ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

STUDIES ON EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM (IV) USING N^1-HYDROXY-N^1,N^2-DIPHENYLBENZAMIDINE AND THIOCYANATE

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Dedicated to the memories of my brother,

GETU YIGZAW

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ABSTRACT

Studies on the Extraction and Spectrophotometric Determination of Titanium (IV) using N^1-Hydroxy - N^1,N^2-diphenylbenzamidine and Thiocyanate

By Yirgalem Yigzaw

Research Advisor Dr. B.S Chandravanshi

Titanium (IV) has been found to react with N^1-Hydroxy-N^1,N^2-diphenylbenzamidine (HDPBA) and thiocyanate to form an orange colored mixed ligand complex which was quantitatively extractable into toluene from 0.5 - 0.25 M HCl solutions. The complex exhibited an absorption maximum in the visible region at 400 nm with a molar absorptivity of 20,000 M^{-1} cm^{-1} and the system obeyed Beer's law in the concentration range of 0.29-3.6 ppm of Ti. The composition of the complex has been established spectrophotometrically to be 1:1:2 (Ti: SCN:HDPBA). The effects of foreign ions and several other experimental variables have been studied to establish the optimum conditions for the extraction and determination of titanium. On the basis of these studies a new method has been developed for the determination of titanium (IV) with HDPBA and thiocyanate by solvent extraction and spectrophotometry. The method is precise, fairly sensitive and highly selective and free from rigid control of experimental variables. Moreover, the method has been successfully applied to the determination of titanium in several synthetic samples corresponding to titanium containing ores, minerals and alloys.

1. INTRODUCTION

1.1 Occurrence and Uses of Titanium [1-5]

Titanium is a relatively abundant element, the average content of the lithosphere being 0.63 % by weight; it is the ninth most abundant element in the earth's crust, in which it is widely distributed.

The main ores of titanium are ilmenite, $FeTiO_3$, and rutile, one of the several crystalline varieties of TiO_2. The former is widely distributed as a black sand on many marine beaches and constitutes the principal source of the element.

Other titanium containing minerals are titanomagnetite $FeO_4(Ti)$, ramsayite (lorenzenite) $Na_2\ (TiO_2\ )_2\ Si_2\ O_7$, titanite $CaTiSiO_5$, lamprophillite $(Ba,Sr,K)Na(TiFe)TiSi_2(O,OH,F)_9$benitoite $BaTiSi_3O_9$ Warwickite $(MgFe)_3TiB_2O_8$ Osbornite TiN, and the Perovskite $CaTiO_3$.

Titanium is a silvery metal with considerable industrial potential owing to its rare combination of properties. It is less dense than iron, much stronger and having a higher melting point than aluminium and almost as corrosion resistant as platinum. These properties make it ideal for use in jet engines, aircraft frames, missiles, some marine equipment, etc., where light weight, strength, and ability to withstand extremes of temperature are important [1,3].

Certain of its properties, such as tensile strength, may be improved by alloying with aluminium. The metal also forms useful alloys with molybdenum, manganese, iron and other metals.

Many diversified applications have been found for titanium and its alloys. Moreover, the number of these applications tend to increase steadily as greater production and improved processes reduce costs [4,5].

Titanium and its alloys are widely used in compressor blades, turbine discs and many other forged parts of the jet engine. Here they offer resistance to high temperature, as well as weight saving. The latter quality is increasing their use in structural aeroplane parts, ranging from engines and air frames to skin and fastenings. Titanium sheet finds application in shroud assemblies, capable shrouds and ammunition tracks.

Titanium alloy sheet is formed into ribs for use as stiffeners, as well as fuselage frames and bulk heads. Other uses of titanium in aircraft include channel sections, flat rubbing strips, landing gear doors, hydraulic lines, baffles, tail cones, longerons, etc. Other uses of titanium alloys include bulk heads, ducts, fire walls, etc.

The light weight of titanium and its alloys, coupled with their corrosion resistance, has brought them into use in ships, especially naval ships. Here many investigations show the important advantages of the metal and its alloys as wet exhaust muffles for submarine diesel engines, and as meter discs, and heat exchanger tubes which offer improved service for widespread use in salt water.

Military applications of titanium extend from cannon and guided missiles to light weight armorplate for tanks.

Throughout the chemical industry, titanium is used extensively both in plant and in the laboratory. Among important present day applications are heat exchangers, autoclave heads, autoclave coils for cooling and heating, chemical processing racks, and valves and tanks where corrosion resistance is necessary.

Titanium is used in some stainless steel in order to stabilize the carbon as carbide. Titanium carbide is an important abrasive.

Ferrotitanium is used as a "scavenger" for the removal of oxygen and nitrogen from molten iron and steel, and copper-titanium and manganese-titanium for brass and bronze.

Smaller quantities of titanium are used for making artificial bones and skull plates for surgery. Titanium metal is considered to be physiologically insert. [2, 4, 5]

1.2 Chemistry of Titanium [1-8]

Titanium is a silvery - white, ductile metal, relatively light (with a density of 4.5 gml^{-3}), high melting (1677°C) and has a very high electrical resistivity (42 micro-ohm-cm at 20°C). It is dimorphic, with a transformation temperature of 882.5°C; below this temperature it exists in a hexagonal lattice, but above in a cubic lattice. [1].

Titanium is a d-block transition element and has the electronic configuration $3d^2 4s^2$. Titanium (IV) is the most stable and common oxidation state; compounds in lower oxidation states, -I, O, II and III, are quite readily oxidized to Ti^{IV} by air, water or other reagents. The energy of removal of four electrons is so high that the Ti^{IV} ion doesn't have a real existence and Ti^{IV} compounds are generally covalent in nature. [3]

The standard electrode potentials in an aqueos medium at 25° C(with reference to the standard hydrogen electrode) are as follows:

$$Ti \rightleftarrows Ti^{2+} + 2e^- \ , \quad -1.630\ V$$

$$Ti + H_2O \rightleftarrows TiO + 2H^+ + 2e^- \ , \quad -1.306\ V$$

$$Ti^{2+} \rightleftarrows Ti^{3+} + e^- \ , \quad -0.368\ V$$

$$Ti^{2+} + H_2O \rightleftarrows TiO^{2+} + 2H^+ + 2e^- , -0.135\ V$$

$$Ti^{3+} + H_2O \rightleftarrows TiO^{2+} + 2H^+ + e^+ \ , -0.100\ V$$

The metal has a tremendous affinity for oxygen, nitrogen and hydrogen at elevated temperatures, but only in the case of hydrogen is the absorption reversible. It is not attacked by mineral acids at room temperature or even by hot aqueous alkali. It dissolves in hot HCl, giving Ti^{III}species, whereas hot nitric acid converts it into a Ti^{4+}hydrous oxide which is rather insoluble in acid or base. It is also attacked by four organic acids in the form of hot, concentrated solutions, namely: oxalic, formic, trichloroacetic and trifluoroacetic, as well as by aluminium trichloride. The best solvents for $Ti^{4+}$are HF or acids to which fluoride ions have been added. Such media dissolves titanium and hold it in solution as fluoro complexes.

Titanium reacts with many metals and non-metals forming interstitial or intermetallic compounds, for example, with Al, Sb, Be, Cr, Fe and B.

Titanium dioxide is one of the stable compounds of titanium which occurs in minerals like rutile. Pure dioxide is colorless. With strong acids TiO_2 reacts to form $[Ti(OH)_3]^+$ or $[Ti(OH)_2]^{2+}$ or $TiO.H_2O$, commonly represented as TiO^{2+} (titanyl ion) as their structures are uncertain. In strong alkalies it dissolves slightly to form probably $[TiO_2(OH)_2]^{2-}$ or $TiO_3.H_2O^{2-}$ (titanate ion). Thus TiO_2 is an amphoteric oxide. [8]

Refractory TiO_2 is best brought into solution by fusing it with $KHSO_4$ and dissolving the cooled melt in dilute H_2SO_4 or HCl. Another good method is to fuse with Na_2CO_3, extract the soluble salts from the cooled melt with water and then dissolve the residue of Na_2TiO_3 in dilute HCl or H_2SO_4 The former method is usually used for the preparation of standard titanium solution. [6,8]

In aqueous solutions of Ti^{IV} there are only oxo species; basic oxo salts, or hydrated oxides may be precipitated. Although these oxo salts have formulas such as $TiSO_4.H_2O$ and $(NH_4)_2TiO(C_2O_4)_2H_2O$ no discrete TiO^{2+} ion is known. Instead, chains or rings, (Ti-O-Ti-O) occur. [3]

One of the most characteristic reactions of aqueous Ti^{IV} solutions is the development of an intense orange color on addition of H_2O_2. This reaction can be used for the colorimetric determination of either Ti or of H_2O_2.

Aqueous solutions of the $[Ti(H_2O)_6]^{3+}$ ion are obtained by reducing aqueous Ti^{IV} either electrolytically or with zinc. The violet solutions reduce O_2 and, hence must be handled in a N_2 or H_2 atmosphere.

There is no aqueous chemistry of Ti^{II} because of its ready oxidation but a few Ti^{II} complexes such as $TiCl_4^{2-}$ can be made in non-aqueous media.

1.3 Analytical Methods for the Determination of Titanium [9-14]

There are many methods, chemical as well as instrumental, for the analysis of titanium in its various samples. The whole coverage of the literature can not be presented here and only a few of the most commonly used ones are described below.

The Gravimetric procedure for the determination of titanium involves the precipitation of the hydrous oxide by ammonium hydroxide (at P^H 6-7) followed by the ignition of the latter to the anhydrous oxide. If other metals are present, it may be necessary to use first a selective precipitating agent to separate the titanium, and then ignite this complex to the dioxide. One example of such selective precipitating agent is tannin (in slightly acidic medium containing acetic acid.) [9]

The standard volumetric method for the determination of titanium involves the reduction of titanium (IV) in a nitrogen atmosphere, by zinc amalgam to the tervalent state. The resulting solution is then titrated against a standard oxidizing agent (one such example is Fe(III)), with thiocyanate as indicator. [11]

Titanium may also be determined potentiometrically in the presence of iron or molybdenum or vanadium by reduction and titration with a standard oxidizing solution.

Atomic absorption spectroscopic methods are common for the determination of titanium in a variety of samples (eg. in cement, nickel alloys, polypropylene, rock samples, steel, etc.) in a fuel rich nitrous oxide /acetylene flame at the 364.3 nm. resonance line. The sensitivity for 1 % absorption is about 2 μg/ml and the limit of determination is 0.2 - 0.4 μg/ml. [12, 13]

Of the colorimetric determinations of titanium, the one with hydrogen peroxide which produces a yellow color when added to an acidic titanium (IV) solution, has long been utilized for the determination of small amounts of the element (up to 0.5 mg of TiO_2 per ml.). Important advantages of hydrogen peroxide for the determination of titanium lie in the high acidity of the medium in which the reaction is carried out and in the lack of interference by the common metals. The great deficiency of the hydrogen peroxide method in trace analysis is its low sensitivity. [14]

Since in the present investigation a spectrophotometric method is employed, a more detailed literature review for the determination of titanium by spectrophotometry or spectrophotometry coupled with solvent extraction is given in the following section.

