SIMULTANEOUS DETERMINATION OF IRON (III) AND COBALT (II) WITH N-PHENYCINNAMOHYDROXAMIC ACID AND THIOCYANATE
AND
DETERMINATION OF IRON (III) WITH N-PHENYLCINNAMOHYDROXAMIC ACID AND AZIDE
BY
SOLVENT EXTRACTION AND SPECTROPHOTOMETRY

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

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

by
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June 1986

ADDIS ABABA UNIVERSITY
School of Graduate Studies

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TO MY FATHER, MOTHER
SISTERS AND BROTHERS

CONTENTS

ACKNOWLEDGEMENTS

I express my deepest appreciation to my advisor Dr. B. S. Chandravanshi for his generous contribution to the accomplishment of this research work, for his tireless and consistent guidance, encouragement and endless intellectual support, and for the time he spent patiently helping me inspite of some tedious and troubling laboratory problems.

I would also like to express my sincere gratitude to Ato Tekle Habte, Zerom Seyoum, Omer Mohammed, Alemayehu Ababaw, Yosief Alem, Tesfay Meresie, Habtom Mebrahtu, Hidat Asghedom, Tadele Tenaw, Abdu De Tango, Adnew Geletu, Yohannes G/Michael, Bekele Dinku, Bizuneh Workie, Shimelis Admassie, Yilma Tamiru and Shenaz Ahmed for their cooperation and moral support. My thanks is also extended to the University of Asmara for giving me an opportunity to participate in the graduate programme. Last but not least I would like to thank the Department of Chemistry of Addis Ababa University for providing laboratory facilities to conduct the research work.

LIST OF TABLES

PAGE

LIST OF FIGURES

PAGE

ABSTRACT

Simultaneous Determination of Iron(III) and Cobalt(II) with N-Phenylcinnamohydroxamic Acid (PCHA) and Thiocyanate and Determination of Iron(III) with PCHA and Azide by Solvent Extraction and Spectrophotometry

by

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R.Advisor Dr. B.S.Chandravanshi

Iron(III) and cobalt(II) have been found to react with thiocyanate in the presence of N-phenylcinnamohydroxamic acid to form pinkish red and blue colored complexes, respectively. Both the complexes were found to be quantitatively extractable into ethylacetate from 0.5-1.5 M hydrochloric acid solutions. The spectra of iron(III) and cobalt(II) complexes exhibited absorption maxima in the visible region at 495 and 625 nm with molar absorptivities of 18000 and 1820 l $mol^{-1}cm^{-1}$, respectively. The coloured systems obeyed Beer's law in the concentration range of 0.2-3.9 ppm of iron and 2-41 ppm of cobalt. The composition of the complexes have been found to be 1:2:2 ($Fe:SCN^-:PCHA$) and 1:4 ($Co:SCN^-$). The effect of foreign ions and other experimental variables in the extraction and determination of iron(III) and cobalt (II) have been studied. On the basis of these studies simple, precise, sensitive, and highly selective methods have been developed for the determination of iron(III) and cobalt(II) and for the simultaneous determination of both metal ions by solvent extraction and spectrophotometry. The methods have been applied successfully for the determination of iron and cobalt in steel and biosamples.

Iron(III) was also found to react with azide in the presence of PCHA to produce an orange coloured complex having a composition of 1:2:2 ($Fe:N_3^-:PCHA$). The complex was found to be stable and quantitatively extractable into ethylacetate from 0.1-0.9 M HCl solutions allowing reproducible and reliable spectrophotometric determination of iron. The complex has maximum absorption at 447 nm with molar absorptivity of 7500 l $mol^{-1}cm^{-1}$ and obeyed Beer's law in the range of 0.5-9 ppm of iron(III). From the study of the effect of foreign ions and several variables, the method was found to be highly selective and largely free from rigid control of experimental variables. The method was found to be effective by applying for the determination of iron in blood and steel samples. Thus, a new rapid, precise, sensitive and highly selective method for determination of iron(III) with PCHA and azide has been developed.

1. INTRODUCTION

Iron is the most useful of the metallic elements and the second most abundant in the earth's crust, after aluminum (1-3). In its elemental form or as steel iron has supplied civilization with most of its tools and machinery,many of its products and the bulk of its structural element in large scale construction. Except in meteorites, it is rarely found in its elemental form but occurs widely in chemical compounds in the earth's crust. Its important ores and minerals are haematite (Fe_2O_3), magnetite (Fe_3O_4), geothite (FeOOH), limonite (hydrated iron oxide), siderite ($FeCO_3$), and pyrite (FeS_2). Natural waters sometime contain considerable amount of iron. Iron is also found in a number of natural substances, plants, and animals and human organs. Iron was the first trace or minor element recognized as being necessary for both plants and animals. Manufactured iron always contian carbide, phosphate, manganese, silicide, and graphite. 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 anemia.

The oxidation state encountered in compounds of iron ranges from 0 to + 6. however, the most common compounds are those of iron (III) and iron (II). In complex compounds iron (II) may be tetracoordinate (e.g $FeCl_4^{-2}$ with tetrahedral configuration), though more often it has coordination number six, e.g. in the octahedral complexes $Fe(H_2O)_6^{+2}$,

$Fe(CN)_6^{-4}$, $Fe(Phen)_3^{+2}$ and sometimes even eight (oxyhemoglobin and carbonyl hemoglobin). The complexes of iron (III) are also more often octahedral as exemplified by $Fe(acac)_3$, $Fe(CN)_6^{-3}$, $Fe(H_2O)_6^{+3}$ and $FeCl_4(H_2O)_2^-$. The tetrahedral complex $FeCl_4^-$ exists in the medium of concentrated hydrochloric acid (4,5). The coordination number of iron (III) in the complex Fe(EDTA) $(H_2O)^-$ is seven (6).

Cobalt in widely distributed in nature making up about 0.001% of the igneous rocks of the earth's crust. It occurs in meteorites, stars, sea and fresh waters,soils, plants and animals. Traces of cobalt are found in many ores of iron, nickel and zinc, but the most important cobalt ores are cobaltite (CoAsS), saltite ($CoAs_2$), erythrite [$Co(AsO_4)_2 \cdot 8H_2O$], and wad (Co_3S_4). Th most important commercial application of cobalt is in making of alloys. Cobalt and its alloys are wear and corrosion resistant even at higher temperature.

The oxidation state of cobalt in its compounds is most frequently +2 and +3. The octahedral complex $Co(H_2O)_6^{+2}$, which is the form of cobalt (II) encountered in solution, has a pink color. The blue tetrahedral complexes, e.g. $Co(H_2O)Cl_3^-$, $CoCl_4^{-2}$ and $Co(SCN)_4^{-2}$ which are considerably dissociated in aqueous medium, begin to predominate at about $[Cl^-] > 9$ M and $[SCN^-] > 3$M, respectively, or when the relative permittivity is decreased by the addition of organic solvents, such as acetone. The octahedral complexes or those with planar configuration are less common.

The most commonly used methods for determination of iron and cobalt are gravimetric (2,7,8), volumetric (7,8), spectrophotometric (7,9-12) and atomic absorption spectroscopy (13,14). Of these methods, spectrophotometry coupled with solvent extraction are the most widely used, which have also been employed in the present investigation. Hence, the basic features of spectrophotometry and solvent extraction are briefly discussed.

1.1 Spectrophotometry

Spectrophotometric methods are based on the measurement of the absorbance for monochromatic light passing through the solution containing the substance to be determined. Provided that the thickness of the absorbing layer, l, and the absorption coefficients, ε_λ, of the substance being determined at a given wavelength are known and the absorbance, A, is measured, it is possible to use Beer-Lambert law in order to determine the unknown concentration, C.

Spectrophotometric methods are commonly used for the determination of inorganic substance with organic reagents (7,8,12,15,16). The realiability 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: $\lambda_{(\text{product})\max} - \lambda_{(\text{reagent})\max} \geq 100$ nm. The reagent for which $\lambda_{(\text{product})\max} \simeq \lambda_{(\text{reagent})\max}$ are less suited for spectrophotometry and are applicable only when the absorption coefficients differ by a factor of at least 2.

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 in color, the molecule of the complex formed or the organic reagent itself must contain chromophoric groups which are characeterized by transitions with molar absorption coefficients in the range 10^3-10^5 l mol^{-1} cm^{-1}. Such chromophoric groups are found among d-π and π-chromophores. The complexes with d-π chromophores are restricted in use to the transition elements, in particular those which can exist in two oxidation states differing by an electron.

The reagent with π-electron groups are most frequently employed in analytical applications. The main reason can be found in the intensity of the transitions (with molar absorption coefficients up to 10^5 l mol^{-1} cm^{-1}) which characterize these chromophoric groups. The selectivity and sensitivity of spectrophotometric method can be increased by introducing suitable substituents into the molecules of the organic reagents.

1.2 Spectrophotometric Determination of Metal Ions

Complexation Reactions: Spectrophotometric determination of metal ions is based on the formation of metal complexes.

The formation of a stable metal complex requires the presence of acidic or basic analytical functional group in the molecule of the reagent, preferably in those positions which allow the formation of a five or six membered chelate ring. Coloured 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.

The complex forming properties of organic reagents can be influenced by introducing suitable substituents into their molecules. The stability of the complex is usually increased by higher basicity of the ligand. When a bulky substituent is close to the functional grouping, the reactivity of the reagent may be decreased or even lost, owing to the steric effect. In this manner it is sometimes possible to increase the selectivity of the reagent. For example, 1-10-phenanthroline forms coloured complex with iron (II) but when methyl groups are introduced in the positions 2 and 9 a reagent is obtained which no longer forms the iron (II)-tris complex. When phenyl groups are introduced in the positions 4 and 7 the absorption maxima is shifted to longer wavelength (533 nm) in comparison with analogous complex of the parent compound having absorption maxima at 510 nm. At the same time, the molar absorption coefficient of the bathophenanthroline complex is twice that of the phenanthroline complex.

A similar example is given by the complex of N-phenylcinnamohydroxamic acid with iron (III). Here the absorption maxima remains the same as that of the parent compound (N-phenylbenzohydroxamic acid) but the molar absorption coefficient is highly increased.

Completeness of Complexation Reaction: Both the accuracy and precision of a photometric determination depends on the completeness of a given reaction. As the reaction solution usually contains components competing in the reaction (buffering and masking agents), it is necessary to consider the conditional constant for the general complexation equilibrium.

$$M + nL \rightleftarrows ML_n \qquad [1]$$

on which the determination is based:

$$\beta'ML_n = \frac{[ML_n]}{C'_M(C'_L)^n} = \frac{\beta_{MLn}}{\alpha_M\alpha_L^n} \qquad [2]$$

where C'_M is total concentration of the metal ion unconsumed in the formation of the complex ML_n, C'_L is total concentration of the ligand unconsumed in the formation of the complex ML_n, α_M and α_L are side reaction coefficients of the metal ion and the ligand, respectively.

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

$$\frac{[ML_n]}{C'_M} = \beta'ML_n(C'_L)^n \geq 10^2 \qquad [3]$$

This expression can be used for the calculation of the necessary minimum excess of the reagent required for the completeness of the reaction.

The Selectivity of Photometric Determination: 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 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.

In the determination of a metal M in the presence of another metal N, if both form colored complexes $ML_n(\beta'_{MLn})$ and $NL_n(\beta'_{NLn})$ 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 the absorbance values of the two complexes, provided that the colorimetric reagent itself does not absorb at the wavelength used:

$$\frac{A_{MLn}}{A_{NLn}} = \frac{\varepsilon_{MLn}[MLn]}{\varepsilon_{NLm}[NLn]} \geq 10^2 \qquad [4]$$

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:

$$\frac{[NL_n]}{C'_N} = \beta'_{NLn}(C'_L)^n \leq 10^{-2} \qquad [5]$$

Combinations of Equations 3 and 5 gives:

$$\frac{\beta'_{MLn}}{\beta'_{MLn}} \geq 10^4 \qquad [6]$$

If the absorption maxima of the two complexes are at different wavelengths, it is possible to determine both M and N by measuring the absorbance at the wavelengths where the differences in absorbance for the two complexes are maximal, and by solving the appropriate simultaneous equations.

Selectivity can often be increased by extraction of the reaction product. Thus it is possible to separate the components to be determined from other interfering substances. Usually a lower limit of determination can be obtained, because the measured compound can be concentrated in the organic phase by use of a suitable volume-ratio. Thus, extraction methods are very vital in inorganic analysis and are superior for the most part to other methods of separations.

1.3 Precision of Photometric Determination

In 1939 Ringbom introduced a method of plotting spectrophotometric data in which % transmittance (or % absorbance) is plotted against the logarithsm of concentration. When these functions are plotted a sigmoid or S-shaped curve is obtained. Ringbom has showed that the accuracy is greatest when the relation:

$$\frac{\Delta C/C}{\Delta T} = \frac{2.303}{\Delta T/\Delta \log C} \qquad [7]$$

reach a minimum ie. at the point of the steepest slope ($\frac{\Delta C/C}{\Delta T}$ is the relative analysis error and $\Delta T/\Delta \log C$ 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 trangency 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.

1.4 Spectrophotometric Methods for Determination of Composition of Complexes

Method of Continuous Variations: The principle of the method is that the mole fraction of the metal ion and ligand is varied between 0 and 1 at constant total concentration, $C = C_L + C_M$, and the absorbance of the solutions of different composition is measured. The absorbance are then plotted against the mole fraction, X_L, of the ligand. If only one complex species has been formed, with composition ML_n, and the absorbance is measured at a wavelength where neither the metal ion nor the ligand but rather only the complex absorbs, then n can be calculated from the abscissa of the maximum of the curve (X_{max}):

$$n = \text{number of ligand} = \frac{X_{max}}{1-X_{max}}$$

absorbance in the presence of excess concentration of auxiliary ligand. Equation 10 can be written as:

$$\log \frac{A-A_{min}}{A_{max}-A} = \log K+n \log [X] + m \log[HL]+m\,pH \qquad [11]$$

Thus, the slope of the curve obtained by plotting $\log \frac{A-A_{min}}{A_{max}-A}$ against log [X] give the number, n, of the auxiliary ligand, X.

1.5 Solvent Extraction

Solvent extraction is the partition of one or more components between two liquids of limited miscibility (17-23). 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 substance. Inorganic constituents are often separated from an aqueous solution to water immiscible organic solvents through the formation of complexes which may be applied to direct analysis by spectrophotometry, gas chromatography, atomic absorption, radiochemical, or other suitable methods.

The thermodynamic condition for a heterogenous equilibria which takes place in partitioning of a substance M between two phases is that the chemical potential μ_M of the substance is equal for the two phases:

$$(\mu_M^0)_I+RT\ell n(a_M^0)_I = (\mu_M^0)_{II}+RT\ell n(a_M^0)_{II} \qquad [12]$$

The quantities $(\mu_M^0)_I$ and $(\mu_M^0)_{II}$ are the standard chemical potentials and $(a_M)_I$ and $(a_M)_{II}$ the activities of substance M in phases I and II, respectively.

In analytical applications the liquid-liquid partition equilibria, which are commonly called extraction equilibria, usually takes place between an aqueous solution (phase I, subscript aq) and an organic solvent (phase II, subscript org) which is immiscible with water. Equation 12 can then be rearranged to give:

$$(\mu_M^0)_{aq} - (\mu_M^0)_{org} = -\Delta G_{D,M} = RT\ell n\frac{(a_M)_{org}}{(a_M)_{aq}} = RT\ell n(K_{D,M})_a \qquad [13]$$

Hence such a partition equilibrium can be characterized by the thermodynamic equilibrium constant $(K_{D,M})_a$.

For practical applications it is necessary to covert the thermodynamic constant $(k_{D,M})_a$ into the concentration partition constant $k_{D,M}$ (called the distribution constant)

$$k_{D,M} = \frac{[M]_{org}}{[M]_{aq}} = k_{D,M}\frac{(a_M)_{aq}}{(a_M)_{org}} \qquad [14]$$

where $[M]_{org}$ and $[M]_{aq}$ represent the equilibrium molar concentrations of the substance M in the particular phase.

Because of its ease, simplicity, speed and wide scope, solvent extraction enjoys a favoured position among the separation techniques.

Extraction systems are classified according to different criteria (8):

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

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

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

d. the kinetics of extraction.

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

If the use of organic reagents is considered for extractions applied in inorganic analysis, the most reasonable classification is that given under (b), in which the extraction systems of chelate compounds and ion-associated are distinguished. The present investigation is based on the extraction of ion-association complexes;hence, the fundamentals of ion-association complexes and their extraction are briefly described in the following section.

