine (7.52 g, 0.07 mole) in absolute ether was added in small portions with stirring to a solution of N-phenylbenzimidoyl chloride (15.0 g, 0.069 mole) in 180 ml of absolute ether placed on ice-salt mixture.

First a light brown oil separated; this solidified into light yellow crystals on continued stirring. The crystals were filtered and washed with ether. The hydrochloride was treated with 32.0 ml of 1.0 N ammonia. The precipitated free base was filtered off, recrystallized twice from petroleum ether (60 - 80°C) benzene (1:2) to give pale yellow crystals. Yield 7.6 g, m.p 160 - 161°C, reported 163°C (64).

2.2 Apparatus and Reagents

Apparatus. A Beckman model 24 UV-Vis spectrophotometer equipped with 1 cm matched quartz cell was used for absorbance measurements. A Beckman CHEMMATE pH meter was used for pH measurements.

A varian Techtron AA6 atomic absorption spectrometer with air -C₂H₂ flame was also used for the determination of iron and cobalt in sample solutions.

Standard Iron(III) Solution. A standard solution of iron(III) was prepared by dissolving 4.0402 g of iron(III) nitrate nonahydrate (3DH, Analar) in 100 ml of 1:5 (V/V) nitric acid and diluted to 1.0 litre with distilled water.

The solution was standardized volumetrically using EDTA (95). Working solutions were prepared by diluting suitable aliquots of the standard solution to known volumes with distilled water.

To standardize the iron(III) solution, 25 ml of it was measured into a conical flask and diluted to 100 ml with distilled water. The pH of the solution was adjusted to 2.5. Five drops of variamine Blue indicator solution was added, the contents of the flask were warmed to 40°C, and titrated with 0.01 M EDTA solution until the initial blue color of the solution turned yellow with the final drops of the reagent.

Standard Cobalt(II) Solution. A standard solution of cobalt(II) was prepared by dissolving 2.8090 g cobalt(II) sulphate heptahydrate (Hopkins and Williams, Analar) in distilled water, acidified with sulphuric acid, and diluted to 1.0 litre with distilled water. The solution was standardized volumetrically using EDTA (95). Working solutions were prepared by diluting suitable aliquots of the standard solution to known volumes with distilled water.

To standardize the cobalt(II) solution, 25 ml of it was measured into a conical flask and diluted to 100 ml with distilled water. The pH of the solution was adjusted to 6. Five drops of xylenol orange indicator solution was added, the contents of the flask were warmed to 40°C, and titrated with 0.01 M EDTA solution until the initial red

color of the solution turned yellow with the final drop of the reagent.

Standard Thiocyanate Solution. A 0.2 M standard solution was prepared by dissolving potassium thiocyanate (Hopkins and Williams, Analer) in distilled water and standardized by Volhard method (2).

Standardization of thiocyanate solution was performed as follows. Standard 0.1 M silver nitrate (25 ml solution) was transferred into a conical flask, 5 ml of nitric acid and 1 ml of iron(III) indicator solution was added to it. Potassium thiocyanate was run in from the burette until a faint brown color was produced which no longer disappeared on shaking.

Reagent (HDPBA) Solution. A 0.005 M solution of the reagent (HDPBA) in redistilled toluene was used for the extraction of iron(III). A 0.003 M of the reagent (HDPBA) in redistilled toluene was used for the extraction of cobalt(II).

Hydrochloric Acid. Concentrated hydrochloric acid (BDH, Analer) was used to adjust the acidity of the solution.

Buffer Solution. Ammonia-ammonium chloride buffer solution of pH 8.5 was used to adjust the pH of the cobalt(II) solution.

Solvents. Toluene (RiedeldeHaen) was distilled twice discarding the first and the last fractions. The fraction

with boiling point of 110°C was used. All other solvents were used after a single distillation.

Drying Agents. Anhydrous sodium sulphate (Riedel-de-Haen) and anhydrous calcium chloride (BDH, Laboratory Reagent) were used for drying the colored extracts and the distilled solvents, respectively.

Solution of Electrolyte. A 2.0 M solution of potassium nitrate (BDH, Analar) in distilled water was used to adjust the ionic strength of the solution.

Solution of Foreign Ions. Solutions of foreign ions were prepared by dissolving known quantities of reagent grade salts in distilled water to give 10 mg of the ion in question per millilitre of solution. The solutions were acidified whenever necessary to prevent hydrolysis.

2.3 Preparation of Sample Solutions

Blood Sample. A 2 ml of aliquot of blood sample was transferred into a 250 ml Kjeldhal flask and decomposed with 10 ml of the mixture of nitric, sulphuric and perchloric acids in the ratio of 3:1:1 (96) by heating over the bunsen burner for about 2 hours. The heating was continued after addition of about 10 ml of dilute hydrochloric acid until the volume of the content was reduced to about 5 ml. It was cooled and the residue was reboiled with 25 ml of distilled water. The solution was cooled

and transferred quantitatively into a 100 ml volumetric flask and diluted to volume with distilled water.

Suitable aliquots of the solution were taken for the analysis.

Vitamin B₁₂. A weighed quantity (0.15 g) of the vitamin B₁₂ was transferred into a 250 ml Kjeldhal flask and decomposed with 20 ml of aquo-regia. The mixture was heated for one hour and 15 ml of 1 N hydrochloric acid was added to it. The solution was evaporated almost to dryness, cooled, and boiled with 50 ml of distilled water. The undissolved matter was filtered and washed several times with distilled water. The filtrate and washings were collected into a 100 ml volumetric flask and diluted to volume with distilled water. The solution was exposed to UV-light to reduce cobalt(III) to cobalt(II) (97). Suitable aliquots of the solution were taken for analysis.

Steel Samples. A weighed quantity (approximately 0.1 g) of the steel sample was transferred to a 400 ml beaker and decomposed with 10 ml concentrated nitric acid. The mixture was heated to remove the oxides of nitrogen and about 10 - 15 ml of concentrated hydrochloric acid was added to it. The solution was evaporated to almost dryness. About 50 ml of distilled water was added and the solution was boiled. Tungsten was precipitated as hydrated tungstic acid. The undissolved silica and tungstic acid were

filtered off and washed several times with hot distilled water. The filtrate and washing were collected into a 500 ml volumetric flask and diluted to volume with distilled water. Suitable aliquots of the solution were taken for the analysis.

2.4 General Procedure for the Extraction and Determination of Iron(III)

An aliquot of the solution containing 5 - 160 μg of iron(III) was transferred into a 100 ml separatory funnel and 5 ml of 0.2 M potassium thiocyanate was added to it. The acidity and volume of the aqueous phase were adjusted to 0.3 - 0.4 M and 10 ml with concentrated hydrochloric acid and distilled water respectively. A 10 ml aliquot of 0.005 M HDPBA in toluene was added to the funnel and the mixture was shaken vigorously for a minute. The funnel was allowed to stand to separate the two phases. The aqueous phase was separated and the organic phase was collected in a 50 ml beaker containing about 2.5 g of anhydrous sodium sulphate. The aqueous phase was again transferred into the funnel and washed with 5 ml of toluene. The colored extract and the washings were transferred into 25 ml volumetric flask. The beaker was washed with a few ml of toluene, the washings were transferred into the volumetric flask and diluted to volume with toluene. The absorbance of the colored solution was measured at 465 nm against the reagent blank.

For calibration, 0.25, 0.50, 1.00, 2.00 and 3.00 ml of the standard solution, $50 \mu\text{g ml}^{-1}$ Fe(III), were used through the procedure.

2.5 General Procedure for the Extraction and Determination of Cobalt(II)

An aliquot of the solution containing 10 - 300 μg of cobalt(II) was transferred into 100 ml separatory funnel and 5 ml of ammonia-ammonium chloride buffer solution was added to it to adjust the pH to 8 - 9. The solution was diluted to 10 ml with distilled water. A 10 ml of aliquot of 0.003 M HDPBA in toluene was added to the funnel and the mixture was shaken for a minute. The funnel was allowed to stand to separate the two phases. The aqueous phase was separated and the organic phase was collected in a 50 ml beaker containing about 2.5 of anhydrous sodium sulphate. The aqueous phase was again transferred into the funnel and washed with 5 ml of toluene. The colored extract and the washings were transferred into the flask, and diluted to volume with toluene. The absorbance of the colored solution was measured at 405 nm against the reagent blank.

For calibration, 0.25, 0.50, 1.00, 2.00 and 3.00 ml of the standard solution, containing $100 \mu\text{g ml}^{-1}$ Co(II), were used through the procedure.

2.6 Procedure for Studying the Effect of Variables

The effect of a particular variable was studied by measuring the absorbance of the system following the general procedures described above for the extraction and determination of the particular metal ion, keeping all experimental variables constant except the one under study.

The quantitative extraction of iron(III) or cobalt(II) from the aqueous phase was examined by changing each variable parameter to its optimum condition and following the general procedure. The extraction was considered to be incomplete when iron(III) or cobalt(II) was detected in the aqueous phase. The presence of iron(III) and Co(II) in the aqueous phase were examined by using 2,2'-bipyridyl and ammonium thiocyanate respectively.

The investigation of the quantitative extraction of iron(III) from the aqueous phase was performed as follows. The aqueous phase was reduced to about 1 - 2 ml by evaporation and 1 ml of 0.1 M hydroxylamine chloride was added to it to reduce iron(III) to iron(II). A 5 ml aliquot of 1% aqueous 2,2'-bipyridyl was added to the solution. The volume of the solution was adjusted to 10 ml and the pH to 4 - 5. The absorbance was measured at 522 nm against reagent blank and the amount of iron(III) was calculated accordingly.

For Co(II), the aqueous phase was reduced to about 1-2 ml

by evaporation. The solution was transferred into 100 ml separatory funnel and 5 ml of 4 M ammonium thiocyanate was adjusted to 10 ml with distilled water and the acidity to 0.5-1.5 M by addition of concentrated hydrochloric acid. A 10 ml aliquot of ethyl acetate was added to the funnel and the mixture was shaken for about a minute. The organic phase was collected in 10 ml volumetric flask after drying over anhydrous sodium sulphate. The absorbance of the solution was measured at 625 nm against the reagent blank and the amount of Co(II) calculated accordingly.

2.7 Procedure for Studying the Effect of Foreign Ions

The effects of foreign ions were studied by adding known quantities of the desired ion to solution containing 50 µg of iron(III) or 100 µg of Co(II). The required amount of particular masking agent was added to the Co(II) solution whenever necessary. Extraction and determination of the metal ions were made according to general procedures described earlier.

2.8 Procedures for the Determination of the Composition of Complexes.

Continuous Variations Method. To determine the ratio of Fe(III) to HDPBA a series of solutions was prepared in which the mole fraction of Fe(III) and HDPBA were varied between 0 and 1 with a

constant total concentration ($4.0 \times 10^{-4} \text{M}$). The concentration of thiocyanate (0.2 M KSCN) and acidity (0.4 M HCl) were kept constant throughout the series.

To determine the ratio of Fe(III) to thiocyanate a series of solution was prepared in which the mole fractions of Fe(III) and thiocyanate were varied between 0 and 1 with a constant total concentration ($4.0 \times 10^{-4} \text{M}$). The concentration of HDPBA ($1.2 \times 10^{-3} \text{M}$) and the acidity (0.4 M HCl) were kept constant throughout the series.

To determine the ratio of Co(II) to HDPBA a series of solutions was prepared in which the mole fractions of Co(II) and HDPBA were varied between 0 and 1 with a constant total concentration ($8.0 \times 10^{-4} \text{M}$). The pH (8.5) was kept constant throughout the series.

The complexes were extracted according to the general procedures and the absorbance of the colored extract was measured at 465 nm against the reagent blank for Fe(III)-SCN-HDPBA system and at 405 nm against the blank for Co(II)-HDPBA system. The absorbances were plotted against the mole fractions of the ligand in each system respectively. The maximum of the curve gave the mole fraction of the ligand in the complex.

Absorptiometric Method. To determine the ratio of Fe(III) to HDPBA a series of solutions was prepared in which the concentration of Fe(III) ($4.0 \times 10^{-5} \text{M}$),

acidity (0.4 M HCl) and thiocyanate (0.05 M) were kept constant and the concentration of HDPBA was varied over a wide range.

To determine the ratio of Fe(III) to thiocyanate a series of solutions was prepared in which the concentration of Fe(III) (4.0×10^{-5} M), acidity (0.4 M HCl) and HDPBA (2.0×10^{-3} M) were kept constant and the concentration of thiocyanate was varied over wide range. The complex was extracted by the general procedure and the absorbance of the colored extract was measured at 465 nm against reagent blank.

Mole Ratio Method. To determine the ratio of Co(II) to HDPBA a series of solutions was prepared in which the concentration of cobalt(II) (8.0×10^{-5} M) and pH (8.5) were kept constant and the concentration of HDPBA was varied. The complex was extracted by the general procedure. The absorbance of the extract was measured at 405 nm against reagent blank and plotted versus the mole ratio of Co(II) to HDPBA. Two straight lines were drawn from the two parts of the curves which intersected each other at a mole ratio of Co(II) to HDPBA.