1.4 Reagents Used for the Spectrophotometric Determination of Titanium

The literature survey revealed that there have been many reagents used for the spectrophotometric determination of titanium. Although all of the reagents reported could not be presented here, some of the most selective and sensitive reagents that have been recently reported in the literature are mentioned below. (The unit of ϵ is $M^{-1}cm^{-1}$ throughout the text).

A method has been described for the spectrophotometric determination of Ti(IV) with nitrilo triacetic acid(I), 4, 5 - dibromophenylfluorone (II), and hexadecyltrimethylammonium bromide (III) based on the color reaction of the multi component complexation of Ti(IV) with the cited reagents as Ti - I - II - III (1: 1: 2: 2) at P^H 2.5 - 4.0 which has an absorption maximum at 576 nm (ϵ = 213000) Beer's law was obeyed for ≤ 0.4 μgml^{-1} of Ti^{IV}.[15] The method has been used for the selective determination of Ti in steel without pre-separation.

Puzanowska - Tarasiewiez et al. have developed the spectrophotometric determination of Ti(IV) (2 - 22 μg) with chlorpromazine hydrochloride in the presence of thiocyanate in HCl medium after extraction of the complex into chloroform. [16] The absorbance was measured at 417 nm (ϵ = 26000). Beer's law was obeyed for 0.2 to 2.2 μgml^{-1} of Ti, and the Sandell sensitivity was 1.8 $ngcm^{-2}$. The coefficient of variation was 0.5 to 1.5 %, depending on the concentration of Ti.

Titanium (IV) was found to react with N-pivaloyl-p-chlorophenylhydroxylamine to form an intensely yellow complex, which can be extracted from 7 to 11M - HCl medium into chloroform. The ϵ value at 380 nm. was 5300, Beer's law was obeyed in the range 0.2 to 12 μgml^{-1} of Ti, and the Sandell sensitivity was 9 $ngcm^{-2}$. Various accompanying ions did not interfere but V^{V}, Mo^{VI}, W^{VI} and Nb^{V} interfere seriously, and Fe^{II}, Sn^{II} and F^{-} to a lesser extent. [17]

Gunawardhana, H.D. [18] has proposed a spectrophotometric determination of titanium with N - phenyldodecanohydroxamic acid (I) and phenylfluorone (II) in HCl - ethanol medium forming the Ti^{IV}- I - II (1: 2: 1) complex, the absorbance of which was measured at 560 nm. (ϵ = 123000). Beer's law was obeyed for $\leq$ 0.4 ppm of $Ti^{IV}$and the detection limit was 10 ppb. Fe^{II}, V^{V}, Mo^{VI},$F^{-}$and Nb^{V} did not interfere in molar amounts $\leq$ 350, 4, 5, 3, 200, and 0.5 times (respectively) that of Ti, nor did Zr^{IV}in up to 0.5 fold molar amount, or in 50 - fold amount if 100 ppm of $F^{-}$was added.

A method has been described by Shijo, Yoshio et al. [19] which uses tridodecylethylammonium bromide, a quaternary ammonium salt, for the extraction of the catechol violet complex of Ti^{IV}into carbontetrachloride from acetate - $SO_4^{=}$ medium (p^H 5.1 - 6.4). The absorption maximum is 586 nm. (ϵ = 51700). The calibration graph is rectilinear from 0.06 to 1.0 $\mu gml^{-1}$of Ti^{IV}in CCl_4

An extraction - spectrophotometric method was developed by Lopez Nunez, R. et al. [20] with alizarine and fluoride which involves treatment of Ti^{IV}solution in 1 M - $H_2SO_4$with aq. F^{-}buffer (P^H=10) and extraction with alizarine solution in isobutyl methyl ketone. The absorbance was measured at 513 nm. (ϵ = 70000); in the determination of 11 μg of Ti, the coefficient of variation was 1.4% (n=11).

Investigation of the reaction of titanium with 3 - hydroxy - 2 - methyl - 1 - p - tolylpyridine - 4 - one in H_2SO_4,HCl and $HClO_4$media has led to the formation of a complex in an excess of ClO_4^{-}that can be extracted into chloroform. The complex has an ϵ value of 16000 at 355 nm. The optimum concentration range is 0.5 to 6

μgml^{-1} over which Beer's law was obeyed. [21]

A spectrophotometric method is described for the determination of Ti^{IV} using 2, 3, 7 - trihydroxy - 9 - o - chlorophenylfluorone (I). The Ti- I complex (1:4) possessed an absorption maximum at 540 nm (ϵ = 207000) in 0.05 to 0.2M - H_2SO_4 Most other metal ions do not interfere except for Zr^{IV}, Sn^{IV}, W^{VI}, Mo^{VI}, Ge^{IV} and Nb^{V}, all of which could be masked. The method was applied to alloys, rocks and minerals with satisfactory results. [22]

Titanium was determined spectrophotometrically at 535 nm (ϵ = 107000) as its complex with 6, 7 - dihydroxy - 2, 4 - diphenyl - 1 - benzopyrylium chloride (I) in the presence of Triton X - 100 at P^{H} 1.6 - 2.1. [23] The ratio of Ti to I was 1: 3. The calibration graph was rectilinear up to 360 μgl^{-1} of Ti. Interference from V^{V}, Nb^{V}, Mo^{VI}, Zr^{IV} and Fe^{III} was masked by the addition of appropriate reagents. The method was applied to determine Ti in steels.

The determination of titanium under high sensitivity condition with 2 - (5 - Chloro - 2 - pyridylazo) - 5 - dimethylaminophenol has been described by Marini, H.J. et al. [24] The reaction between Ti^{IV}, H_2O_2 and the cited reagent (I) was applied to the determination of Ti^{IV} in nodular cast iron and nickel based alloys. The absorbance was measured at 354 nm. (ϵ = 45900). Beer's law was obeyed up to 0.7 ppm. Fe^{III}, Cu^{II}, Ni^{II}, Co^{II}, W^{VI}, Nb^{V}, Ta^{V} and V^{V} interfered seriously but the extraction procedure in the method removed them.

The analytical promise of N - 4 - methoxyphenyl - 2 - furylacrylohydroxamic acid was investigated. [25] The complex formed between Ti and the cited reagent was extracted into chloroform. The absorbance of the $CHCl_3$extract was measured at 390 nm (ϵ = 19000) against a standard solution of the reagent. Beer's law was obeyed over the range 0.1 - 2.5 ppm of $Ti^{IV}$and the Sandell sensitivity was 3 $ngcm^{-2}$The method was used to determine Ti in minerals, alloys, steel, plant tissue and water.

Spectrophotometric study of the ternary complex of titanium (IV), Eriochrome red B and hydrogen peroxide has led to the formulation of a method for its determination. The absorbance of the resulting 1: 1: 1 complex at P^H (7.8 - 8.0) was measured at 550 nm [26]; Beer's law was obeyed from 0.33 to 3.35 ppm of Ti^{IV}.The coefficient of variation was 1.21 % for 2.4 ppm of Ti^{IV}.

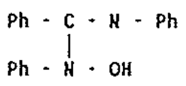
Nazarenko, A.Yu. [27] has described a method for the determination of Ti(IV) with disulphonylfluorone and complex cationic surfactants. The Ti^{IV} - disulphonylphenylfluorone (I) (1:2) complex can be stabilised in solution by a K^+ - Triton X-305 complex and exhibits maximum absorption at 592 nm (ϵ = 140000)and Beer's law was obeyed for 2 - 150 $ngml^{-1}$of Ti under optimum conditions (P^H 3.1 - 3.4). The coefficient of variation is < 15 % (n=4).

The spectrophotometric determination of titanium with 5 - sulphosalicylic acid was reported by Kalianova, M. and Sommer, L. [28] Optimum conditions for this determination are P^H: 2.6, I ≤ 1.5, Ti concentration ≤ 60 μM, reagent concentration 0.15 M, measurement wavelength 360 to 380 nm. Tartrate, citrate, oxalate and ascorbate interfere, but ≤ 80 mM ascorbic acid can be used to reduce Fe^{III}(which otherwise interferes) with only a small decrease in the ϵ value. Fluoride, $H_2PO_4^-$, Nb^V,V^V,Zr^{IV},Mo^{VI}, W^{VI},Cu^{II},$Al^{III}$and V^V interfere seriously.

Mixed ligand complexes of titanium (IV) with bromopyrogallol red (I) and 1 - hexadecylpyridinium ions (II) have been used for the spectrophotometric determination of Ti^{IV}[29]. A Ti - I - II (1: 2: 4) complex was formed under optimum conditions. This complex extractable into chloroform, exhibits a maximum absorption at 630 nm (ϵ = 25900). Beer's law was obeyed from 0.2 to 2 μgml^{-1}. Tolerable amounts of other metals (relative to Ti) are Fe^{II}, Ni^{II} and Al^{III}(10); Mn^{II}(15), Zn^{II} (25) V^{V} (800) and Zr^{IV}, Hf^{IV} and Ta^{V} (1).

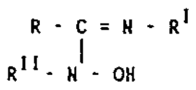
1.5 Analytical Applications of N^{1}- Hydroxy - N^{1}, N^{2}-diphenylbenzamidine (HDPBA)

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



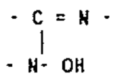
$$\begin{array}{l} \text{Ph}-\text{C}-\text{N}-\text{Ph} \\ \quad\;\;| \\ \text{Ph}-\text{N}-\text{OH} \end{array}$$

I



$$\begin{array}{l} \;\;\text{R}-\text{C}=\text{N}-\text{R}^{I} \\ \qquad\;| \\ \text{R}^{II}-\text{N}-\text{OH} \end{array}$$

II



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

III

where R, R^{I}, R^{II} are phenyl or substituted phenyl rings.

Hydroxyarylbenzamidines are pale yellow crystalline solids which are stable towards heat, light, and air 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 a wide scope as analytical reagents in 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 determinations of metal ions. Most of the metal complexes of hydroxyamidines are intensely colored and are stable. These reaction products can be employed for spectrophotometric determinations 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 an analytical reagent for the first time in 1974 by Satyanarayana and Mishra [30] 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 have been being carried out recently into the 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 [31], spectrophotometric determination of iron (III) [32], solvent extraction and spectrophotometric determination of iron (III) [33, 34], Cobalt (II) [34], Cobalt (III) [35], manganese (VII) [36] and most recently for Mo(V) [37].