1.6 Solvent Extraction of Metal Chelates

If a metal is extracted from an aqueous solution into an organic solvent, the metal ion is transferred across the liquid-liquid boundary as an uncharged particle which can be either an electroneutral complex formed with the organic reagent or an ion-association complex. The extraction of a metal M with the extraction reagent HL, forming a chelate ML_n soluble in an organic solvent, is expressed by the equilibrium:

$$M_{aq} + nHL_{org} \rightleftarrows ML_{n,org} + nH^{+}_{aq} \qquad [15]$$

which is characterized by the extraction constant:

$$K_{ex} = \frac{[ML_n]_{org}[H^+]^n_{aq}}{[M]_{aq}[HL]^n_{org}} = \frac{k_{D,M}\,\beta_n}{(k_{D,L}\beta_{HL})^n} \qquad [16]$$

As shown in Equation 16, 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.

In liquid-liquid partition, a substance M can undergo in both phases various solvation, association, protonation, and complexation equilibria. 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 M in the two phases:

$$D_M = \frac{[M]_{org}}{[M]_{aq}} \qquad [17]$$

This quantity is called the distribution ratio.

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

$$E_M = \frac{100[M]_{org}\,V_{org}}{[M]_{org}\,V_{org}+[M]_{aq}V_{aq}} = \frac{100D_M}{D_M+\frac{V_{aq}}{V_{org}}} \qquad [18]$$

which is the fraction of the substance extracted from the aqueous phase into the organic solvent.

The expression in Equation 16 can, thus be written for the extraction of the chelate ML_n as:

$$D_M = k_{ex} \left(\frac{[HL]_{org}}{[H^+]aq}\right)^n \qquad [19]$$

or

$$\log D_M = \log k_{ex} + n \log[HL]_{org} + npH \qquad [20]$$

As shown in Equation 20, the value of the extraction constant also depends on the concentration of the extracting reagent and the pH of the solution.

The distribution ratio D_M can also be influenced by other factors such as temperature, ionic strength, and kinetics of extraction, which are not explicitly expressed by the quantities in Equation 19. Generally, a change in the temperature changes the value of an equilibrium constant, but it is not possible to predict how it will effect the value of K_{ex}.

There is no general rule for predicting the effect 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.

There is no kinetics effect involved in the value of D_M, provided the distribution ratio has been determined for an equilibrium state.

1.7 Ion-Association Complexes

A decrease in the relative permittivity of the medium usually brings about an increase in the forces of interionic attractions and consequently, various ionic aggregates are formed. The formation of ion-association complexes can be interpreted with the aid of Bjerrum's theory as modified by Fuoss (24). The forces acting between two spherical non-polarizable ions of opposite charge are assumed to be purely coulombic in nature, depending on the relative permittivity, ε, of the medium. If these ions approach at least to the distance, d, as given by the following expression:

$$d = \frac{|Z_+Z_-|e^2}{2\varepsilon KT} \qquad [21]$$

where K is Boltzmann's constant, an ion-association complex can be formed, e.g. by the reaction

$$A^+ + B^- \rightleftarrows [A^+,B^-] \qquad [22]$$

The equilibrium constant of this association equilibrium is given by:

$$(K_{assoc})_a = \frac{a_{A^+B^-}}{a_{A^+}a_{B^-}} = \frac{[A^+,B^-]}{[A^+][B^-]} \frac{\gamma_{A^+B^-}}{\gamma_\pm^2} \qquad [23]$$

The formation of ion-association complexes can thus be treated in the same manner as complexation equilibria. The same analogy holds for the association constant $(K_{assoc})_a$, which can be calculated according to Bjerrum as follows:

$$(K_{assoc})_a = \frac{4\Pi N}{1000}\left(\frac{/Z+Z-/e^2}{\varepsilon KT}\right)^3 Q(b) \qquad [24]$$

where Q(b) is a function of the shortest distance, a, to which the ions forming the complex can approach each other, since $b = /Z_+ Z_-/e^2/ a\varepsilon KT$. If a = d, then b = 2 and Q(b) = 0, so that no ion-pair is formed, because the ions have not reached the distance apart required by Equation 21.

The formation of ion-association complexes is applied in extraction separation based on liquid-liquid partition. The application of theoretical values of $(K_{assoc})_a$ in analytical chemistry is rather difficult, because the value of the activity coefficients are usually not known for the fairly concentrated solutions of electrolytes in which the ion-association complexes are formed. In these solutions the activity coefficients are considerably influenced by the concentration and the kind of ions.

1.8 Extraction of Ion-Association Complexes

The extraction of chelates is based on the consideration of a very simple model extraction system for which the dependence of D_M on the extraction constant, the concentration of the reagent, and the pH value is given by:

$$D_M = K_{ex} \left(\frac{[HL]_{org}}{[H^+]} \right)^n \qquad [25]$$

For similar treatment of the extraction of ion-association complexes perrhenate and tetraphenylarsonium chloride may be used as model substances. It is thus necessary to assume that only the following equilibria are involved:

Organic

Aqueous

$$\begin{tikzcd}
 & (R_4As^+, Cl^-)_{org} \arrow[d, shift left, "K_{D,L}"] & & (R_4As^+, ReO_4^-)_{org} \arrow[d, shift left, "K_{D,M}"] \\
R_4As^+ + Cl^- \arrow[r, shift left, "K_L"] & (R_4As^+, Cl^-)_{aq} \arrow[l, shift left] \arrow[u, shift left] & ReO_4^- + R_4As^+ \arrow[r, shift left, "K_M"] & (R_4As^+, ReO_4^-)_{aq} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

where $R = C_6H_5$.

If the reagent were completely associated in the organic phase and partially dissociated in water, and if the extracted metal were present in the organic phase only in the form of a monomeric association complex and in the aqueous phase as the anion ReO_4^-, the expression for D_{Re} would take the form:

$$D_{Re} = \frac{K_{D,M} \cdot K_M}{K_{D,L} \cdot K_L} \cdot \frac{[(R_4As^+, Cl^-)]_{org}}{[Cl^-]} \qquad [26]$$

However, no real association system behaves in accordance with this simple expression, because it usually involves many other complicated equilibria. The reagent may be dissociated in the organic phase to some extent or may polymerize at higher concentrations, or even be more soluble in water than in the organic solvent. The ion-association complex can undergo dissociation or polymerization in which large aggregates can be formed. The formation of higher aggregates can occur to a considerable extent in the aqueous phase. The association constant can be expressed not only by the law of mass action as:

$$\frac{[R_4As^+, ReO_4^-]}{[R_4As^+][ReO_4^-]} \qquad [27].$$

which reflects the chemical nature of this process, but also by the expression in Equation 21, characterizing the electrostatic nature of the interaction. According to this expression the stability of the complex is increased by decrease in the size of the ions forming the ion-pair. In practice, it is large ions that usually form ion-association complexes.

The expression in Equation 21 also indicates that the stability of the complex, and hence the value of D_M increases when the relative permittivity of the medium is low. In other cases, the ion-association complex, after transfer across the phase boundary dissociates again. It is then more advantageous to use solvents with high relative permittivity.

1.9 Literature Survey

A large number of organic reagents are recommended for the separation, detection, and determination of iron. Just to mention a few of the common organic reagents that are used for spectrophotometric determination of iron are 2,2'-bipyridyl (25), cupferron, 5-methoxy-2-nitrosophenol, and 2,4,6-tri-2-pyridyl-s-triazine (7), 4,7-diphenyl-1,10-phenanthroline (26), 4,7-diphenyl-1,10-phenanthroline disulphonic acid, disodium salt (27), 1,10-phenanthroline (28), isonitrosodimethyldihydroresorcinol (29), 2-(2-pyridyl)-imidazoline (30), 2,2'-dipyridyl ketone-2-pyrimidylhydrazone (31), 2-(p-sulphophenylazo)-1,8-dihydroxynaphthalene 3,6-disulphonic acid (32), 4-(4-methyl-2-thiazolylazo) resorcinol (33), 2,2'-dipyridyl-2-benzothiazolylhydrazone (34), 2-4-dihydroxyacetophenonesemicarbazone (35), as mixed ligand complex with chromeazurols and cetyltrimethylammonium (36), 1,10-phenanthroline and picrate (37), etc.

Thiocyanate used to be, owing to its availability at cheap cost, the most frequently employed reagent for the spectrophotometric determination of iron (38-44). However, the results obtained by the thiocyanate method depend considerably on the exact adjustment of the experimental conditions.

The organic reagents commonly used for the spectrophotometric determination of cobalt are chromazurol S(45), dithizone (46), 1-nitroso-2-naphthol (47), 2-nitroso-1-naphthol (48), nitroso-R-salt (49), 2,2':6,2" terpyridine (50), 3-(o-acetophenyl)-1-methyltriazene N-oxide (51), 2-(p-sulphophenylazo)-1,8-dihydroxynaphthalene 3,6-disulphonic acid (32), benzyl-2-pyridyl ketone-2-pyridylhydroxy-2-acetonaphthoneoxime (54), etc. Thiocynate is also commonly used as a spectrophotometric reagent for cobalt (9-11). It may also be extracted into ketones, alchols, and esters.

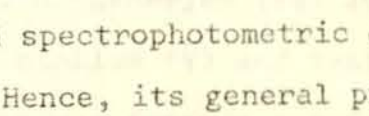
Of the several spectrophotometric reagents recommended comparatively few are well suited for the simple, precise, sensitive, and selective determination of iron and cobalt. Hence, search for the better reagent for iron and cobalt still continues.

The introduction of a third component into a binary complex leads to the formation of a ternary system with advantageous properties (55,56). Generally, the formation of these ternary systems cause a change in properties such as solubility in water and organic solvents and extraction rate, and variation in position and height of the absorption maxima. This allows higher sensitivity and selectivity of determination to be achieved. Recently spectrophotometric methods for the determination of iron based on ternary complex formation has been reported (57-59). The tetrathiocyanatocobaltate (II) can also be extracted as an ion-pair with neotetrazolium chloride (60), propylene carbonate (61) triphenylsulphonium chloride (62).

In the present investigation N-phenylcinnamohydroxamic acid, which has become a popular chelating agent in recent years, has been selected as the main reagent for the extraction and spectrophotometric determination of iron and cobalt. Hence, its general properties and analytical applications are briefly reviewed.

1.10. General Properties and Analytical Applications of N-Phenylcinnamohydroxamic Acid

N-phenylcinnamohydroxamic acid, I, contains an acid group with replaceable hydrogen atom and a basic coordinating group in such a position so as to form a five membered ring, II, on reaction with metal ions.



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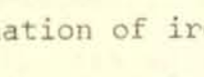


II

N-Phenylcinnamohydroxamic acid was first synthesized by Majumdar and Mukherjee in 1960 (63). It is a pale green crystalline solid, with melting point 159 - 160°C. It is stable towards heat, light and air, and can be stored indefinitely without deterioration. It is a weak acid and its acid dissociation constant has been found to be 1.6×10^{-9} (64). It is stable towards the action of dilute solutions of mineral acids and alkalies, and decomposes in concentrated nitric and sulphuric acid solutions (65). It is slightly soluble in water and fairly soluble in common organic solvents such as alcohol, ethylacetate, chloroform and benzene. Its solution in organic solvents is light yellow and stable for several days if properly stored.

N-Phenylcinnamohydroxamic acid, PCHA, was introduced as an analytical reagent for the first time in 1960 by Majumdar and Mukherjee (66) for the gravimetric determination of niobium (V) and tantalum (V). Its analytical application was further extended for the extraction and spectrophotometric determination of vanadium (V) (67), titanium (IV) and niobium (V) (68), zirconium (IV) and hafnium (IV) (69), and the successive extraction and spectrophotometric determination of iron (III), vanadium (V) and uranium (VI) (70). It has also been used for the gravimetric determination of uranium (71) and zirconium (72). Recently PCHA has been used for the successive extraction and spectrophotometric determination of iron (III) and vanadium (V) (73), for the extraction and spectrophotometric determination of vanadium (V) as a mixed ligand complex with thiocyanate (74) and p-chlorophenol (75), and for the simultaneous determination of iron (III) and vanadium (V) by solvent extraction and spectrophotometry (76).

1.11 Aim and Scope of Present Investigation

The foregoing discussions reveal that PCHA has been used for the extraction and spectrophotometric determination of iron (III) as a binary complex (70,73). It has also been reported that iron (III) is extracted into nonpolar organic solvent only as a binary complex with PCHA even in the presence of thiocyanate (76). However, no attempt has been made to study the mixed complex formation of iron (III) with PCHA and thiocyanate in relatively polar solvents. Also no attempt has been made to study the reaction of cobalt (II) with PCHA both in the absence and presence of thiocyanate and the extraction of iron (III) with PCHA from the azide medium.

Thiocyanate is commonly used as a spectrophotometric reagent for the determination of iron(III) (38-44) and cobalt (II) (9-11). However, both methods suffer from the serious interferences of many metal ions which are commonly associated with iron and cobalt in alloys and complex materials. Furthermore, iron (III)-thiocyanate coloured system is not very stable and requires strict control of experimental parameters while the cobalt (II)-thiocyanate coloured system is not sensitive and cannot be used for the determination of traces of cobalt. Although iron (III) and cobalt (II) form different coloured complexes with thiocyanate, no attempt has been made for the simultaneous determination of the two metal ions by spectrophotometry.

Therefore, from the point of view of occurance, abundance and importance, the development of a new method for the simultaneous determination of iron (III) and cobalt (II) needs no comment. It is also worthwhile to study the extraction of iron (III) with PCHA from the azide medium due to its similarity with thiocyanate.

Hence, in the present investigation, the extraction of iron (III) and cobalt (II) with PCHA from thiocyanate medium has been studied in detail in different experimental condition to develop a new method for the simultaneous determination of the two metal ions by spectrophotometry. The extraction of iron (III) with PCHA from azide medium has also been studied in detail to develop a new spectrophotometric method for determination of iron (III).

The present investigation has led to the development of a simple, precise, and selective method for the simultaneous determination of iron (III) and cobalt (II) with PCHA in the presence of thiocyanate by solvent extraction and spectrophotometry. It has also been resulted in the development of a simple, precise, and selective method for the extraction and spectrophotometric determination of iron (III). Both the methods are applicable to the analysis of iron and cobalt in alloys, steels, and biological samples.

2. EXPERIMENTAL

2.1 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 CHEM-MATE pH meter was used for pH measurements.

Standard Iron (III) Solution: A standard solution of iron (III) was prepared by dissolving 4.0402 g iron (III) nitrate nonahydrate (BDH, 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 (7). A working solution was prepared by diluting a suitable aliquot of the standard solution to a known volume with distilled water.

Standardization of Fe (III) Solution: 25-ml of iron (III) solution was taken 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 content of the flask was warmed to 40°C, and titrated with (0.01M) EDTA solution until the initial blue colour of the solution turned yellow with the final drop 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 (7).

Standardization of Co(II) Solution: 25 ml of cobalt (II) solution was taken 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 content of the flask was warmed to 40°C, and titrated with (0.01M) EDTA solution until the initial red color of the solution turned yellow with the final drop of the reagent.

Reagent Solution: N-Phenylcinnamohydroxamic acid, PCHA, was prepared by the condensation of N-Phenylhydroxylamine with cinnamoyl chloride at low temperature in diethylether medium made alkaline with aqueous suspension of sodium carbonate.

A 0.005 M solution of PCHA in twice distilled ethylacetate was used for the extraction of the metal ions.

Standard Thiocyanate Solution: A 4.0 M standard solution was prepared by dissolving ammonium thiocyanate (Hopkins and Williams, AnalaR) in distilled water and standardized by Volhard method (77).

Standardization of Thiocyanate Solution: 25 ml of the standard 0.1M silver nitrate solution was transferred into a conical flask, 5 ml of 6M nitric acid and 1 ml of iron (III) indicator was added to it. Ammonium thiocyanate was run in from the burette until a faint brown colour was produced which no longer disappeared on shaking.

Standard Azide Solution: A 2.0 M standard solution was prepared by dissolving sodium azide (Hopkins and Williams, AnalaR) in distilled water.

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 wherever necessary to prevent hydrolysis. In general nitrate salts were used for the cations and sodium or ammonium salts were used for the anions.

Solution of Electrolyte: A 4.0 M standard solution of potassium nitrate (BDH, AnalaR) in distilled water was used for adjusting the ionic strength of the solutions.

Solvents: Ethylacetate (Riedel-deHaen) was purified by distillation discarding the first and the last fractions. It was used only after distilling twice. Once used, it was recovered by distillation and used again. All other solvents were used after a single distillation.

Drying Agents: Anhydrous sodium sulphate and calcium chloride were used for drying the colored extracts and the distilled solvents, respectively.

Hydrochloric Acid: Concentrated hydrochloric acid (BDH, AnalaR) was used for adjusting the acidity of the solutions.

2.2 Preparation of Sample Solutions

Blood Sample: A 2 ml aliquot of blood sample was transferred into a 250-ml Kjeldhal flask and decomposed with 10 ml of nitric, sulphuric, and perchloric acids in the ratio of 3:1 :1 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 50-ml volumetric flask and diluted to volume with distilled water (13). A suitable aliquot was taken for the analysis.

