ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

Studies on Extraction and Spectrophotometric Determination of Molybdenum(V) Using N^1-Hydroxy-N^1,N^2diphenylbenzamidine and Thiocyanate

by

Belhu Berhanu
Chemistry Department
Science Faculty

Approved by:

Dr. B.S. Chandravanshi
Advisor
KS Chandravanshi

Prof. G. V. Jere
External Examiner
G V Jere 8.7.91

Dr. B. Hundhammer
Examiner
Hundhammer

Ato Ghirma Moges
Examiner
8.7.91

To

My Father, Mother, Sister, and Brothers

ACKNOWLEDGEMENTS

I am highly indebted to my research advisor and instructor Dr. B.S. Chandravanshi for his consistent supervision, guidance, and keen interest he has shown me throughout the period of the research project.

I am also grateful to Ato Naod Kebede for providing me with cuvettes. My thanks also go to Dr. Fikru Tafesse who allowed me to use the Beckman DU-65 Spectrophotometer.

The generosity moral support and encouragement of colleagues and friends have been invaluable, it is my pleasure to record my gratitude to Kelemu Lemma, Belew Mekonnen, Tadesse Agonafir, Saba Asmelash, Mesfin Bekele, Zerihun Gezahagne, Yirgalem Yigzaw, Mulat Abegaz, Asnaketch Feleke, Getnet Negussie, Daniel Zewge, Mulugeta Desta, Asrat Bekele and G/Egziabheir Kiros.

I would like to thank the Ministry of Labour & Social Affairs for sponsoring my studies in the graduate programme.

Special thanks are due Asmara University Computer Center for enabling me to word process the thesis.

Financial support from Swedish Agency For Research Cooperation with Developing Countries (SAREC) is gratefully acknowledged.

CONTENTS

PAGE

ACKNOWLEDGMENTS iii

LIST OF TABLES Vi

LIST OF FIGURES Viii

ABSTRACT ix

1. INTRODUCTION 1

1.1. Occurrence and Uses of Molybdenum 1

1.2. Chemistry of Molybdenum 3

1.3. Reagents Used for the Spectrophotometric Determination of Molybdenum 5

1.4. Analytical Applications of N^1-Hydroxy-N^1,N^2-diphenylbenzamidine 9

1.5. Aim and Scope of Present Investigation 11

2. THEORETICAL BACKGROUND 13

2.1. Fundamentals of Solvent Extraction 13

2.2. Solvent Extraction of Metal Chelates 14

2.3. Spectrophotometry 18

2.4. Spectrophotometric Determination of Metal Ions 19

2.5. Characteristic Terms in Photometric Analysis 23

2.6. Spectrophotometric Methods for the Determination of Composition of Metal Complexes 26

3. EXPERIMENTAL 30

3.1. Synthesis of N^1-Hydroxy-N^1,N^2-diphenylbenzamidine 30

3.2. Apparatus and Reagents 32

3.3. Procedures 37

3.3.1. Extraction and Determination of Mo(V) 37

3.3.2. Examination of Experimental Variables 38

3.3.3. Investigation of the Effect of Diverse Ions 38

3.3.4. Determination of the Stoichiometric Composition of the Complex 38

4. RESULTS AND DISCUSSION 40

4.1. Color Reaction and Absorption Spectra 40

4.2. Effect of Variables 42

4.3. Evaluation of Photometric Characteristics 53

4.4. Stoichiometry of the Complex 56

4.5. Effect of Diverse Ions 60

4.6. Application 63

4.7. Comparison with Other Spectrophotometric Methods 64

5. CONCLUSION 68

6. REFERENCES 69

LIST OF TABLES

PAGE

1. Extraction behaviour of Mo(V)-SCN-HDPBA complex in different organic solvents 41
2. Extraction behaviour of Mo(V)-SCN complex in AmOH - benzene solvent system 42
3. Effect of hydrochloric acid concentration of the aqueous phase on the extraction of Mo(V)-SCN-HDPBA complex 44
4. Effect of variation of ammonium thiocyanate concentration on the extraction of Mo(V) 45
5. Effect of the concentration of ascorbic acid on the extraction of Mo(V) 47
6. Effect of mode of addition of the reagent (HDPBA) on the extraction of Mo(V) 49
7. Effect of the amount of HDPBA on the extraction of Mo(V) 50
8. Effect of the volume of the aqueous phase on extraction of Mo(V) 51
9. Stability of the complex 52
10. Optimum experimental conditions for extraction and determination of Mo(V) with HDPBA and thiocyanate 52
11. Data for calibration curve and the Ringbom's plot for determination of Mo(V) 53
12. Data for evaluating the limit of determination of Mo(V) and precision of the proposed method 55
13. Photometric characteristics of the complex 56

14. Results of the extraction method for the determination the ratio of Mo(V) to HDPBA in Mo(V)-SCN-HDPBA complex 57

15. Results of the extraction method for the determination the ratio of Mo(V) to SCN^- in Mo(V)-SCN-HDPBA complex 59

16. Tolerance limits of diverse ions in the determination of Mo(V) 61

17. Determination of molybdenum in synthetic steel and ore matrices by the proposed method 64

18. Comparison with other spectrophotometric methods 65

LIST OF FIGURES

PAGE

1. UV spectrum of 5×10^{-5} M HDPBA in ethanol 33

2. IR spectrum of HDPBA (KBr) 34

3. Absorption spectra of (A) 5×10^{-5} M Mo(V)-SCN-HDPBA complex against the reagent blank and (B) 6×10^{-3} M HDPBA in AmOH-benzene 43

4. Effect of HCl concentration of the aqueous phase on the extraction and determination of 120 μg Mo(V) 46

5. Effect of the concentration of thiocyanate on the extraction and determination of 120 μg Mo(V) 46

6. Calibration curve for the determination of Mo(V) 54

7. Ringbom's plot for the evaluation of optimum concentration range for the determination of Mo(V) 54

8. Curve for the determination of Mo(V) to HDPBA ratio in Mo(V)-SCN-HDPBA complex by extraction method 58

9. Curve for the determination of Mo(V) to SCN ratio in Mo(V)-SCN-HDPBA complex by extraction method 58

ABSTRACT

Studies on Extraction and Spectrophotometric
Determination of Molybdenum(V) using
N^1-Hydroxy-N^1,N^2-diphenylbenzamidine
and
Thiocyanate

by

Belhu Berhanu

Research advisor: Dr. B.S. Chandravanshi

Molybdenum(V) has been found to react with N^1-hydroxy-N^1,N^2-diphenylbenzamidine (HDPBA) and thiocyanate to form a reddish-orange complex which is quantitatively extractable into 2.5 % (v/v) amyl alcohol in benzene from 4 - 6 M hydrochloric acid solutions. The complex exhibited a wavelength of maximum absorption at 470 nm with a molar absorptivity of 13100 M^{-1} cm^{-1} and the system obeyed Beer's law in the concentration range of 0.48 - 9.59 ppm of Mo. The composition of the complex has been established spectrophotometrically to be 1:3:1 (Mo:SCN^-:HDPBA). The effects of diverse ions and of several experimental variables have been studied to establish the optimum conditions for extraction and determination of molybdenum. On the basis of these studies a simple, precise, sensitive and a highly selective method has been developed for the determination of molybdenum(V) by solvent extraction and spectrophotometry. The method has been successfully applied to the determination

of molybdenum in several synthetic samples corresponding to molybdenum containing steels and ores.

1. INTRODUCTION

1.1. Occurrence and Uses of Molybdenum [1 - 9]

Molybdenum is ranked fifty third in the order of abundance of the elements in the earth's crust with a concentration of about 1.5 ppm.

The most important ore of molybdenum is the sulphide, molybdenite, MoS_2; of which the largest known deposit is in Colorado,USA, but it is also found in Canada and Chile. Less important ores are: wulfenite, $PbMoO_4$; powellite, $Ca(Mo,W)O_4$; molybdite or molybdenum ochre, $Fe_2O_3.3MoO_6$ [1-3].

Industrial applications of molybdenum and molybdenum containing compounds are immense. Molybdenum compounds may function as a principal catalysts and also as activators and promoters of other catalysts. They are employed industrially in oxidation-reduction reactions, in certain organic synthesis (notably the hydrogenation-cracking, alkylation and reforming of petroleum products). Particularly in the reactions involving petroleum and natural gas, the frequent interchangeability of sulphur and oxygen in molybdenum compounds is a highly useful property, in desulphurization of petroleum products and since traces of sulphur could poison other catalysts but not those of molybdenum catalysts, they are renowned in such technological processes.

Molybdenum compounds, added in relatively small proportions to ceramic glazes and enamels, solve a serious problem in ceramics, particularily in application to vitreous enamels on steels.

Solutions of trivalent molybdenum are used for tanning of skins in the same way as the solutions of salts of trivalent chromium in leather industries .

A very important use of molybdenum disulphide is as a solid lubricant. The very greasy property of molybdenite, gave it particular importance in modern aerospace and mechanical applications.

Corrosion inhibitors, based on soluble molybdates and tungstates have been in use for some time and comparable in their action to chromates. They have the advantage that they are colorless and relatively non toxic. Recently much attention has been given to the use of calcium, zinc, and strontium molybdates as corrosion inhibitors in paint systems. These colorless apparently non-toxic compounds could lead to the formulation of single coat, corrosion inhibitive coating system [2,4,6].

The biological importance of molybdenum was first recognized in the field of agriculture. The effects are quite dramatic in facilitating the plant growth. Traces of molybdenum are necessary for the proper processing of inorganic nitrogen nutrients by plants. Specifically, the

enzyme responsible for the first steps in nitrogen fixation and nitrate assimilation contain molybdenum as part of the active site. This absolute dependence of plant life on molybdenum has motivated scientists to study the relationship between molybdenum and agricultural productivity as well as the bio-inorganic chemistry of the element and its determination.

There are several other motivations for pursuing and understanding of biological molybdenum. Most higher animals also depend on trace amounts of molybdenum. Again these traces are found at the active sites of metalloenzymes that catalyze important metabolic conversions. Persons having diet high in molybdenum often suffer from an inflammation of the extremities due to excess uric acid deposition.

The choice of molybdenum by nature as essential element seems unusual at first glance. Molybdenum is the only metal from second and third transition rows of the periodic table to be required by diverse organisms [7-9].

1.2. *Chemistry of Molybdenum* [1-6]

Metallic molybdenum is silver grey in color and lustrous, moderately heavy (10.22 g cm^{-3}), very high melting (2610^{0}C) and is quite a good electrical conductor (specific conductance of about one third of silver).

It is in Group VIB of the periodic table with electronic configuration of $[Kr]4d^5 5s^1$.

At room temperature it is inert towards oxygen, and it is also resistant to attack of strong acids but slowly reacts with HNO_3 and immediately becomes passive. It dissolves in aqua regia or in a mixture of HF and HNO_3. It is rapidly attacked by fused oxidizing agents such as Na_2O_2, $KClO_3$ and KNO_3.

Molybdenum and tungsten are closely similar to each other and show marked difference from chromium. The closer similarity of the two elements is due to the lanthanide contraction. However the similarity of the two elements is not as strong as (Zr,Hf), and, (Nb, Ta) pairs. As a result, molybdenum and tungsten can be easily separated in the conventional scheme for qualitative analysis of metals.

Molybdenum forms various compounds in which it displays valence states from +6 down to -2. Molybdenum as ionizable cation has not been observed, but cationic species like MoO_2^+, are known to exist. The most important valence are the hexavalent, pentavalent and trivalent states. The lower oxidation states are stabilized by the π acceptor ligands.

A study of the chemistry of molybdenum suggests that oxides are existing having oxidation states of +2 to +6.

In aqueous solution molybdenum compounds with valence states of +6 are the most stable. In hydrochloric acid solution (4 N HCl) the compounds of molybdenum(V) are perfectly stable in air. As the acidity decreases, the tendency of Mo(V) compounds to be oxidized by atmospheric oxygen increases. In alkaline solutions Mo(V) ions are very readily oxidized. Mo(III) in aqueous solution is fairly resistant to oxidation by atmospheric oxygen at high hydrochloric acid concentrations (9 N HCl) owing to the formation of complex ions like $MoCl_6^{3-}$, $MoCl_5^{2-}$, etc. In strongly acidic solutions molybdate anions are reduced to $[MoOCl_5]^{2-}$ ions.

1.3. Reagents Used for the Spectrophotometric Determination of Molybdenum

Several reagents have been reported for spectrophotometric determination of molybdenum. Eventhough the whole coverage of literature would not be presented under this section, some of the most sensitive and selective reagents that have been recently reported in literature and that may have wide analytical applications are reviewed below.

Mo(V) was found to react with N^1-hydroxy-N^1-p-tolyl-N^2-3,4-xylylbenzamidine(I) in 2 to 4.5 M HCl medium in the presence of thiocyanate to form an orange red Mo-I-SCN complex (1 :2 :2), extractable into benzene (λ_{max}= 470 nm) [10]. The analytical range is 5 to 18 ppm Mo. No significant interference from Ni(II), Co(II), Cu(II), Mn(II), Ti(IV), Zr(IV), V(V), Nb(V), Ta(V), or W(VI) was found.

Rodriguez [11] has developed a method using 1,4-dihydroxyphthalamide dithiosemicarbazone forming a yellow 1:1 complex in acidic dimethylformamide-water solution. The yellow complex can be extracted into isopentyl alcohol (λ_{max} = 435 nm, ε = 9400 M^{-1} cm^{-1}).