From the successful application of the reagents (HDPBA and KSCN) for the extraction and spectrophotometric determination of Mo(V), it was thought to worth to extend the analytical application of HDPBA/KSCN to the extraction and spectrophotometric determination of tungsten(V). Hence at the beginning the objective of the research project was to study the reaction of tungten(V) with HDPBA and thiocyanate and the extraction of the resulting mixed ligand complex if any; in order to develop a method for the extraction and spectrophotometric determination of tungsten using the cited reagents, with this objective the research project was undertaken and the first step was to find out a suitable reducing agent for the reduction of W(VI) to W(V). The litrature survey revealed that the most effective reducing agent for the reduction of W(VI) to W(V) is $SnCl_2$ /HCl. Unfortunately the complexing ligands, HDPBA and/or KSCN were found to be attacked by the reducing agent and hence the complexing ligands and the reducing agent (HDPBA/KSCN and $SnCl_2$ /HCl) could not coexist together for the system to work. Other reducing agents were found to be weak and slow. Therefore the original research project was modified to the extraction and spectrophotometric determination of titanium(IV) with HDPBA and thiocyanate.

1.6 Aim and Scope of the Present Investigation

The foregoing literature survey reveals that several spectrophotometric methods involving a variety of reagents for the determination of titanium (IV) as a binary or mixed ligand complex have been reported. These reagents have different advantages and disadvantages in terms of their selectivity, sensitivity, precision, speed, convenience, etc. However, no report has been presented in the literature on the application of HDPBA alone or with other auxiliary reagents for the determination of titanium (IV). Hence, it was worthwhile to study the formation of the mixed ligand complex between Ti (IV),the thiocyanate ion and HDPBA in detail under different experimental conditions in order to develop a new, precise, sensitive and selective method for the extraction and spectrophotometric determination of Ti (IV).

Hence, the detailed objectives of the research project were:

1. to study the extraction and spectral properties of the Ti (IV)-SCN-HDPBA ternary complex in the UV-visible region;
2. to establish the optimum conditions for the extraction and spectrophotometric determination of Ti^{IV} with HDPBA and thiocyanate;
3. to determine the stoichiometric composition of the Ti (IV) -SCN-HDPBA ternary complex species; and
4. to evaluate the sensitivity, selectivity, precision, accuracy and applicability of the system to artificial and/or real samples.

2. THEORETICAL CONSIDERATIONS

2.1 Fundamentals of Solvent Extraction [38 - 44]

Solvent extraction is understood as the partition of one or more components between two liquids of limited miscibility. Such liquid - liquid partition is caused by the different solubilities of a given substance in the two phases. Solvent extraction has been recognized as a popular and versatile technique because of its simplicity, speed and applicability both to major and trace components.

High selectivity of extraction can easily be achieved if the conditions are properly arranged and, wherever necessary, the separation yield can be increased as required by means of successive batch extractions. A further advantage of extraction is that the extract usually has some properties on which the determination of the isolated constituent can be based: absorption of light, fluorescence and radio activity can serve as examples.

In analytical applications the liquid - liquid partition equilibria, which are commonly called extraction equilibria, usually take place between an aqueous solution (Phase I) and an organic solvent (Phase II) which is immiscible with water. Hence, such a partition equilibrium can be characterized (for a given temperature and pressure) by a thermodynamic equilibrium constant $K_{D,A}$. The thermodynamic condition for such equilibrium is that the chemical potentials, μ_A, of the substance are equal for the two phases, i.e.

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

where $(\mu_A{}^0)_I$ and $(\mu_A{}^0)_{II}$ are the standard chemical potentials and $(a_A)_I$ and $(a_A)_{II}$ are the activities of substance A in phase I and II, respectively.

Equation 1 can then be rearranged to give:

$$(\mu^0{}_A)_I = - \blacksquare\ G^\circ_{D,A} = RT \ln (a_A)_{II}/(a_A)_I$$

$$= Rt \ln(K_{D,A})_a \qquad (2)$$

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

$$K_{D,A} = [A]_{II}/[A]_I = (K_{D,A})_a(f_{A,I}/f_{A,II}) \qquad (3)$$

where $[A]_{II}$ and $[A]_I$ represent the equilibrium molar concentrations of the substance A in the particular phase.

2.2 Solvent Extraction of Metal Chelates

If a metal ion is to be extracted from an aqueous solution into an organic solvent, the metal ion must exist as part of an uncharged species which can be either an electroneutral complex (chelate) or an ion-association species that can be transferred across the liquid - liquid boundary. For this organic reagents play a crucial role because they can react with metal ions to give products having the basic prerequisite for extractability i.e. electroneutrality.

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

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

which is characterized by the extraction constant:

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

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 in the aqueous phase:

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

(iii) formation of the extractable chelate, ML_n:

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

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

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

Substituting equation 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 agent HL.

In liquid - liquid partition, a substance M can undergo in both phases various salvation, 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 a 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:

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

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,

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

or

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

As shown in equation 14, the value of the extraction constant also depends on the concentration of the extracting reagent and the P^H of the solution.

The distribution ration D_M can also be influenced by other factors such as temperature, ionic strength of the system, kinetics of extraction, and choice of solvent, which are not explicitly expressed by the quantities in equation 14.

A change in the ionic strength affects the value of the relative permittivity and so the value of K_{ex} which affects the value of D_M. For practical reasons the aqueous phase should contain a certain concentration of a salt, the formation of an emulsion is thus prevented, which makes the separation of the two phases easy.

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 behavior of the chelate in a variety of solvents. Generally, solvents are chosen on the basis of the following considerations: (i) the solvent should have negligible solubility in the aqueous phase so that its effect on the equilibria in the aqueous phase may be kept to the minimum; (ii) it should provide a high distribution ratio for the solute and a low distribution ratio for undesirable impurities; (iii) it must have a sufficiently low viscosity and sufficient density difference from the aqueous phase to avoid the formation of emulsions; and (iv) it must be stable.

The toxicity of some organic solvents must also be considered in the choice of solvent; this is important not only with respect to exposure to solvent vapour but also as regards contact with the skin.

2.3 Spectrophotometry [38, 39, 43-49]

The absorption of radiant energy in the ultraviolet and visible regions of the electromagnetic spectrum form the basis for spectrophotometric methods of trace analysis.

When a monochromatic beam of light passes through a homogenous absorbing medium of length, l, the radiant energy will diminish in proportion to the concentration, c, of the absorbing substance in the light path. Beer's law is the quantitative statement of this phenomena, which can be written mathematically as,

$$A = \epsilon cl \tag{15}$$

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 are commonly used for the determination of inorganic substances with organic reagents. The reliability of the method depends on the nature of the organic reagent used. Organic reagents used in spectrophotometric method should be sufficiently stable and resistant to atmospheric oxidation or to photo 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 a sufficient distance from that of the reagent or of substance being determined: $\lambda_{(product)max} - \lambda_{(reagent)max} \geq 100$ nm.

Reagents for which $\lambda_{(product)max} \sim \lambda_{(reagent)max}$ are less suited for spectrophotometry and can be applied only when the absorption coefficients differ by a factor of at least 10^2.

2.4 Spectrophotometric Determination of Metal Ions [38, 39, 43-49]

Determination of metal ions by spectrophotometry is usually based on the formation of stable metal complexes. This complexation reaction requires the presence of acidic or basic analytical functional groups in the molecules of the complexing reagent (ligand), preferably in those positions which allow the formation of five - or six - membered chelate rings. Colored metal complexes are formed only when the organic reagent has π-electron chromophobic 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 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 determinations extends to the UV region.

The complex - forming properties of organic reagents can be influenced by introducing suitable substituents in to their molecules. The stability of the complex is usually increased by higher basicity of the ligand, this can be achieved, for example, when electron donor substituents (e.g. alkyl groups) are present in the position meta or para to the active grouping. 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 - the reaction of the metal ion with the particular functional group is thus prevented. In this manner it is sometimes possible to increase the selectivity of the reagent.

Completeness of Complexation reaction. On account of the equilibrium involved and the fact that the amount of metal ion is unknown, it is always necessary to use a large excess of the reagent in order to secure a complete and, as far as possible, rapid reaction leading to the formation of a product of a defined composition.

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

$$M^{n+} + nL^{-} \rightleftharpoons ML_n \qquad (16)$$

on which the determination is based

$$\beta^{1}_{MLn} = \frac{[ML_n]}{C_M{}^{1}(C_L{}^{1})^{n}} = \frac{\beta_{MLn}}{\alpha_M \alpha_1{}^{n}} \qquad (17)$$

where $C_M{}^{1}$ is the concentration of metal ion that has not reacted with the complexant L,C^{L} is the concentration of the ligand not bound to the central ion M; α_M and α_L are side reaction coefficients of the metal ion and 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,

$$\frac{[ML_n]}{C^{1}_{M}} = \beta_{MLn}{}^{1}(C_L{}^{1})^{n} \geq 10^{2} \qquad (18)$$

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. It is always necessary to choose a suitable wavelength at which the measurement is made for photometric determination of a given substance to achieve an adequate selectivity. Moreover, the absorption coefficient of the substance being determined should be high and those of other substances present be negligible. Selectivity can also be increased by p^H adjustment or by masking. The masking reagent (and its complex) should be colorless and not form any complexes with the metal being determined or react with the colorimetric reagent.

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

In the determination of a metal ion M, in the presence of another metal N, if both form colored complexes $ML_n(\beta^1{}_{MLn})$ and $NL_n(\beta^1_{NLn})$ 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 absorbance values of the two complexes, provided the colorimetric reagent itself doesn't absorb at th wavelength used:

$$\frac{A_{MLn}}{A_{NLn}} = \frac{\epsilon_{MLn}[ML_n]}{\epsilon_{NLn}[NL_n]} = \frac{\epsilon_{MLn}\beta^1{}_{MLn}C_M[1+\beta^1{}_{NLn}(C_1{}^1)^n]}{\epsilon_{NLn}\beta^1{}_{NLn}C_N[1+\beta^1{}_{MLn}(C_1{}^{\bar{1}})^n]} \geq D^2 \quad (1$$

where C_M and C_N are the total concentrations of M and N, respectively. If the concentrations of M and N are the same and the absorption coefficients of the two complexes are equal, the concentration of the complex NL_n must be negligible if an accurate result is to be obtained for M:

$$\frac{[NL_n]}{C_N{}^1} = \beta^1{}_{NLn}(C_1{}^1)^n \leq 10^{-2} \qquad (20)$$

combination of equations 18 and 19 gives

$$\frac{\beta^1{}_{MLn}}{\beta^1{}_{NLn}} \geq 10^4$$

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 solving the appropriate simultaneous equations. The simultaneous spectrophotometric determination of two solutes in solution can be achieved if there is no reaction between the two solutes. Since absorbances are additive under this condition, one can write

$$A_{\lambda 1} = A_{1(\lambda 1)} + A_{2(\lambda 1)} \qquad (22)$$

$$A_{\lambda 2} = A_{1(\lambda 2)} + A_{2(\lambda 2)} \qquad (23)$$

where $A_{\lambda 1}$ and $A_{\lambda 2}$ are the measured absorbances at the two wavelengths λ_1 and λ_2,and the subscript 1 and 2 refer to the two different substances. The wavelengths λ_1 and λ_2 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 λ_2 and substance 2 absorbs strongly at λ_2 and weakly at λ_1 Now according to Beer's law $A = \epsilon Cl$, where ϵ is the molar absorption coefficient at any particular wavelength, C is the molar concentration. and l is the thickness (length) of the absorbing solution expressed in cm. If l is 1 cm

$$A_{\lambda 1} = \epsilon_{1(\lambda 1)}C_1 + \epsilon_{2(\lambda 1)}C_2 \tag{24}$$

$$A_{\lambda 2} = \epsilon_{1(\lambda 2)}C_1 + \epsilon_{2(\lambda 2)}C_2 \tag{25}$$

The solutions of these simultaneous equations are

$$C_1 = \frac{\epsilon_{2(\lambda 2)}A_{\lambda 1} - \epsilon_{2(\lambda 1)}A_{\lambda 2}}{\epsilon_{1(\lambda 1)}\epsilon_{2(\lambda 2)} - \epsilon_{2(\lambda 1)}\epsilon_{1(\lambda 2)}} \tag{26}$$

$$C_2 = \frac{\epsilon_{1(\lambda 1)}A_{\lambda 2} - \epsilon_{1(\lambda 2)}A_{\lambda 1}}{\epsilon_{1(\lambda 1)}\epsilon_{2(\lambda 2)} - \epsilon_{2(\lambda 1)}\epsilon_{1(\lambda 2)}} \tag{27}$$

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

2.5 Characteristic Terms used in Photometric Analysis [37, 50, 51]

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) depend on the type of instrument used and on the chemical reaction chosen.