Vitamin B_{12}: A weighed quantity (0.2g) of the vitamin B_{12} was transferred into a 250-ml Kjeldhal flask and decomposed with 20 ml of aqua-regia. The mixture was heated for one hour and 15 ml of 1 N hydrochloric acid was added to it. The solution was evaporated to almost dryness, cooled, and boiled with 50 ml of distilled water. The undissolved matter was filtered off 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) (78). A suitable aliquot was taken for the analysis.

Steel Samples: A weighed quantity (approximately 0.1 g) of the steel sample was transferred into 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 tungstic acid. The undissolved silica and tungstic acid were filtered off and washed several times with hot distilled water. The filtrate and washings were collected into a 500-ml volumetric flask and diluted to volume with distilled water. A suitable aliquot was taken for the analysis.

2.3 General Procedure for Extraction of Iron (III) and Cobalt (II) from Thiocyanate Medium

An aliquot of the solution containing 10-90 µg of iron (III) or 100-600µg of cobalt (II) or both metal ions was transferred into a 100-ml separatory funnel and 5 ml of 4 M ammonium thiocyanate was added to it. The acidity and volume of the aqueous phase were adjusted to 0.5 - 1.5M and 10 ml with concentrated hydrochloric acid and distilled water, respectively. A 10 ml aliquot of 0.005 M PCHA in ethylacetate was added to the funnel and the mixture was shaken vigorously for about one minute. The funnel was allowed to stand to separate the two phases. The organic phase was collected in a 50-ml beaker containing about 3 g of anhydrous sodium sulphate. The aqueous phase was washed with 5 ml of the reagent followed by 5 ml of ethylacetate. The coloured extract was transferred into a 25-ml volumetric flask and the beaker was washed with a few ml of ethylacetate. The washings were added to the flask and diluted to volume with ethylacetate. The absorbance of the colored solution was measured at 495 nm for the determination of iron (III), at 625 nm for the determination of cobalt (II), and at both wavelengths for the simultaneous determination of both metal ions against the reagent blank.

For calibration, 0.25, 0.50, 1.0, 1.50 and 2.00 ml of the standard solution (50 µg ml^{-1} Fe(III) or 0.6 mg ml^{-1} Co(II) were used through the procedure.

2.4 General Procedure for Extraction of Iron (III) from Azide Medium

An aliquot of the solution containing 25-175 µg of iron (III) was transferred into a 100-ml separatory funnel and 5 ml of 2 M sodium azide was added to it. The acidity and volume of the aqueous phase were adjusted to 0.4-0.6 M and 10 ml with concentrated hydrochloric acid and distilled water, respectively. A 10 ml aliquot of 0.005 M of PCHA in ethylacetate was added to the funnel and then proceeded as the extraction of iron (III) from thiocyanate medium. The absorbance of the colored solution was measured at 447 nm against the reagent blank.

For calibration 0.50, 0.75, 1.00 and 1.50 ml of the standard solution (100 µg ml^{-1} Fe(III) were used through the procedure.

2.5 Procedure for Studying Effect of Variables

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

The quantitative extraction of iron (III) from the aqueous phase was examined by changing the variable parameter to its optimum condition and following the general procedure. The extraction was considered to be incomplete when iron(III) was found in the aqueous phase.

The quantitative extraction of iron (III) from the aqueous phase was also examined by using 2,2'-bipyridyl. The aqueous phase was reduced to about 1-2 ml by evaporation and 1ml of 0.1M hydroxylamine hydrochloride 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 and pH of the solution was adjusted to 10 ml and to 4-5, respectively. The absorbance was measured at 522 nm against reagent blank and the amount of iron (III) was calculated accordingly.

2.6 Procedures for Determination of Composition

In the continuous variations method a series of solutions was prepared for each system (Fe(III)-SCN-PCHA and Fe(III)-N_3-PCHA) in which the mole fractions of iron (III) and PCHA were varied between 0 and 1 at constant total concentration. The concentration of thiocyanate or azide, the ionic strength, and the acidity were kept constant under optimum conditions throughout the series. The complexes were extracted by the general procedures and the absorbance of the coloured extracts were measured at 447 and 495 nm against reagent blank and Fe(III)-SCN as blank (because Fe(III)-SCN complex absorbs strongly at 495 nm, the reagent blank was replaced by it) for Fe(III)-N_3-PCHA and Fe(III)-SCN-PCHA complexes, respectively. The absorbances were plotted against the mole fractions of PCHA in the two systems.

In the mole ratio method for Fe(III)-SCN-PCHA system a series of solutions was prepared in which the concentrations of iron (III) and thiocyanate, the acidity, and the ionic strength were kept constant and the concentration of PCHA was varied. The complex was extracted by the general procedure, the absorbance of the coloured extract was measured at 495 nm against Fe(III)-SCN as a blank, and plotted against the mole ratio of the metal to PCHA. Two straight lines were drawn from the two parts of the curves which intersect each other at a mole ratio of Fe:PCHA.

In the simple spectrophotometric method a series of solutions was prepared in which the concentrations of iron (III) and azide, the ionic strength and the acidity were kept constant and the concentration of PCHA was varied. The complex was extracted by the general procedure and the absorbance of the coloured extract was measured at 447 nm against the reagent blank (since Fe(III)-N_3 complex was not extractable,.

2.7 Procedure for Studying Effect of Foreign Ions

The effect of foreign ions was studied by adding known quantities of desired ion to solutions containing 50µg of iron(III), 100µg of iron (III) and 500µg of cobalt (II) in Fe(III)-SCN-PCHA, Fe(III)-N_3-PCHA, and Co(II)-SCN systems, respectively. Extraction and determination of the metal ions were made according to the general procedures.

3. RESULTS AND DISCUSSIONS

3.1 Colour Reaction

PCHA was found to react with iron (III) in the presence of thiocyanate or azide to form pinkish red and orange red coloured complexes, respectively. Both the complexes are readily extractable into ethylacetate from the HCl solutions. These sensitive color reactions formed the basis for the development of two new spectrophotometric methods for the determination of iron (III).

Cobalt (II) was found to react with thiocyanate both in the absence and presence of PCHA to form a blue colored complex which is readily extractable into ethylacetate from the HCl solution. The identical reaction condition of iron (III) and cobalt (II) with thiocyanate and PCHA and wide differences in the absorption spectra of the resulting complexes form the basis for the development of a new method for the simultaneous determination of the two metal ions by solvent extraction and spectrophotometry.

3.2 Choice of Solvent for Extraction

Several organic solvents such as benzene, toluene, chlorobenzene, chloroform, ethylacetate, amylacetate and amylalcohol were examined for the choice of proper solvent for extraction of the three complexes. It was found that both the Fe(III)-SCN-PCHA and Co(II)-SCN complexes were quantitatively extractable only into ethylacetate, amylacetate, and amylacohol while the Fe(III)-N_3-PCHA complex was extractable into all the solvents. These results indicate that the Fe(III)-SCN-PCHA and Co(II)-SCN complexes are relatively more polar than the Fe(III)-N_3-PCHA complex. The absorption spectra of the individual complexes were found to be similar in all the solvents in which the particular complex was extractable. However, slight variations in the intensity of the absorption bands were observed. Ethylacetate was found to be the most suitable solvent for the extraction of both the thiocyanato-complexes because the quantitative extraction of the complexes were readily accomplished in it. It was also preferred due to the higher sensitivity of the colour reactions in it than in other solvents. Although benzene, toluene, chlorobenzene and ethylacetate were found to be the suitable solvents for the extraction of azido-complex, ethylacetate was selected because of the carcinogenic nature of aromatic hydrocarbons and higher solubility of the reagent, PCHA, in it than in other solvents. The results are given in Table 1.

Table 1. Effect of Solvents on Extraction of the Complexes.

	ε_{max}, l mol^{-1} cm^{-1}, at λ_{max}		
	Co(II)-SCN complex	Fe(III)-SCN-PCHA complex	Fe(III)-N_3PCHA complex
Benzene	-	-	7650
Toluene	-	-	7690
Chlorobenzene	-	-	7450
Chloroform	-	-	7050
Ethylacetate	1820	18000	7500
Amylacetate	1760	16900	7290
Amylalcohol	1530	14500	6350

3.3 Absorption Spectra

The absorption spectra of the reagent, PCHA, and Co(II)-SCN, Fe(III)-SCN-PCHA, and Fe(III)-N_3-PCHA complexes have been determined in the visible region under different conditions. The reagent showed negligible absorption in the region 700-500 nm, slight increasing absorption in 500-400 nm region and strong absorption beyond 400 nm. Hence, a reagent blank was necessary for the precise measurements of absorbance at wavelengths shorter than 500 nm.

The Co(II)-SCN complex showed an absorption band at 625 nm with a shoulder at around 587 nm. The main absorption band can be assigned to charge transfer electronic transition from metal to the ligand while the weak shoulder is probably due to d-d electronic transition within the metal atom. The absorption spectra have been found to be identical both in the absence and presence of PCHA indicating the formation of a simple binary Co(II)-SCN complex under both conditions. Hence, PCHA was not involved in the complex formation with cobalt(II) in the presence of thiocyanate.

The simple Fe(III)-SCN complex showed a strong absorption band at around 490 nm. The absorption band was found to be affected by the presence of PCHA indicating the formation of a mixed ligand complex. The absorption band was intensified and shifted to 495 nm. Hence, the absorption spectrum of the Fe(III)-SCN-PCHA mixed ligand complex showed an intense absorption band at 495 nm which is due to charge transfer electronic transition from ligand to metal .

The red coloured Fe(III)-N_3 complex in aqueous solution showed an absorption band at 460 nm. However, the binary complex was found to be not extractable into organic solvents. It was only the ternary Fe(III)-N_3-PCHA that was found to be completely extractable into organic solvents. The absorption spectrum of the ternary complex showed an intense and sharp absorption band at 375 nm and a relatively weak and broad band at 447 nm which are due to π-π* and charge transfer (L --> M) electronic transitions, respectively. Although the absorption band at 375 nm is more intense the less intense absorption band at 447 nm was selected for the absorbance measurements because of the strong absorption of the reagent at shorter wavelength. Selected spectra are shown in Figure 1-3.

It has also been found that the absorption spectrum of species extracted into ethylacetate from aqueous solution of Fe(III) in the absence of thiocyanate or azide to be identical to that of PCHA solution itself. This result clearly indicates that there was no complex formation between Fe(III) and PCHA and Fe(III) cannot be extracted with PCHA into ethylacetate from acidic solutions in the absence of thiocyanate or azide.

The position of the absorption band of a particular complex was found to be not affected by the changes in the concentrations of the constituents and hydrochloric acid in a wide range indicating the extraction of a single complex species under each condition.

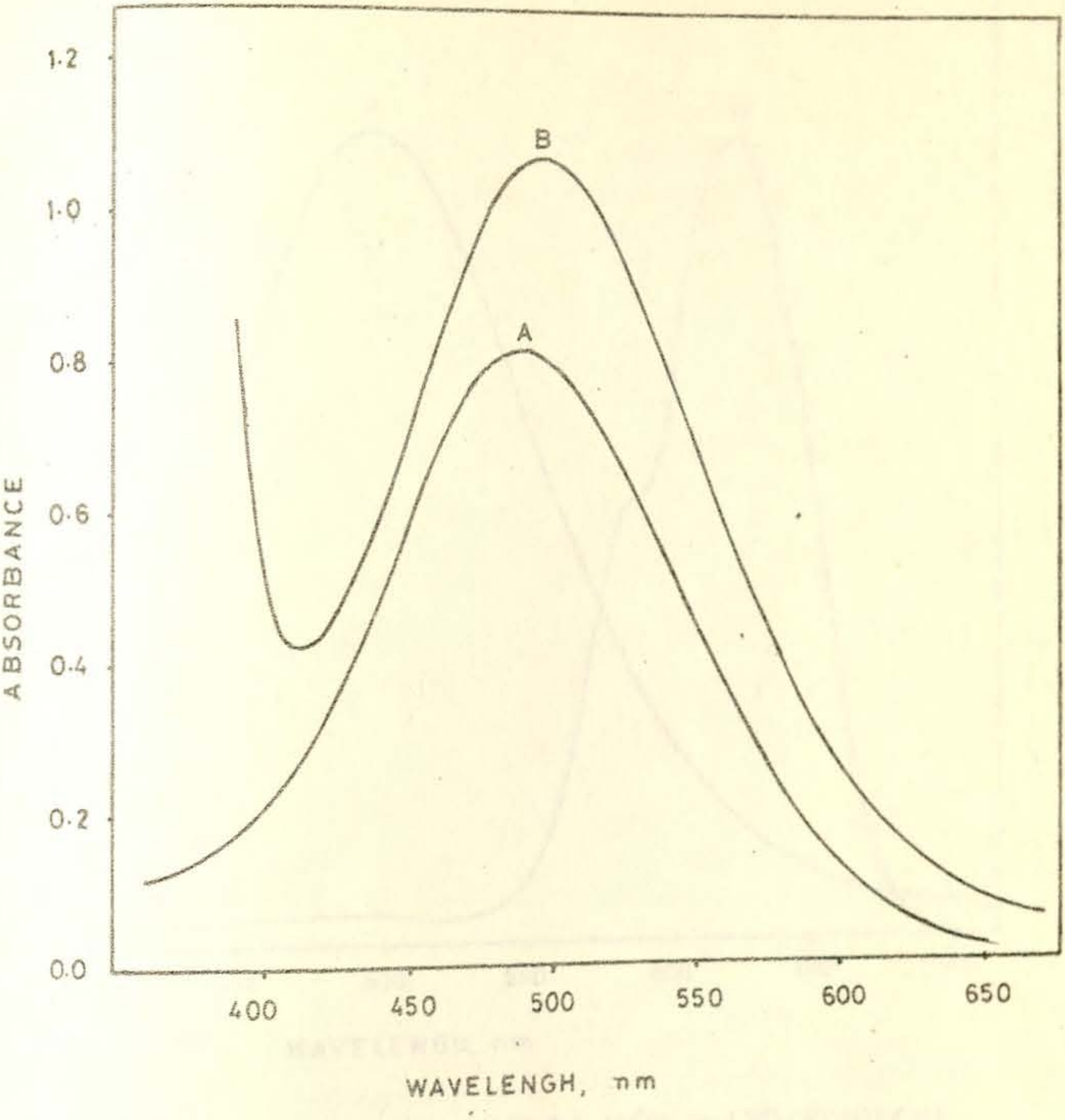


Figure 1. Absorption spectra of (A) 6.0×10^{-5}M Fe(III)-SCN complex (B) 6.0×10^{-5}M Fe(III)-SCN-PCHA complex against reagent blank in ethylacetate.

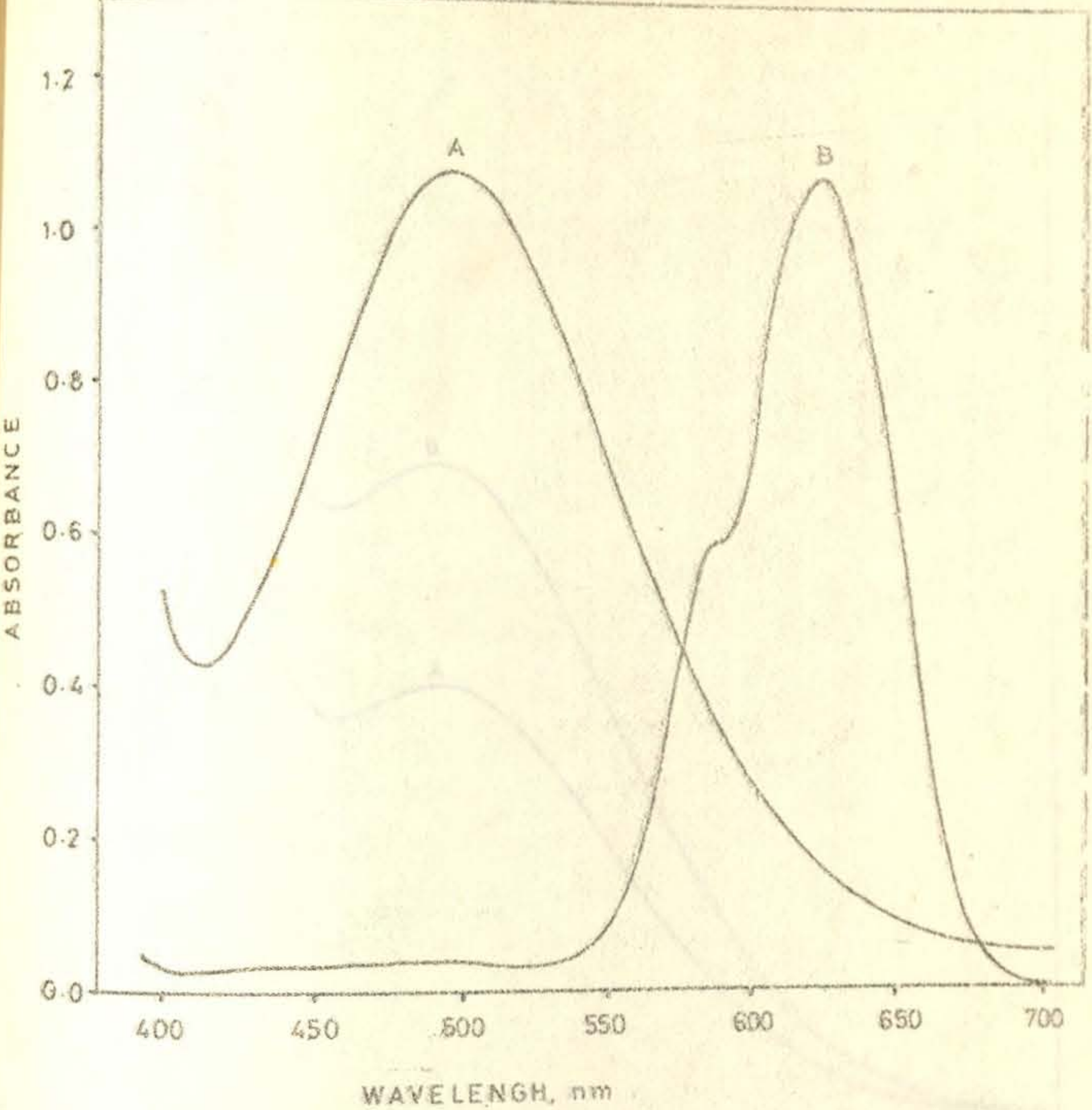


Figure 2 Absorption spectra of (A) 6.0×10^{-5}M Fe(III)-SCN-PCHA complex (B) 6.0×10^{-4}M Co(II)-SCN complex against reagent blank in ethylacetate.