A method has been described for the spectrophotometric determination of micro amounts of molybdenum with N,N'-diarylbenzamidines (HA) and thiocyanate based on the extraction of molybdenum thiocyanate species with dimers (H_2A_2) as 1:2:1 (Mo:SCN:H_2A_2) complexes over a wide acidity range (0.5 - 8 M HCl). The molar absorptivities of the complex lie in the range of (1.65 - 1.85) x 10^4 $M^{-1}cm^{-1}$ at λ_{max} = 465 - 470 nm. The metal ions generally associated do not interfere. The method has been accurately applied to ore, alloy - steels and synthetic mixtures [12].

Imidoylphenylhydrazine {1-[4-methyl-α-(2,5-xylyl-imino)-benzyl]-2-phenyl hydrazine} (I) as a reagent for spectrophotometric determination of Mo(V) in the presence of thiocyanate was employed [13]. The Mo-SCN-I (1:2:1) complex was extracted into benzene and exhibited an absorption maximum at 465 nm (ε = 17300 M^{-1} cm^{-1}). The interference from Fe(III) and Nb(V) was masked with oxalate.

Gudniewska et al. [14] have developed a method for spectrophotometric determination of Mo(V) (5 to 50 μg) with promethazine hydrochloride in the presence of thiocyanate in H_2SO_4 medium after extraction of the orange ion pair complex (λ_{max} = 465 nm) into chloroform. The coefficient of variation is within 0.3 to 1.5 %. Of several ions tested Co^{2+} and Cu^{2+} interfered.

Analytical potentiality of lobeline for spectrophotometric determination of Mo(V) in the presence of thiocyanate was investigated [15]. Chloroform was selected as an extracting solvent for Mo(V)-SCN-lobeline complex (λ_{max} = 465 nm). Beer's law is obeyed from 0.13 - 14 μg mL^{-1}. Prior separation of Cu^{2+} , Ti^{4+}, Co^{2+} and W^{6+} is essential.

A spectrophotometric method for the determination of molybdenum (VI) with toluene-3,4-dithiol in isobutyl methyl ketone has been developed by Pilar et al. [16]. The molar absorptivity of the complex is 75000 M^{-1} cm^{-1} at the absorption maximum (415 nm), and the complex is stable for 15 minutes. Beer's law is obeyed in the range of 0.25 - 1.25 μg mL^{-1} of Mo. Serious interferences are from Fe(III), Cu(II), Co(II), Hg(II) and W(VI).

N-Phenylbenzohydroxamic acid reacts with Mo(VI) in 3.5 - 6.0 M hydrochloric acid to give a complex that is extractable into chloroform. The chloroform extract of the molybdenum complex, on second extraction from a dilute hydrochloric acid medium (0.2 - 0.3 M) in the presence of phenylfluorone in ethanol, forms an intensely colored complex with an absorption maximum at 518 nm and ε = 74000 M^{-1} cm^{-1}. The system obeys Beer's law up to 0.6 ppm of Mo(VI). The interference from V(IV), V(V) and Ti(IV) should be controlled using oxalate and sodium metabisulphate respectively [17].

A method has been reported [18] in which Mo(V) forms a reddish orange complex in the presence of thiocyanate and N-m-tolyl-N'-p-chlorophenyl-o-chlorobenzamidine. The complex exhibited an absorption maximum at 470 nm (1.8×10^4 M^{-1} cm^{-1}). Beer's law is obeyed in the concentration range 0.4 - 5.6 ppm with Sandell sensitivity of 0.005 μg cm^{-2} of Mo(V). The method is suggested to be applied for the determination of Mo(V) in the presence of high concentration of other ions.

Chandrakar and Mishra [19] have developed a method for extractive spectrophotometric determination of Mo(V) using 2-chloro-N,N'-bis-(4-chlorophenyl)-N-hydroxybenzamidine hydrochloride in the presence of thiocyanate. The absorption maximum is at 470 nm, it follows Beer's law in the range of 3 to 24 ppm of Mo(V), the Sandell sensitivity is 0.029 μg cm^{-2} and the coefficient of variation is 1.56 %.

Phosphomolybdenum blue complex has been employed by Luo [20] for spectrophotometric determination of molybdenum(V). The Mo was determined from the absorbance of the complex at 690 nm (ε = 700 M^{-1} cm^{-1}). Beer's law is obeyed for up to 12 mg mL^{-1}. Tungsten was found to interfere.

Salicylaldehyde isonicotinoylhydrazone (SAIH) has been reported as a specific analytical reagent for selective extractive spectrophotometric determination of Mo(VI) [21]. After extraction of the complex into isoamyl alcohol the absorbance was measured at 380 nm (ε =12,100 M^{-1} cm^{-1}). Beer's law is obeyed for 0.2 to 6 μg mL^{-1}.

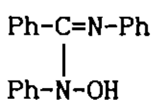
Investigation of molybdenum(V) complexation with 4-benzoyl-3-methyl-1-phenylpyrazolin-5-one in water-ethanolic medium has led to a formation of reddish orange complex of Mo(V) which has absorption maximum at 480 nm to 490 nm (ε_{490} = 2500 M^{-1} cm^{-1}) in aqueous 20 % ethanol. A color development time of 35 minutes is required. Beer's law is obeyed from 1 to 35 μg mL^{-1} of Mo. Iron is found to interfere, hence extraction with acetyl-acetone was recommended [22].

El-Shahat et al.[23] have proposed a spectrophotometric determination of molybdenum with phenylfluorone in HCl-ethanol medium (pH 1.5 to 3.5) to form an intensely colored stable 1:1 complex, the absorbance of the complex was measured at 560 nm. Beer's law was obeyed over the range 40 to 160 μg mL^{-1}; the absorptivity of the complex is 3800 M^{-1} cm^{-1} and Sandell sensitivity is 2.55 μg cm.$^{-2}$ The species Sn(II), Sn(IV), Sb, Ga, Ge, PO_4^{-3}, Nb, Ta, and V interfered when present at concentration exceeding that of Mo. The coefficient of variation of the method was 2 %.

A method of micro determination of Mo(VI) in steel, biological materials and waters has been developed by Abassi [24] using 3-(2-furyl)-N-(4-methoxy phenyl)acrylhydroxamic acid as a reagent and isoamyl alcohol as a solvent. The absorbance was measured at 380 nm (ε = 12100). Beer's law is obeyed for 0.2 to 6 μg mL^{-1} Mo(VI).

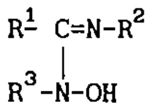
1.4. *Analytical Applications of N^1-Hydroxy-N^1,N^2-diphenyl benzamidine (HDPBA)*

N^1-Hydroxy-N^1,N^2-diphenylbenzamidine, I, and its analogue, II are typical monobasic and bidentate chelating agents having functional grouping III,



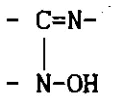
$\begin{array}{l}\text{Ph-C=N-Ph}\\ \quad\;| \\ \text{Ph-N-OH}\end{array}$

I



$\begin{array}{l}R^1\text{-C=N-}R^2\\ \qquad| \\ R^3\text{-N-OH}\end{array}$

II



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

III

where R^1, R^2 and R^3 are phenyl or substituted phenyl groups.

Hydroxyarylbenzamidines are pale yellow crystalline solids and stable towards heat, light, and can be stored indefinitely without deterioration. These compounds are soluble in common organic solvents like alcohol, acetone, chloroform, benzene, and toluene but insoluble in water. Their solutions in organic solvents are light yellow and stable for several days at room temperature.

Hydroxyamidines have wider scope as analytical reagents in a sense that by substitution of a particular group in the three phenyl groups attached to the functional grouping, their complexing properties can be modified. Hence the sensitivity, selectivity, and other analytical characteristics for a particular method can be improved. Some of the metal chelates can be used for gravimetric determination of the metal ions. Most of the metal complexes of hydroxyamidines are intensely colored and are stable. These reaction products can be employed for simple spectrophotometric determination in aqueous systems or for the simultaneous extraction and spectrophotometric determination of metal ions.

N^1-Hydroxy-N^1,N^2-diphenylbenzamidine (HDPBA), the parent compound, was introduced as analytical reagent for the first time in 1974 by Satyanarayana and Mishra [25] for the extraction and spectrophotometric determination of vanadium(V). Since then many workers have tried to exploit the analytical potentialities of HDPBA and its analogues. Several investigations are being carried out until recently for detection and determination of different metal ions in gravimetric analysis, solvent extraction and spectrophotometry.

N^1-Hydroxy-N^1,N^2-diphenylbenzamidine has been used for the gravimetric determination of nickel [26] and spectrophotometric determination of iron(III) [27], and to the solvent extraction and spectrophotometric determination of iron(III) [28,29], cobalt (II) [29], cobalt(III) [30] and manganese (VII) [31].

1.5. *Aim and Scope of Present Investigation*

The foregoing literature survey reveals that there are a wide variety of reagents that could be applied for spectrophotometric determination of molybdenum, which have different advantages and disadvantages in terms of their selectivity, sensitivity, precision, speed, convenience, etc. and the parent compound HDPBA has also not been applied for the spectrophotometric determination of molybdenum. Therefore it has become worth studying the reaction of Mo(V) with HDPBA in the presence of thiocyanate in the present investigation to develop a precise, sensitive and selective method for the determination of Mo(V).

Hence the objectives of the research project were :

(i) to study the spectral properties of the reaction products of Mo(V) with HDPBA and thiocyanate in the UV-Visible region ;

(ii) to establish the optimum conditions for the extraction and determination of Mo(V) with HDPBA and thiocyanate ;

(iii) to determine the stoichiometric compositions of

Mo(V)-HDPBA-SCN complex ; and

(iv) to evaluate the sensitivity , selectivity , precision , accuracy , and the applicability of the proposed method.

The proposed studies has led to the development of a precise , sensitive , and selective method for the determination of Mo(V) with HDPBA and thiocyanate by solvent extraction and spectrophotometry.

2. THEORETICAL BACKGROUND

2.1. Fundamentals of Solvent Extraction [32-39]

Solvent extraction (or liquid-liquid extraction) occupies a very important position among separation methods in chemical analysis because of its simplicity, rapidity, wide applicability, and relatively less contamination problem. This method is based on the distribution of solute between two essentially immiscible solvents.

For the understanding of the fundamental principle on which extraction method of chemical analysis is based, various terms used in expressing the effectiveness of separation will be discussed.

The thermodynamic condition for a heterogeneous 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 in the two phases:

$$(\mu_M^0)_I + RT\ \ln(a_M)_I = (\mu_M^0)_{II} + RT\ \ln(a_M)_{II} \qquad (1)$$

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

In analytical application 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 1 can be rearranged to give:

$$(\mu^{o}_{M})_{aq}-(\mu^{o}_{M})_{org} = \quad -\Delta G^{o}_{D,M} = \frac{RT\ \ln\ (a_{M})_{org}}{(a_{M})_{aq}}$$

$$= RT\ \ln\ (K_{D,M})_{a} \qquad (2)$$

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

For practical applications it is necessary to convert the thermodynamic constant $(K_{D,M})_{a}$, into the concentration partition constant $K_{D,M}$ (called distribution constant)

$$K_{D,M} = \frac{[M]_{org}}{[M]_{aq}} \qquad (3)$$

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

2.2. 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 electro-neutral 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:

$$M_{aq} + nHL_{org} \rightleftharpoons ML_{n,org} + nH^{+}_{aq} \qquad (4)$$

which is characterized by extraction constant:

$$K_{ex} = \frac{[ML_n]_{org}\,[H^{+}]^{n}_{aq}}{[M]_{aq}\,[HL]^{n}_{org}} \qquad (5)$$

The extraction equilibrium expressed by Equation 4, can be considered as composed of the following four equilibria:

(i) distribution of the chelating agent, HL, between the two phases:

$$HL_{aq} \rightleftharpoons HL_{org}; \quad K_{D,L} = \frac{[HL]org}{[HL]aq} \qquad (6)$$

(ii) dissociation of the chelating agent aqueous phase:

$$HL \rightleftharpoons H^{+} + L^{-}; \quad \beta^{-1}_{HL} = \frac{[H^{+}][L^{-}]}{[HL]} \qquad (7)$$

(iii) formation of the extractable chelate, ML_n:

$$M^{n+} + nL^{-} \rightleftharpoons ML_n; \quad \beta_n = \frac{[ML_n]_{aq}}{[M^{n+}][L^{-}]^{n}} \qquad (8)$$

(iv) distribution of the chelate, ML_n, between the two phases:

$$ML_{n,aq} \rightleftharpoons ML_{n,org}; \qquad K_{D,M} = \frac{[ML_n]_{org}}{[ML_n]_{aq}} \qquad (9)$$

Substituting Equations 6 to 9 in Equation 5, one gets:

$$K_{ex} = \frac{K_{D,M}\,\beta_n}{(K_{D,L}\,\beta_{HL})^n} \qquad (10)$$

As shown in Equation 10, 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,

$$D_M = \frac{[M]_{org}}{[M]_{aq}} \qquad (11)$$

This quantity is called the distribution ratio.

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

$$E_M = \frac{100[M]_{org}V_{org}}{[M]_{org}V_{org} + [M]_{aq}V_{aq}} = \frac{100D_M}{D_M + \frac{V_{aq}}{V_{org}}} \qquad (12)$$

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

The expression in Equation 5 can, thus be written for the extraction of the chelate ML_n as,

$$D_M = K_{ex}\left(\frac{[HL]_{org}}{[H^+]_{aq}}\right)^n \qquad (13)$$

or $$\log D_M = \log K_{ex} + n \log [HL]_{org} + n\ pH \qquad (14)$$

As shown in equation 14, 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 13. Generally, a change in temperature changes the value of the equilibrium constant, but it is not possible to predict how it will affect the value of K_{ex}.

There is no general rule for prediction of the effect of 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 kinetic effect involved in the value of D_M, since D_M has been determined for an equilibrium state. However, in some circumstances kinetic masking can be utilized to get selective separation, if the rate of extraction of one species is much faster than that of another.