The occurrence of apparent deviations from Beer's law limits the attainable precision in photometry to 0.5 - 1% (relative) within the range of absorbance values 0.1 - 1. This practical limit is caused by many factors, namely stray light, light reflected on the walls of cuvette, the change 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-reactions with other components of the solution. The presence of a large amount of electrolyte (known as salt effect) causes the deformation of the complex species which results in a change of absorption spectrum.

A further source of photometric error is due to the effect of a change in the concentration of the solution on the value of the refractive index 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 a minimum, was introduced by Ringbom [52]. According to this technique, when 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 a minimum is obtained by constructing tangents to the steepest portion of the curve.

Sensitivity and limit of determination. The sensitivity of a photometric method is defined as the slope dA/dC of the calibration curve C = f(A) at the origin [53].

where C is the concentration of the substance to be determined, and A is the absorbance of the solution. The initial linear portion of the curve can be expressed as:

$$C = (A - A_0)(dA/dC)^{-1} \qquad (28)$$

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 chosen in the region of a high absorption maximum (where ϵ is maximum) and if a 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 (eg. μg) or as the lowest molar concentration, M, or in any other convenient way, eg. as $\mu g ml^{-1}$ percentage, ppm, which shows a statistically significant difference from zero or the average value of the blank.

Of the several method of evaluating the limit of determination, two of the most commonly used methods are described below. According to Kaiser [62] C_{min} is evaluated as:

$$C_{min} = (A-A_0)(dA/dC)^{-1} = 3S_0(dA/dC)^{-1} = 3S_0/\epsilon l \qquad (29)$$

where S_0 is the standard deviation for the blank determination. Sandell [43, 50] defines the limit of determination (or "sensitivity" according to him) as the weight in

$\mu gml^{-1}$of solution which corresponds to an absorbance A = 0.001 measured in cuvette of cross-sectional area 1 cm^2 and l = 1 cm. Its dimensions are μgcm^{-2}. According to this definition, C is given by

$$C_S = \frac{M}{\epsilon} \quad (\mu gml^{-1}) \tag{30}$$

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 the Determination of the Composition of Metal Complexes [54, 55]

The stoichiometric composition of metal complexes can be determined by several spectrophotometric techniques. However, the most commonly used ones are: the method of continuous variations [46, 56], the mole ratio [47], and the extraction [44] methods.

Method of continuous variation. The underlying principle of this method is that the mole fraction of the 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 solutions. Considering a single defined equilibrium:

$$M + nL \rightleftarrows ML_n \tag{31}$$

if the absorbance is measured at the 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_L) or f(X_M), gives the stoichiometry of the complex being formed in solution:

$$n = \frac{X_{L(max)}}{1 - X_{L(max)}} = \frac{1 - X_{M(max)}}{X_{M(max)}} \qquad (32)$$

<u>The mole ratio method</u>. For a single and stable complex in solution, the stoichiometry can be simply determined from the break on the absorbance versus component concentration plot, maintaining the concentration of one component constant (usually the metal). 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.

<u>Extraction method</u>. Considering the formation of a mixed ligand complex ML_nX_m in an extraction system, the equilibria involved can be represented by:

$$M_{aq}^{n+} + mX_{aq} \rightleftarrows MX_{m,aq} \qquad (33)$$

$$MX_m + nHL_{org} \rightleftarrows MX_m(HL)_{n,org} \qquad (34)$$

summing 33 and 34,

$$M_{aq}^{n+} + mX_{aq} + nHL_{org} \rightleftarrows MX_m(HL))_{n,org}$$

The extraction constant for $MX_m(HL)_n$ is given by

$$K_{ex} = \frac{[MX_m(HL)_n]_{org}}{[M_{aq}][X_{aq}]^m[HL_{n,org}]^n} \qquad (36)$$

Rearrangement of equation 36 gives

$$\frac{[MX_m(HL)_n]_{org}}{[M]_{aq}} = K_{ex}[X]^m{}_{aq}[HL]^n{}_{org} \qquad (37)$$

Since $[M]_{aq} = C_M - [MX_m(HL)_n]_{org}$, equation 37 can be written as

$$\frac{[MX_m(HL)_n]_{org}}{C_M - [MX_m(HL)_n]_{org}} = K_{ex}[X]^m{}_{aq}[HL]^n{}_{org} \qquad (38)$$

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

$$[MX_m(HL)_n] = A/\epsilon \text{ and } C_M = A_{max}/\epsilon$$

(for $l = 1$ cm), where A is the equilibrium absorbance in the presence of excess concentration of auxiliary ligand, X. Rewriting equation 38,

$$\frac{A/\epsilon}{(A_{max}-A)/\epsilon} = \frac{A}{A_{max}-A} = K_{ex}[X]^m{}_{aq}[HL]^n{}_{org} \qquad (39)$$

Equation 39 can be expressed in logarithmic form as,

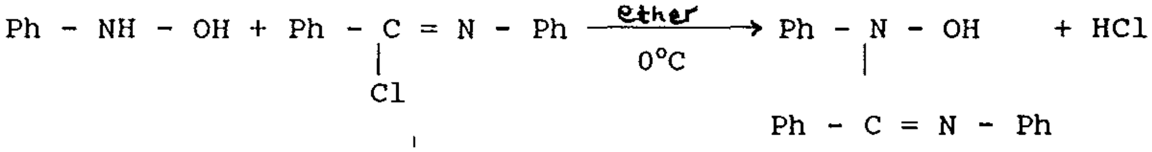
$$\log(A/A_{max}\ A) = \log K_{ex} + m\log[X]_{aq} + n\log[HL]_{org} \qquad (40)$$

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

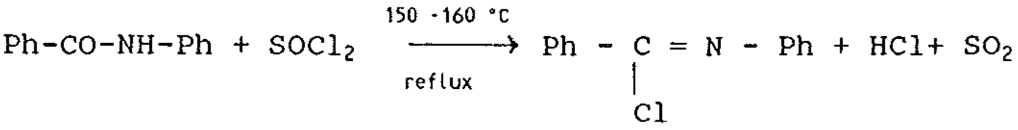
3.1 Synthesis of N^1- Hydroxy - N^1,N^2-diphenylbenzamidine (HDPBA)

HDPBA was prepared by the condensation of N - phenylbenzimidoyl chloride with N - phenylhydroxylamine at 0°C in ether medium [30]. Thus, the preparation of N^1 - Hydroxy - N^1, N^2- diphenylbenzamidine required the synthesis of N - phenylbenzimidoyl chloride and N - phenylhydroxylamine.



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

Preparation of N-Phenylbenzimidoyl Chloride. The synthesis of N-phenylbenzimidoyl chloride was made by chlorinating bezanilide using thionyl chloride as a chlorinating agent [57]. 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.



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

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.

$$\mathrm{Ph - CO - Cl + Ph - NH_2 \xrightarrow[reflux]{NaOH} Ph - CO = NH - Ph + HCl}$$

Preparation of N - Phenylhydroxylamine. N - Phenylhydroxylamine was prepared by the reduction of nitrobenzene with zinc and ammonium chloride in aqueous solution at 60 - 65 °C [57].

$$\mathrm{Ph - NO_2 \xrightarrow[60\text{-}65^\circ C]{Zn/NH_4Cl} Ph - NH - OH}$$

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 over twenty five minutes by mechanical stirring, so that the temperature of the reaction mixture did not rise above 60 - 65 °C due to the exothermicity of the reaction. The product was separated from the zinc oxide and unreacted zinc by filtration under suction. Sodium chloride (150 g) was added to the filtrate to effect the crystallization of N - phenylhydroxyl amine. The product was recrystallized from benzene, yield 11 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 - phenylbenzimidol chloride (21.5 g, 0.1 mole) in ether (100 ml), stirred continuously and placed on an ice bath.

The light yellow crystals were obtained from 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 benzine to give pale yellow crystals yield 10 g.

3.2 Apparatus and Reagents

Apparatus. A Beckman model 24 UV -visible spectrometer equipped with 1 cm matched quartz cells and Beckman recorder was used for recording the absorption spectra and absorbance measurements of the complex in the visible region.^G

Standard titanium (IV) solutions. The standard solution of Ti(IV) ($7.5*10^{-3}$ M) was prepared by fusing 0.3 g of TiO_2 with 2.5 g of potassium hydrogen sulphate. The cooled melt was leached with 10 % (v/v) sulphuric acid and diluted to 500 ml with 10 % (v/v) sulphuric acid.

Reagent (HDPBA) solution. . A $7.5*10^{-3}$ M solution of the reagent(HDPBA) was prepared by dissolving the right amount in doublly distilled toluene.

Standard thiocyanate solution. A 4.0 M solution of potassium thiocyanate (Riedel de Haen) was prepared by dissolving the appropriate amount of the salt in distilled water.y

Solvents. Toluene and other solvents were used after double distillation.

Hydrochloric acid. Dilute hydrochloric acid (2 M, 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.

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

Solutions of Li^+, Na^+, K^+, Be^{2+}, Hg^{2+}, Cu^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Sr^{2+}, Pb^{2+}, Ni^{2+}, UO_2^{2+}, La^{3+}, Fe^{3+}, Bi^{3+}, Cr^{3+}, Th^{4+}, Tl^{1+} and Y^{3+} were prepared by dissolving the respective nitrate salts (BDH or Riedel de Haen) in distilled water to give 10 $mgml^{-1}$ of the ion in solution.

Molybdate, tungstate, 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 or 20 $mgml^{-1}$ of the ion in solution.

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

Sample solutions. Stock solutions of synthetic matrices of compositions similar to the ones present in ores and minerals were prepared by mixing known quantities of the solution of constituent ions.