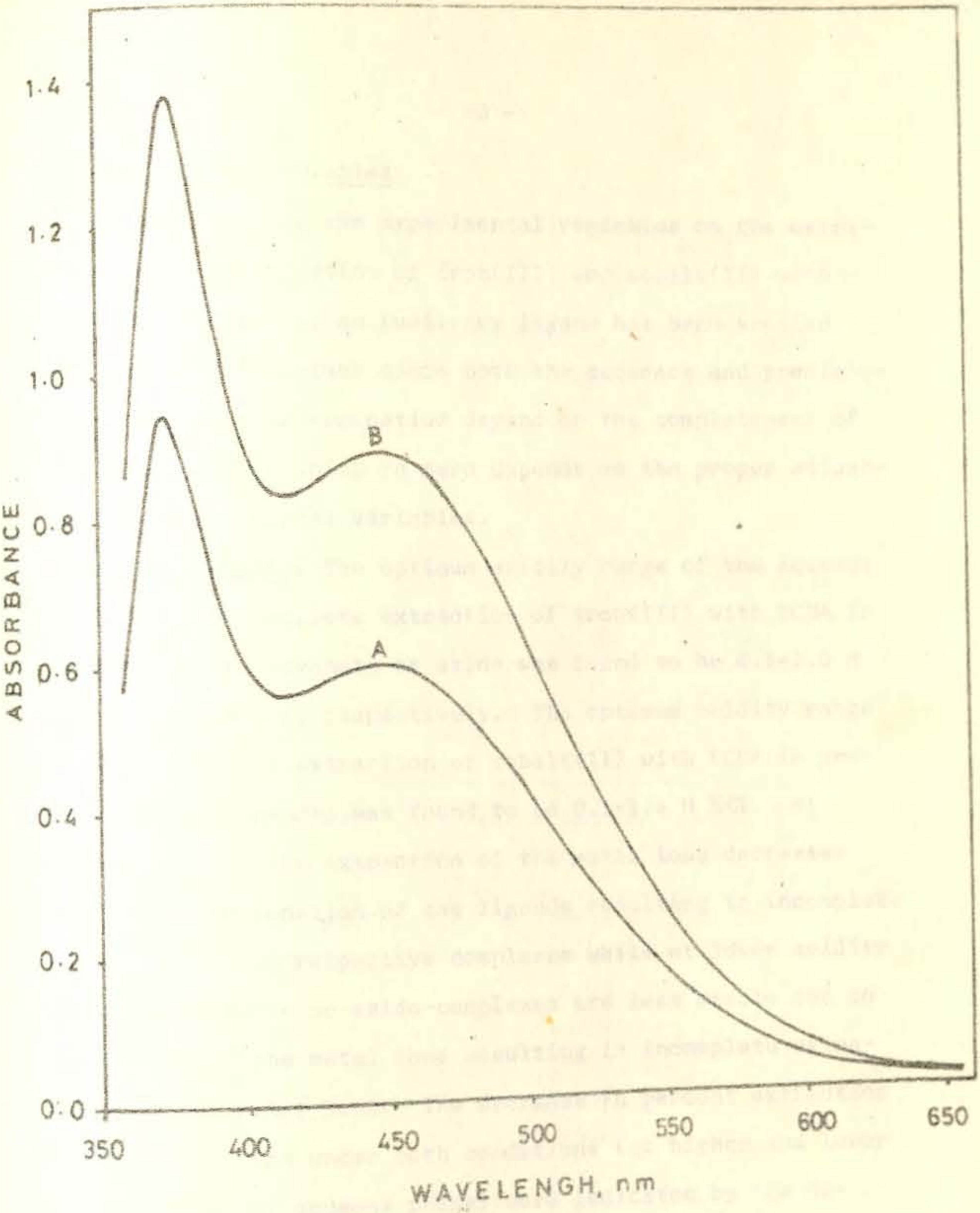


Figure 3 Absorption spectra of (A) 8.0×10^{-5}M Fe (III)- N_3-PCHA complex (B) 1.2×10^{-4}M Fe (III)- N_3 - PCHA complex against regeant blank in ethylacetate.

3.4 Effect of Variables

The effect of the experimental variables on the extraction and determination of iron(III) and cobalt(II) with PCHA in presence of an auxiliary ligand has been studied. This is very important since both the accuracy and precision of photometric determination depend on the completeness of a given reaction which in tern depends on the proper adjustment of experimental variables.

Effect of Acidity: The optimum acidity range of the aqueous phase for the complete extraction of iron(III) with PCHA in presence of thiocyanate or azide was found to be 0.5-2.0 M and 0.1-0.9 M HCl, respectively. The optimum acidity range for the complete extraction of cobalt(II) with PCHA in presence of thiocyanate was found to be 0.1-1.5 M HCl. At higher acidity the extraction of the metal ions decreases due to the protonation of the ligands resulting in incomplete formation of the respective complexes while at lower acidity the thiocyanato - or azido-complexes are less stable due to hydrolysis of the metal ions resulting in incomplete extraction of the metal ions. The decrease in percent extraction of the metal ions under both conditions (at higher and lower acidities of the aqueous phase) were indicated by the decrease in the absorbance value of the coloured extracts in the organic phase. The presence of metal ions in the aqueous phase at higher and lower acidities can easily be detected by changing the acidity to the optimum range. The results are given in Table 2 and 3.

Table 2. Effect of Acidity of the Aqueous Phase on the Extraction of Iron(III) and Cobalt(II) from Thiocyanate Medium $[Fe(III)] = 4.0 \times 10^{-5} M$, $[Co(II)] = 4.0 \times 10^{-4} M$.

Acidity of the aqueous phase	Fe(III)-SCN-PCHA System	Co(II)-SCN System
	Absorbance at 495 nm	Absorbance at 625 nm
pH=4	-	0.665
pH=3	-	0.694
pH=2	0.416	0.701
pH=1	0.676	0.717
0.5M HCl	0.724	0.715
1.0 M HCl	0.723	0.719
1.5M HCl	0.722	0.719
2.0M HCl	0.722	0.679
2.5M HCl	0.668	0.582
3.0M HCl	0.611	0.476
4.0M HCl	0.591	0.303

Table 3. Effect of Acidity of the Aqueous Phase on the Extraction of Iron(III) from Azide Medium $[Fe(III)] = 8.0 \times 10^{-5} M$

Acidity of the Aqueous phase, [HCl]	Absorbance at 447 nm
pH=2	0.510
0.1	0.602
0.2	0.603
0.3	0.601
0.4	0.605
0.5	0.602
0.6	0.603
0.7	0.602
0.8	0.604
0.9	0.602
1.0	0.483

Effect of Amount of Auxiliary Ligands: The optimum concentration range of thiocyanate or azide in the aqueous phase for the complete extraction of iron(III) was found to be 1.25-2.50M and 0.50-2.0M, respectively. The optimum concentration range of the thiocyanate for the complete extraction of cobalt(II) was found to be 1.50-3.0M. At lower concentrations of thiocyanate or azide the formation of iron(III) mixed ligand complex was incomplete. At higher concentrations of thiocyanate or azide, water soluble thiocyanato- or azido - complexes becomes stable resulting in an incomplete extraction of the metal. Similarly, at lower concentration of thiocyanate the formation of cobalt(II) simple complex was incomplete while at higher concentrations of thiocyanate, water soluble cobalt(II)-thiocyanate complex becomes stable resulting in an incomplete extraction of the metal ion. The decrease in percent extractions of the metal ions at lower or higher concentrations of thiocyanate or azide was indicated by the decrease in the absorbance values of respective systems. The results are given in Table 4 and 5.

Table 4. Effect of Concentration of Thiocyanate in the Aqueous Phase on the Extraction of Iron(III) and Cobalt(II).
$[Fe(III)] = 4.0 \times 10^{-5}M$, $[Co(II)] = 4.0 \times 10^{-4}M$, $[HCl] = 1.0M$

	Fe(III)-SCN-PCHA System	Co(II)-SCN System
$[SCN^-]$	Absorbance at 495 nm	Absorbance at 625 nm
0.10	0.094	–
0.20	0.260	–
0.30	0.403	0.052
0.40	0.497	0.118
0.50	0.582	0.165
0.75	0.655	0.423
1.00	0.703	0.561
1.25	0.724	0.656
1.50	0.722	0.724
2.00	0.726	0.723
2.50	0.723	0.719
3.00	0.687	0.721

Table 5. Effect of Azide Concentration in the Aqueous Phase on the Extraction of Iron(III)
$[Fe(III)] = 8.0 \times 10^{-5}M$, $[HCl] = 0.5M$

Concentration of	$Fe(III)-N_3-PCHA$ System
Azide, M	Absorbance at 447 nm
0.10	0.110
0.15	0.201
0.20	0.282
0.25	0.351
0.30	0.423
0.35	0.504
0.40	0.577
0.50	0.605
1.00	0.605
1.50	0.608
2.00	0.603
2.50	0.569
3.00	0.517

Effect of Amount of PCHA: A 5 - and 25-fold molar excess of the reagent, PCHA, was found to be necessary for the complete extraction of iron(III) from thiocyanate and azide medium, respectively, whereas it was found to have no effect on the extraction of cobalt(II) from the thiocyanate medium under optimum experimental conditions. The necessity of the higher concentration of PCHA for the complete extraction of Fe(III) from azide medium indicates the greater stability of Fe(III)-azide complex than that of Fe(III)-thiocyanate in the aqueous phase. A large excess of the reagent up to 50-fold molar excess had no adverse effect on the extraction of both metal ions from the aqueous phase. Nevertheless, the extent of absorption of the reagent increases with its increasing concentration and therefore one needs the reagent blank for the measurement of the absorbance of the respective complexes. The results are given in Table 6.

Table 6. Effect of Amount of PCHA on the Extraction of Iron(III).

	Thiocyanate-system $[Fe(III)] = 4.0 \times 10^{-5} M$	Azide-system $[Fe(III)] = 8.0 \times 10^{-5} M$
[Fe(III)] : [PCHA]	Absorbance at 495 nm	Absorbance at 447 nm
1:0	0.441	-
1:05	0.508	-
1:1	0.572	0.027
1:2	0.673	0.068
1:3	0.694	0.110
1:4	0.716	0.171
1:5	0.722	0.205
1:6	0.720	0.260
1:8	0.721	0.368
1:10	0.723	0.424
1:15	0.725	0.522
1:20	0.724	0.578
1:25	0.721	0.603
1:30	0.723	0.607
1:50	0.724	0.608

Ionic Strength, Temperature, and Volume of the Aqueous Phase: The wavelength of maximum absorption and absorbance values of the colored extract of the three complexes were not affected by the change in ionic strength of the aqueous phase between 0.1 and 1.0 M with respect to potassium nitrate. Variation in the temperature of the aqueous phase between 20° and 40°C did not produce any change in the absorbance value of the colored extract of the three complexes. It has also been found that the volume of the aqueous phase can be varied from 10-50 ml with respect to a fixed volume of 10 ml of the organic phase without any variation in the absorbance or extraction efficiency of cobalt(II)-complex. In the case of iron(III) complexes the volume of the aqueous phase can be varied from 10-25 ml with respect to a fixed volume of 10 ml of the organic phase without any variation in the absorbance or extraction efficiency. However, more repetitive extractions were found to be necessary for the complete extraction of Fe(III) from larger volumes of the aqueous phase. The results are given in Table 7.

Order of Addition of Reagents: It has been found that there is no change in the absorbance or in the color intensity of the three complexes extracted into ethylacetate if the order of addition of reagents is changed.

Extraction Time and Stability of Complexes: The iron (III) mixed ligand complexes and cobalt(II) simple complex were completely extracted into ethylacetate within two minutes. The absorbance values of the ethylacetate extracts of

Fe(III)-SCN-PCHA, Fe(III)-N_3-PCHA, and Co(II)-SCN complexes remained constant for about six hours, for at least seven days, and for at least two days at room temperature, respectively. The results are given in Table 8.

Table 7. Effect of Ionic Strength, Temperature, and Volume of Aqueous Phase on Extraction of Iron(III) and Cobalt(II).
$[Co(II)]=4.0x10^{-4}M$ $[Fe(III)]=4.0x10^{-5}M$ $[Fe(III)]=8.0x10^{-5}M$

	Co(II)-SCN system	Fe(III)-SCN-PCHA System	Fe(III)-N_3-PCHA System
Variable	Absorbance at 625 nm	Absorbance at 495 nm	Absorbance at 447 nm
$[KNO_3]$			
0.1M	0.722	0.721	0.604
1.0M	0.724	0.723	0.603
Temperature			
20°C	0.724	0.723	0.600
40°C	0.721	0.722	0.601
$*V_{org}:V_{aq}$			
1:1.0	0.723	0.723	0.601
1:2.5	0.721	0.724	0.600
1:5.0	0.722	0.589	0.566

$*V_{org}$ = 10 ml.

3.5 Composition of the Complexes

The composition of the complexes was determined by different spectrophotometric methods. The continuous variations (79) and mole ratio (80) methods were used to determine the ratio of Fe(III) to PCHA in Fe(III)-SCN-PCHA complex while the ratio of Fe(III) to PCHA in Fe(III)-N_3-PCHA.

Table 8. Stability of the Complexes with Time.

	[Co(II)]=4.0x10^{-4}M	[Fe(III)]=4.0x10^{-5}M	[Fe(III)]=8.0x10^{-5}M
	Co(II)-SCN system	Fe(III)-SCN-PCHA system	Fe(III)-N_3-PCHA system
	Absorbance at 625 nm	Absorbance at 495 nm	Absorbance at 447 nm
0 min	0.723	0.720	0.603
30 min	0.724	0.721	0.604
60 min	0.723	0.721	0.603
2 hrs	0.725	0.720	0.602
4 hrs	0.723	0.721	0.602
6 hrs	0.722	0.721	0.604
8 hrs	0.723	0.701	0.603
1 day	0.724	0.688	0.604
2 days	0.723	-	0.602
7 days	-	-	0.603

complex was determined by continuous variations and simple spectrophotometric method(12). The ratio of metal to auxiliary ligand (thiocyanate or azide) in all the three complexes was determined by the simple spectrophotometric method. In the continuous variations method the maximum absorbance was observed at the mole fraction of 0.33 of the metal ion in both systems. These results indicate the ratio of Fe(III) to PCHA to be 1:2 in both the complexes. The results are given in Table 9 and the curves are shown in Figure 4 and 5.

The results obtained by the mole ratio method indicated the ratio of Fe(III) to PCHA to be 1:2. The results are given in Table 10 and the curve is shown in Figure 6.

The mole ratio method could not be applied to determine the ratio of Fe(III) to PCHA in the Fe(III)-N_3-PCHA system because of the gradual attainment of mixed ligand complex formation equilibrium with increasing concentration of PCHA. Hence, a simple spectrophotometric method was used to determine the ratio of Fe(III) to PCHA in the Fe(III)-N_3-PCHA system.

Table 9. Results of Continuous Variations Method for Fe(III)-SCN-PCHA and Fe(III)-N_3-PCHA Complexes.