The proper selection of a solvent for the extraction of a metal chelate requires a study of the behaviour of the chelate in a variety of solvents to determine the one resulting in high distribution of the chelate and low distribution for interferants. In addition to a consideration of a distribution of a metal chelate in a particular solvent, the ease of recovery of the chelate and the solvent is important for subsequent analytical processing. Thus the boiling point of the solvent or the ease of stripping by chemical reagent should have a place in the selection of a solvent. Similarly the degree of miscibility of the two phases, the specific gravities, viscosity, tendency to form emulsion and stability should be considered. Some times it is possible to achieve many of the desired characteristics of a solvent by employing a mixed solvent system.

2.3. *Spectrophotometry* [32,33,38-45]

When a monochromatic light passes through a homogeneous absorbing medium of length, l, the radiant energy will decrease in proportional to the amount or concentration, c, of the absorbing substance in the light path, this is the basis for spectrophotometric determination of chemical analysis.

The quantitative statement of this phenomenon is described by Beer's law as,

$$A = \varepsilon c l \tag{15}$$

where A is the absorbance and ε is the proportionality constant known as molar absorptivity or molar absorption coefficient, which is a measure of the extent of interaction between the molecule of substance and the monochromatic radiant energy. If the value of ε and l are known, the concentration of the unknown solution can be evaluated using Beer's law.

Spectrophotometric methods, coupled with, solvent extraction are commonly used for the determination of inorganic substances with organic reagents. In particular they are applied for the determination of small amounts of nearly all common and most rare elements in a great variety of natural materials and industrial products.

2.4. Spectrophotometric Determination of Metal Ions [32,33,38-45]

Spectrophotometric determination of metal ions is usually based on the formation of metal complexes. The formation of a stable metal complex requires the presence of acidic or basic analytical functional groups in the molecule of the reagent, preferably in those positions which allow the formation of a five or six-membered chelate ring. Since these complexes mostly have color, the quantification of such complexes is accessible in the visible part of the spectrum. Colorless species can also be investigated, since the usable range of spectrophotometric determination extends to the UV region.

Completeness of complexation reaction. Both the accuracy and the 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

$$M + nL \rightleftharpoons ML_n \tag{16}$$

on which the determination is based;

$$\beta'_{ML_n} = \frac{[ML_n]}{C'_M (C'_L)^n} = \frac{\beta_{ML_n}}{\alpha_M \alpha_L^n} \tag{17}$$

where C'_M is the total concentration of the metal ion in the formation of the complex ML_n, C'_L is the 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,

$$\frac{[ML_n]}{C'_M} = \beta'_{ML_n}(C'_L)^n \geq 10^2 \qquad (18)$$

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 (β'_{MLn}) and NL_n (β_{NLn}') with similar absorption spectra, correct results for ML_n are obtained if the condition in Equation 18 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,

$$\frac{A_{ML_n}}{A_{NL_n}} = \frac{\varepsilon_{ML_n}[ML_n]}{\varepsilon_{NL_n}[NL_n]} \geq 10^2 \qquad (19)$$

If the concentration 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 accurate result is to be obtained for M,

$$\frac{[NL_n]}{C'_N} = \beta'_{NL_n}(C_L)^n \leq 10^{-2} \qquad (20)$$

combination of Equations 18 and 20 gives,

$$\frac{\beta'_{ML_n}}{\beta'_{NL_n}} = 10^4 \qquad (21)$$

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 wavelength where the difference in absorbance are maximal, and by solving the appropriate simultaneous equations.

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

2.5. *Characteristic Terms used in Photometric Analysis* [32,46,47]

Accuracy and precision of photometric determination. The accuracy (the agreement between the result obtained in photometric analysis and the true amount of the substance being determined) and the precision (reproducibility of measurements, e.g. expressible in terms of the standard deviation) depends on the type of the instrument used and on the chemical reaction choosen.

Deviation from Beer's law are caused by many factors, namely stray light, light reflected on the walls of the cuvette, the changes in temperature during measurement (which may affect the molar absorption coefficient) and the band width of the radiation from the monochromator.

The equilibrium concentration of the complex is influenced by side-reaction with other components of the solution. The presence of large amount of electrolyte (known as salt effect) causes the deformation of the complex species which results in the change of the absorption spectrum.

A further source of photometric error is due to the change in refractive index due to the change in the concentration of the absorbing species and thus, the amount of light scattered from the beam passing through the cuvette. A useful method for the determination of concentration limits within which the photometric error is minimum, was introduced by Ringbom [48]. According to this technique, percent transmittance, T, is plotted against the logarithm of concentration, a sigmoid or S-shaped curve is obtained. The concentration range within which the relative photometric analysis error is minimum is obtained by constructing tangents to the steepest portion of the curve.

Sensitivity and limit of determination. The sensitivity of a quantitative photometric method is defined as the slope, dA/dC, of the calibration curve C = f(A) at the origin [49], where C is the concentration of the substance to be determined, and A the absorbance of the solution. The initial linear portion of the curve can be expressed as:

$$C = (A-A_0)\ (dA/dC)^{-1} \qquad (22)$$

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

The limit of determination is defined as the lowest concentration (C_{min}) of a given substance which can be determined by employing a specified procedure. This can be expressed as the lowest weight amount (e.g. μg) or as the lowest molar concentration, M, or in any other convenient way, e.g. as μg mL^{-1}, percentage, ppm, which shows a statistically significant difference from zero or the average value of the blank.

Of several methods of evaluating the limit of determination, two of the most commonly used methods are described. According to Kaiser [57] C_{min} is evaluated as

$$C_{min} = (A-A_0)(dA/dC)^{-1} = 3S_0(dA/dC)^{-1} = \frac{3S_0}{\varepsilon l} \qquad (23)$$

where S_0 is the standard deviation for the blank determination. Sandell [38,46] defines the limit of determination (or Sensitivity) as the weight in μg mL^{-1} of solution which corresponds to an absorbance A = 0.001 measured in a cuvette of cross sectional area 1 cm^2 and l = 1 cm. Its dimension are μg cm^{-2}. According to this definition, C, is given by

$$C_s = \frac{M}{\varepsilon} \; (\mu g \; mL^{-1}) \qquad (24)$$

where M is the molar mass or atomic weight of the analyte metal ion.

In this mode of expressing the limit of determination the spread of the blank determination is not taken into account.

2.6. *Spectrophotometric Methods for Determination of Composition of Metal Complexes* [39,50,51]

Several methods are available for the spectrophotometric determination of the stoichiometric composition of the metal complexes. The most commonly used techniques include the method of continuous variations [42,52], the mole ratio [43], and the extraction [39] methods.

Method of continuous variation. The principle of this method is that the mole fraction of ligand, $X_L = C_L \; (C_M + C_L)^{-1}$, and that of a metal, $X_M = C_M \; (C_M + C_L)^{-1}$, are varied between 0 and 1 maintaining the total concentration constant, $C_L + C_M = C_T$, in the whole series of solution. Considering a single defined equilibrium:

$$M + nL \rightleftharpoons ML_n \qquad (25)$$

if the absorbance is measured at wavelength where neither the metal ion nor the ligand but only the complex absorbs, the coordinates of the maximum of the plot $A = f(X_M \text{ or } X_L)$ gives the stoichiometry of the complex being formed in solution:

$$n = \frac{X_{L(max)}}{1 - X_{L(max)}} \qquad (26)$$

The mole ratio method. The stoichiometry of a single and stable complex in solution can be simply determined from the break on the absorbance versus component concentration plot, maintaining the concentration of one component constant (usually the metal) and the other one vary successively (usually the ligand). The absorbance increases approximately linearly with the mole ratio and then becomes constant. The abscissa of the point of intersection, i.e.,the break, of the two tangents gives the number of ligands in the complex, if it was the ligand concentration that was varied.

Extraction method. Consider the formation of a mixed ligand complex ML_nX_m in an extraction system. The equilibria involved can be represented by,

$$M^{n+}_{aq} + mX_{aq} \rightleftharpoons MX_{m,aq} \qquad (27)$$

$$MX_{m,aq} + nHL_{org} \rightleftharpoons MX_m(HL)_{n,org} \qquad (28)$$

Summing 27 and 28,

$$M_{aq} + mX_{aq} + nHL \rightleftharpoons MX_m(HL)_{n,org} \qquad (29)$$

The extraction constant, K_{ex} for the complex $MX_m(HL)_n$ is given by

$$K_{ex} = \frac{[MX_m(HL)_n]_{org}}{[X]^m_{aq}\ [HL]^n_{org}\,[M^{n+}]_{aq}} \qquad (30)$$

Rearrangement of Equation 30 yields,

$$\frac{[MX_m(HL)_n]_{org}}{[M]_{aq}} = K_{ex}\,[X]^m_{aq}\,[HL]^n_{org} \qquad (31)$$

Since $[M]_{aq} = C_M - [MX_m(HL)_n]_{org}$, Equation 20 can be written as

$$\frac{[MX_m(HL)_n]_{org}}{C_M - [MX_m(HL)_n]_{org}} = K_{ex}\,[X]^m_{aq}\,[HL]^n_{org} \qquad (32)$$

where C_M is the total concentration of the metal ion. If only one stable complex, $MX_m(HL)_n$, is formed, which has selective light absorption at the selected wavelength, then it follows from Beer's law that

$$[MX_M(HL)_n] = \frac{A}{\varepsilon} \quad \text{and} \quad C_M = \frac{A_{max}}{\varepsilon}$$

(for l = 1 cm), where A is the equilibrium absorbance and A_{max} is the maximum absorbance in the presence of excess concentration of auxiliary ligand, X. Rewriting Equation 32,

$$\frac{A}{A_{max} - A} = K_{ex}\,[X]^m_{aq}\,[HL]^n_{org} \qquad (33)$$

Equation 33 can be expressed in logarithmic form as,

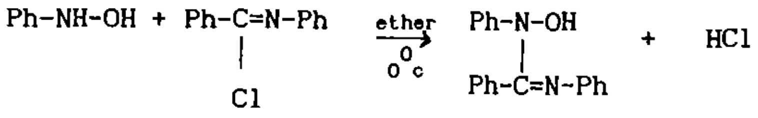
$$\log\left(\frac{A}{A_{max} - A}\right) = \log K_{ex} + m \log [X]_{aq} + n \log [HL]_{org} \quad (34)$$

Thus, the slope of the plot of log $(\frac{A}{A_{max} - A})$ against log $[X]$ at constant concentration of HL in the organic phase gives the number of the auxiliary ligand, X, in the mixed ligand complex; similarly the slope of the plot of log $(\frac{A}{A_{max} - A})$ versus log $[HL]_{org}$ at constant $[X]_{aq}$ gives the number of ligand, HL, in the mixed ligand complex, $MX_m(HL)_n$.

3. EXPERIMENTAL

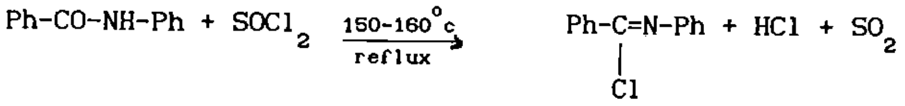
3.1. Synthesis of N^1-Hydroxy-N^1,N^2-diphenylbenzamidine (HDPBA)

HDPBA was prepared by the condensation of N-phenylbenzimidoyl chloride with N-phenylhydroxylamine at 0 °C in ether medium [25]. Thus the preparation of N^1-hydroxy-N^1, N^{2}diphenylbenzamidine required the synthesis of N-phenylbenzimidoyl chloride and N-phenylhydroxylamine.



$$\mathrm{Ph{-}NH{-}OH} + \mathrm{Ph{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}N{-}Ph} \xrightarrow[0^{\circ}c]{ether} \mathrm{\underset{\displaystyle Ph{-}C{=}N{-}Ph}{\underset{|}{Ph{-}N{-}OH}}} + \mathrm{HCl}$$

Preparation of N-phenylbenzimidoyl chloride. The synthesis of N-phenylbenzimidoyl chloride was made by chlorinating the benzanilide using thionyl chloride as a chlorinating agent [53]. A 20 % excess of thionyl chloride (BDH) was mixed with benzanilide (20 g, 0.1 mole) and heated for 30 minutes at 110 °C. The mixture was further heated under reflux (150-160 °C) until the reaction mixture turned to a clear brownish liquid. The excess thionyl chloride was removed by distillation under partial vacuum. The imidoyl chloride was used as such for the synthesis of HDPBA.



$$\mathrm{Ph{-}CO{-}NH{-}Ph} + \mathrm{SOCl_2} \xrightarrow[reflux]{150\text{-}160^{\circ}c} \mathrm{Ph{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}N{-}Ph} + \mathrm{HCl} + \mathrm{SO_2}$$

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

$$\text{Ph-CO-Cl} + \text{Ph-NH}_2 \xrightarrow{\text{NaOH}} \text{Ph-CO-NH-Ph} + \text{HCl}$$

Preparation of N-phenylhydroxylamine. N- Phenylhydroxylamine was prepared by the reduction of nitrobenzene with zinc and ammonium chloride in aqueous soltion at 60- 65 °C [53].

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

Nitrobenzene (50 g, 41.6 mL.) was added to 800 mL of distilled water to which 25 g of ammonium chloride was already dissolved. To the mixture 60 g of zinc dust was added gradually in twenty five minutes time by mechanical stirring, so that the temperature of the reaction mixture could not rise beyond 60-65 °C due to exothermicity of the reaction. The product was separated from the zinc oxide and unreacted zinc by suction. Sodium chloride (150 g) was added to the filtrate to effect the crystallization of N-phenylhydroxylamine. The product was recrystallized from benzene, yield 12 g. The final product was immediately used for the synthesis of HDPBA.