3. RESULTS AND DISCUSSION

3.1 Complex Formation and Absorption Spectra

Complexes of iron and cobalt with HDPBA and thiocyanate were studied by extraction and spectrophotometry.

Iron(III) forms red complex with thiocyanate in acidic medium which is readily extractable into polar oxygen containing solvents such as ethyl acetate and amyl alcohol. The absorption spectrum of the iron(III)-thiocyanate complex was found to be not affected by HDPBA in these solvents indicating that there is no mixed ligand complex formation.

The iron(III) thiocyanate complex was found to be not extractable into non-polar organic solvents such as toluene, benzene and chloroform. It was also found that iron(III) in acidic medium was not extractable in the presence of HDPBA into toluene, benzene, chloroform, ethyl acetate and amyl alcohol which shows that there is no complex formation between iron(III) and HDPBA. On the other hand iron(III) was found to be readily extractable in the presence of HDPBA into toluene, benzene and chloroform from thiocyanate medium indicating the formation of mixed ligand complex.

Iron(II) was not found to form a complex with HDPBA solution in benzene, toluene, chloroform, ethyl acetate and amyl alcohol in the presence or absence of thiocyanate.

Cobalt(II) forms a complex with thiocyanate in acidic

medium which is extractable into amyl alcohol and ethyl acetate. The absorption spectrum of the Co(II)-thiocyanate complex was found to be not affected by the addition of HDPBA in these solvents which shows that there is no mixed complex formation of Co(II) with thiocyanate and HDPBA.

The Co(II)-thiocyanate complex was found to be not extractable into non-polar solvents such as toluene, benzene and chloroform. Cobalt(II) in acidic medium was not also extractable in the presence of HDPBA into toluene, benzene, chloroform, ethyl acetate and amyl alcohol. However in basic medium cobalt(II) was found to be extractable in the presence of HDPBA into toluene, benzene and chloroform with formation of a yellow-brown complex. The presence or absence of thiocyanate does not have any effect on the absorption spectrum of Co(II)-HDPBA complex as thiocyanate does not form a stable complex with cobalt(II) in basic medium.

It was also found that cobalt(III) does not form a complex with HDPBA in toluene, benzene, chloroform, ethyl acetate and amyl alcohol ether in the presence or absence of thiocyanate.

Thus the complex formation reaction of iron(III) with thiocyanate and HDPBA in the acidic medium and the complex formation reaction of cobalt(II) with HDPBA in the basic medium formed the basis for the development of new extraction-spectrophotometric methods for the deter-

mination of iron(III) and cobalt(II) respectively.

Several organic solvents such as benzene, toluene, chlorobenzene, chloroform, amyl alcohol and ethyl acetate were tested as solvent for the extraction of the Fe(III)-SCN-HDPBA and Co(II)-HDPBA complexes from the aqueous phase. It was found that either complexes was not extractable into amyl alcohol and ethyl acetate, the complexes were partially extractable into chloroform and chlorobenzene and completely extractable into benzene and toluene. These results indicate that both Fe(III)-SCN-HDPBA and Co(II)-HDPBA complexes are extracted as electroneutral species. The absorption spectra of the individual complexes were found to be similar in all solvents in which the complexes are extractable. Although both benzene and toluene were found to be suitable for the quantitative extraction of the complexes, toluene was preferred since it is less toxic and less volatile than benzene. It was also preferred due to the higher sensitivity of the color reaction in it than in benzene.

The absorption spectra of HDPBA and of the Fe(III)-SCN-HDPBA and Co(II)-HDPBA complexes have been determined in the visible region under various conditions. The reagent showed no absorption maxima in the visible region. However it showed negligible absorption in the region 700-600 nm, slight increasing absorption in the region 600-400 nm, strong absorption below 400 nm (Fig.1).

Thus a reagent blank was necessary for precise measurement

of absorbance at wavelengths shorter than 600 nm in recording the absorption spectra of the complexes.

The orange-red Fe(III)-SCN-HDP3A complex (Fig.1) showed an intense absorption band at 465 nm with a molar absorptivity of $1.0 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. The absorption band is probably due to charge transfer electronic transitions from ligand to metal ($L \rightarrow M$).

The absorption spectrum of the Co(II)-HDP3A complex (Fig. 2) showed a sharp absorption band at 405 nm with molar absorptivity of $7.0 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$. The absorption band can be assigned to charge transfer electronic transitions from metal to ligand ($M \rightarrow L$).

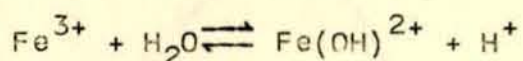
For each system the position of the absorption band was found to be unaffected by the changes in the concentration of the constituents and the acidity (or pH) over a wide range indicating the extraction of a single complex species.

3.2 Effect of Variables

The effect of the experimental variables on the extraction and determination of the Fe(III)-SCN-HDP3A and Co(II)-HDP3A complexes into toluene has been investigated in order to establish the optimum conditions for the extraction and determination of iron and cobalt.

Effect of Acidity (or pH). The effect of the concentration of hydrochloric acid in the aqueous phase on the extraction

of Fe(III)-SCN-HDPBA was studied in the range 1.0 - 0.01 M. When the hydrochloric acid concentration is greater than 0.6 M the complex formation was retarded due to protonation of the ligands. For hydrochloric acid concentration lower than 0.1 M, the complex becomes less stable due to hydrolysis of the metal ion resulting in an incomplete extraction of iron(III).



Hence the optimum acidity range for the complete extraction of Fe(III)-SCN-HDPBA was found to be 0.1 - 0.6 M HCl.

The influence of pH of the aqueous phase on the extraction of Co(II)-HDPBA was studied in the range 5.5 - 11.5. When the pH is less than 7.5, the extraction of Co(II) decreases, because the free ligand concentration may not be sufficient to give complete complex formation. When the pH is greater than 9.5, the decrease in extraction was probably due to formation of anionic or hydroxo complexes. Hence the optimum range was found to be 7.5-9.5.

The decrease in percent extraction of both metal ions beyond the optimum condition (at higher and lower acidities or pH) was indicated by the decrease in absorbance values of the colored extracts. The presence of metal ions in the aqueous phase beyond the optimum acidities (or pH) were detected and determined by changing

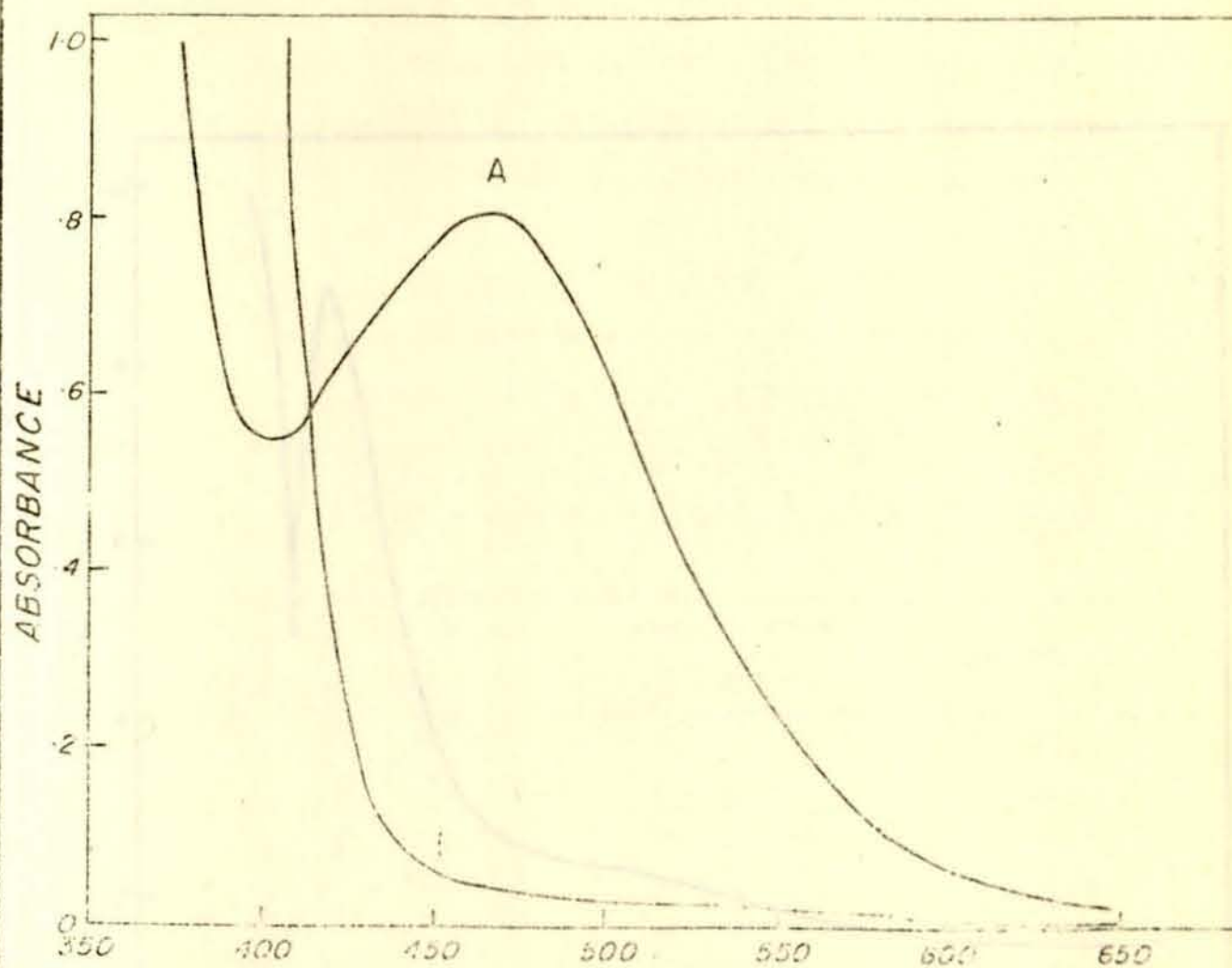


Figure 1 Absorption spectra of A) $8 \times 10^{-5} \text{ M Fe (III) - SCN - HDPBA}$ complex against reagent blank B) Absorption spectra of reagent blank

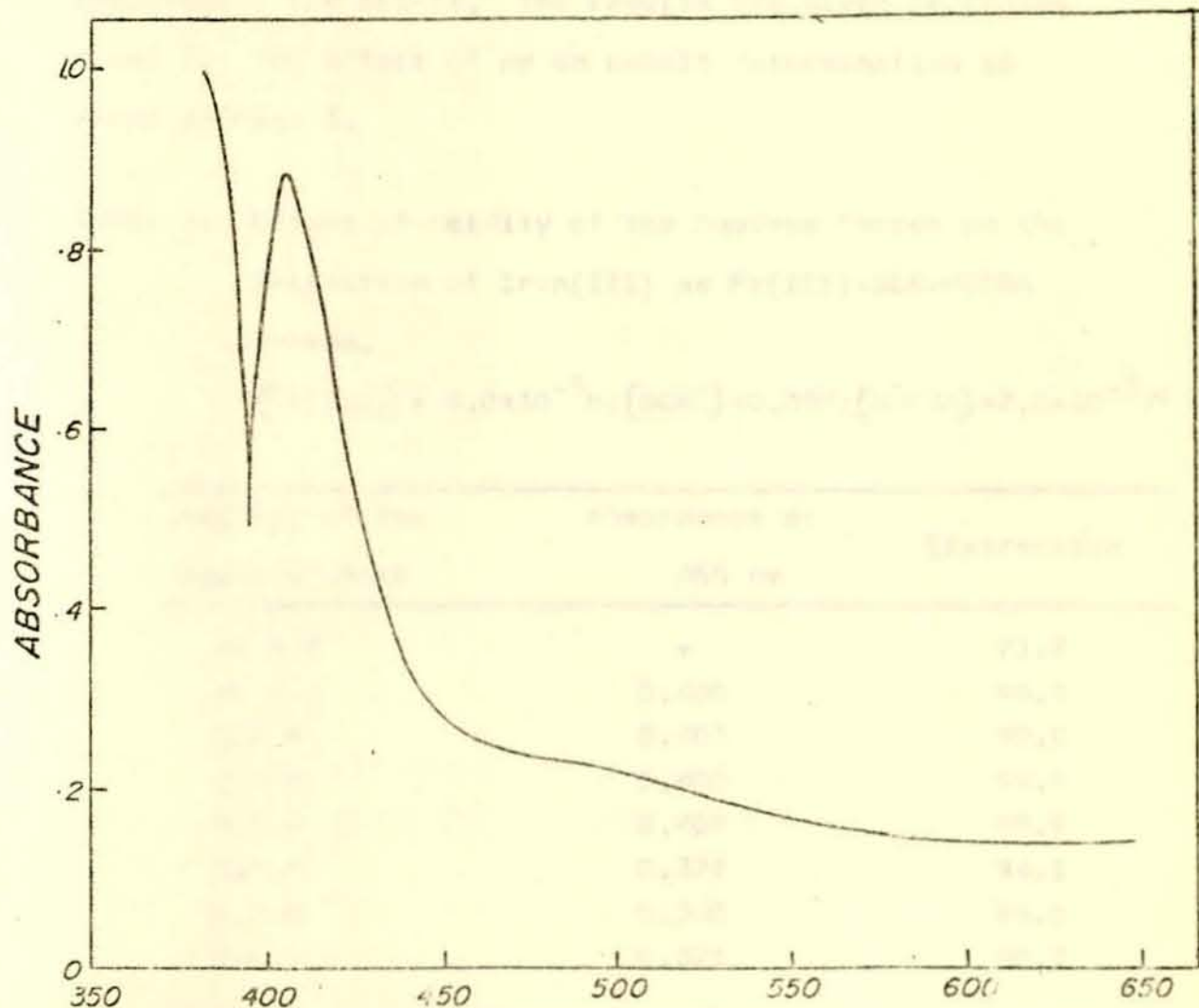


Figure 2 Absorption spectra of $1.15 \times 10^{-4} \text{ M}$ of $\text{Co(II)}-\text{HDPBA}$ complex against reagent blank

the acidities (or pH) to the optimum range and following the general procedures. The presence of metal ions in the aqueous phase were also detected and determined by using other reagents, i.e. 2,2'-bipyridyl for iron and thiocyanate for cobalt. The results are given in Tables 1 and 2. The effect of pH on cobalt determination is shown in Fig. 3.