3.3 Procedures

3.3.1 Extraction and Determination of Ti(IV)

An aliquot of the solution containing up to 100 μg of Ti(IV) was placed in a 100 ml separatory funnel. To this were added 0.5 ml of 2 M hydrochloric acid and 1.0 ml of potassium thiocyanate (40 % w/w) and the aqueous phase volume was made to 10 ml with distilled water. A 10 ml aliquot of 7.5×10^{-3} M solution of HDPBA in toluene was added to the funnel, the mixture was shaken vigorously for 2-3 minutes, and the funnel was allowed to stand for 2 minutes. The organic phase was collected in a 50-ml beaker containing 2 g of anhydrous sodium sulphate and stirred with a glass rod. The aqueous phase was shaken with another 10 ml of HDPBA solution, the organic phase was again collected in the same beaker. The aqueous phase was equilibrated with yet another 5 ml portion of HDPBA solution in the funnel and the organic extract was added to the 50-ml beaker for the third time. The dried extract was then transferred to a 25-ml volumetric flask and filled to the mark with pure solvent. The spectrum of the extract was taken over the range 700 - 350 nm using the reagent blank as the reference.

For calibration, 0.05, 0.10, 0.15 and 0.20 ml of the standard Ti(IV) stock solution (360 μgml^{-1}) were used through the general procedure.

3.3.2 Examination of Experimental Variables

The effect of a particular experimental variable was studied by measuring the absorbance of the system by following the general procedure described for the extraction and determination of Ti(IV) in section 3.1.1, keeping all the experimental variables constant except the one under study.

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 36 μg of Ti(IV). The extraction and determination of the metal ion were made according to the procedure described in section 3.3.1.

3.3.4 Determination of the Stoichiometric Composition of the Complex

Extraction Method. To determine the Ti(IV) to HDPBA ratio in the complex, Ti - SCN - HDPBA, a series of solutions were prepared in which the concentration of

Ti(IV), SCN^- and HCl were kept constant at 3 x 10^{-5} M, 0.4 M and 0.1 M respectively. The concentration of HDPBA was varied in the range 2.5 x 10^{-4} - 3 x 10^{-3}. The complex was extracted by the general procedure described in section 3.3.1. The same was done for the determination of the Ti(IV) to SCN^- ratio in the complex, Ti(IV) - SCN - HDPBA, by keeping constant the concentration of HDPBA at 7.5 x 10^{-3} M and others as in the previous case, and varying the concentration of SCN^- from 1.25 x 10^{-3} - 3 x 10^{-2} 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 $\log(A/(A_{max} - A))$ was plotted against $\log(SCN^-)$ and log(HDPBA) respectively.

3.3.5 Procedure for Testing the Presence of Ti(IV) in the Extract

The extract was evaporated nearly to dryness and the residue was decomposed with about 5 ml of concentrated H_2SO_4. The solution was heated to dryness to evaporate most of the sulphuric acid and cooled. The residue was leached and diluted to 10 ml with 10 % (v/v) sulphuric acid. A drop of the sulphuric acid test solution was treated with a drop of 3 % hydrogen peroxide on a spot plate. Appearance of an intense yellow color indicated the presence of Ti(IV) in the test solution [58].

4. RESULTS AND DISCUSSION

4.1 Reaction Conditions and Absorption Spectra

The extractability of titanium (IV) as the Ti(IV)- SCN binary complex from aqueous solutions of different acidity (1.0, 0.5, 0.3, 0.2, 0.15, 0.1, 0.07, 0.05 and 0.03 M HCl) into toluene was examined. However, the organic phase was found to be colorless.These results indicated that there was no formation and / or extraction of Ti(IV)-SCN in the organic phase. This was further supported by the absence of Ti(IV)in the organic phase by the H_2O_2 spot test [58].

In the second trial the extractability of titanium(IV) from aqueous solutions of different acidity as above was tried with HDPBA solution (7.5 x 10^{-3} M) in toluene as a binary complex species [Ti(IV) - HDPBA] and it was found that there was no colored reaction product in the organic phase . These results again indicated that there was no formation and / or extraction of a Ti(IV) - HDPBA binary complex. This was further evidenced by the absence of Ti(IV) in the organic phase by the H_2O_2 spot test [58].

In the third trial, attempts were made to extract Ti(IV) in the presence of thiocyanate from aqueous solution of different acidity (1.0, 0.5, 0.3, 0.2, 0.18, 0.15, 0.1, 0.07, 0.05 and 0.03 M HCl) into a toluene solution of HDPBA. These attempts resulted in the extraction of titanium (IV) as a mixed ligand complex , Ti(IV)-SCN -

HDPBA , from aqueous solution into toluene as indicated by the orange colored extract in the organic phase.This was further supported by the presence of Ti(IV) in the organic phase by the H_2O_2 spot test [58].

These studies confirmed that there is no formation of an extractable Ti(IV) - SCN or Ti(IV) - HDPBA binary complex, and there is only formation of a Ti(IV) - SCN - HDPBA ternary complex, extractable into toluene under the experimental conditions used.

The absorption spectrum of the complex in toluene was recorded using the reagent blank as reference in the spectral range 700 - 350 nm. The absorption spectra of the complex extracted at different acidities were more or less similiar , indicating the extraction of titanium (IV) as a single complex species i.e., Ti(IV) - SCN - HDPBA , ternary complex. This ternary complex species exhibited maximum absorption at a wavelength of 400 nm with a molar absorptivity of 20,000 $M^{-1}cm^{-1}$(fig 1).

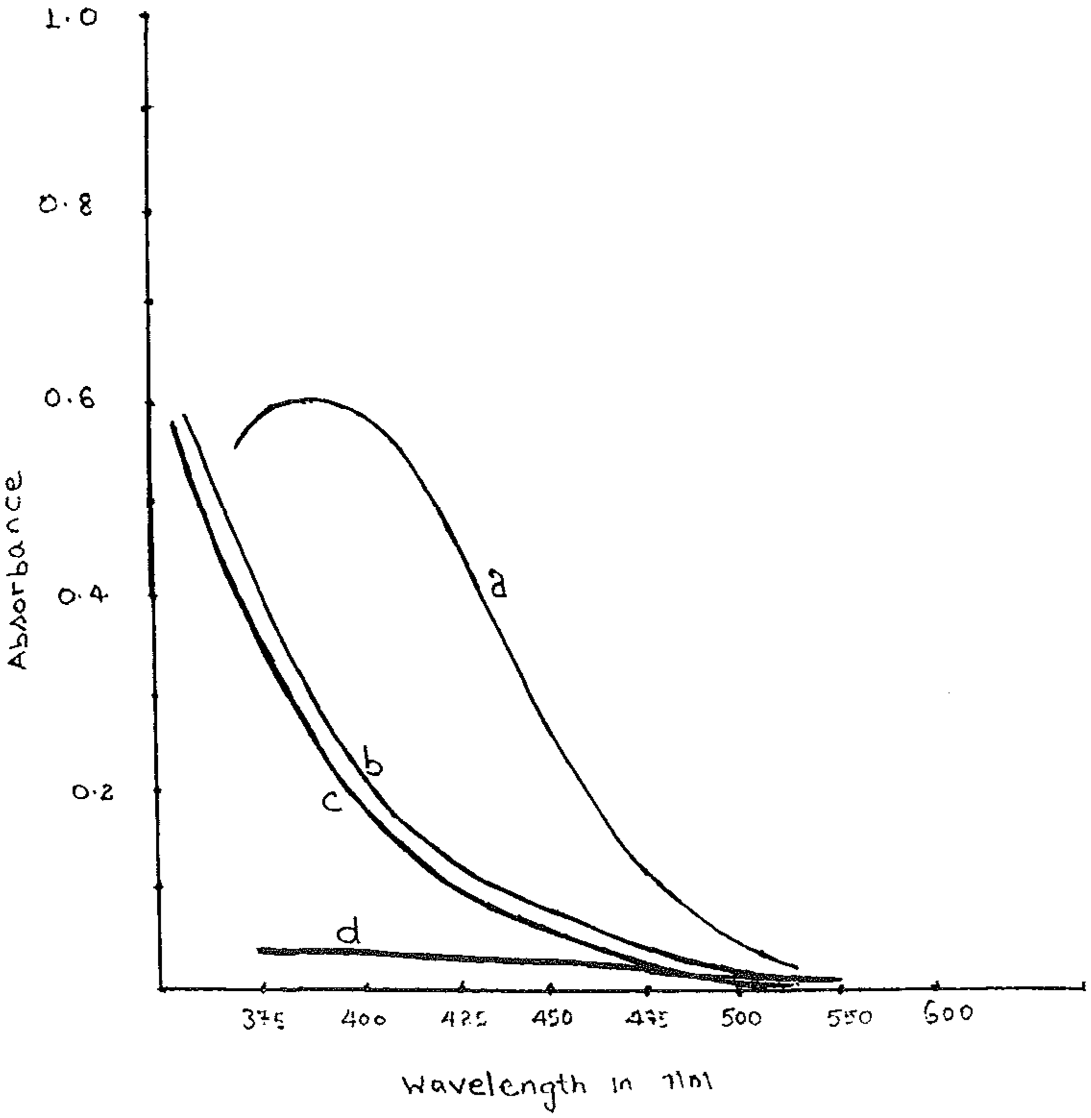


Fig. 1 Absorption Spectra of 3×10^{-5} M
(a) Ti(IV)-SCN-HDPBA, (b) Ti(IV)-HDPBA,
(c) SCN-HDPBA, (d) Ti(IV)-SCN
against the reagent blank.

4.2 Effect of Variables

The effects of different experimental variables on the extraction and determination of the Ti(IV) - SCN - HDPBA ternary complex have been investigated in order to establish the optimum conditions for the extraction and determination of Ti(IV).

Choice of solvent. Different organic solvents were tried for the extraction of the ternary complex , Ti(IV) - SCN - HDPBA, from the aqueous phase. The results are summarized in Table 1.

Table1 *Spectral behavior of Ti(IV) - SCN - HDPBA complex in different organic solvents. Ti(IV) = 36 μg, [HDPBA] = 7.5 x* 10^{-3} *M, [HCl] = 0.1 M,* $[SCN^-]$ *= 0.4 M*

Solvent	λ_{max},nm	$^*\epsilon_{max}$,$M^{-1}cm^{-1}$
Benzene	400	20,000 ± 135
Toluene	400	20,000 ± 160
Xylene	400	20,000 ± 1416
1-Chlorobenzene	400	16,400 ± 750
1,2-dichlorobenzene	400	12,800 ± 1000
Carbontetrachloride	400	22,300 ± 1850
Chloroform	400	1,500 ± 150
Ethylacetate	385	15,500 ± 905
Amylacetate	375	11,300 ± 50

* Extinction coefficient ± average fluctuation for three determinations.

These results show that benzene and toluene gave the most sensitive and reproducible results and therefore toluene was selected for further work for its lesser carcinogenicity than benzene.