		Fe(III)-SCN-PCHA system $C_{total}=2.0\times10^{-3}M$ $[SCN^-] = 2.0M$ $[HCl] = 1.0M$	Fe(III)-N_3-PCHA system $C_{total}=5.0\times10^{-3}M$ $[N_3^-] = 1.0M$ $[HCl] = 0.5M$
Mole fraction of iron (III)	Mole fraction of PCHA	Absorbance at 495 nm	Absorbance at 447 nm
1.00	0.00	0.000	0.000
0.90	0.10	0.025	0.046
0.80	0.20	0.048	0.095
0.70	0.30	0.072	0.150
0.60	0.40	0.093	0.183
0.50	0.50	0.108	0.231
0.40	0.60	0.122	0.266
0.33	0.67	0.133	0.283
0.30	0.70	0.125	0.271
0.25	0.75	0.109	0.262
0.20	0.80	0.092	0.216
0.10	0.90	0.048	0.103
0.00	1.00	0.000	0.000

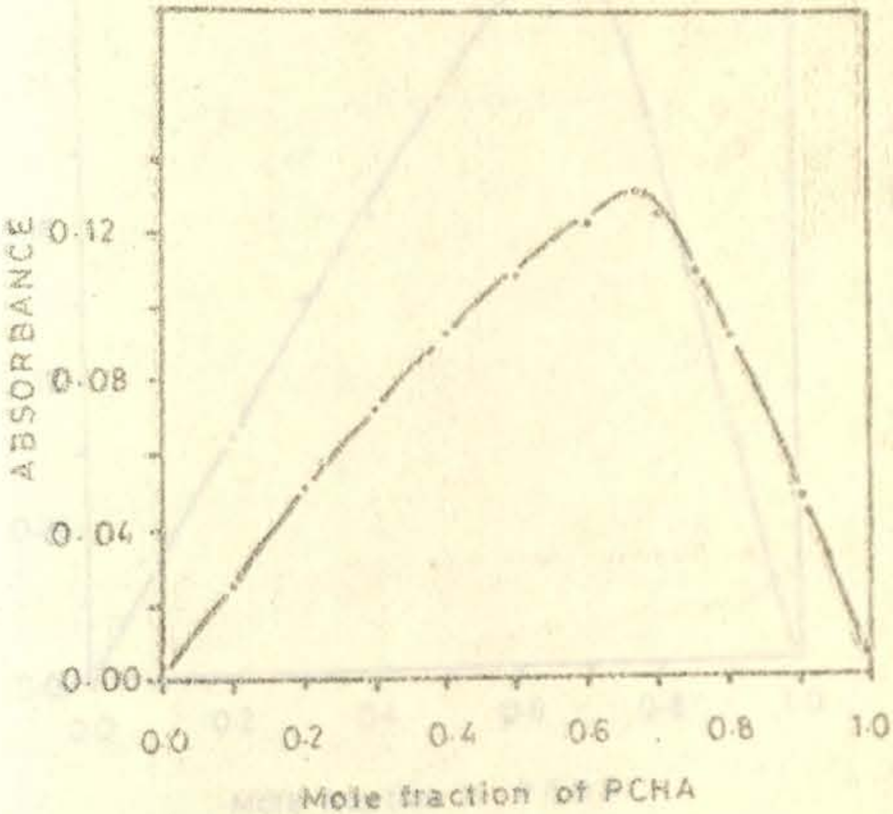


Figure 4 Curve for determination of composition of Fe(III)-SCN-PCHA complex by continous variations method

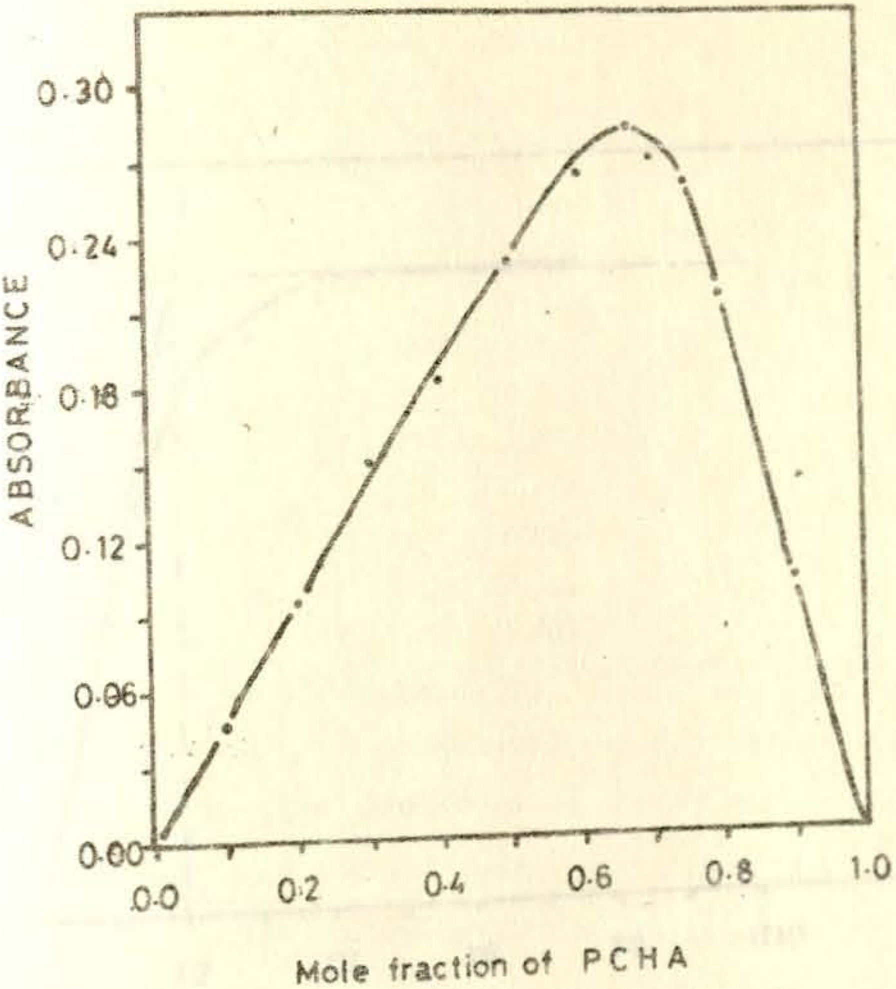


Figure 5 Curve for determination of composition of $Fe(III)-N_3^--PCHA$ complex by continous variations method.

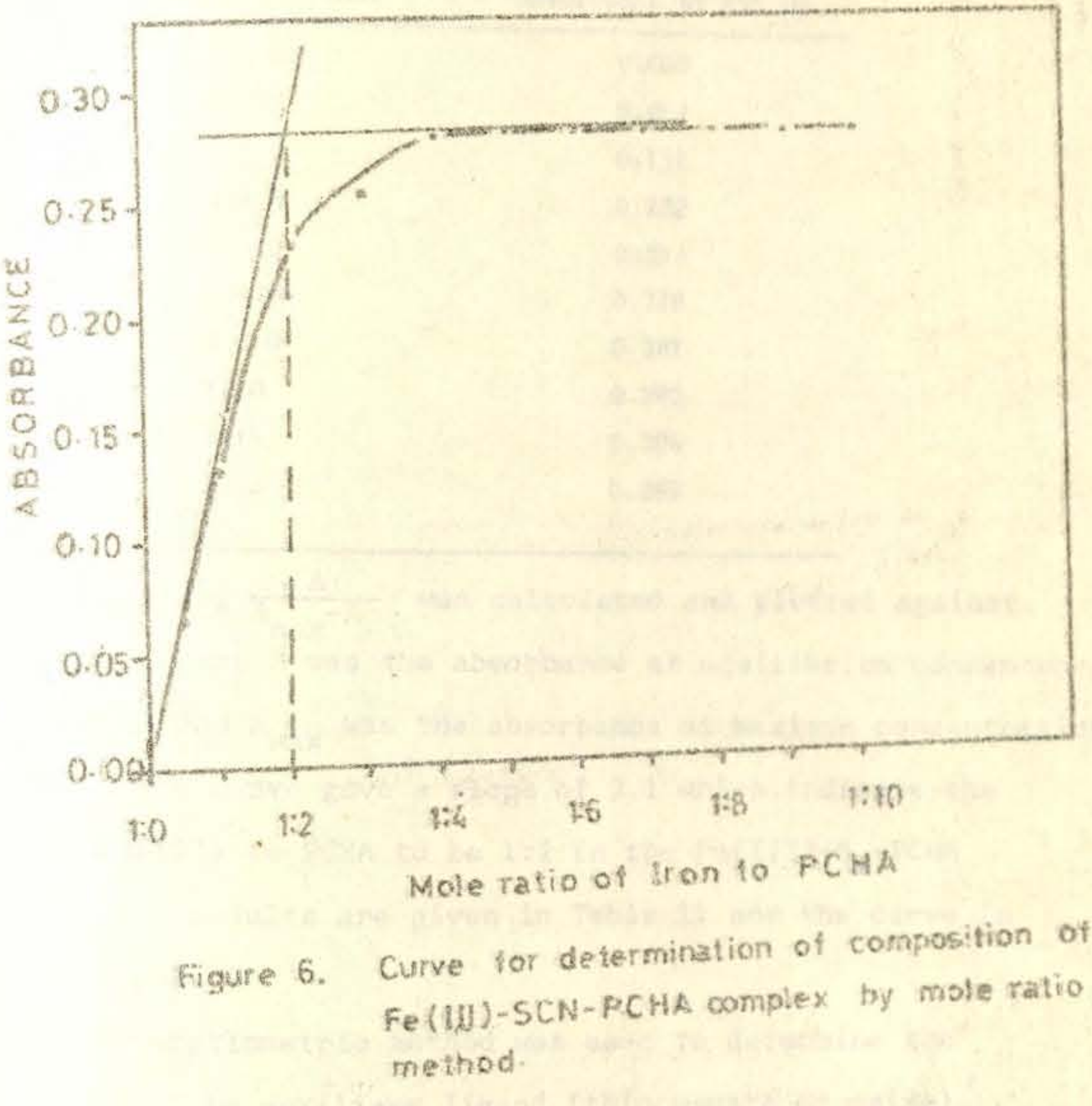


Figure 6. Curve for determination of composition of Fe(III)-SCN-PCHA complex by mole ratio method.

Table 10. Results of Mole Ratio Method for Fe(III)-SCN-PCHA Complex.

$[Fe(III)]=4.0 \times 10^{-5}M$, $[SCN^-] = 2.0M$, $[HCl]=1.0M$

[Fe(III)]: [PCHA]	Absorbance at 495 nm
1:0.0	0.000
1:0.5	0.067
1:1.0	0.131
1:2.0	0.232
1:3.0	0.253
1:4.0	0.278
1:5.0	0.281
1:10	0.282
1:15	0.284
1:50	0.285

The quantity log $\frac{A}{A_{max}-A}$ was calculated and plotted against log [PCHA] (where A was the absorbance at equilibrium concentration of PCHA and A_{max} was the absorbance at maximum concentration of PCHA). The curve gave a slope of 2.1 which indicate the ratio of Fe(III) to PCHA to be 1:2 in the Fe(III)-N_3-PCHA complex. The results are given in Table 11 and the curve is shown in Figure 7.

The absorptiometric method was used to determine the ratio of metal to auxiliary ligand (thiocyanate or azide) in all the three systems. A series of solutions was prepared for each system in which the concentrations of metal and PCHA, the ionic strength, and the acidity were kept constant and the concentration of thiocyanate or azide was varied. The complexes were extracted by the general procedures and the absorbances were measured at their λ_{max}

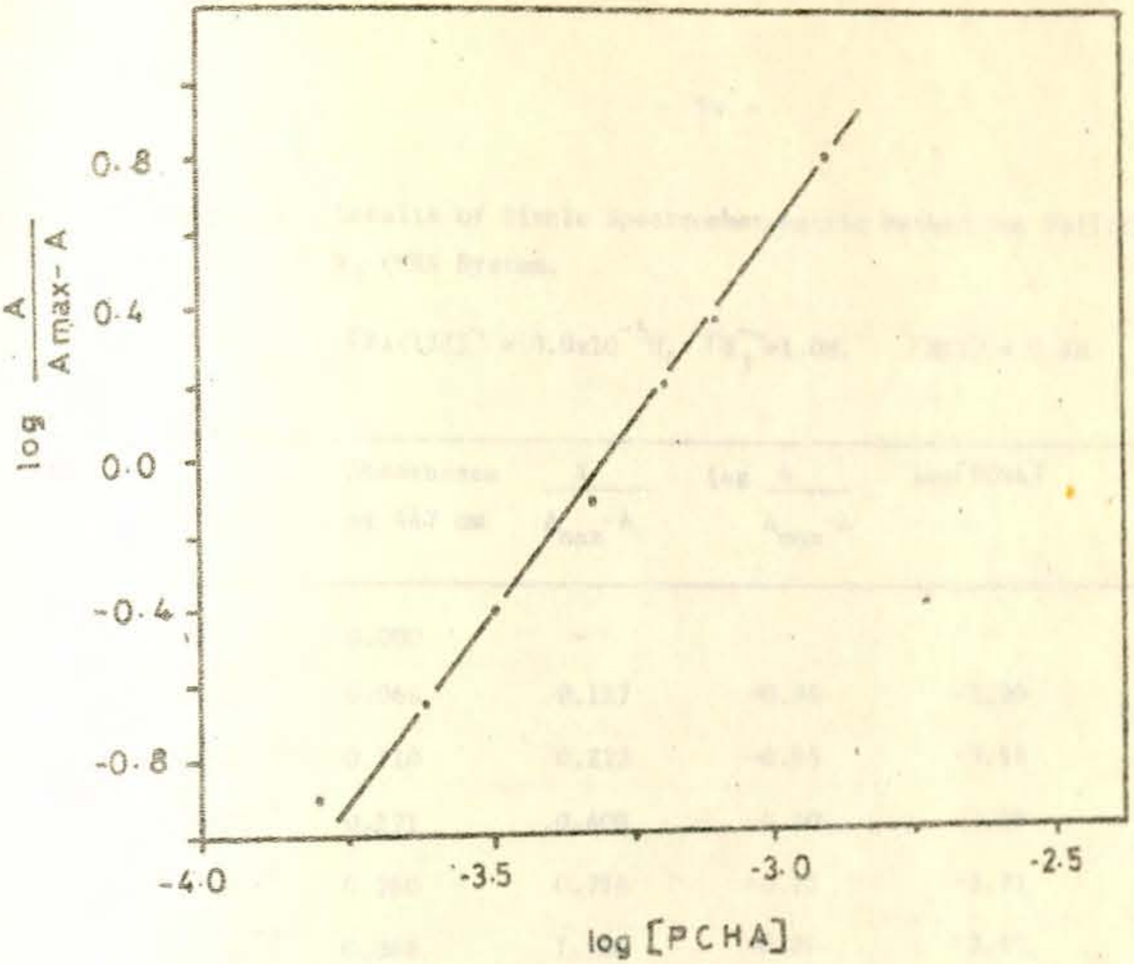


Figure 7. Curve for determination of Iron (III) to PCHA ratio in Fe (III)-N_3-PCHA system

Table 11. Results of Simple Spectrophotometric Method for Fe(III)-N_3^--PCHA System.

$[Fe(III)] = 8.0\times10^{-5}M$, $[N_3^-]=1.0M$, $[HCl] = 0.5M$

$[PCHA]$	Absorbance at 447 nm	$\frac{A}{A_{max}-A}$	$\log \frac{A}{A_{max}-A}$	$\log[PCHA]$
0.00	0.000	-	-	-
1.6×10^{-4}	0.068	0.127	-0.90	-3.80
2.4×10^{-4}	0.110	0.223	-0.65	-3.62
3.2×10^{-4}	0.171	0.400	-0.40	-3.50
4.8×10^{-4}	0.260	0.758	-0.12	-3.32
6.4×10^{-4}	0.368	1.566	+0.20	-3.19
8.0×10^{-4}	0.424	2.369	+0.38	-3.10
1.2×10^{-3}	0.522	6.444	+0.81	-2.92
2.0×10^{-3}	0.603	-	-	-

against the corresponding reagent blank. The quantity $\log \frac{A}{A_{max}-A}$ was calculated for each system and plotted against $\log [SCN^-]$ or $\log [N_3^-]$ (where A_{max} was the maximum absorbance in presence of excess of thiocyanate or azide). A straight line was obtained in each system, the slope of which gave the number of auxiliary ligand (thiocyanate or azide) in the ternary complexes. Slopes of 1.98, 2.2 and 3.8 were found which indicated the ratio of 1:2 ($Fe:N_3^-$), 1:2 (Fe:SCN$^-$), and 1:4 (Co:SCN$^-$) in the Fe(III)-N_3-PCHA, Fe(III)-SCN-PCHA, and Co(II)-SCN complexes, respectively. The results are given in Table 12-14 and the curves are shown in Figure 8-10.