Table 1. Effect of Acidity of the Aqueous Phases on the Extraction of Iron(III) as Fe(III)-SCN-HDPBA System.

$$[\text{Fe(III)}] = 4.0 \times 10^{-5} \text{ M}; [\text{SCN}^-] = 0.05 \text{ M}; [\text{HDPBA}] = 2.0 \times 10^{-3} \text{ M}$$

Acidity of the aqueous phase	Absorbance at 465 nm	%Extraction
pH = 2	*	71.2
pH = 1	0.400	99.9
0.2 M	0.403	99.9
0.4 M	0.400	99.9
0.6 M	0.402	99.9
0.7 M	0.378	94.5
0.8 M	0.340	85.0
1.0 M	0.321	80.2

*no absorption maximum.

Table 2. Effect of pH of the aqueous phase on the extraction of Co(II) by HDPBA in CH_2Cl_2 system.

$[\text{Co(II)}] = 8.0 \times 10^{-3} \text{ M}$; $[\text{HDPBA}] = 1.2 \times 10^{-2} \text{ M}$

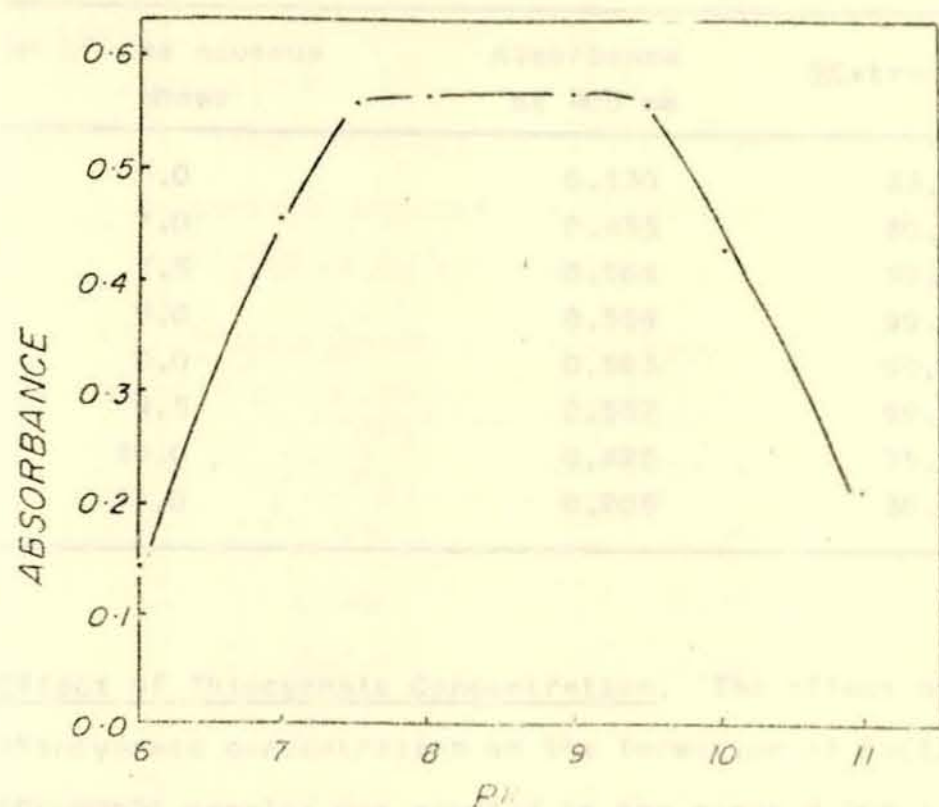


Figure 3. pH effect of the aqueous phase on the extraction of Co(II) -HDPBA complex

Table 2. Effect of pH of the Aqueous Phase on the Extraction of Cobalt(II) as Co(II)-HDPBA System

$$[\text{Co(II)}] = 8.0 \times 10^{-5} \text{ M}; [\text{HDPBA}] = 1.2 \times 10^{-3} \text{ M}$$

pH of the aqueous phase	Absorbance at 405 nm	%Extraction
6.0	0.130	23.1
7.0	0.455	80.8
7.5	0.561	99.9
8.0	0.559	99.9
9.0	0.563	99.9
9.5	0.557	99.9
10.0	0.425	75.7
11.0	0.205	36.4

Effect of Thiocyanate Concentration. The effect of thiocyanate concentration on the formation of Fe(III)-SCN-HDPBA complex was studied in the range 0.005-1.00 M. At low concentrations of thiocyanate the formation of the mixed ligand complex was incomplete. At high concentrations of thiocyanate water soluble thiocyanate complexes become stable resulting in incomplete extraction of iron(III). The optimum concentration range of thiocyanate for the extraction of iron(III) was found to be 0.03 - 0.2 M.

The decrease in percent extraction of iron(III) at lower or higher concentrations of thiocyanate was indicated by a decrease in absorbance of the colored extract

and also by the presence of iron(III) in the aqueous phase. The results are given in Table 3.

The extraction of cobalt(II) as Co(II)-HDPBA complex was found unaffected by the presence or absence of thiocyanate in the aqueous phase.

Table 3. Effect of Concentration of Thiocyanate in the Aqueous Phase on the Extraction of Iron(III) as Fe(III)-SCN-HDPBA System.

$$[\text{Fe(III)}] = 4.0 \times 10^{-5} \text{ M}; [\text{HCl}] = 0.4 \text{ M} \quad [\text{HDPBA}] = 2.0 \times 10^{-3} \text{ M}$$

[SCN]	Absorbance at 465 nm
0.005	0.292
0.01	0.367
0.02	0.385
0.03	0.401
0.04	0.400
0.05	0.398
0.10	0.401
0.20	0.401
0.30	0.386
0.40	0.351
0.50	0.321
1.00	0.275

Effect of the Amount of HDPBA. A 30-fold molar excess of

HDPBA was required to ensure the complete extraction of iron(III) and maximum color development for the Fe(III)-SCN-HDPBA complex. A 6-fold molar excess of HDPBA was required for the complete extraction of Co(II) and maximum color development of Co(II)-HDPBA. The reagent absorbs significantly at the wavelength of maximum absorption for the Co(II)-HDPBA and a large excess of the reagent is required for the extraction of iron(III). Hence all measurements were done against reagent blanks. Up to a 100-fold molar excess of HDPBA had no effect on the extraction of either iron(III) or the cobalt(II) complexes. The results are given in Tables 4 and 5.

Table 4. Effect of the Amount of HDPBA on the Extraction of Iron(III) as Fe(III)-SCN-HDPBA System

$$[\text{Fe(III)}] = 4.0 \times 10^{-5} \text{ M}, [\text{HCl}] = 0.4 \text{ M}, [\text{SCN}^-] = 0.05 \text{ M}$$

Concentration of HDPBA, 10^{-4} M	$[\text{Fe(III)}] : [\text{HDPBA}]$	Absorbance at 465 nm
0.8	1:2	0.024
1.2	1:3	0.052
1.6	1:4	0.084
2.4	1:6	0.148
3.2	1:8	0.207
4.0	1:10	0.252
4.8	1:2	0.281
6.0	1:15	0.320
8.0	1:20	0.350
12	1:30	0.399
20	1:50	0.401
40	1:100	0.401

Table 5. Effect of the Amount of HDP3A on the Extraction of Cobalt(II) as Co(II)-HDP3A System.

$$[\text{Co(II)}] = 8.0 \times 10^{-5} \quad \text{pH} = 8.5$$

Concentration of HDP3A, 10^{-4}M	$[\text{Co(II)}] : [\text{HDP3A}]$	Absorbance at 405 nm
0.00	1:0	0.002
0.8	1:1	0.180
1.6	1:2	0.301
2.4	1:3	0.440
3.2	1:4	0.515
4.0	1:5	0.551
4.8	1:6	0.563
5.6	1:7	0.561
6.4	1:8	0.564
8.0	1:10	0.560
20	1:25	0.563
40	1:50	0.561
80	1:100	0.562

Effect of Ionic Strength, Temperature and Volume of the Aqueous Phase. The wavelength of the absorption maximum and the absorbance values of Fe(III)-SCN-HDP3A and Co(II)-HDP3A system remained unchanged when the ionic strength of the aqueous phase was varied between 0 and 1.5 M with respect to potassium nitrate.

The absorbance of the colored extracts were not influenced by variation in temperature of both extraction systems between 20 and 40°C.

The effect of the volume of the aqueous phase on the

degree of extraction of Fe(III)-SCN-HDPBA and Co(II)-HDPBA was studied in the range 10-100 ml with a fixed volume of 10 ml of toluene.

It has been found that the volume of the aqueous phase of Fe(III)-SCN-HDPBA system can be varied from 10-40 ml with respect to a fixed volume of 10 ml of the organic phase without any variation in absorbance or extraction efficiency. For larger volumes a decrease in absorbance was observed which indicates incomplete extraction of iron(III); therefore repetitive extractions were found necessary for the complete extraction of iron(III) from larger volumes of the aqueous phase.

The volume of the aqueous phase of the Co(II)-HDPBA system can be varied from 10-100 ml with respect to a fixed volume of 10 ml of the organic phase without any variation in the absorbance value of the complex or the extraction efficiency of the system.

The volume effect is explained by equation 31. Accordingly the decrease in the extraction efficiency at higher ratio of $V_{aq}:V_{org}$ in the Fe(III)-SCN-HDPBA system indicates that the distribution ratio of iron(III) is relatively smaller than that of cobalt(II). The results are shown in Table 6.

Table 6. Effect of Ionic Strength, Temperature and Volume of the Aqueous Phase on the Extraction of Iron(III) and Co(II)

$$[\text{Fe(III)}] = 4.0 \times 10^{-5} \text{ M}$$

$$[\text{Co(II)}] = 8.0 \times 10^{-5} \text{ M}$$

Variable	Fe(III)-SCN-HDPBA	Co(II)-HDPBA
	Absorbance at 465 nm	Absorbance at 405 nm
<u>[KNO₃]</u>		
0.0	0.402	0.562
0.1	0.400	0.559
1.0	0.399	0.560
1.5	0.402	0.561
<u>Temperature</u>		
20°C	0.401	0.560
40°C	0.398	0.562
<u>V_{aq}:V_{org}</u>		
1:1	0.401	0.563
2.5:1	0.403	0.562
4:1	0.399	0.558
5:1	0.386	0.560
10:1	0.212	0.562

Order of Addition of Reagents. For both systems it was found that there is no change in the absorbance or in the color intensity of the complexes extracted into toluene if the order of addition of reagents is reversed.

Time of Extraction and Stability of Complexes. An equilibrium period of 1 minute (with shaking) was sufficient

for complete extraction of the iron(III) mixed ligand complex and the Co(II)-HDP3A complexes. Prolonged extraction had no harmful effect on the determination.

The Fe(III)-SCN-HDP3A complex was stable for 6 hours and the Co(II)-HDP3A for 12 hours. After 6 hours the colored extract of the Fe(III)-SCN-HDP3A system slowly became turbid probably due to the decomposition of the complex. The colored extract of the Co(II)-HDP3A system after 12 hours changed to dark brown and finally becomes turbid; probably due to oxidation of the Co(II) to Co(III) by dissolved oxygen (98). The results are given in Table 7.

Table 7. Effect of Time on the Stability of Complexes

$$[\text{Fe(III)}] = 4.0 \times 10^{-5} \text{ M}$$

$$[\text{Co(II)}] = 8.0 \times 10^{-5} \text{ M}$$

Time	Fe(III)-SCN-HDP3A	Co(II)-HDP3A
	Absorbance at 465 nm	Absorbance at 405 nm
30 min	0.403	0.563
1 hr	0.400	0.561
2 hrs.	0.402	0.561
4 hrs.	0.402	0.563
6 hrs.	0.403	0.561
7 hrs.	0.411	0.564
10 hrs.	*	0.561
12 hrs.	*	0.563
16 hrs.	*	0.596
20 hrs-	*	0.606

* Changed turbid.