Effect of acidity. The dependence of the absorbance (the degree of extraction of Ti(IV) as the Ti(IV) - SCN - HDPBA ternary complex) on the acidity of the aqueous phase was examined by varying the molarity of HCl. The results are given in Table 2. The extraction of Ti(IV) as the ternary complex species was found to be complete in the range 0.05 - 0.15 as is shown by the absorbance values and therefore the middle one (0.1 M HCl) was chosen for subsequent work. When the acidity of the aqueous phase was less than 0.05 M HCl , the decrease in extraction was probably due to formation of anionic or hydroxocomplexes . Similarly when the acidity of the aqueous phase was greater than 0.15 M HCl the extraction of Ti(IV) decreased because the free ligand concentration may not be sufficient due to protonation to give complete complex formation.

Table 2. *Effect of acidity of the aqueous phase on the extraction of Ti(IV) - SCN - HDPBA ternary complex Ti(IV) = 36 μg , [HDPBA] = 7.5 x 10^{-3} M , [SCN^-] = 0.4 M*

[HCl]	A at 400 nm
2.00	0.204
1.00	0.236
0.50	0.396
0.30	0.450
0.25	0.493
0.20	0.568
0.18	0.582
0.15	0.600
0.10	0.600
0.07	0.605
0.05	0.601
0.03	0.568
0.00	0.204

Effect of potassium thiocyanate. The effect of the concentration of thiocyanate has been studied over a wide range at constant and optimum acidity (0.1 HCl). The optimum thiocyanate concentration for quntitative extraction of the Ti(IV) - SCN - HDPBA ternary complex was found to be 0.2 - 1.0 M . At lower thiocyanate concentration , lower absorbance values were 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 3.

Table 3 *Effect of potassium thiocyanate concentration in the aqueous phase on the extraction of Ti(IV) - SCN - HDPBA complex; Ti(IV) = 36 μg, [HDPBA] = 7.5 X 10 $^{-3}$ M , [HCl] = 0.1 M*

[KSCN]	A at 400 nm
2.0	0.467
1.5	0.500
1.0	0.594
0.8	0.591
0.6	0.591
0.5	0.598
0.4	0.600
0.2	0.596
0.1	0.586
0.08	0.575
0.06	0.554
0.05	0.525

Effect of concentration and mode of introduction of the reagent, HDPBA. The effect of concentration and mode of addition of the extractant (HDPBA in toluene) was studied to determine the minimum concentration of HDPBA required and the right mode of its addition for the complete extraction of Ti(IV) - SCN - HDPBA from a fixed volume of the aqueous phase (10 ml) .

The results in Table 4 show that a minimum of 7.5x10^{-3} M HDPBA (a molar ratio of 1:120 [Ti(IV):HDPBA]) was required with (10 + 10 + 5) ml mode of introduction of the reagent for quantitative extraction of the ternary complex. Increasing the HDPBA concentration to 1.0 x 10^{-2} M (a 160 - fold molar excess) was found to have no effect on the extraction of the ternary complex. Higher concentrations of the reagent greater than 1.0 x 10^{-2} M (molar ratio > 160 - fold) were not expermentally possible due to the limited solubility of HDPBA in the solvent (toluene)

Table 4 *Effect of concentration of the reagent (HDPBA) and its mode of introduction on extraction of Ti(IV) - SCN -HDPBA complex*
Ti(IV) = 36 µg, $[SCN^-]$ = 0.4 M, [HCl] = 0.1 M, Vaq = 10 ml

[HDPBA]	Mode of introduction		
	25 ml	(15 + 10) ml	(10+10+5) ml
	Absorbance at 400 nm		
0.0100	0.470	0.565	0.594
0.0075	0.438	0.554	0.600
0.0050	0.464	0.543	0.585
0.0025	0.197	0.322	0.365
0.0010	0.063	0.294	0.315

Effect of ionic strength of the aqueous phase. The molarity of KCl was varied from 0.0 - 2.0 M in the aqueous phase in order to see the dependence of the degree of extraction of the ternary complex on the ionic strength of the aqueous phase. The results obtained (Table 5) indicate that it is independant of the ionic strength of the aqueous phase.

Table 5 *Effect of ionic strength of the aqueous phase on the extraction of the Ti(IV) - SCN -HDPBA complex; Ti(IV) = 36 μg, [HDPBA] = 7.5 x 10^{-3}, [HCl] = 0.1 M, [SCN^-] =0.4 M*

[KCl]	A at 400 nm
0.0	0.601
0.5	0.606
1.0	0.595
1.5	0.594
2.0	0.605

<u>Effect of volume ratio.</u> It was found that complete extraction of the Ti(IV) - SCN - HDPBA ternary complex from the aqueous phase was possible from 1:1 to 2.5:1 ratios of the aqueous phase to the organic phase. At higher volume ratios, the extraction was found to be incomplete (Table 6)

Table 6 *Effect of the volume of the aqueous phase on extraction of the Ti(IV) - SCN- HDPBA complex. Ti(IV) = 36 μg, V_{org} (10+10+5) ml, [HCl] = 0.1 M, [SCN^-] = 0.4 M [HDPBA] = 7.5 x 10^{-3} M*

V_{aq}	*V_{aq}/V_{org}	A at 400 nm
10	1.0	0.603
25	2.5	0.595
30	3.0	0.537
50	5.0	0.494
100	10.0	0.347

* Initial volume ratio

Extraction time and stability of the complex. The Ti(IV) - SCN -HDPBA complex required 2 -3 minutes of shaking time for the quantitative extraction of the complex from the aqueous phase into the organic phase. The stability of the complex was also studied and it was stable up to 2 hours from the time of extraction.

Table 7 *Stability of the complex*

Time (min.)	A at 400 nm
0	0.600
30	0.604
60	0.607
90	0.608
120	0.609
150	0.667

The higher absorbance value beyond 2 hours was due to precipitate formation by the decomposition of the complex.

The optimum conditions for the quantitative extraction and determination of Ti(IV) with HDPBA in the presence of thiocyanate are summarized in Table 8.

Table 8 *Optimum expermental conditions for extraction and determination of Ti(IV) with HDPBA and thiocyanate ion.*

Parameter	Optimum condition
Aqueous phase, [HCl]	0.05 - 0.15 M
Aqueous phase, [SCN$^-$]	0.1 - 1.0 M
Concentration / mode of introduction of the extractant	7.5 x10^{-3}/(10+10+5) ml
Extraction time	2 - 3 minutes
Stability of the complex	2 hours
Solvent for extraction	Toluene

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

4.3 Evaluation of photometric characteristics

Using the optimum conditions of the experimental variables, the agreement with of Beer's law was examined and it has been found that the colored system obeyed Beer's law from 0.29 - 3.6 ppm. The optimum concentration range in which the photometric analysis error is minimal has been evaluated from Ringbom's plot. The results are given in Table 9, and the curves are shown in Figures 2 and 3

Table 9 *Data for calibration curve and the Ringbom's plot*
[HCl] = 0.1 M, [SCN$^-$] = 0.4 M, [HDPBA] = 7.5 x 10^{-3} M

Ti(IV) μg ml^{-1}	[Ti(IV)]x10^{-6}	A at 400 nm	log[Ti(IV)]x10^{-6}	Transmittance (%)
0.14	3	0.073	-5.5	84.53
0.29	6	0.119	-5.2	76.03
0.72	15	0.298	-4.8	50.35
1.44	30	0.600	-4.5	25.12
2.90	60	1.198	-4.2	6.34
3.60	75	1.431	-4.1	3.72
4.30	90	1.694	-4.0	2.02

The Sandell sensitivity of the method, i.e., the concentration that corresponds to an absorbance of 0.001, and the limit of determination, i.e., the minimum concentration that corresponds to an absorbance value three times the standard devation of the blank[50] have also been evaluated. The reproducibility (precision) of the method has also been evaluated from the relative standard deviation of ten measurements each containing 36 μg Ti(IV) (Table 10). The summary of the photometric characterstics are given in Table 11.

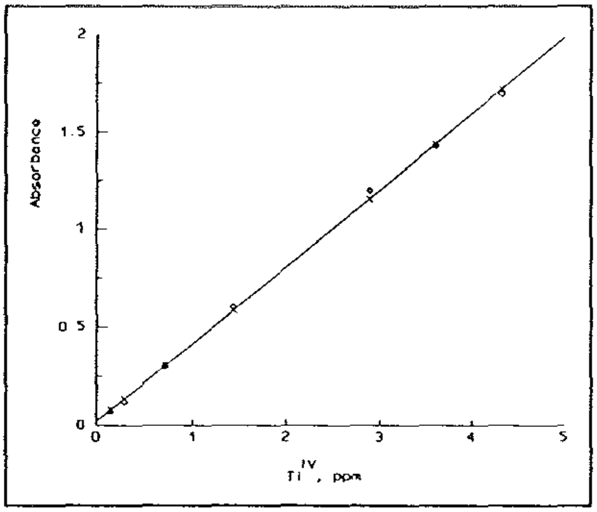


Fig. 2 Calibration curve for the determination of Ti(IV)

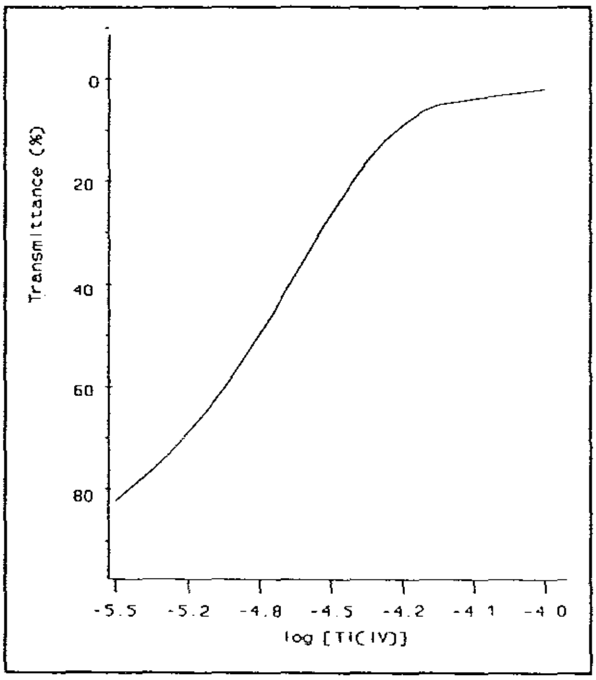


Fig. 3 Ringbom's plot for the evaluation of optimum concentration rangefor the determination of Ti(IV)

Table 10 *Data for evaluating the limit of determination and precision*

Measurements n	Absorbance at 400 nm Blank	 Sample
1	0.107	0.598
2	0.093	0.605
3	0.096	0.602
4	0.092	0.600
5	0.096	0.607
6	0.099	0.605
7	0.100	0.597
8	0.095	0.605
9	0.097	0.599
10	0.096	0.604

$x^{-}_{b} = 0.097$ $x^{-}_{s} = 0.602$

$\sigma_b = 4.3 \times 10^{-3}$ $\sigma_s = 3.2 \times 10^{-3}$

These results show that the proposed method for the extraction and determination of Ti(IV) with HDPBA and thiocyanate is highly sensitive and gives reproducible results.