Preparation of N^1-hydroxy-N^1,N^2-diphenylbenzamidine. N-Phenylhydroxylamine (10.9 g, 0.1 mole) in ether (100 mL) was added in small portions from a separatory funnel to a solution of N-phenylbenzimidoyl chloride (21.5 g, 0.1 mole) in ether (180 mL), stirred continuously and placed on an ice bath.

The light yellow crystals were obtained from the ether phase by overnight standing together with the one obtained just at completion of the reaction. The crystals were filtered and washed with ether. The hydrochloride salt was treated with 32 mL of 1 N ammonia. The precipitated free base was filtered off, recrystallized twice from benzene to give pale yellow crystals. Yield 9.2 g, mp 169-170 °C, reported [25] 171 °C.

The UV spectrum of the compound showed an absorption band at $\lambda_{max(ethanol)}$ = 317 nm with ε_{max} = 1.28×10^4 M^{-1} cm^{-1} (Fig. 1).

Infrared spectrum of the compound showed ν_{O-H} = 3200-3000 cm^{-1}, $\nu_{C-H(Ar)}$ = 3100 cm^{-1}, $\nu_{C=N}$ = 1580 cm^{-1}, ν_{C-N}= 1440 cm^{-1} and ν_{N-O} = 940 cm^{-1} (Fig. 2).

3.2. Apparatus and reagents

Apparatus. A Beckman DU-65 spectrophotometer was used for recording the UV spectrum of HDPBA.

A Perkin-Elmer 727B infrared spectrophotmeter was used for recording the IR spectrum of HDPBA.

A Beckman model 24 UV-Vis spectrophotometer equipped with 1 cm matched quartz cells and Beckman recorder was used

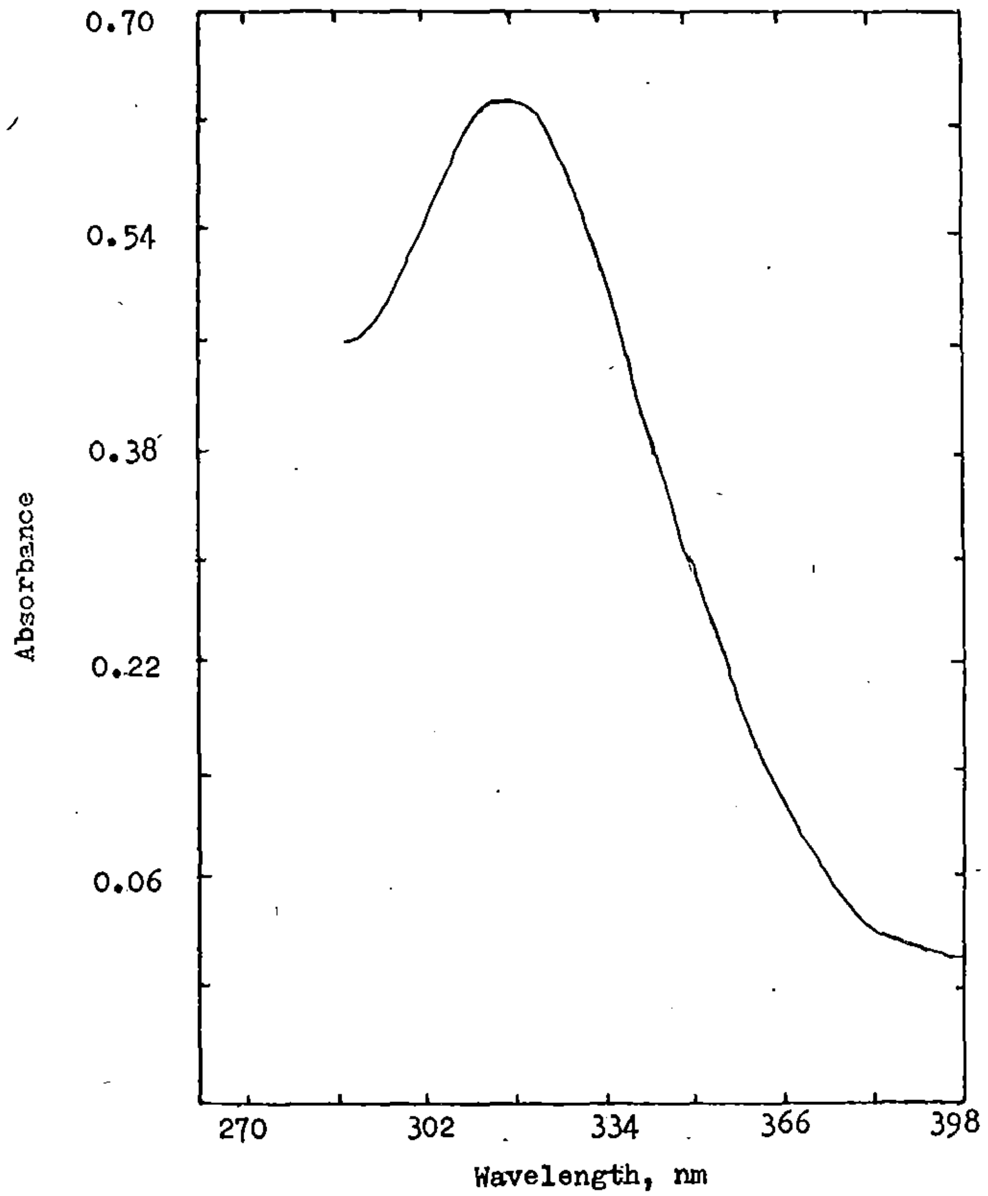


Fig. 1. Absorption spectrum of 5 X 10^{-5} M HDPBA in ethanol.

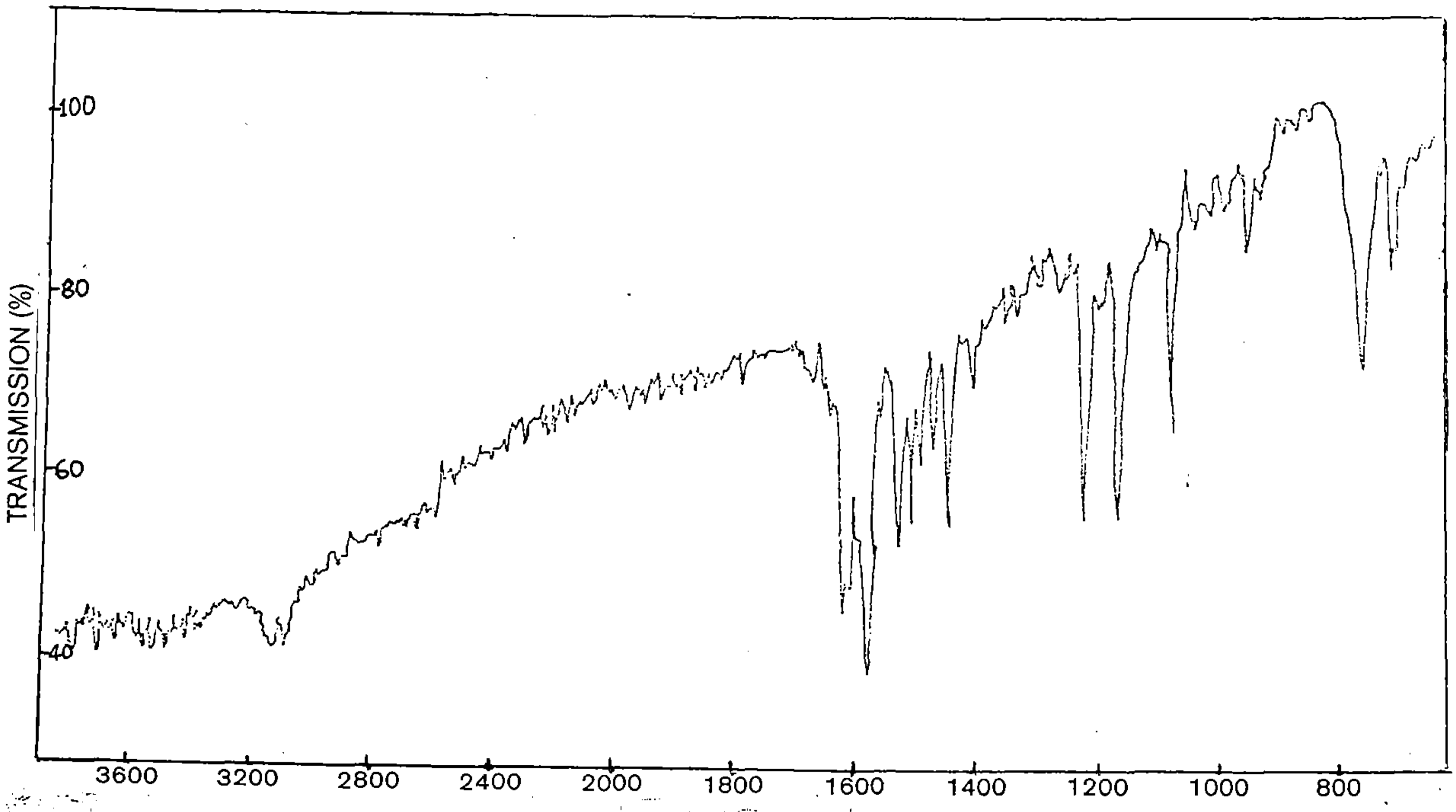


Fig.2. Infrared spectrum of HDPBA (kBr)

for recording the absorption spectra and absorbance measurements of the complex in the visible region.

Standard molybdenum (VI) solution. The solution was prepared by dissolving 5.0000 g of ammonium molybydate (Hopkins & Williams) in a litre of distilled water.

Reagent (HDPBA) solution. A 0.0075 M solution of the reagent (HDPBA) was prepared in 2.5 % (v/v) amyl alcohol solution in benzene.

Ascorbic acid solution. A 20 % (w/v) ascorbic acid (Hopkins & Williams) was prepared by dissolving the solid compound in distilled water.

Standard thiocyanate solution. A 7.0 M solution of ammonium thiocyanate (Riedel de Haen) was prepared by dissolving appropriate amount of the salt in distilled water.

Solutions of diverse ions. Solutions of Ti(IV), 2.5 mg mL^{-1}, was prepared by fusing 0.42 g TiO_2 (BDH) with 4.2 g $KHSO_4$ (BDH), leaching the cool melt with 10 % (v/v) sulphuric acid and diluting the solution to 100 mL with 10 % (v/v) sulphuric acid.

Solutions of Zr(IV), 10 mg mL^{-1} and Pd(II), 5 mg mL^{-1}, were prepared by dissolving $ZrCl_4$ (BDH), and $PdCl_2$ (SPEX) in concentrated hydrochloric acid.

Solutions of Li(I), Na(I), K(I), Be(II), Hg(II), Cu(II), Mg(II), Zn(II), Mn(II), Co(II), Sr(II), Pb(II), Ni(II), UO_2(II), La(III), Fe(III), Bi(III), Cr(III), Th(IV), Tl(III) and Y(III) were prepared by dissolving the respective nitrate salts (BDH or Riedel de Haen) in distilled water to give 5, 10 or 20 mg mL^{-1} of the ion in solution.

Tungstate, borate, vanadate, arsenate, citrate, phosphate, sulphate, tartrate, antimonate, oxalate, acetate, fluoride, EDTA, and perchlorate solutions were prepared by dissolving sodium, potassium or ammonium salts (BDH or Riedel de Haen) in distilled water to give 5, 10, 20 or 500 mg mL^{-1} of the ion in solution.

Appropriate concentrations of Pt(IV) solutions were prepared from a 5 % (w/w) stock solution of chloroplatinic acid ($H_2PtCl_6.6H_2O$, SPEX).

Solutions of thiourea (Hopkins and Williams), 20 mg mL^{-1},was prepared by dissolving the solid compound in distilled water.

Sample solutions. Stock solutions of synthetic steel and ore samples of desired compositions were prepared by mixing known quantities of the solution of constituent ions. The solutions were diluted to 50 mL each and acidified with concentrated hydrochloric acid to give 1 M solution with respect to hydrochloric acid.

Hydrochloric acid. Concentrated hydrochloric acid (37 %, Riedel de Haen) was used to adjust the acidity of the solution.

Drying agent. Anhydrous sodium sulphate (Riedel de Haen) was used for drying the organic extracts.

Solvents. Solvents were used after distillation.

3.3 Procedures

3.3.1 Extraction and Determination of Mo(V)

An aliquot of the solution containing 10 to 250 μg molybdenum(VI) was transferred into a 100 mL of separatory funnel. Solutions of concentrated hydrochloric acid, 20 % (w/v) ascorbic acid, and 7 M ammonium thiocyanate (4, 2 and 2.1 mL respectively) were added and the aqueous phase volume was made to 10 mL with distilled water. A 10 mL aliquot of 7.5 x 10^{-3} M solution of HDPBA in amylalcohol-benzene(2.5 : 97.5) was added to the funnel, the mixture was shaken vigourously for 3 minutes, and the funnel was allowed to stand for 3-4 minutes. The organic phase was collected in 50 mL beaker containing 2 g of anhydrous sodium sulphate and stirred with glass rod. The aqueous phase was shaken with another 10 mL HDPBA solution and finally washed with 5 mL of the mixed solvent. The dried extract was transferred into a 25 mL volumetric flask and diluted to volume with the solvent. The absorbance of colored solution was measured at 470 nm against the reagent blank.

For calibration 0.10, 0.20, 0.50, 0.75, 0.90 and 1.00 mL samples of the stock solution containing 240 μg mL^{-1} Mo(V) were used.