3.3 Composition of the Complexes

The composition of the complexes was determined by several spectrophotometric methods. The continuous variations (12) and the absorptiometric (6) methods were used to determine the ratio of Fe(III) to HDPBA and Fe(III) to SCN^- in Fe(III)-SCN-HDPBA system. The mole ratio (13) and continuous variations were applied to determine the ratio of Co(II) to HDPBA.

In the continuous variations method the maximum absorbance was observed at the mole fraction of 0.67 of the thiocyanate and also at the mole fraction of 0.67 of the HDPBA in the Fe(III)-SCN-HDPBA system. These results indicate the ratio of iron(II) to thiocyanate is 1:2 and the ratio of iron(III) to HDPBA is also 1:2 in the Fe(III)-SCN-HDPBA complex. The results are given in Tables 8 and 9. The curves are shown in Fig. 4 and 5.

In the absorptiometric method, for the Fe(III)-SCN-HDPBA the quantity $\log \frac{A}{A_{\max} - A}$ was plotted against the

$\log (\text{HDPBA})$ or (SCN^-) ; where A was the absorbance for a particular concentration of HDPBA or thiocyanate and $A_{\max}$ was the absorbance in the presence of excess HDPBA or thiocyanate. The curve $\log \frac{A}{A_{\max} - A}$ versus $\log$

(HDPBA) gave a slope of 2.04 which indicates the ratio of Fe(III) to HDPBA is 1:2. The curve $\log \frac{A}{A_{\max} - A}$

versus $\log (\text{SCN}^-)$ gave a slope of 1.85 which indicates the ratio of Fe(III) to thiocyanate is 1:2. The results are

Table 8. Results of Continuous Variations Method for Fe(III)-SCN-HDPBA System to Determine Fe(III): HDPBA Ratio

$$C_T = [\text{Fe(III)}] + [\text{HDPBA}] = 4.0 \times 10^{-4} \text{ M}, [\text{HCl}] = 0.4 \text{ M},$$

$$[\text{SCN}] = 0.2 \text{ M}$$

Mole fraction of Iron(III)	Mole fraction of HDPBA	Absorbance at 465 nm
0.0	1.0	0.001
0.1	0.9	0.182
0.2	0.8	0.291
0.3	0.7	0.331
0.33	0.67	0.343
0.4	0.6	0.337
0.5	0.5	0.298
0.6	0.4	0.241
0.7	0.3	0.196
0.8	0.2	0.141
0.9	0.1	0.076
1.0	0.0	0.000

Table 9. Results of Continuous Variations Method for Fe(III)-SCN-HDPBA Complex to Determine Iron(III): SCN⁻ Ratio

$$C_T = [\text{Fe(III)}] + [\text{SCN}^-] = 4.0 \times 10^{-4} \text{ M}$$

$$[\text{HCl}] = 0.4 \text{ M}, [\text{HDPBA}] = 1.2 \times 10^{-3} \text{ M}$$

Mole fraction of Iron(III)	Mole fraction of SCN ⁻	Absorbance at 465 nm
0.00	1.00	0.002
0.10	0.90	0.095
0.20	0.80	0.149
0.30	0.70	0.195
0.33	0.67	0.201
0.40	0.60	0.191

Table 9 contd.

Mole fraction of Iron(III)	Mole fraction of SCN^-	Absorbance at 465 nm
0.50	0.50	0.173
0.60	0.40	0.144
0.70	0.30	0.113
0.80	0.20	0.080
0.90	0.10	0.041
1.00	0.00	0.001

given in Tables 10 and 11. The curves are shown in Fig. 6 and 7.

Table 10. Results of Absorptiometric Method for Fe(III)-SCN-HDPBA Complex to Determine Iron(III):HDPBA Ratio.

$[\text{Fe(III)}] = 4.0 \times 10^{-5} \text{ M}$, $[\text{SCN}^-] = 0.05 \text{ M}$ $[\text{HCl}] = 0.4 \text{ M}$

$A_{\text{max}} = 0.401$

$[\text{HDPBA}]$ 10^{-4} M	$\frac{A}{A_{\text{max}} - A}$	$\log \frac{A}{A_{\text{max}} - A}$	$\log [\text{HDPBA}]$	Absorbance at 465 nm
0.8	0.06	-1.19	-4.09	0.024
1.2	0.15	-0.82	-3.92	0.052
1.6	0.27	-0.57	-3.79	0.084
2.4	0.59	-0.23	-3.62	0.148
3.2	1.07	0.03	-3.49	0.207
4.0	1.70	0.23	-3.39	0.252
4.8	2.34	0.37	-3.32	0.281
6.0	3.98	0.60	-3.22	0.320
8.0	7.07	0.85	-3.09	0.350

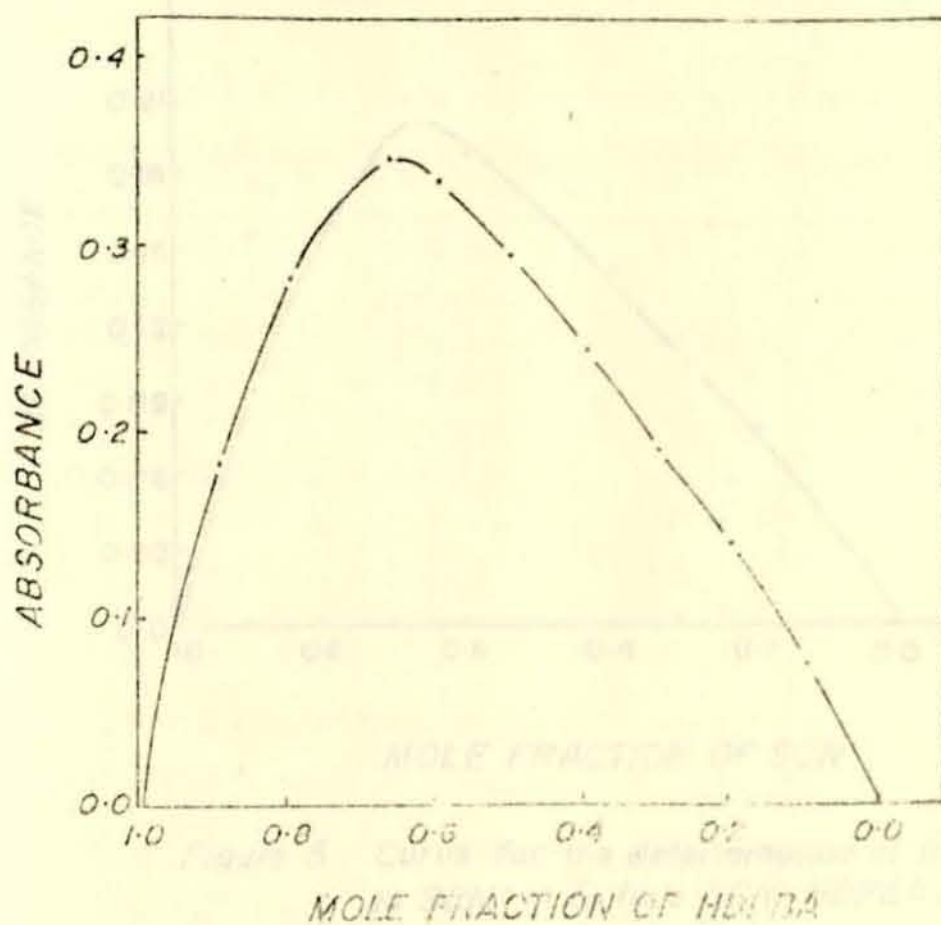


Figure 4 Curve for the determination of ratio, iron (III) to HDPBA in Fe (III) - SCN - HDPBA complex by continuous variation method

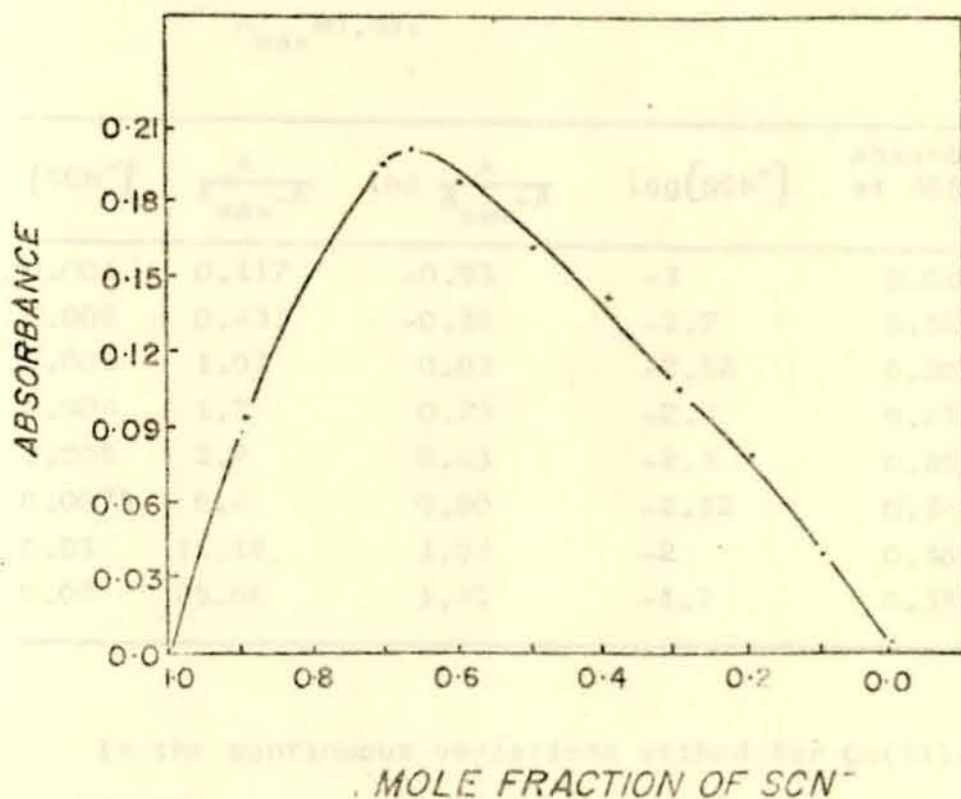


Figure 5 Curve for the determination of iron(III) to SCN^- in $\text{Fe(III)}-\text{SCN}^-$ -HDPBA complex by continuous variation method

Table 11. Results of Absorptiometric Method for Fe(III)-SCN-HDPBA Complex to Determine Fe(III):SCN⁻ Ratio

$$[\text{Fe(III)}] = 4.0 \times 10^{-5} \text{ M}, [\text{HCl}] = 0.4 \text{ M}, [\text{HDPBA}] = 2.0 \times 10^{-3} \text{ M}$$

$$A_{\text{max}} = 0.401$$

$[\text{SCN}^-]$	$\frac{A}{A_{\text{max}} - A}$	$\log \frac{A}{A_{\text{max}} - A}$	$\log [\text{SCN}^-]$	Absorbance at 465 nm
0.001	0.117	-0.93	-3	0.042
0.002	0.433	-0.36	-2.7	0.121
0.003	1.07	0.03	-2.52	0.207
0.004	1.7	0.23	-2.4	0.252
0.005	2.7	0.43	-2.3	0.292
0.0075	6.4	0.80	-2.12	0.347
0.01	11.12	1.04	-2	0.367
0.02	25.66	1.41	-1.7	0.385

In the continuous variations method for Co(II)-HDPBA system the maximum absorbance was observed at the mole fraction of 0.75 of the HDPBA which indicates the ratio of the metal ion to HDPBA to be 1:3 in the Co(II)-HDPBA complex.

In the mole ratio method for Co(II)-HDPBA system the two straight lines drawn from the two parts of the curve intersected at a mole ratio of 1:3 (Co(II):HDPBA). This result indicates the ratio of cobalt(II) to HDPBA to be 1:3. The results are given in Tables 12 and 13 and the curves are shown in Fig. 8 and 9.