Table 11 *Photometric characterstics of the complex*

λ_{max}	400 nm
ϵ_{max} , $M^{-1}cm^{-1}$	20,000
Sandell Sensitivity,μgcm^{-2}	$2.4x10^{-3}$
Concentration range from Beer's law, ppm	0.29 - 3.6
Optimum concentration range from Ringbom's plot, ppm	0.29 - 2.9
Limit of determination, ppm	0.029
Relative standard deviation, (n = 10)	0.53 %

4.4 Stoichiometry of the complex.

The Stoichiometry of the complex was determined by the extraction method. The other most frequently used methods (the mole ratio [47], and the continuous variation [46,56]) were found to be unsuitable for the present study due to the necessity of excess molar fold of the reagent (HDPBA) and thiocyanate to initate the complexation equilibria.

Using the extraction method the ratio of Ti(IV) to HDPBA was determined by plotting the quantity log A/A_{max} - A = (log D_{Ti}) 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 2.3, which indicates a 1:2 ratio of Ti(IV) to HDPBA in the ternary complex (Table 12, Fig 4)

Table 12 *Results of the extraction method for the determination of the ratio of Ti(IV) to HDPBA in Ti(IV) - SCN - HDPBA ternary complex.*
[Ti(IV)] = 3 x 10^{-5} M, [HCl] = 0.1 M, [SCN$^-$] = 0.4 M

[HDPBA]x10^{-3}	A at 400 nm	A_{max}-A	log A/A_{max}-A	log[HDPBA]
7.50	*0.600	-	-	-
3.00	0.447	0.153	0.47	-2.52
2.50	0.391	0.209	0.27	-2.60
2.25	0.364	0.236	0.19	-2.65
2.00	0.256	0.344	-0.13	-2.70
1.50	0.190	0.410	-0.33	-2.82
0.75	0.078	0.522	-0.82	-3.12
0.50	0.029	0.571	-1.30	-3.30
0.25	0.005	0.595	-2.10	-3.60

* A_{max}

Similarly the plot of log A/A_{max}- A versus log[SCN$^-$] was made to determine the ratio of Ti(IV) to thiocyanate. The slope of the curve was found to be 1.23 which indicated the Ti(IV) to SCN$^-$ ratio in the ternary complex to be 1:1. The results are given in Table 13 and Fig 5.

Table 13 *Results of extraction method for the determination of the ratio of Ti(IV) to SCN^- in the Ti(IV) - SCN -HDPBA ternary complex [Ti(IV)] = 3×10^{-5} M, [HCl] = 0.1 M, [HDPBA] = 7.5×10^{-3} M*

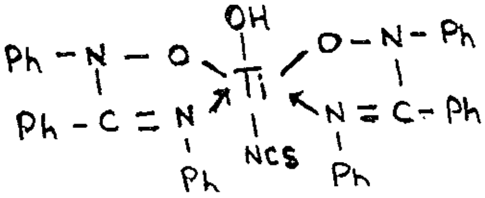
$[SCN^-]$	A at 400 nm	A_{max}-A	log A/A_{max}-A	log$[SCN^-]$
0.40000	*0.600	-	-	-
0.03000	0.473	0.105	0.650	-1.52
0.02000	0.448	0.130	0.540	-1.70
0.01000	0.332	0.246	0.130	-2.00
0.00500	0.187	0.391	-0.320	-2.30
0.00250	0.106	0.472	-0.650	-2.60
0.00125	0.055	0.523	-0.980	-2.90

* A_{max}

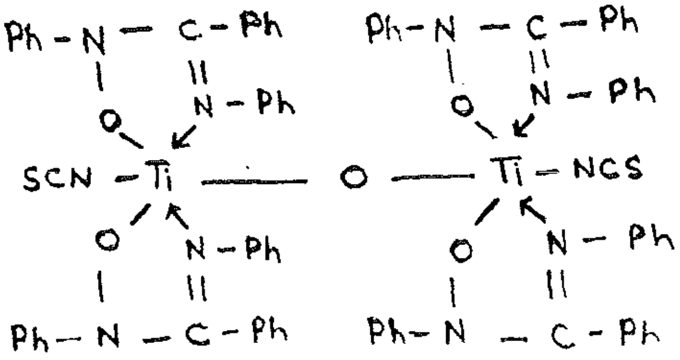
Thus the overall stiochiometry of the Ti(IV) - SCN -HDPBA ternary complex was found to be 1:1:2 (Ti : SCN : HDPBA).

From the extractability of titanium as an electroneutral species and from the results of stoichiometric studies, the following structures are proposed for the ternary complex species.

i)



ii)



From soft-hard acid-base (SHAB) theory the linkage of SCN^- to the metal would be more likely through the nitrogen atom. However, for an accurate structural elucidation further structural investigation is required which is not the objective of this research project.

4.5 Effects of Diverse Ions

To evaluate the selectivity of the proposed method, the effects ofseveral ions on the extraction and determination of titanium (IV) have been studied . The ions that react with Ti(IV) or that undergo complexation with thiocyanate and/or HDPBA as to cause insufficient reagent for the complete complexation to be present in solution affect the determination by reducing the absorbance value (negative interference) ; whereas those ions which react with thiocynate and/or HDPBA and give extractable colored products and whose absorption bands overlap with that of Ti(IV) - SCN - HDPBA ternary complex interferred by increasing the absorbance value (positve interference). As a result these ions have lower tolerance limits.

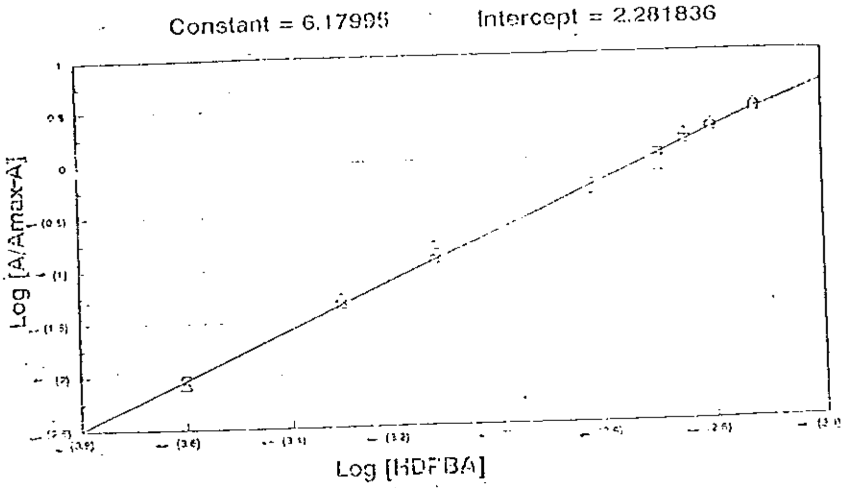


Fig. 4 Curve for the determination of Ti(IV) to HDPBA ratio in Ti(IV)-SCN-HDPBA system by extraction method.

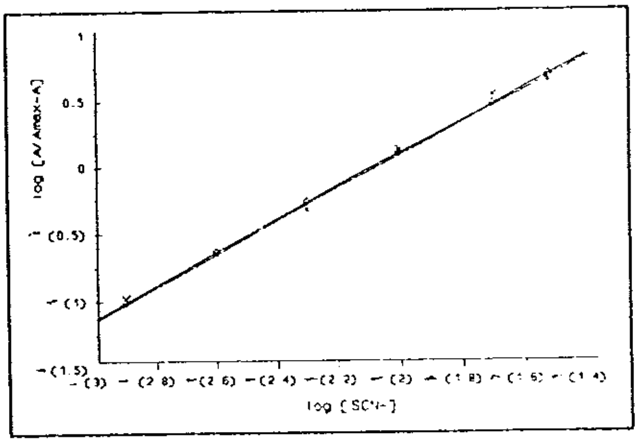


Fig.5 Curve for the determination of Ti(IV) to SCN$^-$ ratio in Ti(IV)-SCN-HDPBA system by extraction method

Table 14 *Tolerance limits of diverse ions in the determination of Ti(IV). Ti(IV) =36 μg, [HDPBA] =7.5 x 10^{-3}M, [HCl]=0.1 M, [SCN^-]= 0.4 M*

Ion	Tolerance limit, mg	Direction of interference
Li^+,Na^+,K^+,Be^{2+},Ca^{2+}		
Ba^{2+},Sr^{2+},Cd^{2+},Pb^{2+}		
Al^{3+},As^{5+},Sb^{5+},Co^{2+}		
Ni^{2+},Mn^{2+},La^{3+},Y^{3+},Tl^+		
Ag^+	20 each	*
Th^{4+}	10	b
UO_2^{2+}	10	a
Hg^{2+}	5	b
Ce^{4+}	5	a
Sn^{2+},Bi^{3+}	2.5 each	b
Zr^{4+}	2.5	a
Cr^{3+}	1.0	a
Pd^{2+}	1.0	b
Pt^{4+},Cu^{2+}	0.125 each	a
Ta^{5+}	0.0625	a
Nb^{5+},W^{6+}	0.0500 each	a
VO_2^{2+}	0.0280	a
Mo^{6+},Fe^{3+}	0.0125 each	a
NO_3^-	30	*
Cl^-	700	*
SO_4^{2-},I^-,$ClO_4\overline{c}$,	20 each	*
Citrate,Tartrate	50 each	b
Borate	20	*
Oxalate	2.5	b
EDTA	10	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 limits of diverse ions taken as an amount (mg) which causes an error less than 2% are given in Table 14. These results show that most of the ions which are normally associated with titanium in ores do not interfere when present at 100 times to the weight of titanium, by the proposed method. However the ions Ta^{V},Mo^{VI},W^{VI},Fe^{III},Nb^{V}, V^{V}, Cu^{II} and Pt^{IV}have lower tolerance limits. The proposed method is also free from interference by some common masking agents and hence the ions W^{VI},Nb^{V} ,Ta^{V} , having lower tolerance limits could be further improved by the use of masking agents. Hence the proposed method could be applied for the analysis of titanium in ores , alloys and industrial samples.

4.6 Applications

The analytical potentiality of the proposed method was testedbyapplying it to the determination of titanium in various samples. Due to the absence of real samples, synthetic matrices corresponding to ores and mineral samples were used.

The results are given in Table 15. These results indicate that the proposed method is precise and reliable for the determination of titanium in ores and minerals containing trace amount of titanium.

Composition of synthentic matrices

Sample I

Ti^{IV}36 μg ; Ta^{V},36 μg ; Nb^{V},36 μg ;Fe^{III},6 μg ; Sn^{2+},500 μg;Cr^{3+}, 500 μg ; Mn^{2+},1000 μg ;Al^{3+}, 1000 μg.

sample II

Ti^{IV},18 μg ; Al^{III},3000 μg ; Zn^{II},250 μg ; Cr^{III},500 μg ; Mg^{II},2000 μg ;Ca^{II}, 2000 μg ; Fe^{III},3 μg ;Co^{II},1000 μg ; Hg^{II}, 1000 μg; Pb^{II},100 μg.