3.3.2. Examination of Experimental Variables

The effect of a particular experimental variable was studied by measuring the absorbance of the system following the general procedure described for extraction and determination of Mo(V) in Section 3.3.1.,keeping all the experimental variables constant except the one under investigation.

3.3.3. Investigation of the Effect of Diverse Ions

The effects of diverse ions were studied by adding known amounts of the foreign ion to a solution containing 120 μg of Mo(V). The extraction and determination of the metal ions were made according to the procedure described earlier in Section 3.3.1.

3.3.4. Determination of the Stoichiometric Composition of the Complex

Extraction method. To determine the Mo(V) to HDPBA ratio in the complex, a series of solutions were prepared in which the concentration of Mo(V), SCN^-, ascorbic acid and HCl were kept constant at 5 X 10^{-5} M, 1.5 M, 0.288 M and 4.8 M respectively. The concentration of HDPBA was varied in the range of 2 X 10^{-4} - 3 X 10^{-3} M. The complex was extracted by the general procedure described in Section 3.3.1. The same was done for the determination of Mo(V) to SCN^- ratio in the complex by keeping constant the concentration of HDPBA at 6 X 10^{-3} M and others like in the previous case, and varying the concentration SCN^- from 0.6 M to 1.25 M. The volumes of aqueous and organic phases (10 mL each) were also constant. The complex was extracted by the general procedure described in Section 3.3.1. The quantity log $\left(\frac{A}{A_{max} - A}\right)$ was plotted against log $[SCN^-]$ and log [HDPBA] alternatively.

4. RESULTS AND DISCUSSION

4.1. Color Reaction and Absorption Spectra

It is well established that Mo(V) reacts with thiocyanate in acidic solution to give a reddish-orange complex [5,55,56]. The Mo(V)-SCN complex was readily extractable into amyl alcohol and other similar solvents. However the complex was not extractable into benzene and other non-polar solvents. The extraction of Mo(V) with HDPBA into non-polar solvents was also tried in the absence of thiocyanate and it was found that Mo(V) was not extractable with HDPBA. Another trial was made to extract Mo(V) with HDPBA into non-polar solvents in the presence of thiocyanate, and Mo(V) was found to react with HDPBA and thiocyanate in 4-6 M hydrochloric acid medium to give a reddish-orange solution extractable into non-polar solvents. Therefore, several organic solvents were examined for the extraction of Mo(V)-HDPBA-SCN complex from the aqueous phase. The results of the experiments are summarized in Table 1.

Based upon the results in Table 1 choice was made to use the mixed solvent system (AmOH-benzene). However the Mo(V)-SCN complex itself was found to be completely extractable into the mixed solvent from 99 : 1 to 10 : 90 (AmOH : benzene), partially extractable in the range 10 : 90 - 4 : 96 (AmOH : benzene) and not extractable below 3:97 (AmoH : benzene). The results are summarized in Table 2. Hence attempt was made to use 2.5 : 97.5 (AmOH : benzene) solvent

Table 1. Extraction behaviour of Mo(V)-HDPBA-SCN complex in different organic solvents

Solvent	λ_{max}	Apperance of aq. phase left after extraction	Remark
Benzene	470	Colored aq. phase	Extraction was incomplete
Chloroform	469	Colored aq. phase	Extraction was incomplete
Chlorobenzene	-	- -	No distinct separation of the two phases
1,2 dichlorobenzene	475	Colored aq. phase	Extraction was incomplete
Toluene	470	Colored aq. phase	Extraction was incomplete
xylene	-	-	Unstable & incomp. extraction

system for the extraction of Mo(V)-HDPBA-SCN mixed ligand complex which was found to completely extract the mixed ligand complex and hence gives the most sensitive color reaction than others.

Table 2. Extraction behaviour of Mo(V)-SCN complex in AmOH-benzene solvent system

% (v/v) AmOH in benzene	Apperance of aq. & org. phase left after extraction	Remarks
100.0	Colorless aq.	Completely Extractable
10.0	Colorless aq.	Completely Extractable
5.0	Both colored	Partially extractable
4.0	Both colored	Partaially extractable
3.0	Colorless org.	Unextractable
2.5	Colorless org.	Unextractable
1.0	Colorless org.	Unextractable

The absorption spectrum of Mo(V)-HDPBA-SCN complex was recorded in the mixed solvent and the complex exhibited an absorption maximum at 470 nm with molar absorptivity of 13100 M^{-1} cm^{-1} (Fig. 3). The absorption spectrum of the reagent, HDPBA, was also recorded in the visible region in the mixed solvent (Fig. 3). The reagent showed negligible absorption in the region 700 - 470 nm, slight increasing absorption in the region 470 - 440 nm, and strong absorption beyond 440 nm. Hence all absorbance measurements of the complex were carried out against the reagent blank.

4.2. *Effect of Variables*

The effect of experimental variables on the extraction and determination of Mo(V)-HDPBA-SCN complex has been investigated in order to establish the optimum conditions for the extraction and determination of Mo(V).

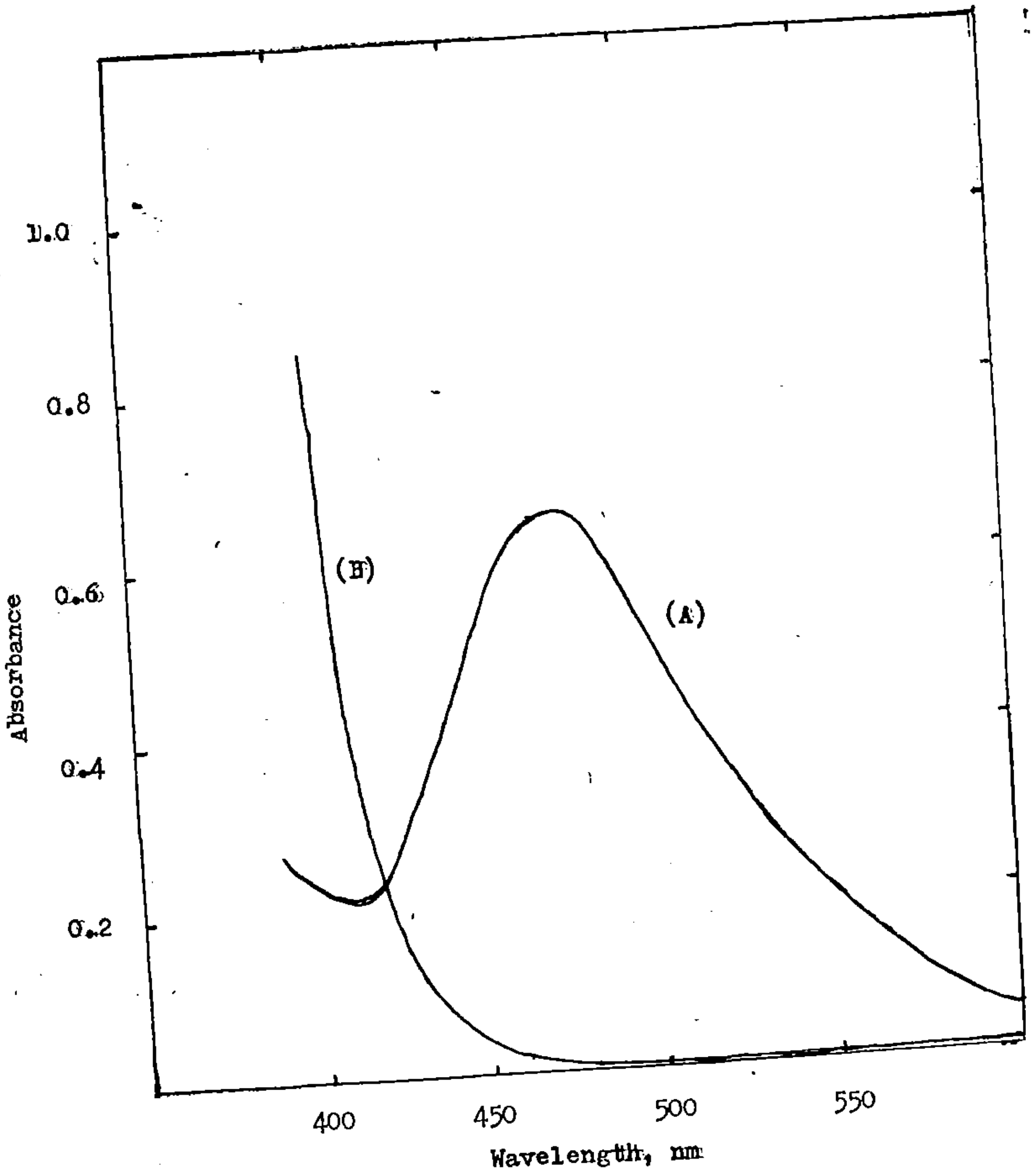


Fig. 3. Absorption spectra of (A) 5 X 10^{-5} M Mo(V)-SCN-HDPBA complex against the reagent blank and (B) 6 X 10^{-3} M HDPBA in AmOH-benzen

Effect of acidity. The effect of acidity of the aqueous phase on extraction of Mo-HDPBA-SCN was studied. The optimum acidity range for complete extraction of Mo(V) was found to be 4 - 6 M HCl in the aqueous phase. At lower acidity the absorbance decreases probably due to incomplete reduction of Mo(VI) to Mo(V) which results in a decrease in the extent of complex formation and hence in a decrease in the extraction of Mo(V). At higher acidity the absorbance decreases possibly due to the protonation of the ligand which results in a decrease in the extent of complex formation of Mo(V). The results are summarized in Table 3 and Fig. 4.

Table 3. Effect of hydrochloric acid concentration of the aqueous phase on the extraction of Mo(V)-HDPBA-SCN complex

(Mo(V) = 120 µg, $[SCN^-]$= 1.5 M, [HDPBA] = 6 $\times 10^{-3}$ M)

[HCl]	Absorbance at 470 nm
1.00	0.153
2.00	0.404
3.00	0.616
3.50	0.636
4.00	0.655
4.50	0.659
5.00	0.655
5.50	0.658
6.00	0.656
6.50	0.618

Effect of ammonium thiocyanate. The effect of the concentration of thiocyanate on the extraction and determination of Mo(V) has been studied over a wide range. The optimum thiocyanate concentration for quantitative extraction of Mo(V)-SCN-HDPBA complex varies from 1.25 - 1.75 M. At lower thiocyanate concentrations, lower absorbance values are obtained due to incomplete formation of the mixed ligand complex, while at higher concentrations of thiocyanate, formation of the mixed ligand complex was retarded resulting in low absorbance values. The results are summarized in Table 4 and Fig. 5.

Table 4. Effect of variation of ammonium thiocyanate concentration on the extraction of Mo(V)

(Mo(V) = 120 μg, [HCl] = 4.8 M, [HDPBA] = 6 x 10^{-3} M)

$[SCN^-]$	Absorbance at 470 nm
0.50	0.111
0.75	0.369
1.00	0.598
1.25	0.654
1.50	0.655
1.75	0.657
2.00	0.618

Potassium thiocyanate was also tried, however there was a precipitate formation with other components in the aqueous

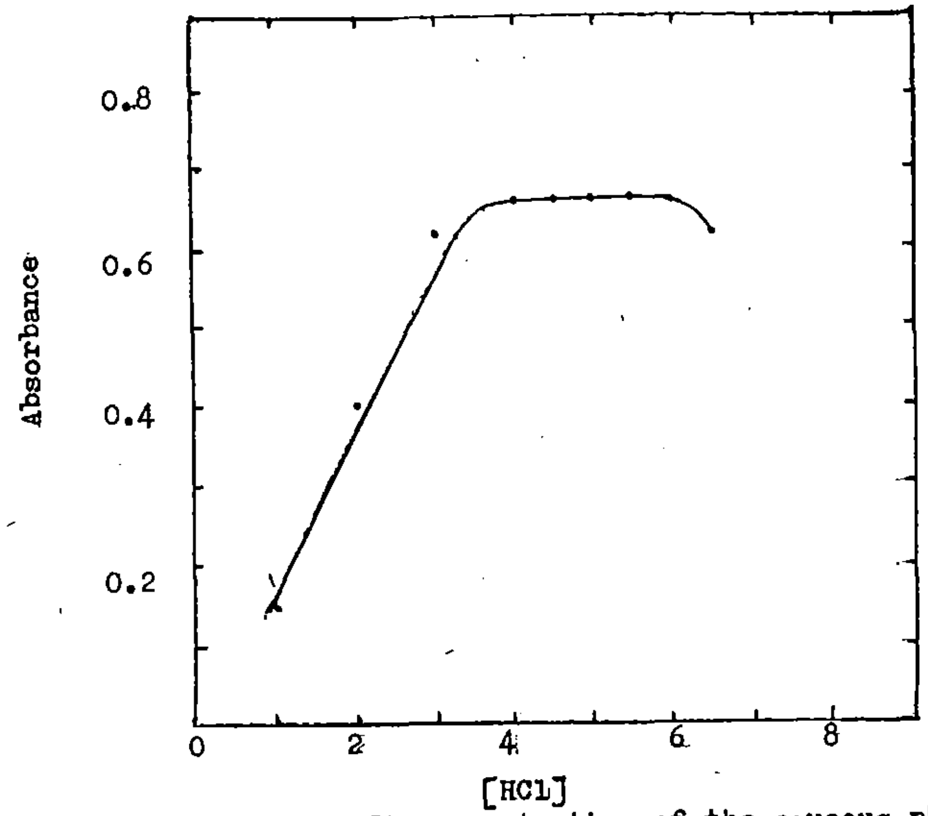


Fig. 4. Effect of HCl concentration of the aqueous phase on the extraction and determination of 120 μg Mo(V).