Table 12. Results of Absorptiometric Method for Fe(III)-N_3-PCHA Complex

$[Fe(III)] = 8.0 \times 10^{-5}N$, $[HCl]=0.5M$, $[PCHA]=4.0 \times 10^{-3}M$

$[N_3^-]$	Absorbance at 447 nm	$\log \frac{A}{A_{max}-A}$	$\frac{A}{A_{max}-A}$	$[\log N_3^-]$
0.00	-	-	-	-
0.10	0.110	0.22	-0.65	-1.00
0.15	0.200	0.50	-0.30	-0.82
0.20	0.282	0.77	-0.06	-0.70
0.25	0.351	1.39	+0.14	-0.60
0.30	0.423	2.31	+0.36	-0.52
0.35	0.504	5.03	+0.70	-0.46
0.40	0.572	17.80	+1.25	-0.40
0.50	0.603	-	-	-

Table 13. Results of Absorptiometric Method for Fe(III)-SCN-PCHA Complex.

Fe(III) =4.0×10^{-5}M, HCl =1.0M, PCHA =2.0×10^{-3}M

$[SCN^-]$	Absorbance at 495 nm	$\frac{A}{A_{max}-A}$	$\log\frac{A}{A_{max}-A}$	$\log[SCN^-]$
0.00	0.000	-	-	-
0.10	0.094	0.149	-0.83	-1.00
0.20	0.260	0.56	-0.25	-0.70
0.30	0.403	1.26	+0.10	-0.52
0.40	0.497	2.19	+0.34	-0.40
0.50	0.582	4.10	+0.61	-0.30
0.75	0.655	9.49	+0.98	-0.13
1.00	0.704	35.20	+1.55	0.00
1.25	0.724	-	-	-0.097

Table 14. Results of Absorptiometric Method for Co(II)-SCN Complex.

$[Co(II)] = 4.0\times10^{-4}$, $[HCl] = 1.0M$

$[SCN^-]$	Absorbance at 625 nm	$\frac{A}{A_{max}-A}$	$\log\frac{A}{A_{max}-A}$	$\log[SCN^-]$
0.00	-	-	-	-
0.25	0.018	0.025	-1.59	-0.602
0.50	0.165	0.295	-0.530	-0.300
0.75	0.423	1.41	+0.148	-0.125
1.00	0.561	3.44	+0.537	0.000
1.25	0.656	9.65	+0.984	+0.097
1.50	0.724	-	-	+0.176

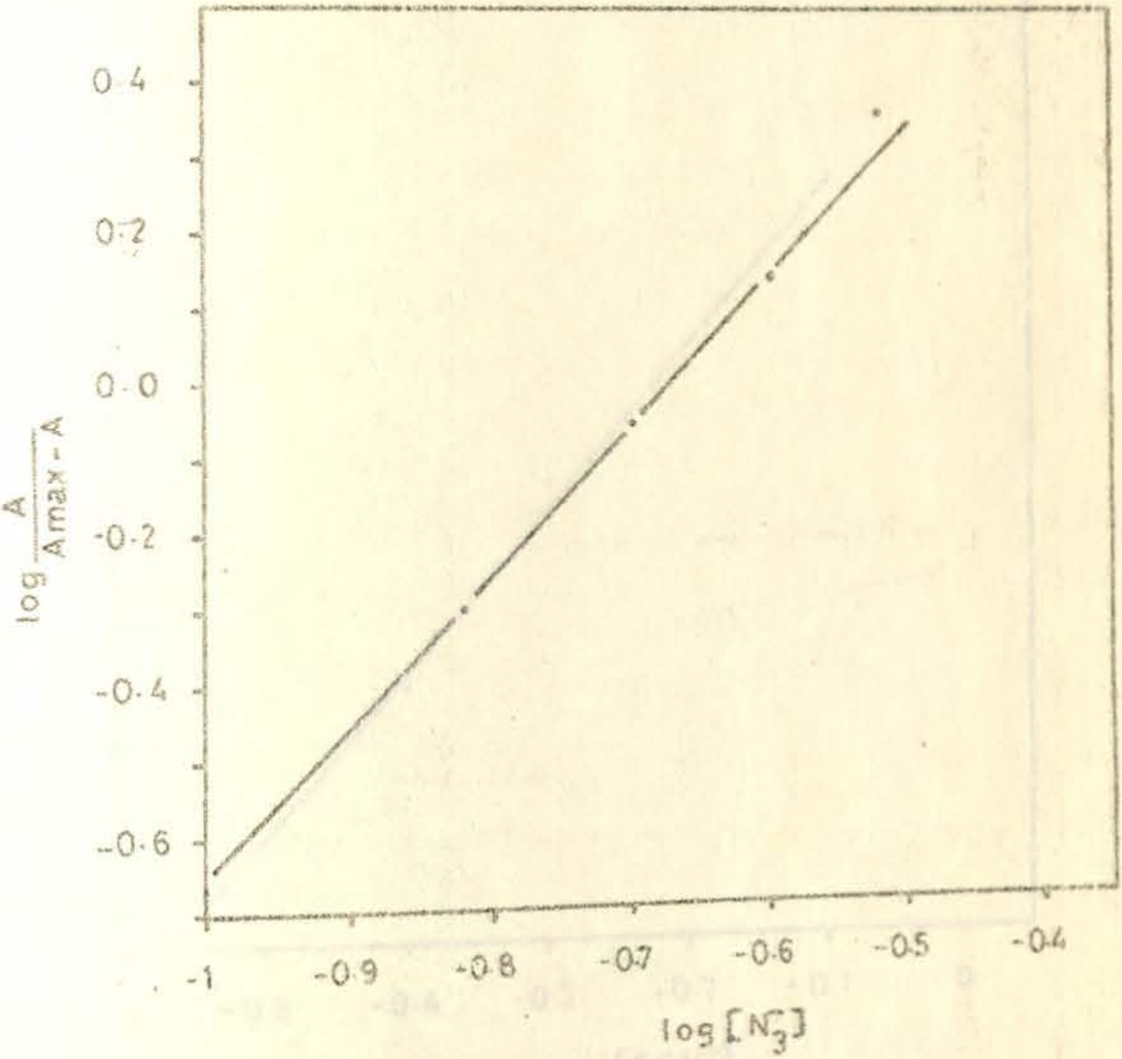


Figure 8 Curve for determination of Iron (III) to N_3^- ratio in Fe (III)-N_3-PCHA system.

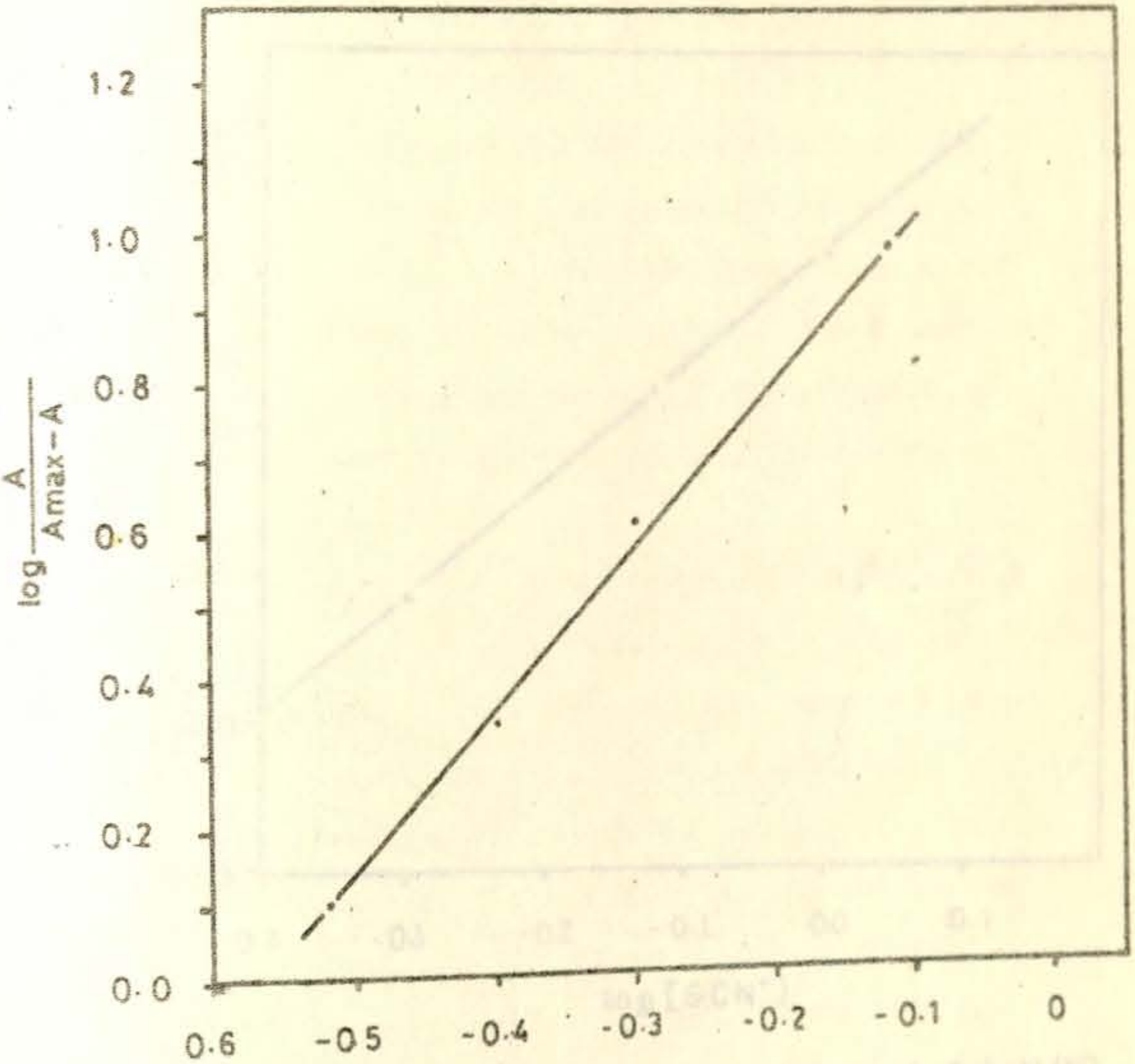


Figure 9. Curve for determination of Iron (III) to SCN⁻ ratio in Fe (III)-SCN-PCHA system.

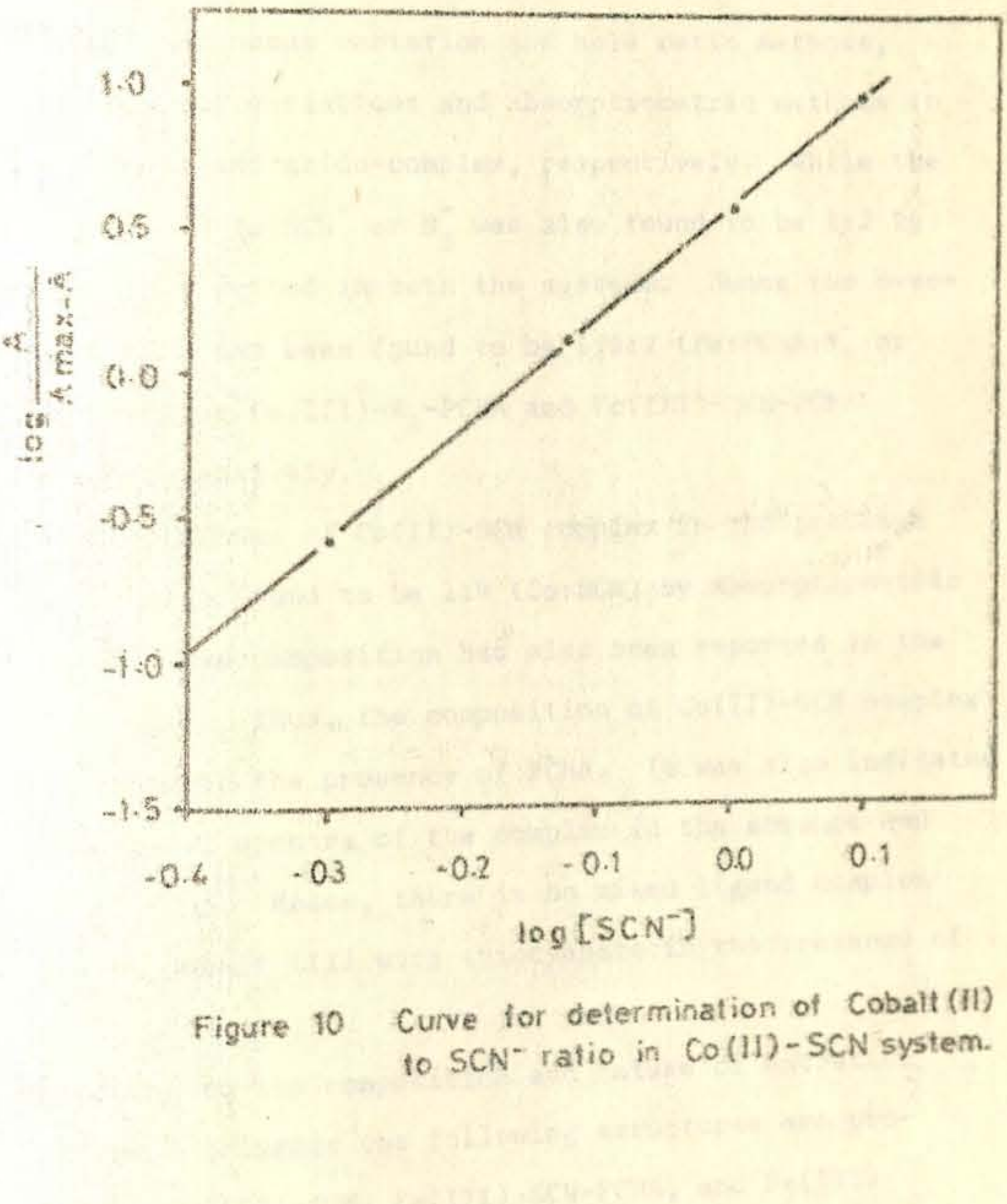


Figure 10 Curve for determination of Cobalt (II) to SCN⁻ ratio in Co(II) - SCN system.

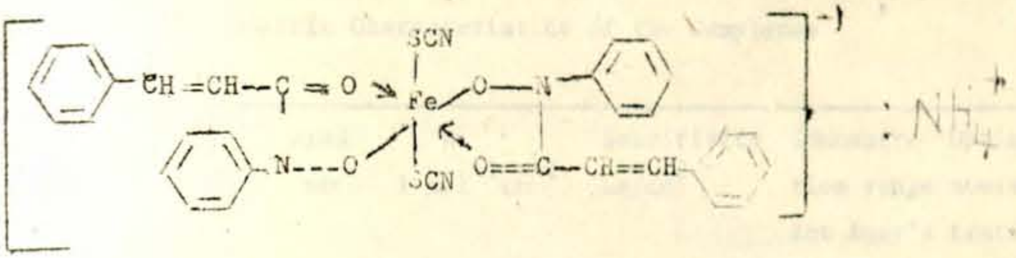
Thus the ratio of Fe(III) to PCHA was found to be 1:2 by both the continuous variation and mole ratio methods, and by continuous variations and absorptiometric methods in the thiocyanato-and azido-complex, respectively. While the ratio of Fe(III) to SCN^- or N_3^- was also found to be 1:2 by absorptiometric method in both the systems. Hence the overall composition has been found to be 1:2:2 (Fe:PCHA:N_3^- or SCN^-) in both the Fe(III)-N_3-PCHA and Fe(III)-SCN-PCHA complexes, respectively.

The composition of Co(II)-SCN complex in the presence of PCHA has been found to be 1:4 (Co:SCN) by absorptiometric method. The same composition has also been reported in the literature (61). Thus, the composition of Co(II)-SCN complex did not change in the presence of PCHA. It was also indicated by the identical spectra of the complex in the absence and presence of PCHA. Hence, there is no mixed ligand complex formation of cobalt (II) with thiocyanate in the presence of PCHA.

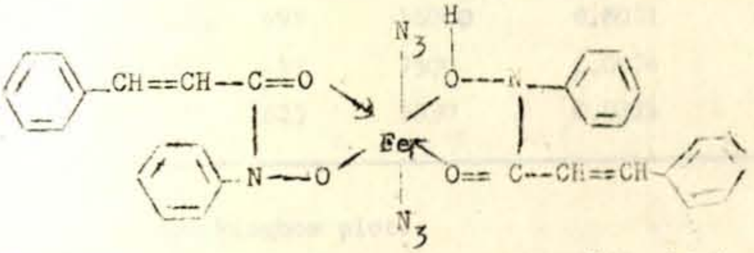
According to the composition and nature of extration into different solvents the following structures are proposed for the Co(II)-SCN, Fe(III)-SCN-PCHA, and Fe(III) N_3-PCHA complexes, respectively.

$$Co(SCN)_4^{2-}:2NH_4^+$$

Tetrathiocyanatocobatate(II).



Bis-(N-phenylcinnamohydroxamic acid)dithiocyanatoferrate(III).



Bis-(N-phenylcinnamohydroxamic acid)diazidoiron(III).