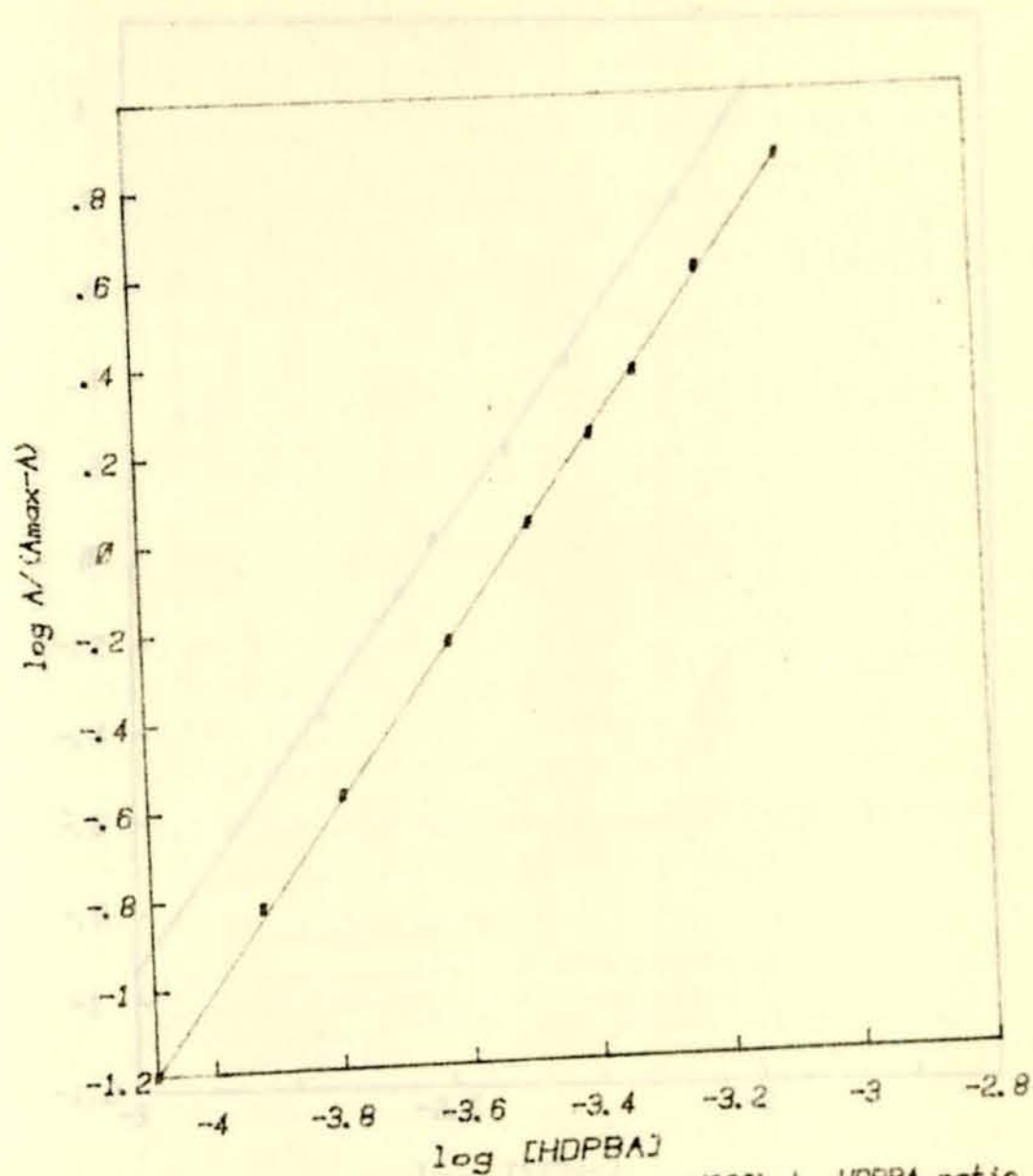


Fig 6 Curve for determination of iron(III) to HDPBA ratio in Fe(III)-SCN-HDPBA system by absorptiometric method

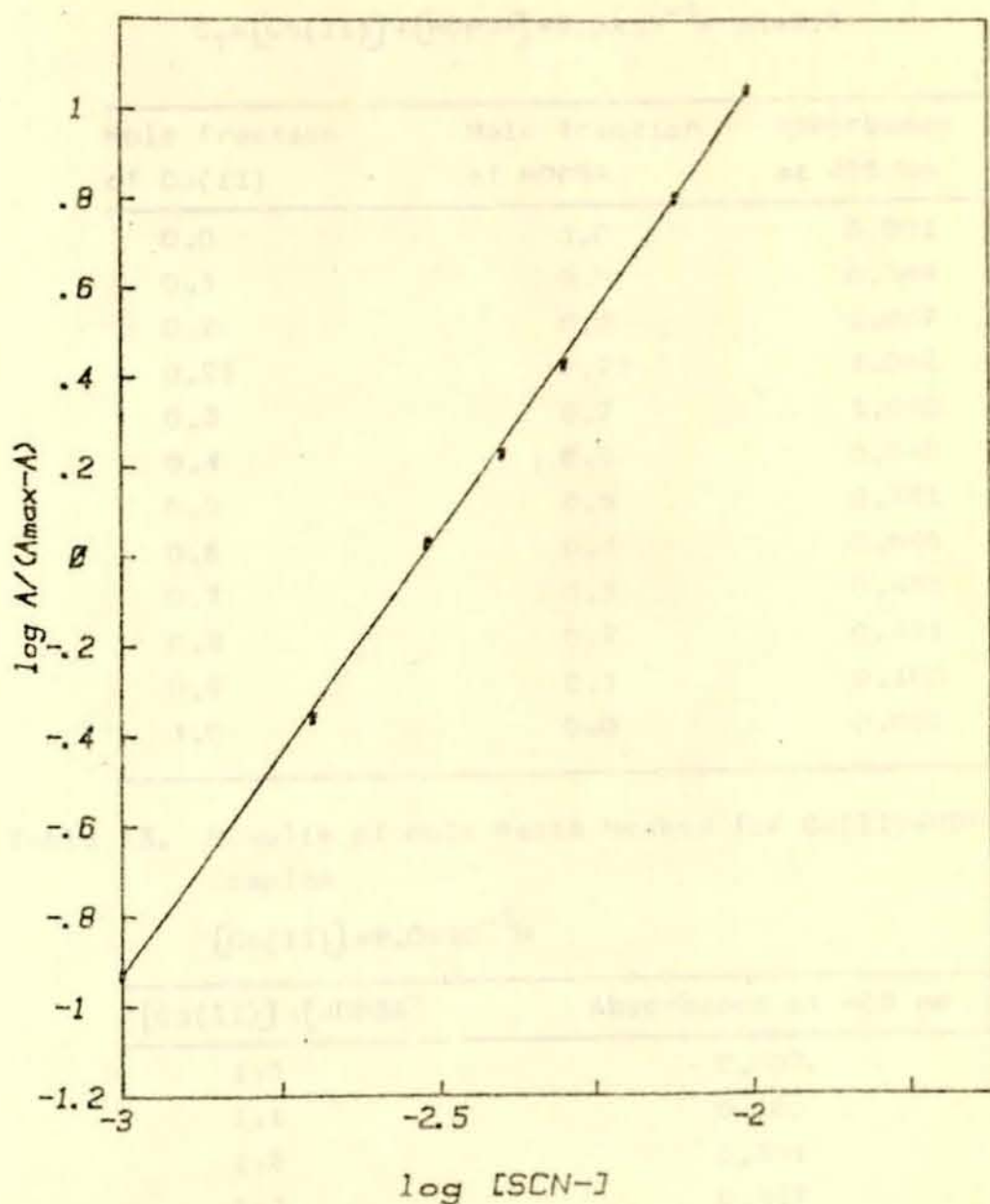


Fig 7 Curve for determination of iron(III) to SCN^- ratio in $\text{Fe(III)}-\text{SCN}-\text{HDPBA}$ system by absorptiometric method

Table 12. Results of Continuous Variations Method for Co(II)-HDPBA Complex

$$C_T = [\text{Co(II)}] + [\text{HDPBA}] = 8.0 \times 10^{-4} \text{ M } \text{pH} = 8.5$$

Mole fraction of Co(II)	Mole fraction of HDPBA	Absorbance at 405 nm
0.0	1.0	0.001
0.1	0.9	0.564
0.2	0.8	1.047
0.25	0.75	1.082
0.3	0.7	1.020
0.4	0.6	0.840
0.5	0.5	0.781
0.6	0.4	0.640
0.7	0.3	0.452
0.8	0.2	0.301
0.9	0.1	0.160
1.0	0.0	0.001

Table 13. Results of Mole Ratio Method for Co(II)-HDPBA Complex

$$[\text{Co(II)}] = 8.0 \times 10^{-5} \text{ M}$$

$[\text{Co(II)}] : [\text{HDPBA}]$	Absorbance at 405 nm
1:0	0.002
1:1	0.160
1:2	0.301
1:3	0.417
1:4	0.497
1:5	0.535
1:6	0.563
1:7	0.561
1:8	0.564
1:9	0.560
1:10	0.563
1:25	0.561
1:50	0.564

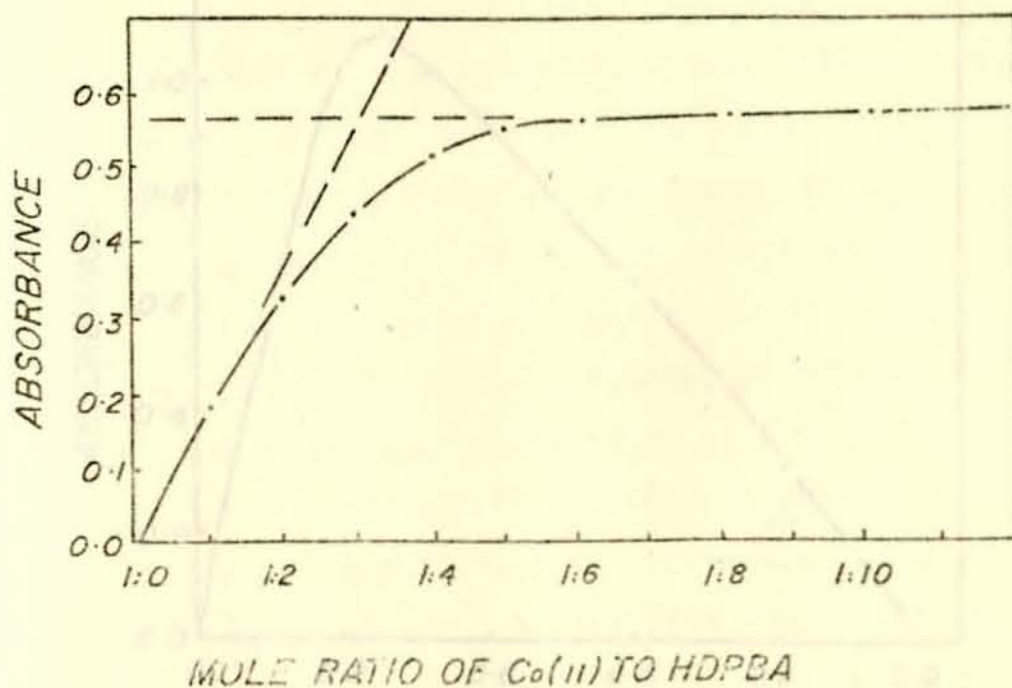


Figure 8 Curve for the determination of composition of Co(II)-HDPBA complex by the mole ratio method