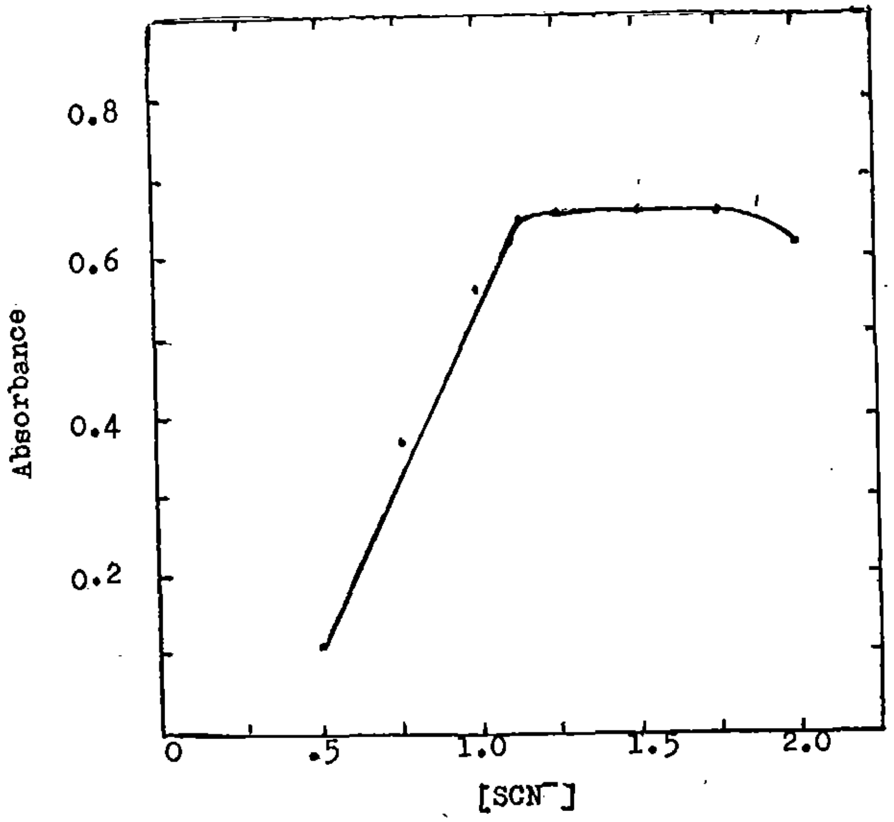


Fig. 5. Effect of the concentration of thiocyanate on the extraction and determination of 120 μg Mo(V).

phase probably due to the limited solubility of potassium salts in contrast to that of ammonium salts.

Effect of ascorbic acid. Ascorbic acid was used for the reduction of Mo(VI) to Mo(V) in the aqueous phase. The results (Table 5) showed a minimum of 0.057 M ascorbic acid was required for the complete reduction of Mo(VI) to Mo(V) and higher concentrations up to 0.388 M was found to have no adverse effect. Higher concentrations of ascorbic acid (>0.388 M) was not studied due to limited solubility.

Table 5. Effect of the concentration of ascorbic acid on the extraction of Mo(V)

(Mo(V) =120 μg, [HCl] = 4.8 M, $[SCN^-]$ = 1.5 M)

[Ascorbic acid]	Absorbance at 470 nm
0.000	0.578
0.014	0.611
0.057	0.657
0.114	0.656
0.228	0.655
0.300	0.656
0.320	0.660
0.388	0.658

The absorbance value at zero concentration of ascorbic acid may lead to the conclusion that there is a possibility of the mixed ligand complex formation by Mo(VI) but this is not the case due to the reducing ability of HCl towards Mo(VI) to Mo(V) [2]. Therefore the use of ascorbic acid in the range between 0.057 to 0.388 M is necessary for the complete reduction of Mo(VI) to Mo(V) and for the control of aerial oxidation of Mo(V) to Mo(VI).

For the reduction of Mo(VI) to Mo(V) stannous chloride was also tried, however the Mo(V)-SCN complex in the aqueous phase was found to decolorize immediately, probably due to the reduction and decomposition of thiocyanate at higher acidity used in the system.

Amount and mode of addition of the reagent. For a fixed volume of the aqueous phase (10 mL) different modes of addition of the reagent solution were tried and the results are summarized in Table 6.

These results indicate that a minimum of 20 mL of the reagent solution (7.5 x 10^{-3} M) was necessary for the complete extraction of Mo(V) from a fixed volume of 10 mL of the aqueous phase. However when the 20 mL aliquot of the reagent solution was used at once it resulted in an incomplete extraction of the metal. Therefore batch extractions were found to be necessary for the complete extraction of the metal from the aqueous phase.

Three different modes of batch extractions were tried and all the three modes gave similar results. Hence for all subsequent works a (10 + 10) mL mode was used.

The effect of concentration of the reagent on the

Table 6. Effect of the mode of addition of the reagent on the extraction of Mo(V)

Mo(V) = 120 μg, $[SCN^-]$ = 1.5 M, [HCl] = 4.8 M, V_{aq} = 10 mL, $V_{org\ (final)}$ = 25 mL)

Volume of HDPBA added in mL	[HDPBA]	Absorbance at 470 nm
20	7.5×10^{-3}	0.600
10 + 10	"	0.657
15 + 5	"	0.655
10 + 5 + 5	"	0.657
10 + 5	"	0.632
5 + 5 + 5	"	0.634

extraction of Mo(V) from the aqueous phase was also studied. The results are summarized in Table 7.

A 5.0×10^{-3} M of HDPBA (a molar ratio of 1:80 [Mo(V)] : [HDPBA]) was found to be the minimum required for complete extraction of Mo(V)-HDPBA-SCN complex from the aqueous phase. A 1.0×10^{-2} M of HDPBA (a 160 fold molar excess of the ligand, HDPBA) has been found to have no effect on the extraction of the complex. Higher concentrations of the reagent greater than 1.0×10^{-2} M (molar ratios > 160 fold) were not experimentally possible due to the limited solubility of HDPBA in the mixed solvent system.

Table 7. Effect of the amount of HDPBA on the extraction of Mo(V).

(Mo(V) = 48 µg, [HCl] = 4.8 M, [SCN] = 1.5 M, V_{aq} = 10 mL
V_{org} = (10 + 10) mL, $V_{org\ (final)}$ = 25 mL)

[HDPBA]	[Mo(V)]:[HDPBA]	Abs. at 470 nm
0.0010	1 : 16	0.342
0.0025	1 : 40	0.500
0.0050	1 : 80	0.647
0.0075	1 : 120	0.655
0.0100	1 : 160	0.653

Effect of the volume of the aqueous phase. It has been found that the volume ratio of aqueous phase to the organic phase to be 1 : 1 for complete extraction of Mo(V). However, more repetitive extractions seem to be necessary for complete extraction of Mo(V) from larger volumes of the aqueous phase.

It is also possible to achieve complete extraction from larger volume of the aqueous phase ($V_{aq}:V_{org}$ = 2:1) by using higher concentration of HDPBA (1.0 x 10^{-2} M). The results are summarized in Table 8. These results also indicate that the distribution ratio of the metal is not very high in the solvent system used.

Extraction time and stability of the complex. The Mo(V)-HDPBA-SCN complex requires 3-4 minutes of shaking time

Table 8 Effect of the volume of the aqueous phase on extraction of Mo(V)

(V_{org} = 10 + 10 mL, $V_{org\ (final)}$ = 25 mL, Mo(V) = 120 µg, [HCl] = 4.8 M, [SCN^-] = 1.5 M)

Volume of aqueous phase mL	$^*V_{aq}$: V_{org}	[HDPBA] stock	Absorbance at 470 nm
10	1:1	0.0075	0.656
20	2:1	0.0075	0.599
25	2.5:1	0.0075	0.369
50	5:1	0.0075	0.278
20	2:1	0.0100	0.660

*Reagent was added in two portions (10 mL each). This is the ratio of V_{aq} to V_{org} at the time of extraction.

for the complete extraction from the aqueous to organic phase. The stability of the complex was studied and the results are shown in Table 9. The complex was found to be stable for 1 hour and then decomposes. The higher absorbance values beyond 1 hour were due to precipitate formation by the decomposition of the complex.

The optimum conditions for the extraction and determination of Mo(V) with HDPBA and ammonium thiocyanate are summarized in Table 10.

Table 9. Stability of the complex

Time (min)	A at 470 nm
0	0.656
15	0.656
30	0.656
45	0.656
50	0.656
55	0.656
60	0.657
70	0.719*
75	0.765*

* The solutions was turbid.

Table 10. Optimum experimental conditions for extraction and determination of Mo(V) with HDPBA and thiocyanate

Parameter	Optimum condition
Aqueous phase, HCl	4.0 - 6.0 M
Aqueous phase, NH_4SCN	1.25 - 1.75 M
Aqueous phase, ascorbic acid	0.057 - 0.388 M
*Organic phase, HDPBA	5.0×10^{-3} - 1.0×10^{-2} M
$V_{aq} : V_{org}$	1:1
Extraction time	3-4 min
Stability of the complex	60 min
Solvent used for extraction	2.5 % AmOH in benzene

*The reagent solution should be added in two equal portions.

Thus the proposed method is free from the rigid control of experimental conditions.

4.3. *Evaluation of photometric characteristics*

The concentration range obeyed by Beer's law has been determined and the optimum concentration range in which photometric analysis error is minimum has been evaluated from Ringbom's plot. The results are given in Table 11, and the curves are shown in Figures 6 and 7.

Table 11. Data for calibration curve and the Ringbom's plot for determination of Mo(V)
($[HCl] = 4.8$ M, $[SCN^-] = 1.5$ M, $[HDPBA] = 6 \times 10^{-3}$ M)

$[Mo(V)].10^5$	log [Mo(V)]	Absorbance at 470 nm	Transmittance (%)
0.5	-5.30	0.065	86.10
1.0	-5.00	0.134	73.45
2.0	-4.70	0.270	53.70
5.0	-4.30	0.655	22.13
7.5	-4.13	0.983	10.40
9.0	-4.03	1.199	6.32
10.0	-4.00	1.321	4.78

The sensitivity of the method, i.e. the concentration that corresponds to an asorbance of 0.001, and the limit of determination, i.e. the minimum concentration that corresponds to an absorbance three times of the standard deviation of the blank [46] have also been evaluated. The precision of the method has also been evaluated from the relative standard deviation of ten measurements each containing 120 μg Mo(V)

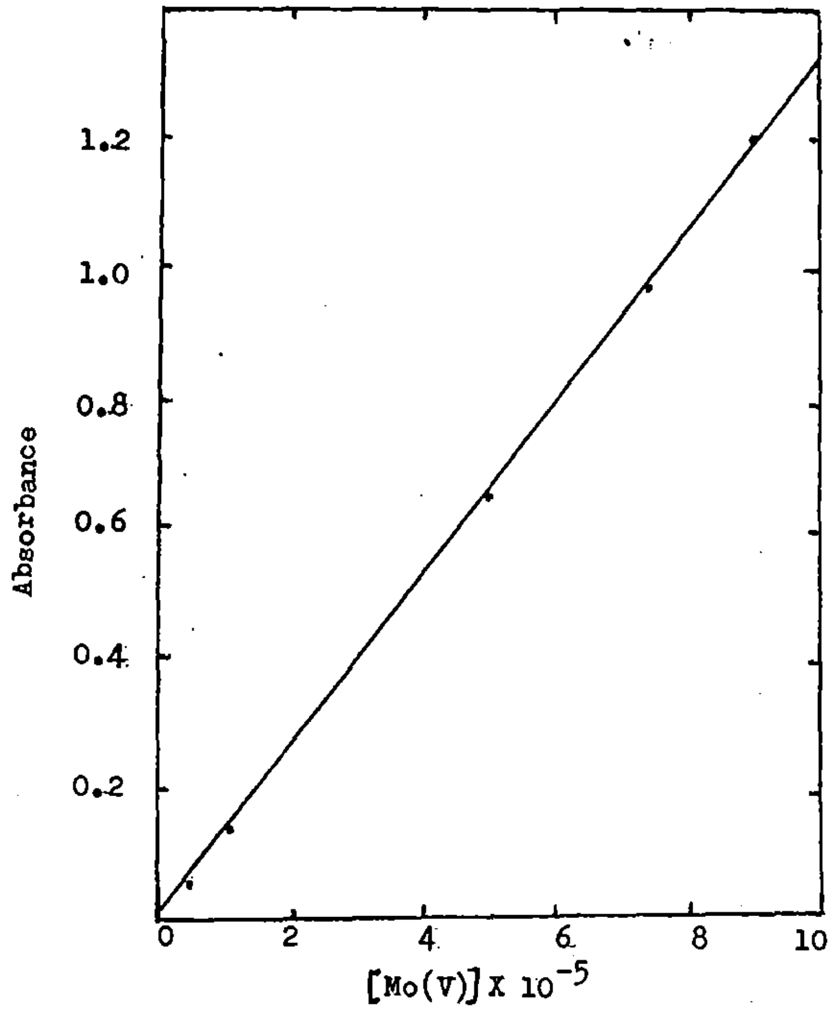


Fig. 6. Calibration curve for the determination of Mo(V).