3.6 Photometric Characteristics of the Complexes

The molar absorptivities and photometric sensitivities (9), the concentration range obeyed by Beer's law, and the optimum concentration range for the photometric determination evaluated from Ringbom's plot (81) are summarized in Table 15. The calibration curves data are given in Tables 16-18 and the curves are shown in Figures 11-16. These results show that the Fe(III)-SCN-PCHA method is highly sensitive and can be applied for the determination of trace quantities of iron. Although Co(II)-SCN method is not very sensitive, it is more sensitive than some of recently reported methods (62,82) which are also based on the formation of cobalt(II)- thiocyanate complexes.

Table 15. Photometric Characteristics of the Complexes

Coloured System	λmax nm	ε $l\ mol^{-1}\ cm^{-1}$	Sensitivity $\mu g/cm^2$	Concentration range for Beer's law (ppm)	Optimum concentration range* (ppm)
Fe(III)-SCN-PCHA	495	18000	0.0031	0.2-3.9	0.35-3.0
Fe(III)-N_3-PCHA	447	7500	0.0074	0.5-9.0	0.75-8.0
Co(II)-SCN	625	1820	0.0324	2-41	3.7-36

*Evaluated from Ringbom plot.

Table 16. Calibration Curve Data for Determination of Iron(III) by Fe(III)-SCN-PCHA System

Concentration of iron(III)			Absorbance at 495 nm
M	µg/25	ppm	
0.33×10^{-5}	4.65	0.186	0.060
1×10^{-5}	13.96	0.559	0.180
2×10^{-5}	27.92	1.118	0.362
3×10^{-5}	41.88	1.677	0.542
4×10^{-5}	55.85	2.236	0.721
5×10^{-5}	69.80	2.795	0.904
6×10^{-5}	83.76	3.354	1.075
7×10^{-5}	97.72	3.913	1.259

Table 17. Calibration Curve Data for Determination of Iron (III) by $Fe(III)-N_3-PCHA$ System

Concentration of iron(III)			
M	µg/25 ml	ppm	Absorbance at 447 nm
$1x10^{-5}$	13.96	0.559	0.075
$2x10^{-5}$	27.93	1.117	0.150
$4x10^{-5}$	55.85	2.234	0.301
$8x10^{-5}$	111.70	4.468	0.603
$12x10^{-5}$	167.58	6.702	0.902
$16x10^{-5}$	223.44	8.932	1.200

Table 18. Calibration Curve Data for Determination of Cobalt(II) by Co(II)-SCN system

Concentration of cobalt(II)			
M	µg/25 ml	ppm	Absorbance at 625 nm
$0.33x10^{-4}$	49.08	1.96	0.061
$1x10^{-4}$	147.25	5.89	0.182
$2x10^{-4}$	294.50	11.78	0.362
$4x10^{-4}$	589.00	23.56	0.724
$6x10^{-4}$	883.50	35.34	1.086
$7x10^{-4}$	1030.75	41.23	1.264

3.7 Precision

The precision of the methods was evaluated by performing six independent analyses made on samples each containing 55.85 µg of iron(III) per 25 ml, 111.7 µg of iron(III) per 25 ml, and 589 µg of cobalt(II) per 25 ml for Fe(III)-SCN-

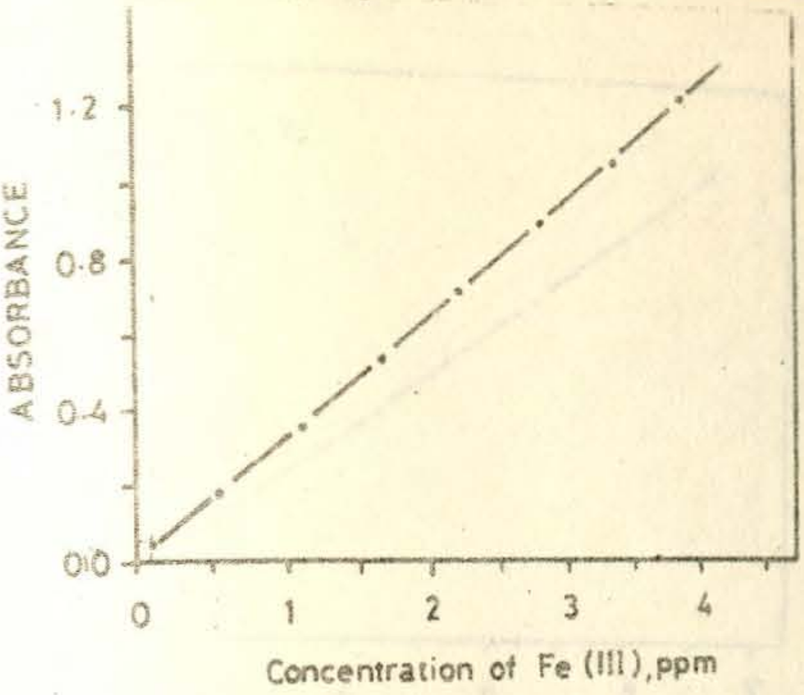


Figure 11 Calibration curve for determination of Iron (III) by Fe (III)-SCN-PCHA system.

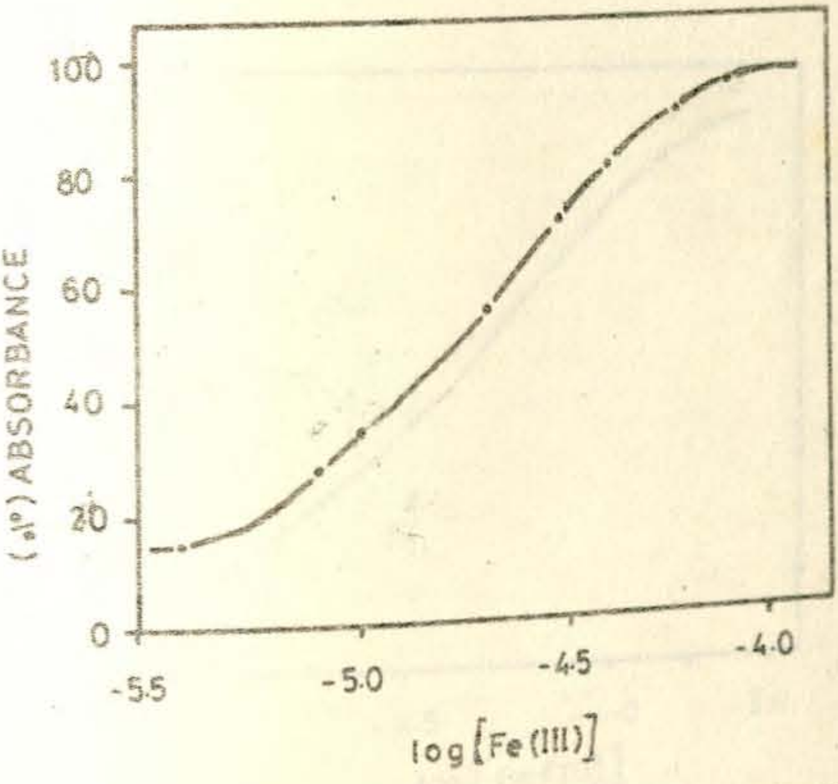
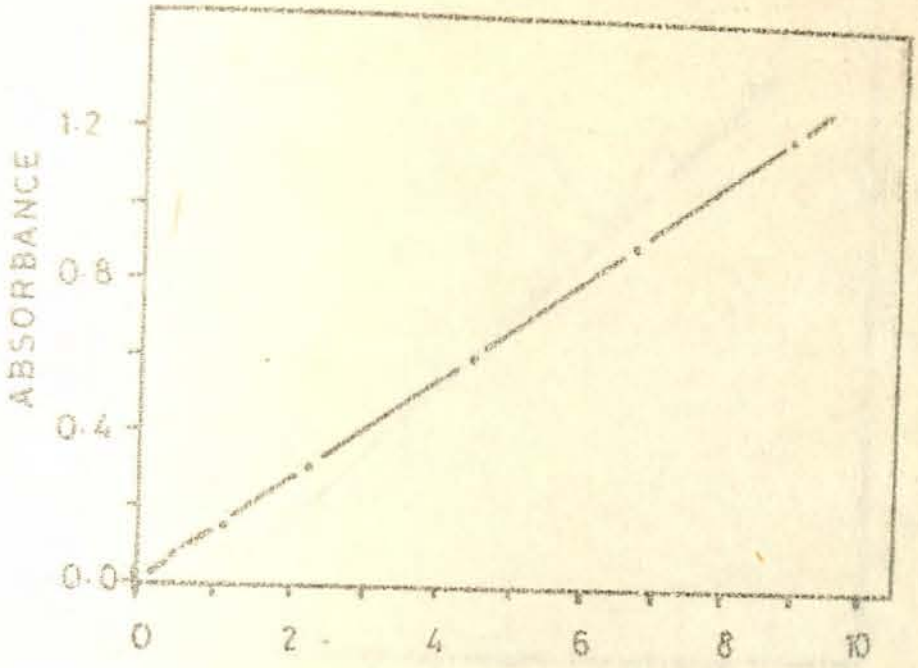
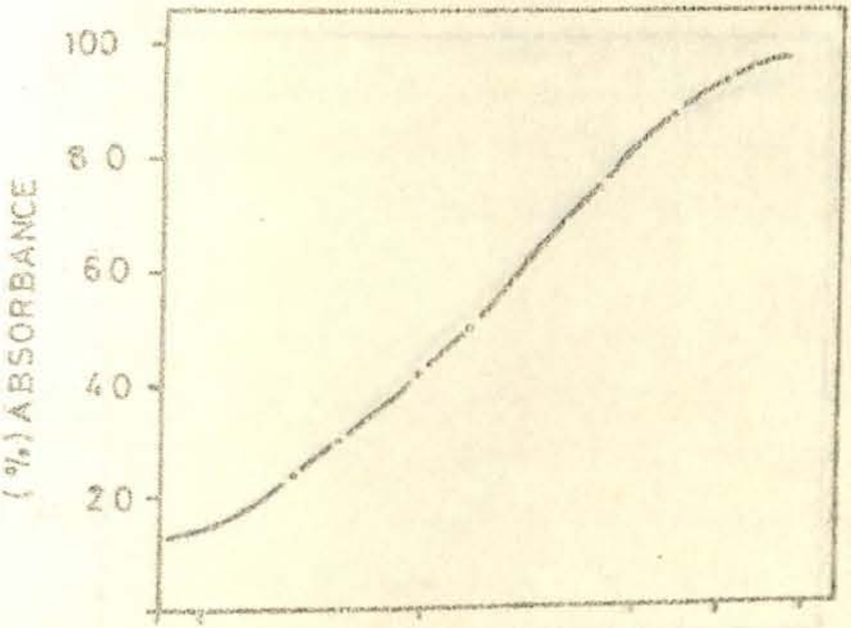


Figure 12 Ringbom's plot for the evaluation of optimum concentration range for determination of Iron(III) by Fe(III)-SCN-PCHA system.



Concentration of Fe (III), ppm

Figure 13 Calibration curve for determination of Iron (III) by Fe (III)-N_3^--PCHA system.



log [Fe (III)]

Figure 14 Ringbom's plot for evaluation of optimum concentration range for determination of Iron (III) by Fe (III)-N_3^--PCHA system

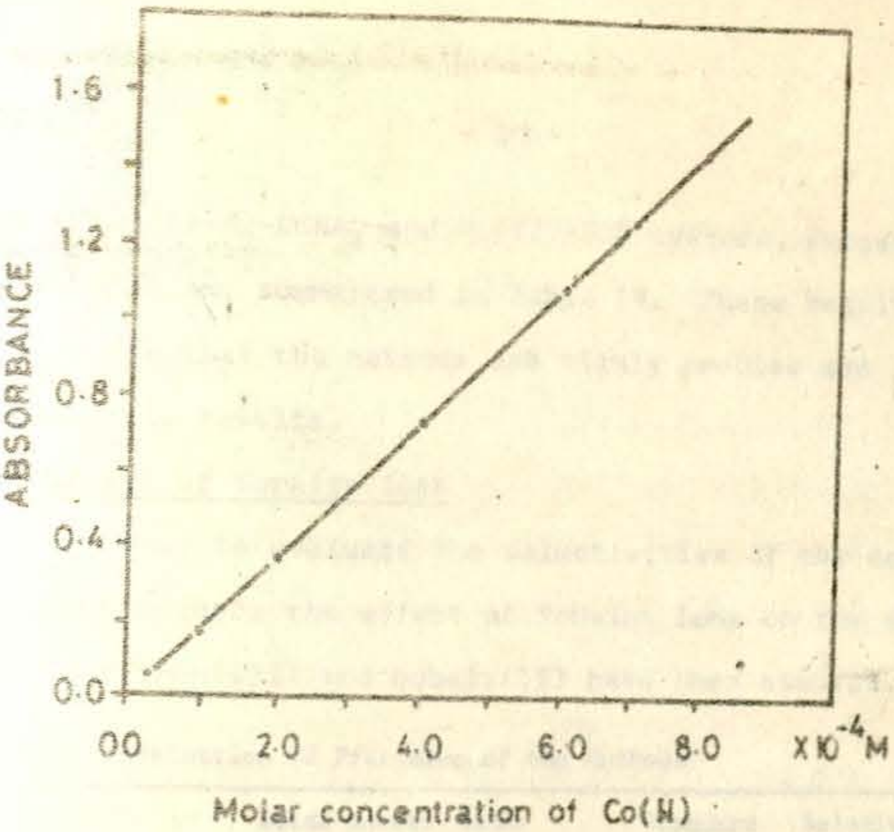


Figure 15 Calibration curve for determination of Cobalt (II).

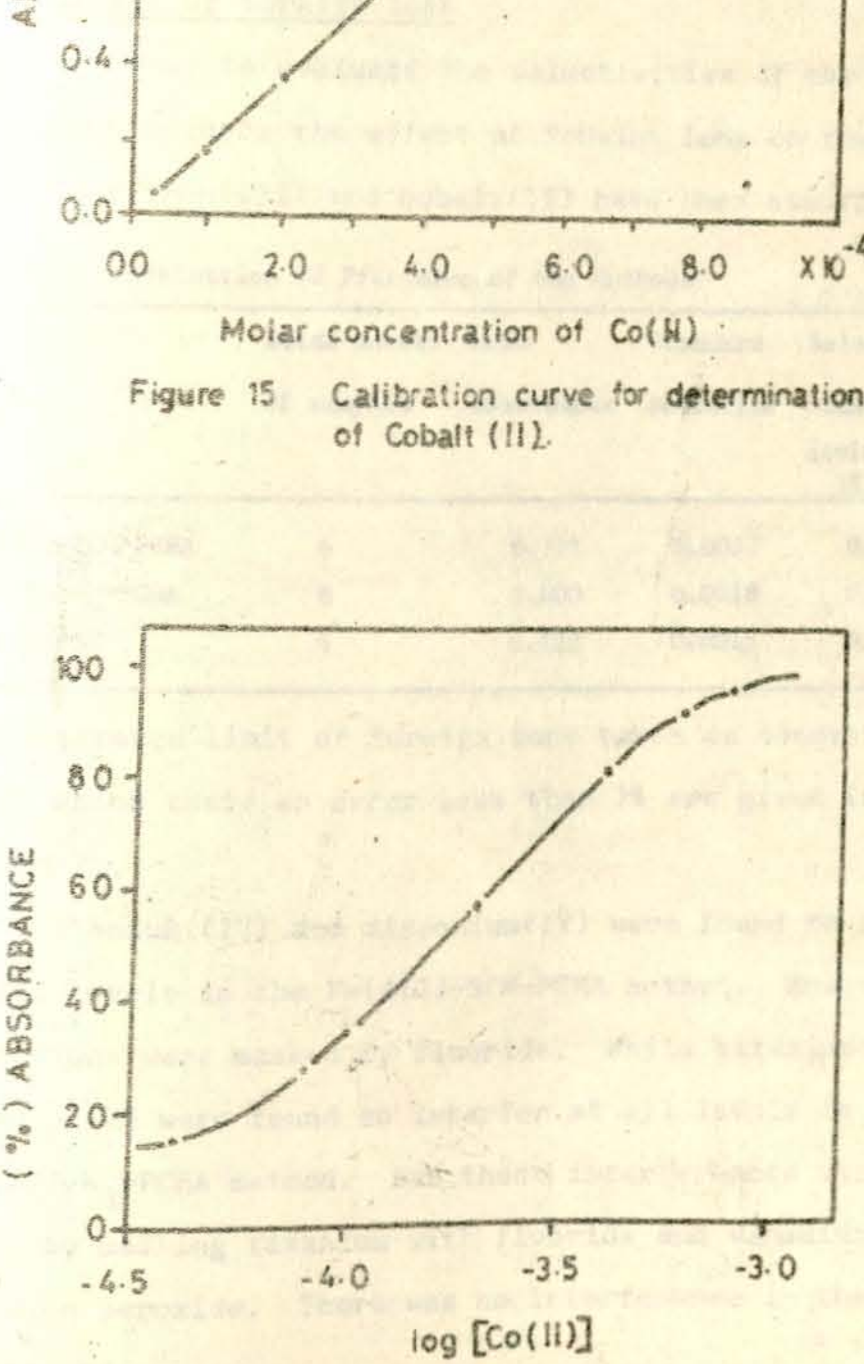


Figure 16 Ringbom's plot for the evaluation of optimum concentration range for determination of Cobalt (II).