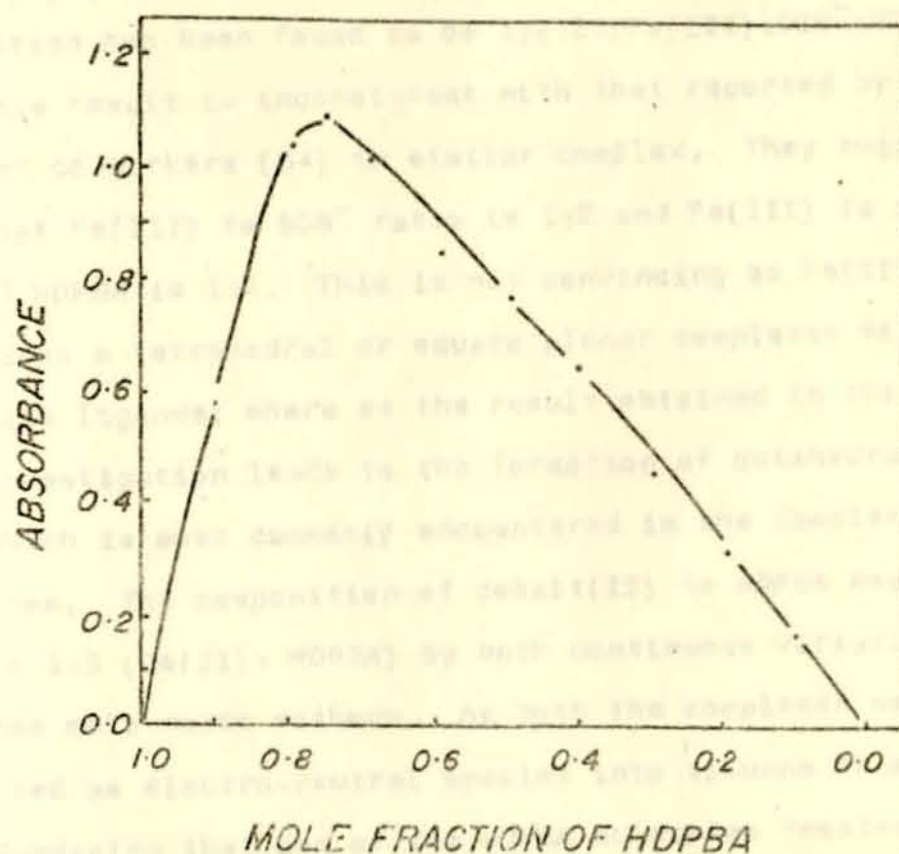
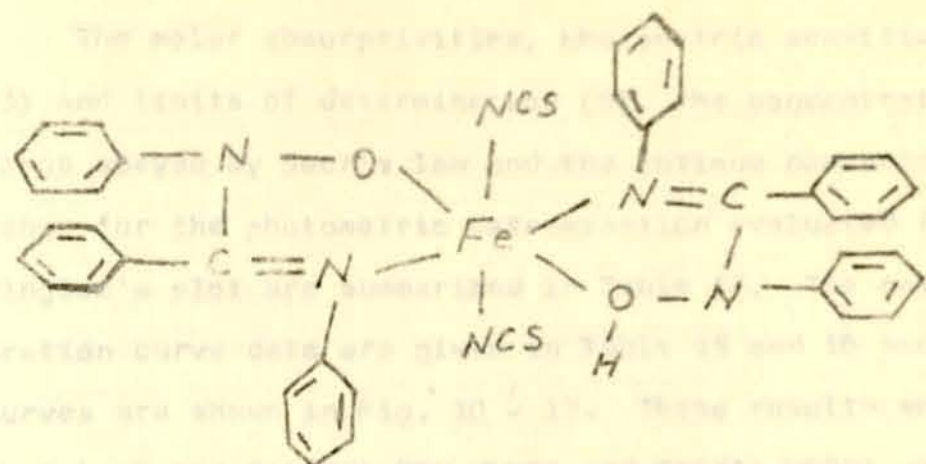
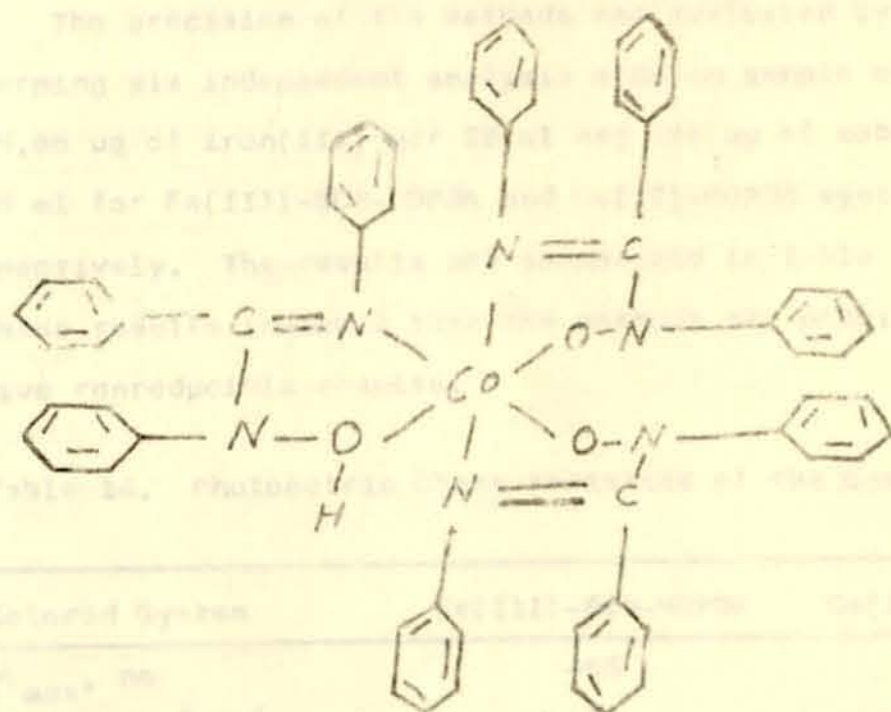


Figure 9 Curve for the determination of composition of $\text{Co(II)}-\text{HDPBA}$ by continuous variation method

Thus the ratio of Fe(III) to HDPBA was found to be 1:2 by both methods. The same result was also found for the Fe(III) to SCN⁻ ratio. Therefore the overall composition has been found to be 1:2:2 (Fe(III):SCN⁻:HDPBA). This result is inconsistent with that reported by Mishra and co-workers (84) in similar complex. They suggested that Fe(III) to SCN⁻ ratio is 1:2 and Fe(III) to analogues of HDPBA is 1:1. This is not convincing as Fe(III) hardly forms a tetrahedral or square planar complexes with bidentate ligands; where as the result obtained in the present investigation leads to the formation of octahedral complex which is most commonly encountered in the complexes of iron. The composition of cobalt(II) to HDPBA was found to be 1:3 (Co(II): HDPBA) by both continuous variations and the mole ratio methods. As both the complexes were extracted as electro-neutral species into toluene it may be suggested that one of the HDPBA molecules remained protonated, hence the formula of the complexes may be [Fe(L)(HL)(SCN)₂] and [CoL₂HL], respectively. The possible structures of the complexes are shown below.



Dithiocyanato-bis(N-hydroxy-N,N'-diphenylbenzamine)iron(III)



Tris(N-hydroxy-N,N'-diphenylbenzamine)cobalt(II)

3.4 Photometric Characteristics of the Complexes

The molar absorptivities, photometric sensitivities (3) and limits of determination (8), the concentration range obeyed by Beer's law and the optimum concentration range for the photometric determination evaluated from Ringbom's plot are summarized in Table 14. The calibration curve data are given in Table 15 and 16 and curves are shown in Fig. 10 - 13. These results show that both the Fe(III)-SCN-HDPBA and Co(II)-HDPBA are sensitive and can be applied for the determination of trace quantities of iron and cobalt.

The precision of the methods was evaluated by performing six independent analysis made on sample containing 55.85 μg of iron(III) per 25 ml and 118 μg of cobalt per 25 ml for Fe(III)-SCN-HDPBA and Co(II)-HDPBA systems respectively. The results are summarized in Table 17. These results indicate that the methods are precise and give reproducible results.

Table 14. Photometric Characteristics of the Complexes

Colored System	Fe(III)-SCN-HDPBA	Co(II)-HDPBA
λ_{max} , nm	465	405
ϵ , $\text{l mol}^{-1}\text{cm}^{-1}$	1.0×10^4	7.0×10^3
^a Sandell sensitivity, $\mu\text{g cm}^{-2}$	0.006	0.008
^b Limit of determination, $\mu\text{g ml}^{-1}$	0.014	0.042
Concentration range from Beer's law, $\mu\text{g ml}^{-1}$	0.22-6.60	0.47-11.80

Table 14 Contd.

Colored System	Fe(II)-SCN-HDPBA	Co(II)-HDPBA
Optimum concentration		
Range from Ringboms		
plot $\mu\text{g ml}^{-1}$	0.55-4.40	0.94-4.72

- a- Concentration that corresponds to an absorbance of 0.001.
 b- Concentration that corresponds to an absorbance three times the standard deviation of the blank.

Table 15. Calibration Curve Data for Determination of Iron(III) by the Fe(III)-SCN-HDPBA System

Concentration of Iron(III)			Absorbance at 465 nm
M	$\mu\text{g}/25\text{ml}$	ppm	
8.0×10^{-6}	11.8	0.47	0.056
1.6×10^{-5}	23.6	0.94	0.110
2.0×10^{-5}	29.5	1.18	0.136
4.0×10^{-5}	59.0	2.36	0.276
8.0×10^{-5}	118.0	4.72	0.561
1.6×10^{-4}	236.0	9.44	1.112
2.0×10^{-4}	295.0	11.80	1.387

Table 16. Calibration Curve Data for Determination of Cobalt(II) by the Co(II)-HDPBA System

Concentration of Cobalt(II)			
M	$\mu\text{g}/25\text{ml}$	ppm	Absorbance at 405 nm
8.0×10^{-6}	11.8	0.47	0.056
1.6×10^{-5}	23.6	0.94	0.110
2.0×10^{-5}	29.5	1.18	0.136
4.0×10^{-5}	59.0	2.36	0.276
8.0×10^{-5}	118.0	4.72	0.561
1.6×10^{-4}	236.0	9.44	1.112
2.0×10^{-4}	295.0	11.80	1.387

Table 17. Evaluation of Precision of the Methods

Method	Total number of samples	Mean absorbance	Standard deviation	Relative standard deviation (%)
Fe(III)-SCN-HDPBA	6	0.41	0.001	0.25
Co(II)-HDPBA	6	0.561	0.003	0.60

3.5 Effect of Foreign Ions

To evaluate the selectivities of the newly developed methods the effect foreign ions on the determination of iron(II) and cobalt(II) have been studied. Reasonable amounts of alkali, alkaline-earth metals and most of the

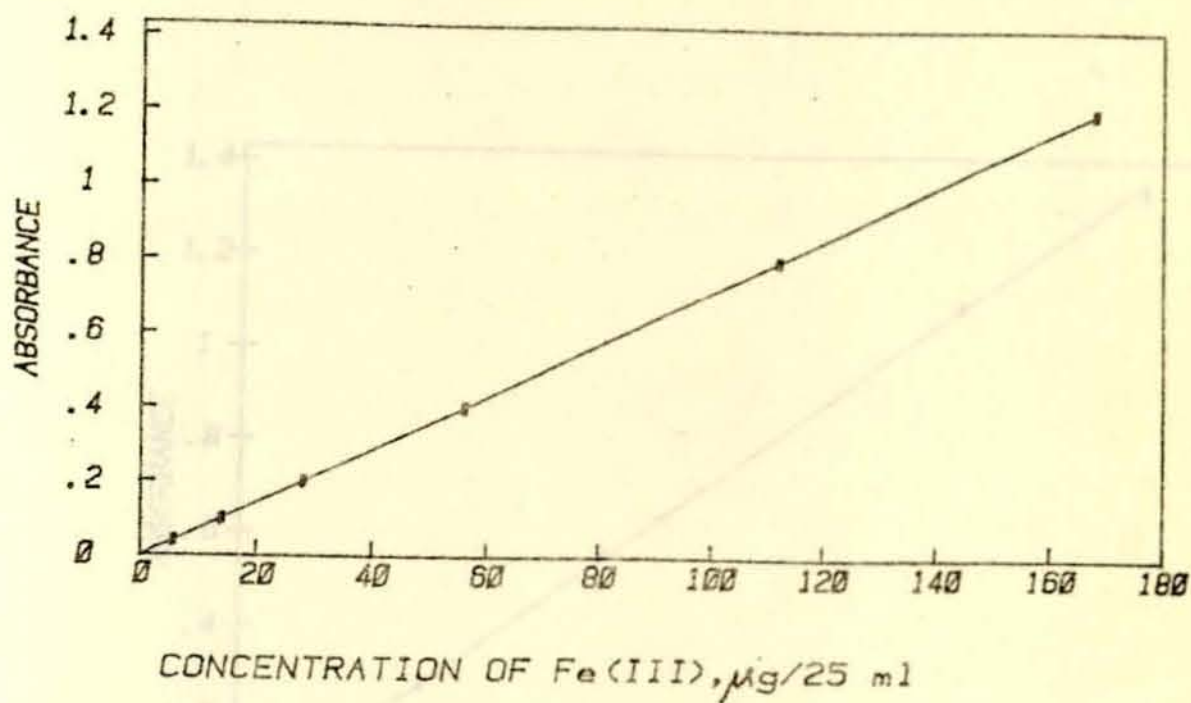


Fig 10 Calibration Curve for the determination of Fe(III)

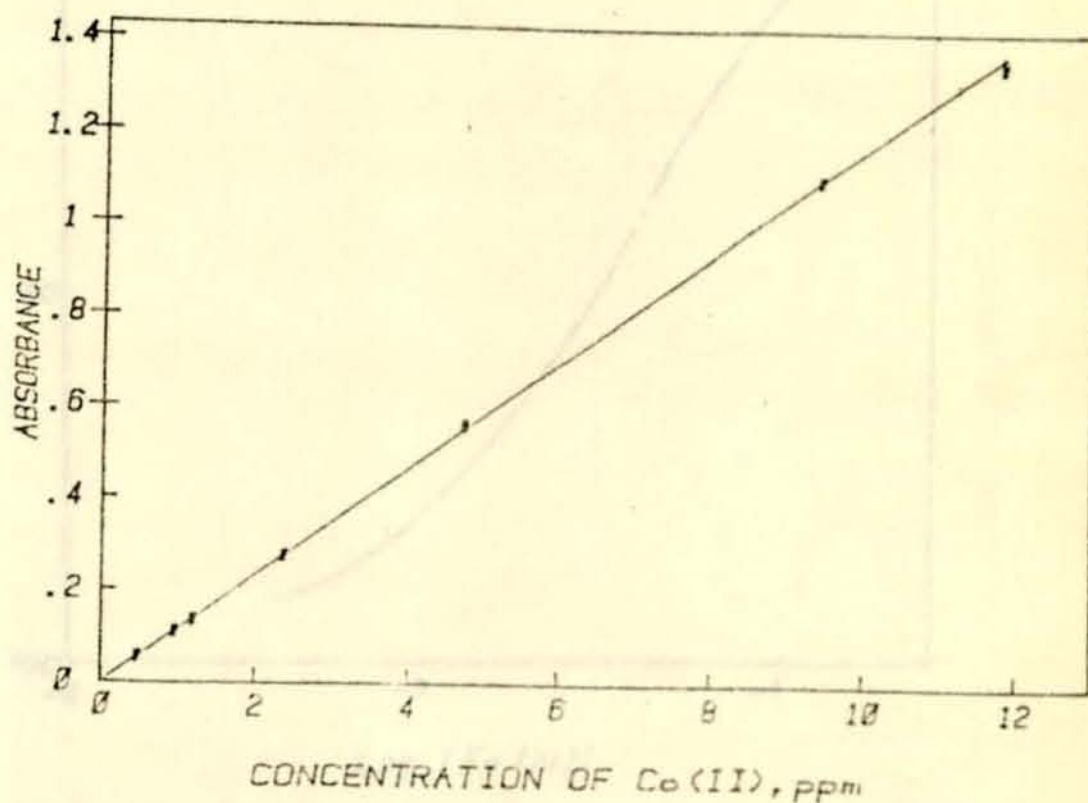


Fig 11 Calibration Curve for the determination of Cobalt(II)