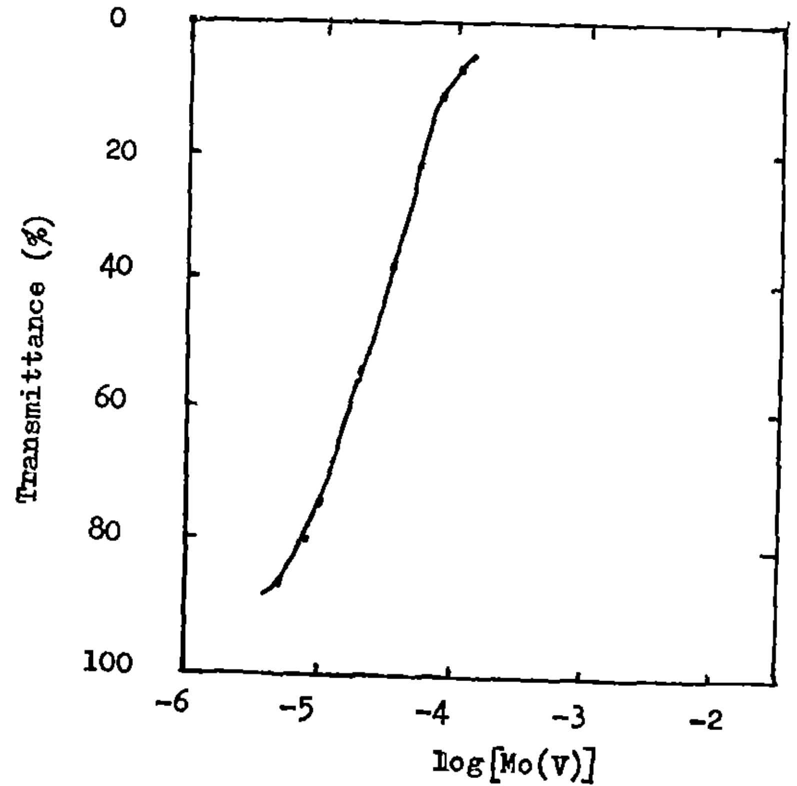


Fig. 7. Ringbom's plot for the evaluation of optimum concentration range for the determination of Mo(V).

(Table 12). The summary of the photometric characteristics are given in Table 13.

Table 12. Data for evaluating the limit of determination of Mo(V) and precision of the proposed method

(Mo(V) = 1.20µg, $[SCN^-]$ = 1.5 M, [HDPB] = 6 X 10^{-3} M)

Measurements (n)	Absorbance of the sample	Absrbance of the blank
1	0.658	0.069
2	0.650	0.063
3	0.667	0.067
4	0.652	0.069
5	0.645	0.066
6	0.657	0.065
7	0.656	0.067
8	0.651	0.068
9	0.661	0.067
10	0.650	0.066
	$\bar{X}_s$ = 0.655	$\bar{X}_b$ = 0.067
	σ_s = 0.0046	σ_b = 0.00176

These results show that the proposed method for the extraction and determination of Mo(V) with HDPBA and thiocyanate is highly sensitive and give reproducible results.

Table 13. Photometric characteristics of the complex

λ_{max}	470 nm
ε_{max} M^{-1} cm^{-1}	13100
Sensitivity, μg cm^{-2}	0.00732
Concentration range from Beer's law in μg mL^{-1}	0.480 - 9.59
Optimum concentration range from Ringbom's plot, μg mL^{-1}	0.9 - 7.1
Limit of determination, μg mL^{-1}	0.039
Relative standard devaition, % (n = 10)	0.97

4.4. *Stoichiometry of the Complex*

Two of the most common methods of determining the stoichiometry of the complex (mole ratio [43], and continuous variation [42,52] methods) were found to be inapplicable for the system investigated due to the necessity of excess molar fold of the reagent (HDPBA) and thiocyanate to initiate the complexation equilibria. Hence the stoichiometry of the complex was determined using the extraction method [39].

The ratio of molybdenum(V) to HDPBA was determined by the extraction method in which the quantity log $\frac{A}{A_{max} - A}$ (= log D_{Mo}) was plotted against log [HDPBA], where A is the absorbance at an equilibrium concentration of HDPBA, and A_{max} is the absorbance at the optimum concentration of HDPBA. The slope of the plot was found to be 0.90, which shows a 1:1 ratio of Mo(V) to HDPBA in the complex (Table 14, Fig 8).

Table 14. Results of the extraction method for the determination of the ratio of Mo(V) to HDPBA in Mo(V)-SCN-HDPBA complex

($[Mo(V)] = 5 \times 10^{-5}$ M, $[HCl] = 4.8$ M, $[SCN^-] = 1.5$ M)

$[HDPBA].10^{4}$ M	A at 470 nm	$A_{max} - A$	$\log\frac{A}{A_{max}-A}$	log[HDPBA]
8	0.395	0.260	0.182	-3.10
10	0.441	0.214	0.314	-3.00
15	0.472	0.183	0.412	-2.82
20	0.519	0.136	0.582	-2.72
25	0.535	0.120	0.649	-2.60
30	0.561	0.094	0.776	-2.52
35	0.612	0.043	1.153	-2.50
40	0.649	0.006	2.034	-2.40
60	0.655	-	-	-2.22

Similarly the plot of $\log \frac{A}{A_{max} - A}$ versus $\log[SCN^-]$ was made and the slope was calculated to be 2.70, which indicates the Mo(V) to SCN^- ratio in the complex to be 1:3. The results are given in Table 15 and Fig. 9.

Thus the overall stoichiometry of the Mo(V)-SCN-HDPBA has been established as 1:3:1 (Mo:SCN:HDPBA), which is further evidenced by the existence of the Mo(V) thiocyanato complex in acidic medium as $MoO(SCN)_3$ [55, 56].

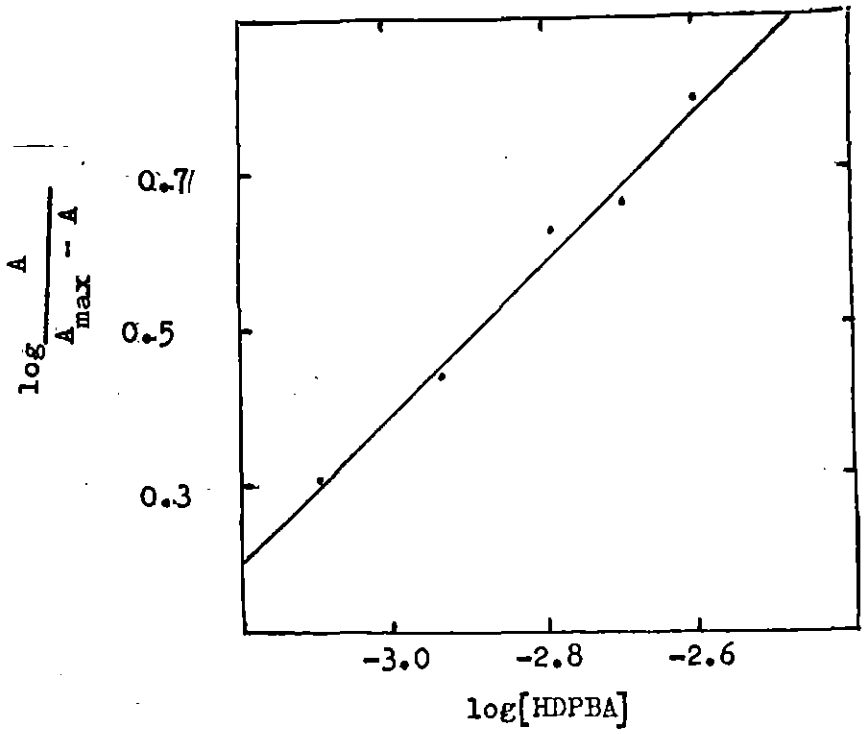


Fig. 8. Curve for the determination of Mo(V) to HDPBA ratio in Mo(V)-SCN-HDPBA complex by extraction method.

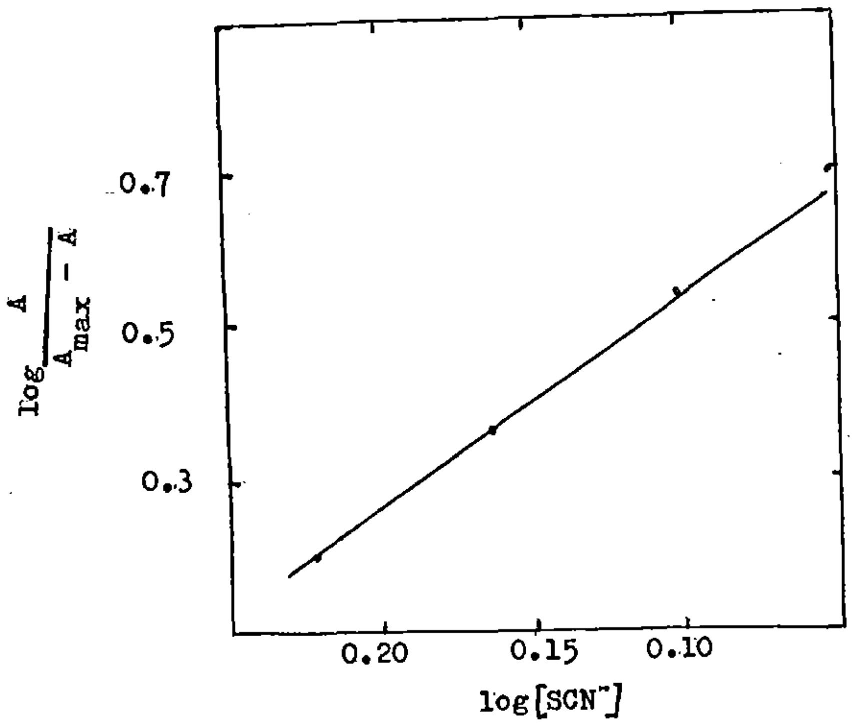


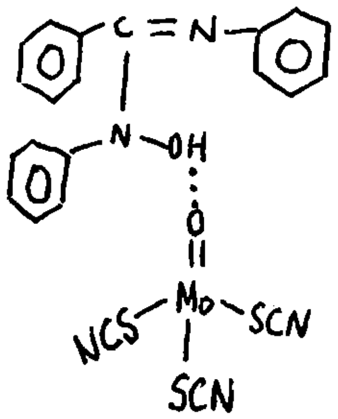
Fig. 9. Curve for the determination of SCN ratio to Mo(V) in Mo(V)-SCN-HDPBA complex by the extraction method.

Table 15. Results of the extraction method for the determination of the ratio of Mo(V) to SCN^- in Mo(V)-SCN^--HDPBA complex

([Mo(V)] = 5×10^{-5} M, [HCl] = 4.8 M, [HDPBA] = 6×10^{-3} M)

$[SCN^-]$.10	A at 470 nm	$A_{max}-A$	$\log\frac{A}{A_{max}-A}$	$\log[SCN^-]$
6.0	0.391	0.264	0.171	-0.22
7.0	0.456	0.199	0.360	-0.16
8.0	0.508	0.147	0.539	-0.10
9.0	0.543	0.112	0.686	-0.05
10.0	0.570	0.085	0.826	0.00
11.0	0.651	-	-	-
12.0	0.655	-	-	-
12.5	0.655	-	-	-

From the extractability of the complex into a less polar solvent, consideration of the presence of Mo=O group, and the above stoichiometry the following structure is proposed for the complex.



As already discussed that the optimum condition for the extraction of the mixed ligand complex is from strongly acidic medium which could result in a protonation of the ligand (HDPBA) as a result the ligand losses its chelating ability. Hence it could not directly coordinate with the metal, instead it is linked to the complex through hydrogen bonding which facilitated the extraction of the complex into a relatively non polar solvent, which improves the selectivity of the method in comparison to the method based on a simple thiocyanato complex

4.5. *Effects of Diverse Ions*

For the evaluation of the selectivity of the proposed method the effects of diverse ions on the extraction and determination of molybdenum(V) have been investigated. It has been found that ions that react with Mo(V) or that form complexes with thiocyanate or HDPBA as to deprive molybdenum of sufficient reagent for the complete color development, influence the determination by reducing the absorbance value (negative interference); while those ions which react with constituents of the complex and whose absorption bands overlap with that of Mo(V)-SCN-HDPBA complex interfered by increasing the absorbance values (positive intereference) As a result these ions have lower tolerance limits.

Table 16. Tolerance limits of diverse ions in the determination of Mo(V)

($Mo(V)$ = 120 µg, [HDPBA] = 6 X 10^{-3}M , [HCl] = 4.8 M, [SCN^{-}] = 1.5 M)

Ion	Tolerance limit (mg)	Direction of interference
Li^{+}, Na^{+}, K^{+}, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Sn^{2+}, Pb^{2+}, As^{5+}, Sb^{5+},	20 each	*
Bi^{3+}, W^{6+}, Fe^{3+}	10 each	a
Co^{2+}	5.0	a
Ti^{4+}	2.5	a
Pt^{4+}	4.8	a
Th^{4+}	5.0	a
Pd^{2+}, Zr^{4+}	5.0 each	a
Ni^{2+}, U^{6+}, Cu^{2+} Cr^{3+}, Mn^{2+}, V^{5+} La^{3+}, Ce^{4+} Y^{3+}, Er^{3+}, Tl^{3+}	10 each	*
Ta^{5+}	1.0	b
Nb^{5+}	0.25	b

Table 16. continued

I^-, ClO_4^-, OAc^-, SO_4^{2-}, $B_4O_7^{2-}$, Citrate, Tartrate, Thiourea, PO_4^{3-}	20 each	*
Fluoride	500	a
Oxalate	30	b
EDTA	50	b

[*] Not studied beyond the indicated level.

[a] Amount more than the tolerance limit results in positive interference.

[b] Amount more than the tolerance limit results in negative interference.

The tolerance limit of diverse ions taken as an amount (mg) which cause an error less than 2 % are given in Table 16. These results show that most of the ions which are normally associated with molybdenum in ores and alloys do not interfere up to 200 times to the weight of molybdenum by the proposed method. The proposed method is also free from the interference from the common masking agents and hence the ions having lower tolerance limit could further be improved by the use of common masking agents. Hence the proposed method could be applied for the analysis of molybdenum in ores, alloys, minerals, industrial and biological samples.