Sample III

Ti^{IV}, 12 μg ; Cu^{II},25 μg ; V^{V} ,6 μg ; Mo^{VI},6 μg ; W^{VI},12 μg ; Ni^{II}, 100 μg ; Mn^{II},100 μg ; Fe^{III},3 μg ; Al^{III},1000 μg ; Na^{I}; 1000 μg .

Sample IV

Ti^{IV},12 μg ; U^{VI},1000 μg ; Th^{IV},2000 μg ,Ce^{IV},1000 μg ; Zr^{IV},1000 μg ; La^{III},3000 μg.

Table 15 *Determination of titanium in synthetic matrices by the proposed method.*

Sample	Titanium added, μg	*Titanium found , μg
I	36	36.16 + 0.17
II	18	17.65 + 0.17
III	12	12.37 + 0.45
IV	12	12.56 + 0.15

* Mean + 95% confidence limit of three determinations

4.7 Comparison with Other Spectrophotometric Methods

A comparison has been made for the determination of titanium by the proposed method and other spectrophotometric methods with respect to the sensitivity and selectivity. Even though some of the reported methods are more sensitive than the propsed method, their selectivities are poorer than the proposed method (Table 16).

Thus the proposed method is fairly sensitive and highly selective and therefore could be applied for the determination of titanium in diverse samples.

Table 16 **Comparison With Other Spectrophotometric Methods**

No.	Reagent	Emax $M^{-1}Cm^{-1}$ and/or Conc. Range, ppm	Interference	Ref.
1.	Nitrilotriacetic acid, 4,5 - dibromophenylfluorone and hexadecyltrimethylammonium bromide	213,000 $M^{-1}Cm^{-1}$	not studied	{15}
2.	Chloropromazine hydrochloride	26,000 $M^{-1}Cm^{-1}$, 0.2 - 2.2 ppm	not studied	{16}

3.	N-pivaloyl -p-chloro - phenyl-hydroxylamine	0.2 - 12 ppm 5,300 $M^{-1}Cm^{-1}$	V^{V+},Mo^{VI+},W^{VI+},Nb^{V}, Fe^{III},Sn^{II} and F^-	{17}
4.	N-phenyldodeCanohydroxamic acid and phenylfluorone	$\leq$ 0.4 ppm 123,000 $M^{-1}Cm^{-1}$	Nb^{V+}, Zr^{IV+}	{18}
5.	Catechol Violet and tridodecyl ethylammonium bromide	51,700 $M^{-1}Cm^{-1}$	———	{19}
6.	Alizarin and fluoride	70,000 $M^{-1}Cm^{-1}$	———	{20}
7.	3-hydroxy-2-methyl-1-p-tolyl-pyridine-4-one	0.5-6 ppm 16,000 $M^{-1}Cm^{-1}$	———	{21}

No.	Reagent	Emax $M^{-1}Cm^{-1}$ and/or Conc. Range, ppm	Interference	Ref.
8.	2,3,7, - trihydroxy- 9-o-chlorophenyl Fluorone	207,000 $M^{-1}Cm^{-1}$	Zr^{IV},Sn^{IV},W^{VI},Mo^{VI},Ge^{IV} and Nb^{V},	{22}
9.	6,7-dihyodroxy- 2,4-diphenyl-1-benzopyrylium chloride and Triton X-100	107,000,$M^{-1}Cm^{-1}$	V^{V},Nb^{V},No^{VI},Zr^{IV+}, and Fe^{III},	{23}
10.	2-(5-chloro-2-pyrdylazo)-5-dimethyl aminophenol and hydrogon peroxide	0 - 0.7 ppm 45,900 $M^{-1}Cm^{-1}$	Fe^{II},Cm^{II},Ni^{I},Co^{II}, W^{VI},Nb^{V}, Ta^{V} and V^{V}	{24}

11.	N-4-methoxyphenyl-2-furylacrylohydroxamic acid	19,200 $M^{-1}Cm^{-1}$	—	{25}
12.	Eriochrome red B and hydrogen peroxide	0.33 - 3.35ppm	—	{26}
13.	5-sulphosalicylic acid	17,300	Tartrate, citrate, oxalate, ascorbate, Fe^{III}, F^-, Nb^V, U^{VI}, Zr^{IV}, Mo^{VI}, W^{VI}, Cu^{II}, Al^{III} and V^V,	{28}
14	Bromopyrogallol red and 1- hexadecyl pyridinium ion	0.2 - 2ppm 25,900 $M^{-1}Cm^{-1}$	Zr, Hf, Ta	{29}

5. CONCLUSION

A new method has developed for the determination of titanium (IV) 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 rigid control of experimental variables. It is believed that the method could be applied to the analysis of diverse samples containing titanium.

6. REFERENCES

1. A.F. Trotman-Dickson "Comprehensive Inorganic Chemistry," Pergamon press, Oxford, 1975.
2. P. Parker,, "Encyclopedia of Science and Technology," 6th ed, vol. 1O, McGraw-Hill, New York, 1987.
3. F.A Cotton and G.Wilkinson, "Basic Inorganic Chemistry, " 5th ed, Wiley, New York, 1989.
4. Van Nostrand, "Scientific Encyclopedia, " 3rd ed., D.Van Nostrand, New York, 1958.
5. A.H. Clifford and G.H Gessner, "The Encyclopedia of Chemistry," 3rd ed., Van Nostrand Reinhold, New York, 1973.
6. J.J. Lingane, "Analytical Chemistry of Selected Metallic Elements, " Reinhold, New York, 1966.
7. V. Alexeyev, "Quantitative Analysis," Mir Publishers, Moscow, 1969.
8. S. Praksh, R. Madan, M. Tuli and Basu, " Advanced Inorganic Chemistry ,"6th ed., S. Chand, New Delhi, 1983.
9. L. Erdey, " Gravimetric Analysis, " part II, Pergamon Press, New York, 1965.
10. A.I. Busev, V.G. Tiptsova, and V.M. Ivanov, "Analytical Chemistry of Rare Elements, " Mir publishers Moscow, 1981
11. J. Bassett, R.C. Denney, C.H. Jeffery, and J. Mendham, "Textbook of Quantitative Inorganic Analysis, " Longman , New York, 1981.

12. K.C Thompson and R.J. Reynholds, " Atomic Absorption, Flourescence and Flame Emission Spectrscopy," 2nd ed. Charles Grriffin, London, 1978

13. J.C van Loon,"Analytical Atomic Absorption Spectroscopy," Academic Press, 1980.

14. C.L. Wilson and D.W Wilson, "Comprehensive Analytical Chemistry," Elsevier, New York, 1962.

15. D. Wang, N. Zheng, F.Luo, Q.Pan, *Fenxi Huaxue, 12(9), 1984; Anal. Abst. 1985, 47, 819.*

16. H.Puzanowska - tarasiewicz, M.Tarasiewicz, W.Misiuk, *Microchem.J., 1984, 29, 341; Anal. Abstr., 1985, 47, 3B75.*

17. *N.Baccon, Fresenius, Z. Anal. Chem., 1983, 8, 796; Anal. Abstr., 1984, 46, 7B81.*

18. H.D. Gunawardhana, *Analyst, 1983, 108, 952-958.*

19. *Y. Shijo, T. Shimizu, and K. Sakai, Bull. Chem. Soc. Jpn. 1952, 55 (10), 3187-3189.*

20. *R. Lopez Nunez, M. Callejon Mochon, A. Guiraum Perez, Talanta 1986,33 (7), 587-591 ., Anal. Abstr., 1987, 498, 10B126.*

21. *B.Tamhina, V.Vojkovic, Microchem. Acta, 1986, 135-145.*

22. *G. Xu., Z. Wang, H. Shen, Fenxi Huaxue, 1987, 15, 1-4.; Anal. Abstr., 1987, 49, 10B119.*

23. *G. Xu, H. Qi, H. Shen, Huaxue Shiji, 1986, 8, 332-334; Anal. Abstr. 1987, 49, 10B120.*

24. H.J. Marini, R.I. Anton, and R.A. Olsina, *Bull. Chem. Sos. Jpn., 1987, 60(7), 2635 - 2640.*

25. S.A. Abassi, *Anal. Lett. 1987, 20(11), 1697-1717; Anal.Abstr., 1988, 50, 5B102.*

26. D.M. Sanchez Ledesma, C.Perez Conde, *Quim. Anal., 1985, 4(2), 135-144.; Anal. Abstr., 1986, 48, 5B104.*

27. A.Yu. Nazarenko, *Zh. Anal. Khim., 1985, 40(5), 828-833.; Anal. Abstr., 1986, 48, 5B103.*

28. M. Kilianova, L. Sommer, *Purkynianae Brun., 1984, 14, 147-159; Anal. abstr., 1986, 48, 5B106.*

29. L.I. Gango and L.V. Kovaleva, *Zh. Anal. Khim, 1982, 37(7), 1209-1211; Anal. Abstr., 1983, 44, 6B112.*

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

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

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

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

34. Gebray Asgodom, M.Sc. Thesis, Addis Ababa University, Addis Ababa, 1988.

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

36. Dejene Ayele and B.S. Chandravanshi, *Anal. Lett., 1990, 23, 1729.*

37. Belhu Berhanu, M.Sc. Thesis, Addis Ababa University, Addis Ababa, 1991.

38. Z. Holzbecher, L. Devis, M. Kral, L.Sucha, and F. Vlacil, "Hand book of organic Reagents in Inorganic Analysis", Ellis Hoodwood Sussex, 1976.

39. H. Freiser, *Anal. chem., 1957, 29, 290.*

40. G.H., Morrison and H. Freiser,"Solvent Extraction in Analytical chemistry, " Wiley, New York, 1957

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

42. C.L. Wilson and D.W. Wilson, "Comprehensive Analytical Chemistry", Vol. IA, Elsevier, Amsterdam, 1959.

43. E.B. Sandell, "Colometric Determination of Traces of Metals",3rd ed. Interscience, New York, 1965.

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

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

46. W.C. Vosburgh and G.R. Cooper, *J. Amer. Chem. Soc., 1941, 63, 437.*

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

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

49. H.A. Strobel, "Chemical Instrumentation",2nd ed. ,Addison Wesley, California,1973.

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

51. K.L. Cheng, "Trace analysis, Physical Methods", Wiley, New York, 1965.

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

53. J.E. Barney, *Talanta, 1067, 14, 1363; Chem. Abstr., 1968, 68, 18294n.*

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

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

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

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

58. F. Feigl and V. Anger "Spot Test in Inorganic Analysis", Elsevier, New York,1972.

59. B.S. Furnise, A.J. Hannaford, V. Rogers, P.W.G. Smith and A.R. Tatchel, "Vogels Text Book of Practical Organic Chemistry", 4th ed., Longman, London, 1978, P.318.

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

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

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

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

64. H. Freiser and Q. Fernando, "Ionic Equlibria in Analytical Chemistry", Wiley, London, 1963.

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

66. A. Muller and E. Demann, "Transition Metal Chemistry", Verlag Chemie, Weinheim, 1981.