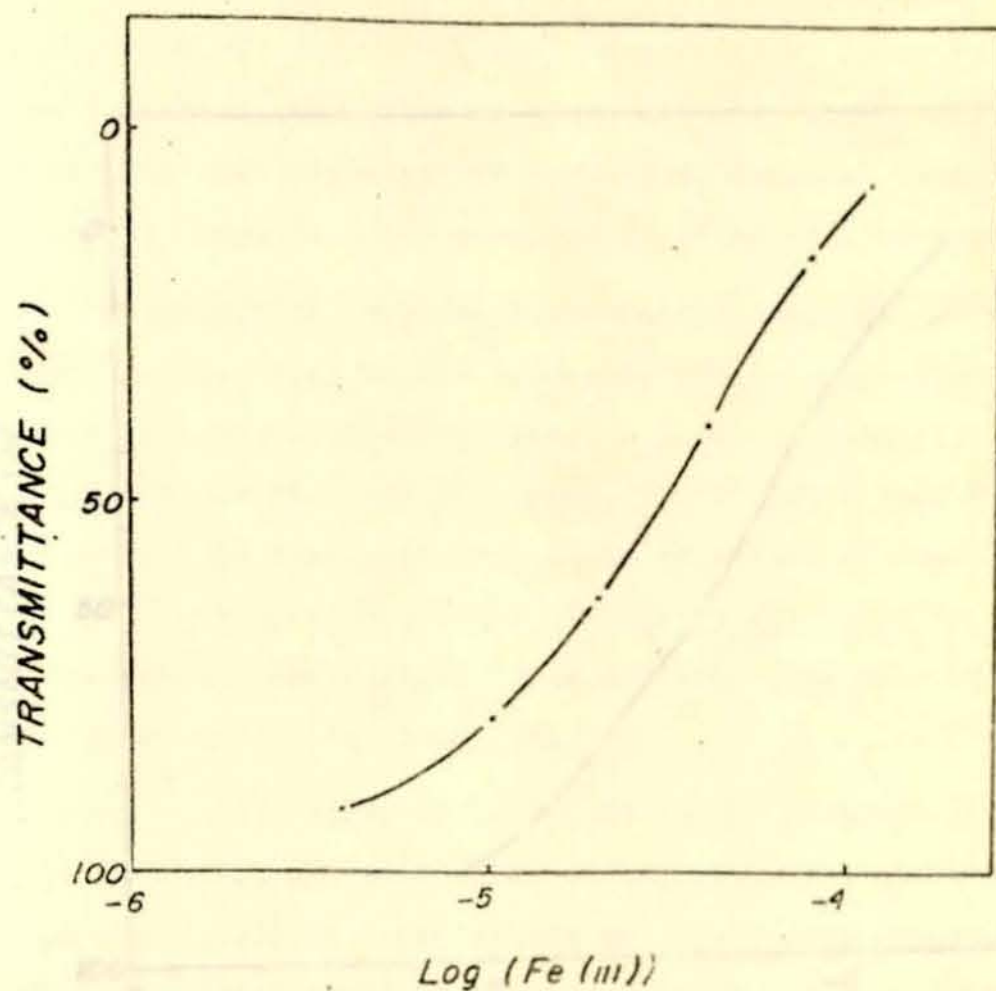


Fig 12 Ringbom's plot for the evaluation of optimum concentration range for the determination of iron (III) by Fe-SCN-1:1DPBA system

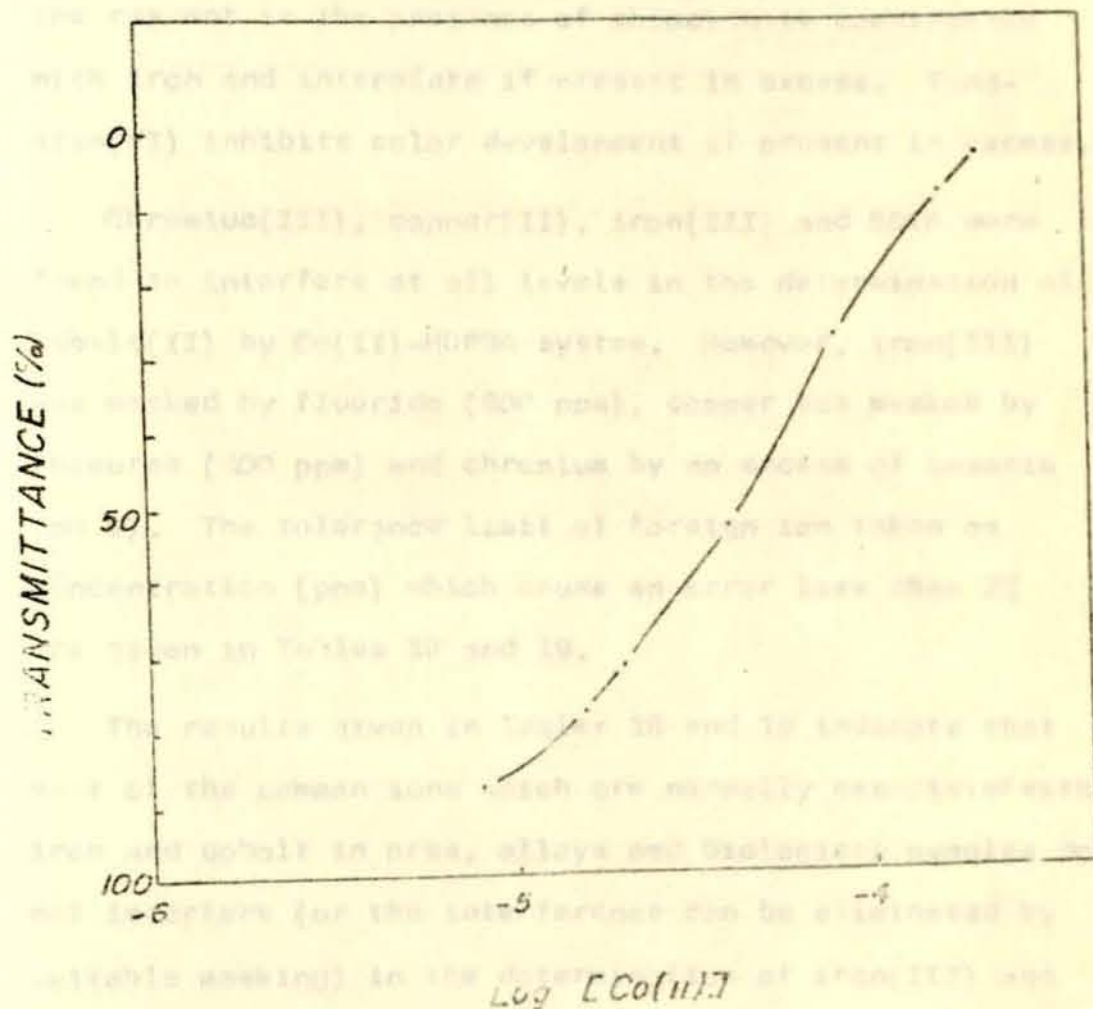


Figure 15 Ringbom's plot for the evaluation of optimum concentration range for the determination of Co(II) by Co-HDPBA system

anions except EDTA, oxalate and citrate were found not to interfere in the determination of iron. Copper(II) molybdenum(VI) and Vanadium(V) were found to react with the reagent in the presence of thiocyanate coextracted with iron and interfere if present in excess. Tungsten(VI) inhibits color development if present in excess.

Chromium(III), copper(II), iron(III) and EDTA were found to interfere at all levels in the determination of cobalt(II) by Co(II)-HDPBA system. However, iron(III) was masked by fluoride (800 ppm), copper was masked by thiourea (400 ppm) and chromium by an excess of ammonia (pH 9). The tolerance limit of foreign ion taken as concentration (ppm) which cause an error less than 2% are given in Tables 18 and 19.

The results given in Tables 18 and 19 indicate that most of the common ions which are normally associated with iron and cobalt in ores, alloys and biological samples do not interfere (or the interference can be eliminated by suitable masking) in the determination of iron(III) and cobalt(II) by Fe(III)-SCN-HDPBA and Co(II)-HDPBA, respectively. Hence the proposed method for iron can be applied to the analysis of ores, alloys, steels and biological samples. Except in steels in which iron is interfering, cobalt can be determined in ores, biological samples and most alloys.

Table 18. Tolerance Limit of Foreign Ions in the Determination of Iron(III)

$[\text{Fe(III)}] = 2.0 \text{ ppm}$; $[\text{SCN}^-] = 0.05 \text{ M}$; $[\text{HCl}] = 0.4 \text{ M}$

Ion	Tolerance limit*, ppm
Na^+	400
K^+	400
Ca^{2+}	400
Mg^{2+}	400
Be^{2+}	400
Li^+	400
Al^{3+}	400
Sn^{2+}	400
Ba^{2+}	400
Zn^{2+}	400
Tl^+	400
Ti^{4+}	80
La^{3+}	400
Hg^{2+}	400
Bi^{3+}	400
Co^{2+}	400
Cr^{3+}	400
Sn^{4+}	400
Cd^{2+}	400
VO_2^+	10
Ni^{2+}	400
Cu^{2+}	10

Ion	Tolerance limit*, ppm
Th ⁴⁺	400
Mn ²⁺	400
Ce ⁴⁺	400
MoO ₄ ²⁻	10
WO ₄ ²⁻	10
Nitrate	400
Chloride	400
Acetate	400
Sulphate	400
Citrate	200
Thiourea	400
EDTA	60
Phosphate	400
Fluoride	400
Oxalate	40

*400 ppm was maximum concentration tested

Table 19. Tolerance Limit of Foreign Ions in the Determination of Cobalt(II).

[Co(II)] = 4.0 ppm; pH=8.5

Ion	Tolerance limit*, ppm
Na ⁺	400
K ⁺	400
Ca ²⁺	400
Mg ²⁺	400

Ion	Tolerance limit*, ppm
Be ²⁺	400
Li ⁺	400
Al ³⁺	400
Sn ²⁺	400
Ba ²⁺	400
Zn ²⁺	400
Ti ⁺	400
Ti ⁴⁺	400
La ³⁺	80
Hg ²⁺	400
Bi ³⁺	40
Fe ³⁺	40 ^a
Cr ³⁺	10 ^b
Sn ⁴⁺	400
Cd ²⁺	400
VO ₂ ⁺	20
Ni ²⁺	100
Cu ²⁺	10 ^c
Th ⁴⁺	400
Mn ²⁺	400
Ce ⁴⁺	80
MoO ₄ ²⁻	400
WO ₄ ²⁻	400
Nitrate	400
Chloride	400
Acetate	400
Sulphate	400
Citrate	400
Thiourea	400
EDTA	-
Phosphate	400
Fluoride	400
Borate	400
Oxalate	400

*400 ppm was maximum concentration tested.

^a masked by Fluoride (800 ppm).

^b masked by excess ammonia (pH 9).

^c masked by thiourea (400 ppm).

3.6 Application

In order to assess the analytical potentiality of the newly developed methods, the Fe(III)-SCN-HDPBA system has been applied to the analysis of blood and steel samples for iron content and Co(II)-HDPBA system to the analysis of vitamin B₁₂ for cobalt determination. The iron and cobalt of the samples were also determined by atomic absorption spectroscopy (AAS) to compare the results obtained by the newly developed methods.

Steel Sample. Since standard samples were not available, synthetic samples having the same constituents with identical proportion as that of the British Standard Steel No 64 a and 24 ¹/₄ were prepared. Extraction and determination of iron in steel samples were undertaken following the general procedure described earlier. The iron contents of samples were also determined by AAS. The experimental results are given in Table 20; which indicate the reliability of the proposed method. It can also be noted that the proposed method gives precise and accurate results in comparison to that of AAS.

Composition of steel

Sample No 64 a. C, 0.80; Cr, 4.40; V, 1.57; Mo, 4.11;
W, 5.66; Fe, 83.45%.

Sample No 24 ¹/₁. W, 19.61; Cr, 5.03, Mo, 0.52; V, 1.57;
Co, 5.67; C, 0.85, Si, 0.33; S, 0.033;
P, 0.021; Mn, 0.295; Ni, 0.075; Cu,
0.10; Sn, 0.025; Fe, 65.8%.