4.6. *Application*

The analytical potentiality of the proposed method was assessed by applying it for the determination of molybdenum in various samples. Due to the absence of real samples synthetic matrices corresponding to the British Chemical Standards steel samples No. 64a and 241/1 as well as molybdenum containing ores were analysed by the proposed method.

Table 17 shows a summary of the experimental results. These results indicate that the proposed method is precise and reliable for the determination of molybdenum at trace levels in diverse samples.

Composition of synthetic steel and ore matrices

BCS steel No 241/1: W , 19.61 μg; Cr , 5.03 μg; Mo , 0.5 μg;
V , 1.57 μg; Co, 5.67 μg; C , 0.85 μg;
Si , 0.33 μg; S , 0.033 μg; P , 0.022 μg;
Mn , 0.295 μg; Ni , 0.075 μg; Cu , 0.10 μg;
Sn , 0.025 μg; Fe , 65.87 μg.

BCS steel No 64a: C , 0.80 μg; Cr , 4.40 μg; V , 1.57 μg;
Mo , 4.11 μg; W , 5.66 μg; Fe , 83.45 μg.

Ore matrix 96 μg Mo + 1.2 mg Co + 0.8 mg Ca + 0.5
mg Mg + 4.2 mg Pb + 1.1 mg Fe + 3.7 mg W

Table 17 Determination of molybdenm in synthetic steel and ore matrices by the proposed method

Sample	Molybdenum content µg	*Molybdenum found µg	RSD (%)
241/1	2.50	2.54	0.89
	5.00	4.97	0.76
64a	20.55	20.83	0.63
	41.10	41.30	0.61
Ore matrix	48.00	48.34	0.72
	96.00	95.68	0.82

*Average of triplicate determintions

4.7. *Comparison with Other Spectrophotometric Methods*

A compartive study has been made for the determination of molybdenum by the proposed method and other spectrophotometric methods in regard to sensitivity and selectivity of the methods.

The proposed method has been found to be more sensitive than most of the reported methods. Eventhough some of the reported methods are more sensitive than the proposed method their selectivity is poorer than the proposed method. While the selectivity of the proposed method is found to be superior to most others (Table 18).

Table 18. Comparison with other spectrophotometric methods

No.	Reagent	ϵ_{max} M^{-1} cm^{-1} or Concentration range, ppm	Interference	Ref.
1.	N^1-Hydroxy-N^1-p-tolyl-N^2-3,4-xylyl benzamidine and thiocyanate	0.5-18 ppm	Fe(III)	[10]
2.	1,4-Dihydroxyphthalamide dithiosemicarbazone	9400 $M^{-1}cm^{-1}$	not studied	[11]
3.	N,N^1-Diaryl benzamidines and thiocyanate	16500-18500 $M^{-1}cm^{-1}$	--	[12]
4.	Imidophenyl hydrazine and thiocyanate	17300	Fe(III),Nb(V)	[13]
5.	Promethazine hydrochloride and thiocyanate	5-50 ppm	Co(II),Cu(II)	[14]
6.	Lobeline and thiocyanate	0.13-14 ppm	Cu(II),Ti(IV), Co(II),W(VI)	[15]

Table 18 continued

No.	Reagent	εmax M^{-1} cm^{-1} Concentration range, ppm	Interference	Ref.
7.	Toluene-3,4-dithiol	75000 $M^{-1}cm^{-1}$	Co(II),Cu(II) Hg(II),W(VI) Fe(III)	[16]
8.	N-Phenylbenzohydroxamic acid	74000 $M^{-1}cm^{-1}$	Ti(IV),V(IV) V(V)	[17]
9.	N-m-tolyl-N'-p-chlorophenyl-o-chlorobenzamidine and thiocyanate	18000 $M^{-1}cm^{-1}$	--	[18]
10.	2-Chloro-N',N-bis-(-chlorophenyl)-N-hydroxybenzamidine and thiocyanate	3-24 ppm	not studied	[19]
11.	Phosphomolybdenum blue	700 $M^{-1}cm^{-1}$	W(VI)	[20]
12.	Salicylaldehyde isonicotinoyl hydrazone	12100 $M^{-1}cm^{-1}$	not studied	[21]

Table 18 continued

No.	Reagent	εmax M^{-1} cm^{-1} Concentration range, ppm	Interference	Ref.
13.	4-Benzoyl-3-methyl-1-phenylpyrazolin-5-one	2500 $M^{-1}cm^{-1}$	Fe(III)	[22]
14.	Phenylfluorone	3800 $M^{-1}cm^{-1}$	Sn(II), Sn(IV) Ga, Ge, PO_4^{-3}, Nb, Ta, V	[23]
15.	3-(2-Furyl)-N-(4-methoxyphenyl) acrylhydroxamic acid	12100 M^{-1} cm^{-1}	--	[24]
16.	N^1-Hydroxy-N^1,N^2 diphenylbenzamidine and thiocyanate	13100 $M^{-1}cm^{-1}$	--	Proposed method

5. CONCLUSION

A new method has been developed for the determination of molybdenum(V) with N^1-hydroxy-N^1,N^2-diphenylbenzamidine and thiocyanate by solvent extraction and spectrophotometry. The proposed method is fairly sensitive and highly selective. The method is precise and free from a rigid control of experimental conditions. It is believed that the method could be applicable to the analysis of diverse samples containing molybdenum.

6. REFERENCES

1. N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements,' 2nd ed., Pergamon Press, London, 1985.
2. F.A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 5th ed., Wiley, New York, 1988.
3. A.F. Trotman-Dickson, 'Comprehensive Inorganic Chemistry,' Pergamon Press, Oxford, 1975.
4. McGraw-Hill, 'Encyclopedia of Science and Technology,' 6th ed., Vol. 10, McGraw-Hill, New York, 1987.
5. A.I. Busev, V.G. Tiptsova, and V.M. Ivanov, 'Hand Book of the Analytical Chemistry of Rare Elements,' Humphrey, London, 1970.
6. Kirk-Othmer, 'Encyclopedia of Chemical Technology,' 2nd ed., vol. 20, Wiley, New York, 1969.
7. B.K. Burgess, *Chem. Rev.*, 1990, *90,* 1377.
8. S.J.N. Burgameyer and E.I. Stiefel, *J. Chem. Educ.*, 1985, *62,* 943.
9. K.G. Swedo and J. Enemark, *J.Chem. Educ.*, 1979, *56*, 70.
10. R.K. Singh and R.K. Mishra, *Bull. Chem. Soc. Jpn.*, 1980, *53*, 1736; *Anal. Abstr.*, 1981, *44*, 1B137.
11. M.T. Rodriguez, *Analyst*, 1982, *54*, 52.
12. K.S. Patel, R.M. Verma, and R.K. Mishra, *Anal. Chem.*, 1982, *54*, 52.
13. K.S. Patel, and and R.K Mishra, *Ann. Chim.(Rome)*, 1983, *73*, 91; *Anal. Abstr.*, 1983, *44*, 1B110.
14. A. Gudniewska, *Fresenius* Z. *Anal. Chem.*, 1983, *315*, 355;

Anal. Abstr., 1983, *45*, 6B136.

15. K. Nytko and H. Sirkorska-Tomicka, *Microchem. J.*, 1980, *25*, 548; *Anal. Abstr.*, 1981, *41*, 2B147.

16. M. Pilar, J. Francisco and F. Bermejo, *Analyst*, 1987, *112*, 473.

17. H. Gunawardhana and S. Fernado, *Canadian J. Chem.*, 1987, *65*, 1124.

18. L.P. Chandrakar and R. Singh, *Analyst*, 1987, *112*, 1511.

19. L.P. Chandrakar and R.K. Mishra, *J. Indian Chem. Soc.*, 1986, *63*, 920; *Anal. Abstr.*, 1988, *50*, 1B204.

20. G. Luo, *Fenxi Shiyanshi*, 1987, *6*, 55; *Anal. Abstr.*, 1988, *50*, 4B123.

21. E. Kalventis, *Anal. Lett.*, 1988, *21*, 107; *Anal. Abstr.*, 1988, *50*, 7B126.

22. A.I. Khalitova, N.V. Melchakova, V.M. Peshkova, and M.A. Smerdova, *Vestn. Mosk. Univ., Ser.2: Khim.*, 1986, *27*, 202; *Anal. Abstr.*, 1986, *48*, 12B119.

23. M.F. El-Shahat, M.Z. Mostafa, M. Monshi, *Microchem. J.*, 1985, *31*, 56; *Anal. Abstr.*, 1985, *47*, 12B172.

24. S.A. Abassi, *Anal. Lett.*, 1987, *20*, 2021; *Anal. Abstr.*, 1988, *50*, 8B174.

25. K. Satyanarayana and R.K. Mishra, *Anal. Chem.*, 1974, *46*, 1609.

26. K. Satyanarayana and R.K. Mishra, *Indian J. Chem.*, 1975, *13*, 295.

27. K. Satyanarayana and R.K. Mishra, *J. Indian Chem. Soc.*, 1976, *53*, 63.

28. G. Moges and B.S. Chandravanshi, *Bull. Chem. Soc. Jpn.*, 1984, *57*, 866.

29. Gebray Asgedom, M.Sc. Thesis, Addis Ababa University, Addis Ababa, 1988.

30. G. Moges and B.S. Chandravanshi, *Ann. Chim. (Rome)*, 1984, *74*, 627.

31. Dejene Ayle and B.S. Chandravanshi, *Anal. Lett.*, 1990, *23*, 1729.

32. Z. Holzbecher, L. Davis, M. Kral, L. Sucha and F. Vlacil, 'HandBook of Organic Reagents in Inorganic Analysis,' Ellis Horwood, Sussex, 1976.

33. J. Basset, R.C. Denney, G.H. Jeffery, and J. Mendhan, 'Vogèl s Textbook of Quantitative Inorganic Analysis,' 4th ed., Longman, London, 1978.

34. H. Freiser, *Anal. Chem.*, 1957, *29*, 290.

35. G.H. Morrison and H. Freiser, 'Solvent Extraction in Analytical Chemistry,' Wiley, New York, 1957.

36. G.H. Morrison and H. Freiser, *Anal. Chem.*, 1968, *40*, 522R.

37. C.L. Wilson and D.W. Wilson, 'Comprehensive Analytical Chemistry,' Vol. IA, Elsevier, Amesterdam,. 1959.

38. E.B. Sandell, 'Colorimetric Determination of Traces of Metals,' 3rd ed., Interscience, New York, 1965.

40. L. Meites and H.C. Thomas, 'Advanced Analytical Chemistry,' McGraw-Hill, New York, 1958.

41. M.C. Patric, *Anal. Chem.*, 1978, *50*, 2165.

42. W.C. Vosburgh and G.R. Cooper, *J. Amer. Chem. Soc.*,

1941, *63*, 437.

43. A.S. Meyer, Jr. and J.H. Ayres, *J. Amer. Chem. Soc.*, 1957, *79*, 49.

44. H.A. Laitinen and W.E. Haris, 'Chemical Analysis,' 2nd ed., McGraw-Hill, Tokyo, 1975.

45. H.A. Strobel, 'Chemical Instrumentation,' 2nd ed., Addison-Wesley, California, 1973.

46. Analytical Methods Committee, *Analyst*, 1987, *112*, 199.

47. K.L.Cheng, 'Trace Analysis, Physical Methods,' Wiley, New York, 1965.

48. A. Ringbom, Z. *Anal. Chem.*, 1939, *115*, 332; *Chem Abstr.*, 1939, *33*, 2839.

49. J.E. Barney, *Talanta,* 1967, *14*, 1363; *Chem. Abstr.*, 1968, *68*, 18294n.

50. L. Sommer and M. Langova, CRC Critical Riviews in Analytical Chemistry, 1988, *19*, 225.

51. F.G.C. Rossoti and H. Rossoti, 'The Determination of Stability Constants and Other Equilibrium Constants,' McGraw-Hill, New York, 1961.

52. P. Job, *Ann. Chim. (Paris)*, 1982, *9*, 113; *Chem. Abstr.*, 1928, *22*, 2120.

53. H.O. House, 'Modern Synthetic Reactions,' 2nd ed., Benjamin-Cummings, Philipines, 1972.

54. B.S. Furnise, A.J. Hannaford, V. Rogers, P.W.G. Smith and A.R. Tatchel, 'Vogel's Textbook of Practical Organic Chemistry,' 4th ed., Longman, London, 1978, p. 318.

55. D.D. Perrin, *J. Amer. Chem. Soc.*, 1958, *80*, 3540,

56. C.F. Hiskey and V.W. Meloche, *J. Amer. Chem. Soc.*, 1940, *62*, 1565.

57. H. Kaiser, Z. *Anal. Chem.*, 1965, *209*, 1; *Chem. Abstr.*, 1966, 65, 12h.

58. W.F. Hillerbrand and G.E.F. Lundell, 'Applied Inorganic Analysis,' 2nd ed., Wiley, New York, 1953.

59. H. Freiser and Q. Fernando, 'Ionic Equilibria in Analytical Chemistry,' Wiley, London, 1963.

60. J.J. Lingane, 'Analytical Chemistry of Selected Metallic Elements,' Reinhold, New York, 1966.

61. R.O.C. Norman, 'Principles of Organic Synthesis,' 2nd ed., Chapman, London, 1978.

62. P.J. Durrant and B.D. Durrant, 'Introduction to Advanced Inorganic Chemistry,' 2nd ed., William Clowes, London, 1970.

63. A. Muller and E. Diemann, 'Transition Metal Chemistry,' Verlag Chemie, Weinheim, 1981.

64. M.S. Sethi and M. Satake, 'Chemistry of Transition Elements,' South Asians, New Delhi, 1987.