PCHA, Fe(III)-N_3-PCHA, and Co(II)-SCN systems, respectively. The results are summarized in Table 19. These results clearly indicate that the methods are highly precise and give reproducible results.

3.8 Effect of Foreign Ions

In order to evaluate the selectivities of the newly developed methods the effect of foreign ions on the determination of iron(III) and cobalt(II) have been studied.

Table 19. Evaluation of Precision of the Methods

Method	Total number of samples	Mean absorbance	Standard deviation	Relative Standard deviation (%)
Fe(III)-SCN-PCHA	6	0.721	0.0027	0.37
Fe(III)-N_3-PCHA	6	0.603	0.0018	0.30
Co(II)-SCN	6	0.723	0.0015	0.21

The tolerance limit of foreign ions taken as concentration (ppm) which cause an error less than 2% are given in Table 20 and 21.

Titanium (IV) and zirconium(IV) were found to interfer at all levels in the Fe(III)-SCN-PCHA method. However, both metal ions were masked by fluoride. While titanium(IV) and vanadium(V) were found to interfer at all levels in the Fe(III)-N_3-PCHA method. But these interferences were overcomed by masking titanium with fluoride and vanadium(V) with hydrogen peroxide. There was no interference in the Co(II)-SCN method.

The results given in Table 20 and 21 clearly indicate that almost all common ions which are normally associated with iron and cobalt in ores, alloys, steels, and biological samples do not interfer in the simultaneous determination of iron(III) and cobalt(II) with PCHA and thiocyanate and also in the Fe(III)-N_3-PCHA method. Hence, the methods are highly selective and can be applied for the determination of iron and cobalt in any type of sample.

Table 20. **Tolerance Limit of Foreign Ions in the Determination of Iron(III) and Cobalt(II).**

Concentration of Iron(III) = 2 ppm

Concentration of Cobalt(II) = 20 ppm

$[SCN^-] = 2.0M$, $[HCl] = 1.0M$

Ion	Tolerance limit, ppm		
	Iron determination	Cobalt determination	Simultaneous determination
Na^+	400	400	400
K^+	400	400	400
Li^+	400	400	400
Ca^{2+}	400	400	400
Sr^{2+}	400	400	400
Ba^{2+}	400	400	400
Mg^{2+}	400	400	400
Be^{2+}	400	400	400
Al^{3+}	400	400	400
La^{3+}	400	400	400
Tl^+	400	400	400
Zn^{2+}	400	400	400
Cd^{2+}	400	400	400
Hg^{2+}	400	400	400
Sn^{2+}	400	400	400

Table 20 Continued

Ion	Tolerance limit, ppm		
	Iron determination	Cobalt determination	Simultaneous determination
Sn^{4+}	400	400	400
Pb^{2+}	400	400	400
Bi^{3+}	400	400	400
VO_2^+	80	20	20
Ce^{4+}	200	300	200
Th^{4+}	400	200	200
UO_2^{2+}	400	400	400
Cu^{2+}	10	40	10
Ni^{2+}	400	400	400
Cr^{3+}	400	400	400
Mn^{2+}	400	400	400
MoO_4^{2-}	12	40	12
WO_4^{2-}	200	200	200
Ti^{4+}	80*	120	80*
Zr^{4+}	80*	160	80*
Acetate	400	400	400
Chloride	400	400	400
Nitrate	400	400	400
Sulphate	400	400	400
Citrate	200	400	200
Tertarate	400	400	400
Phosphate	400	400	400
Fluoride	400	400	400
Oxalate	200	400	200
EDTA	400	400	400
Borate	200	400	200

*Masked by Fluoride (400 ppm).

Table 21. Tolerance Limit of Foreign Ions in the Determination of Iron(III).

Concentration of Iron(III) = 4 ppm

$[N_3^-] = 1.0$ M, $[HCl] = 0.5$ M

Ion	Tolerance limit, ppm
Na^+	400
K^+	400
Li^+	400
Ca^{2+}	400
Sr^{2+}	400
Ba^{2+}	400
Mg^{2+}	400
Be^{2+}	400
Al^{3+}	400
La^{3+}	400
Tl^+	400
Zn^{2+}	400
Cd^{2+}	400
Hg^{2+}	400
Sn^{2+}	120
Sn^{4+}	120
Bi^{3+}	400
*VO_2^+	40
Ce^{4+}	400
Th^{4+}	160
UO_2^{2+}	400
Cu^{2+}	60
Ni^{2+}	400
Co^{2+}	400
Cr^{3+}	400
Mn^{2+}	400
MoO_4^{2-}	400
WO_4^{2-}	40

Table 21 Continued

Ion	Tolerance limit, ppm
$^{**}Ti^{4+}$	40
Zr^{4+}	320
Acetate	400
Chloride	400
Nitrate	400
Sulphate	400
Citrate	40
Tartarate	320
Borate	400
Phosphate	400
Fluoride	3000

*Masked by H_2O_2(2 ml of 30%).

**Masked by Fluoride (3000 ppm).

3.9 Simultaneous Determination of Iron(III) and Cobalt(II)

The simultaneous spectrophotometric determination of two solutes in solution can be done if there is no reaction between the two solutes because absorbances are additive property (7). Hence, it can be written as:

$$A_{\lambda 1} = A_1(_{\lambda 1}) + A_2(_{\lambda 1}) \qquad [28]$$

$$A_{\lambda 2} = A_1(_{\lambda 2}) + A_2(_{\lambda 2}) \qquad [29]$$

where $A_{\lambda 1}$ and $A_{\lambda 2}$ are the measured absorbances at the two wavelengths λ_1 and λ_2, and the subscripts 1 and 2 refer to the 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 $A = \varepsilon Cl$, 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:

$$A_{\lambda_1} = \varepsilon_1(\lambda_1) \cdot C_1 + \varepsilon_2(\lambda_1) \cdot C_2 \qquad [30]$$

$$A_{\lambda_2} = \varepsilon_1(\lambda_2) \cdot C_1 + \varepsilon_2(\lambda_2) \cdot C_2 \qquad [31]$$

Solution of these simultaneous equations gives:

$$C_1 = \frac{\varepsilon_{2(\lambda_2)} \cdot A_{\lambda_1} - \varepsilon_{2(\lambda_1)} A_{\lambda_2}}{\varepsilon_{1(\lambda_1)} \varepsilon_{2(\lambda_2)} - \varepsilon_{1(\lambda_2)} \varepsilon_{2(\lambda_1)}} \qquad [32]$$

$$C_2 = \frac{\varepsilon_{1(\lambda_1)} A_{\lambda_2} - \varepsilon_{1(\lambda_2)} A_{\lambda_1}}{\varepsilon_{1(\lambda_1)} \varepsilon_{2(\lambda_2)} - \varepsilon_{1(\lambda_2)} \varepsilon_{2(\lambda_1)}} \qquad [33]$$

Therefore by measuring the absorbance of the mixture at wavelengths λ_1 and λ_2, the concentrations of the two components can be calculated, if ε_1 and ε_2 are known. The values of the molar absorption coefficients ε_1 and ε_2 can be deduced from measurements of the absorbances of pure solutions of substances 1 and 2.

In the present investigation iron (III) and cobalt(II) are completely extracted together into ethylacetate from the aqueous phase under identical conditions and the absorption spectra of the two metal complexes don't overlap.

Iron(III)-SCN-PCHA complex absorbs strongly at 495 nm and weakly at 625 nm, and cobalt(II)-SCN complex absorbs strongly at 625 nm and weakly at 495 nm (Figure 2). Thus by measuring the absorbance of the ethylacetate extract at 495 and 625 nm the concentration of the two metal ions can be determined in the original solutions.

Hence, in order to verify the proposed method, a series of solutions was prepared by mixing varying amounts of iron(III) and cobalt(II) solutions and the two metal ions were extracted by the general procedure described earlier. The absorbance of the extracts was measured at 495 and 625 nm against reagent blank and the concentration of the two metal ions in the original sample solutions were calculated by solving the simultaneous equations. The results are given in Table 22. These results indicate that the two metals can be determined precisely and accurately in a given sample by the proposed method.

Table 22. Results of Simultaneous Determination of Iron(III) and Cobalt(II).

[Fe(III)] Added	[Co(II)] Added	Molar ratio [Fe(III)]: [Co(II)]	Absorbance at 495 nm	Absorbance at 625 nm	[Fe(III)] found	[Co(II)] found
$6.0x10^{-5}$	$8.0x10^{-5}$	3:4	1.092	0.268	$6.02x10^{-5}$	$8.08x10^{-5}$
$4.0x10^{-5}$	$2.0x10^{-4}$	1:5	0.728	0.440	$3.95x10^{-5}$	$1.98x10^{-4}$
$2.0x10^{-5}$	$4.0x10^{-4}$	1:20	0.399	0.774	$2.03x10^{-5}$	$4.04x10^{-4}$
$8.0x10^{-6}$	$6.0x10^{-4}$	1:75	0.195	1.106	$8.12x10^{-6}$	$6.00x10^{-4}$

3.10 Application

In order to asses the analytical potentiality of the newly developed methods, the methods have been applied to the analysis of blood, steel, and vitamin B_{12} samples for iron and cobalt, respectively.

Blood Sample: The amount of iron in blood sample, prepared by following the procedure described earlier, was determined by Fe(III)-SCN-PCHA method and Fe(III)-N_3-PCHA method. The iron content of the blood sample was also determined by 2,2'-bipyridyl as standard method to compare the results obtained by newly developed methods. In all the methods the results obtained were essentially the same, and fall within the range of content of iron in whole blood reported for an adult man. The reported range is from 45-145 mg/100 ml (14). Hence, both Fe(III)-SCN-PCHA and Fe(III)-N_3-PCHA methods are reliable and applicable for the determination of iron in biosamples. The results are given in Table 23.

Table 23. Determination of Iron in Blood Sample

Method	*Fe Found mg/100 ml	Relative standard deviation (%)
Fe(III)-SCN-PCHA	77.18	0.25
Fe(III)-N_3-PCHA	77.14	0.76
2,2'-bipyridyl	77.41	0.30

* Average of three determinations.

Steel Sample: Since standard samples were not available, synthetic samples having the same constituents with identical proportion as that of the British Chemical Standard Steel No. 64a and 241/1 were prepared. Extraction and determination of iron in steel samples were undertaken following the procedures described earlier. The experimental results are given in Table 24.

Composition of Steel:

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

Sample No. 241/1: 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, 65.87%.

Table 24. Determination of Iron in Synthetic Steel Samples

Method	Sample No.	Iron Content (%)	*Iron Found (%)	Relative Standard deviation (%)	Relative Error (%)
Fe(III)-SCN-PCHA	64a	83.45	82.83	0.28	0.75
Fe(III)-N_3-PCHA	64a	83.45	82.89	0.22	0.67
Fe(III)-N_3-PCHA	241/1	65.87	65.25	0.43	0.91

*Average of triplicate analyses.

In order to ascertain the reliability of the newly developed method for the simultaneous determination of iron(III) and cobalt(II), the method was applied to the analysis of British Chemical Standard Steel No. 241/1. The iron(III) and cobalt(II) were extracted from the sample solution by the general procedure and the concentration of the two metal ions were calculated by solving the simultaneous equations. The results of the analysis are given in Table 25.

Table 25. Simultaneous Determination of Iron(III) and Cobalt(II) in Steel Sample No. BCS 241/1

Iron Content (%)	*Iron found (%)	Relative standard deviation (%)	Relative error (%)	Cobalt content (%)	*Cobalt found (%)	Relative standard deviation (%)	Relative error (%)
65.87	65.33	0.124	0.82	5.67	5.64	0.72	0.53

*Average of triplicate analyses.

The experimental results indicate that the newly developed methods are reliable.

Vitamin B_{12}: The cobalt(II)-thiocyanate method was applied to the analysis of vitamin B_{12}. The cobalt content of the sample was determined by the general procedure described earlier. The experimental result (Table 26) is in good agreement with the actual value indicating the accuracy of the method.

Table 26. Determination of Cobalt in Vitamin B_{12}

Cobalt Content (%)	*Cobalt found (%)	Relative standard deviation (%)	Relative error (%)
4.35	4.323	0.16	0.62

*Average of triplicate analyses.

3.11. Comparison with Other Methods

The comparative study of the proposed methods for cobalt and iron, in regard to selectivity and sensitivity with other spectrophotometric methods are summarized in Table 27 and 28.

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

The sensitivity and selectivity of the present methods for iron have been compared with other methods. The selectivity of the present methods is comparable to most of the other methods while the sensitivity of Fe(III)-SCN-PCHA method is relatively higher than most of the other methods and that of Fe(III)-N_3-PCHA method is comparable to most of the other methods.

Table 27. Comparison with Other Methods for Iron

Reagent	λmax nm	Optimum acidity range	Sensitivity μg Fe/cm^2	Inferference	Ref.
1,10-phenanthroline	508	pH=2-9	0.0047	Cu^{2+}, Hg^{+}, Ni^{2+}, Cd^{2+}, Co^{2+}, PO_4^{3-}	28
Ammonium thiocyanate	480	0.5-1.0M HCl	0.0080	Ag^{+}, Hg^{+}, V^{4+}, Mo^{6+}, Cd^{2+}, F^{-}, PO_4^{4-}, AsO_4^{3-}	44
Oxalate with purpurin	600	pH=8-10	0.0098	V^{5+}, As^{5+}, Bi^{3+}, Be^{2+}, Th^{4+}, Zr^{4+}	83
N-hydroxy N,N-diphenyl benzamidine with azide	530	ph=2-5	0.0120	V^{5+}	59
N-hydroxy N,N-diphenyl benzamidine with thiocyanate	460	0.5-1.0M HCl	0.0047	V^{5+}, Mo^{6+}	58
PCHA/thiocyanate	440	pH=1.1-2.5	0.0068	Zr^{4+}, Ti^{4+}, W^{6+}	76
PCHA	440	pH=1-4	0.0070	V^{5+}, Ti^{4+}, Zr^{4+}, Mo^{6+}, W^{6+}	73
PCHA with azide	447	0.1-0.9M HCl	0.0074	Ti^{4+}, V^{5+}	Present Method
PCHA with thiocyanate	495	0.5-2.0M HCl	0.0031	Ti^{4+}, Zr^{4+}	Present Method

Table 28. Comparison with Other Methods for Cobalt

Reagent	λ_{max} nm	Optimum acidity range	Sensitivity µg Co/cm^2	Interference	Ref.
Ammonium thiocyanate	620	pH=4-5	0.0550	Ni^{2+}, Fe^{3+}, V^{5+}, Cu^{2+}, Cr^{3+}, Cr^{6+}	8
1-Nitroso-2-naphthol	550	ph=4.5-5	0.0075	Cu^{2+}, Fe^{2+}, Mn^{2+}	47
Neotetrazolium chloride with thiocyanate	620	pH=3.5-5	0.0196	Fe^{3+}, EDTA, all metal ions which form colored complexes with thiocyanate	60
Triphenylsulphonium chloride with thiocyanate	625	pH=6-8	0.1447	Cr^{3+}, U^{6+}, Hg^{2+}, Zn^{2+}, Bi^{3+}, Fe^{2+}, CN^-, EDTA	52
Propylene carbonate with thiocyanate	625	pH=2.5-6.2	0.0327	Fe^{2+}, Cu^{2+}, Hg^{2+}, Cr^{3+}	61
1,5bis(di-2-pyridylmethylene) thiocarbonohydrazide	48	ph=10.4-11	0.0011	Cr^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, Bi^{3+}	84
Ammonium thiocyanate	625	0.1-1.5M HCl	0.0324	--	Present Method

4. CONCLUSION

New methods have been developed for the determination of iron(III) and cobalt(II) and for the simultaneous determination of iron(III) and cobalt(II) with thiocyanate and N-phenylcinnamohydroxamic acid by solvent extraction and spectrophotometry. The methods are highly selective, and the method for iron is highly sensitive while the method for cobalt is fairly sensitive. The methods are also simple, precise, accurate, and free from the rigid control of the experimental variables. Therefore, the methods are applicable for the successful determination of iron and cobalt in ores, alloys, rocks, soils, and biological samples. Hence, the methods will have wide analytical potentialities.

Another new simple, rapid, precise, and reliable method has been developed for the extraction and spectrophotometric determination of iron(III) with PCHA and azide. The newly developed method is sensitive and highly selective, and free from the rigid control of experimental variables. The proposed method can be applied for determination of iron in diverse samples.

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DECLARATION

I, the undersigned, declare that this thesis is my work and that all sources of material used for the thesis have been duly acknowledged.

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