Table 20. Determination of Iron in Synthetic Steel
Samples

Method	Sample No	Iron Content (%)	* Iron Found (%)	Relative Standard Deviation	Relative error (%)
Fe(III)-SCN-HDPBA	64a	83.45	83.07	0.52	0.45
AAS	64a	83.45	84.58	2.02	1.35
Fe(III)-SCN-HDPBA	24 ¹ / ₁	65.87	65.29	0.75	0.88
AAS	24 ¹ / ₁	65.87	64.92	2.50	1.44

*Average of triplicate analyses.

Blood Sample. The amount of iron in blood sample, prepared by following the procedure described earlier, was determined by Fe(III)-SCN-HDPBA and AAS methods. The results obtained by both methods are comparable, and fall within the range of content of iron in whole blood reported for an adult man, i.e. 45 - 145 mg/100 ml (99). However, it can be noted that the proposed method is more precise than AAS. Hence the proposed method can be applied for the determination of iron in biosamples. The results are given in Table 21.

Table 21. Determination of Iron in Blood Samples

Method	*Iron found mg/100 ml	Relative standard deviation (%)
Fe(III)-SCN-HDPBA	65.78	0.55
AAS	67.02	1.60

*Average of triplicate analysis

Vitamin B₁₂: The Co(II)-HDPBA and AAS methods were applied to the analysis of vitamin B₁₂. The cobalt content of the sample was determined by the general procedure described earlier for the Co(II)-HDPBA system and also by AAS method. The experimental results are in good agreement with the actual value indicating the accuracy of the methods. The results are given in Table 22.

Table 22. Determination of Cobalt in Vitamin B₁₂

Method	Cobalt content (%)	*Cobalt found (%)	Relative standard deviation (%)	Relative error (%)
Co(II)-HDPBA	4.35	4.31	0.89	0.91
AAS	4.35	4.40	1.50	1.14

*Average of triplicate analyses

3.7 Comparison with Other Spectrophotometric Methods

A comparative study of the proposed methods for the determination of iron and cobalt with the recently reported spectrophotometric methods in regard to sensitivity, selectivity, concentration range for determination and interference is made in Tables 23 - 26.

The comparison reveals that, of the many organic reagents used for the determination of iron (Tables 23 and 24) the reagents 4-(4-methyl-2-thiazolylazo)resorcinol (101) and N-phenylcinnamohydroxamic acid and thiocyanate (56) are more sensitive than the proposed reagent. These reagents are highly selective as the proposed reagent. The reagents 2,6-bis[1-(2-methoxyethylimino)ethyl]pyridine and sodium picrate (29) and 3-hydroxy-2-methyl-1,4-naphthaquinone monoxime (36) are also sensitive than the proposed reagent; but the problem with these methods in interference from many species that are associated in real samples. Moreover, 2,6-bis[1-(2-methoxyethylimino)ethyl]pyridine method involves the use of nitrobenzene as solvent which is highly toxic and at the same time long equilibration period is required for the extraction. The reagents salicylaldehyde (100), 3-(4-sulphophenylazo)-chromotropic acid (41), 2-(phenoxyacetyl)acetophenone (37) and N-phenylcinnamohydroxamic acid and azide (40) are far less sensitive and less selective than the proposed reagent and therefore they require prior separation and may not be used for trace analysis.

The thiocyanate method (3) for ion determination is not selective (Cu^{2+} , Bi^{3+} , Ti^{4+} , Mo^{6+} , U^{6+} and F^- interfere), color intensity is highly dependent on the concentration of thiocyanate and temperature. It is also unstable and slightly deviates from Beer's law. HDPBA (65) is also not sensitive ($\epsilon = 3600$) and not selective (Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , V^{5+} , Mo^{6+} and U^{6+} interfere). Whereas the proposed method which involves the use of both thiocyanate and HDPBA to form a mixed ligand complex is more sensitive and highly selective than the individual reagents. The method is also found to be free from rigid control of experimental conditions.

Thus the comparison indicates that the proposed method for the determination of iron is more sensitive than many of the literature reported methods while the proposed method is more selective than most of the literature reported methods.

Of the spectrophotometric reagents recommended for cobalt (Tables 25 and 26), the reagent isonitrosothiocamphor (46) is more sensitive than the proposed reagent; while the proposed reagent has the same selectivity as that of isonitrosothiocamphor. Cyclohexylthioglycolate (52) and isophthalodihydroxamic acid (102) are more sensitive than the proposed reagent, but they suffer from serious interferences from many species and need long equilibration time. The reagents biacetylmonoxime-2-pyridylhydrazone (44), 4-formyl-3-methyl-1-phenyl-2-pyrazolin-5-one and pyridine (59), t-butyl hydroperoxide

and EDTA (60), ammonium thiocyanate (56) and N-hydroxy-N,N'-diphenylbenzimidine and azide (80) are less sensitive and less selective than the proposed method.

Thus the newly proposed reagents for the spectrophotometric determination of cobalt is found to be moderately sensitive in comparison to the others but the selectivity is much better than that of the other methods.

Hence the newly proposed methods could be preferred in selecting the methods for the determination of iron and cobalt.

1. 2,2'-bipyridine	393	0.0-2.0	1000	201
2. 2,2'-bipyridine	393	0-80	1000	27
3. 2,2'-bipyridine	470	0.0-5.00	1000	26
4. 2,2'-bipyridine	500	0.02-0.20	1000	21
5. 2,2'-bipyridine	595	0.1-1.5	1000	20
6. 2,2'-bipyridine	412	0.2-5	1000	20
7. 2,2'-bipyridine	420	0.2-5	1000	20
8. 2,2'-bipyridine	420	0.2-5	1000	20
9. 2,2'-bipyridine	420	0.2-5	1000	20
10. 2,2'-bipyridine	420	0.2-5	1000	20
11. 2,2'-bipyridine	420	0.2-5	1000	20
12. 2,2'-bipyridine	420	0.2-5	1000	20
13. 2,2'-bipyridine	420	0.2-5	1000	20
14. 2,2'-bipyridine	420	0.2-5	1000	20
15. 2,2'-bipyridine	420	0.2-5	1000	20
16. 2,2'-bipyridine	420	0.2-5	1000	20
17. 2,2'-bipyridine	420	0.2-5	1000	20
18. 2,2'-bipyridine	420	0.2-5	1000	20
19. 2,2'-bipyridine	420	0.2-5	1000	20
20. 2,2'-bipyridine	420	0.2-5	1000	20

Table 23. Sensitivities of the Methods for Iron Determination

Reagent	λ_{max} nm	Concentration range for de- termination, $\mu\text{g ml}^{-1}$	Molar absor- ption coeffi- cient $1 \text{ ml}^{-1} \text{ cm}^{-1}$	Referen
1. 2,6-bis(1-(2-methoxyethyl)pyridine and sodium picrate	596	0.0-6.8	12000	29
2. Salicylaldehyde	440	0.1-10	5190	100
3. 4-(4-Methyl-2-thiazolylazo) resorcinol	735	0.0-2.0	24900	101
4. 2-(Phenoxyacetyl) acetophenone	393	5-80	6813	37
5. 3-Hydroxy-2-methyl-1,4-naphthaquinone monoxime	470	0.0-5.58	12100	36
6. 3-(4-Sulphophenylazo) chromotropic acid	580	0.02-0.24	4800	41
7. N-Phenylcinnamohydroxamic acid and thiocyanate	495	0.2-3.9	18000	56
8. N-Phenylcinnamohydroxamic acid and azide	447	0.5-9	7500	40
9. Thiocyanate	480	-	7000	3
10. N-hydroxy-N,N'-diphenylbenzamidine	520	1.8-16	3600	65
11. N-Hydroxy-N,N'-diphenylbenzamidine and thiocyanate	465	0.22-6.60	10000	

Table 24. Selectivities of the Methods for Iron Determination

	Reagent	pH	*Interference	Reference
1.	2,6-bis(1-2-Methoxy-ethylimino)ethyl pyridine and sodium picrate	3.2-3.9	EDTA, Co^{2+} , Cu^{2+} , Cn	29
2.	Salicylaldehyde	5	Ti^{4+} , Ag , Sb^{3+} , Cr^{3+} , Cd , PO_4^{3-} , citrate, oxalate, WO_4^{2-}	100
3.	4-(4-Methyl-2-thiozolylozo) resorcinol	8.9-11.6	-	101
4.	2-(Phenoxyacetyl) acetophenone	5.5	Al^{3+} , EDTA	37
5.	3-Hydroxy-2-methyl-1,4-naphthaquinone monoxime	5	(Cu^{2+} , Pd^{2+}) ^a , oxalate, NO_2^- , PO_4^{3-} , EDTA	36
6.	3-(4-Sulphophenylazo) chromotropic acid	5.5-6.0	Cu^{2+} , Ni^{2+} , citrate, tartarate, AsO_4^{3-} , PO_4^{3-} , F^- , Be , Zn , Cd , Al	41
7.	N-Phenylcinnamohydroxamic acid and thiocyanate	0.5-2.0M	(Ti^{4+} Zr^{4+}) ^a	
8.	N-Phenylcinnamohydroxamic acid and azide	0.1-0.9M HCl	(Ti^{4+} , V^{5+}) ^a	40
9.	Thiocyanate	0.05-1M HCl	Cu^{2+} , Bi^{3+} , Ti^{4+} , Mo^{6+} , U^{6+}	3
10.	N-hydroxy-N,N'-diphenylbenzamidine	8-11	Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , V^{5+} , Mo^{6+} , U^{6+}	65
11.	N-Hydroxy-N,N'-diphenyl benzamidine and thiocyanate	0.1-0.6M HCl		

*Those that cannot be tolerated more than 2-fold excess amount are considered as interfering.

^aInterference can be eliminated by masking.

Table 25. Sensitivities of the Methods for Cobalt Determination

Reagent	λ_{max} , nm	Concentration range for determination, $\mu\text{g ml}^{-1}$	Molar absorption coefficient, $\text{l mol}^{-1}\text{cm}^{-1}$	Reference
1. t-Butylhydroperoxide and EDTA	580	20-190	249	60
2. Isophthalodihydroxamic acid	330	1-3	13000	108
3. Cyclohexylthioglycolate	500	0.116-1.16	20030	52
4. 4-Formyl-3-methyl-1-phenyl-2-pyrazolin-5-one and pyridine	490	8-19	689	59
5. Isonitrosothiocamphor	350	0.2-1.5	17000	46
6. Biacetylmonoxime-2-pyridylhydrazone	430	0.8-15	3700	44
7. N-Hydroxy-N,N'-diphenylbenzamine and azide	520	1.6-11.2	1980	80
8. Ammonium thiocyanate	625	2-41	1820	56
9. N-Hydroxy-N,N'-diphenylbenzamine	405	0.47-11.80	7000	

Table 26. Selectivities of the Methods for Cobalt Determination

Reagent	pH	⁺ Interference	Reference
1. t-butylhydroperoxide and EDTA	11.6	Mn ²⁺ , CN ⁻ , NH ₄ ⁺ , Cr ³⁺ , Al ³⁺	60
2. Isophthalodihydroxamic acid	basic	Fe, Cu ²⁺ , Mn ²⁺ , Mg ²⁺ , Be ²⁺ , EDTA, Al ³⁺ ^a	102
3. Cyclohexylthioglycolate	8.5-10.5	OS, Pb, Zn, Cd, Hg, W, In, Mo, As, Rh, Al, Mn, V, Fe ²⁺	
4. 4-Formyl-3-methyl-1-phenyl-2-pyrazolin-5-one and pyridine	3.5-5.0	-	59
5. Isonitrosothiocamphor	1M HCl	(Cu ²⁺ , Pd ²⁺) ^a	46
6. Biacetylmonoxime-2-pyridylhydrazine	5.5-60	(Ag ⁺ , Pd ²⁺) ^a , Au, EDTA	44
7. N-Hydroxy-N-N'-diphenylbenzamine and azide	7.4-7.8	Mn ²⁺ , CN ⁻ , Cu ²⁺ , Fe ³⁺	80
8. Ammonium thiocyanate	0.1-1.5M HCl	Fe ³⁺ , VO ₂ ⁺	56
9. N-Hydroxy-N-N'-diphenylbenzidine	7.5-9.5	(Cu ²⁺ , Fe ³⁺ , Cr ³⁺) ^a	

⁺Those that cannot be tolerated more than 2-fold excess amount are considered as interfering.

^aInterference can be eliminated by masking.

4. CONCLUSION

New methods have been developed for the determination of iron(III) with N-Hydroxy-N,N'-diphenylbenzamidine and thiocyanate and Co(II) with N-Hydroxy-N,N'-diphenylbenzamidine by solvent extraction and spectrophotometry. The proposed methods are more selective than most of the other methods reported in the literature, however, the methods are only moderately sensitive. The methods are precise, accurate and free from rigid control of experimental variables. The proposed methods are applicable to the analysis of diverse samples for iron and cobalt.

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