STUDIES ON EXTRACTION AND SPBCTROPHOTOMETRIC DETERMINATION OP KIQBIUM(V) USING N-4-CHLOROPHENYLCINNAMOHYDROXAMIC ACID AND THIOCYANATE

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Taddese Wondirau

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TO MY UNCLE AND SISTER

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A B S T R A C T

Studies on Extraction and Spectrophotoraetric Determination of Niobium (V) Using N.4-Chlorophenylcinnamohydroxaraic Acid and Thiocyanate

by

Taddese Wondimu

Research &dvisor -Dr.B.f/\Uhandravsnshi

Niobium(TT)' has been found to react with N.4-chloro.phenylcinnamohydroxamic acid(CPCHA) and thiocyanate to form a golden yellow mixed ligand complex which is quantitatively extractable into chloroform from 5*5-6«5M hydrochloric acid solutions. The complex exhibited a wavelength of maximum absorption at 568 nm with a molar absorptivity of 47500M^{-i}.cm^{-1} and the system obeyed Beer's lav/ in the concentration range of 0«177-2.73 ppm of Nb, The composition of the com.plex has been established spectrophotometrically to be 1:1:2 (Nb:SCN´:CFCHA). The effects of diverse ions and of several other experimental variables have been studied to establish the optimum conditions for extraction and determination of niobium. On the basis of these studies a simple, precise, sensitive, and a highly selective method has been developed for the determination of niobium(V) by solvent extraction and spectrophotometry„ The method has been n

successfully applied to the determination of niobium in several synthetic samples corresponding to niobium containing Ores, minerals, and alloys.

I I T H O D D C T I O N

1„1„ Terminology, Occurrence and Uses of Niobium

The name niobinm (symbol Nb), from Niobe, has been recommended, to be used exclusively, by the Commission on Inorganic Nomenclature and the Atomic Weights Commission, however, the name columbium (symbol Cb), in honour of the country it was found in, is still used, particularly by the American Industries (1). The Metal is frequently referred to as a 'rare element' because it has come to common use relatively recently, (since 1866) (2), and it is of very rare occurrence in the earth's crust, the crustal abundance of the element being only 24 ppm, which is largely in the state of dispersal (3,4)„ However, it is reported that in stars of the S-type, such as R-andromedae, niobium is 'over-abundant'„

The metal does not exist in the free state in nature. It almost always occurs together with the element tantalum. Though estimates vary largely, recent reports show that niobium is approximately ten to twelve times more abundAant than tantalum (5). The most important sources of the element are the columbite-tantalite series of minerals of general formula $(Fe,Mn)(Nb,Ta)_2O_6$, which are found in granite pegmatites and in residual or alluvial deposits derived from such rocks, Pyrochlore, $(Ca,Na,Ce)(Nb,Ta,Ti)_2(O,OH,F)_y$, and euxenite, $(Y,Er,Ce,La,U)(Nb,Ta,Ti)_2(O,OH)_\Lambda$ have gradually

assumed industrial importance as reserves of columbite are insufficient to support large scale production of niobium. Other minerals of very rare occurrence from pegmatites include: microlite, $(Ca,Na)_2(Ta,Nb)_2O_6(O,OH,F)$, dysanalite, $(Ca,Na,Ce)(Ti,Nb,Ta)O_3$, stibiotantalite, $Sb(Ta,Nb)O_4$, fBrsmite $(Ca,Ce,)(Nb,Ti)_2(O,F)_6$, hatchettolite, $(Ca,Fe,U)(Nb,Ta,Ti)_2(O,OH,F)_7$, and samarskite, $(Y,U,Fe,Th)(Nb,Ta)_2O_6$.

There is no indication that the element has any particular biological significance. However, the metal is widely used in industry (1,6,7). It is employed in chromium-nickel type stainless steels in the form of ferroniobium or ferroniobium-tantalum as a stabilizer to prevent carbide precipitation, thereby inhibiting intergranular corrosion and improves strength at high temperature. Numerous high temperature alloys containing niobium are used in components for aircraft jet engines and turbine wheels. It is a potential constituent of nuclear fuels and fuel cladding materials. In welding technology, niobium bearing electrodes are in use. The carbide of niobium is very hard and resistant to wear and is used in dies and cutting tools and as abrassive.

1.2. General Properties and Chemistry of Niobium(1,5,8)

The metal is located in Group VA of the periodic table of the elements, having electronic structure $[Kr]\,4d^4 5s^1$, which is different from its group congeners, vanadium and tantalum. It has a steel-grey colour and a bright metallic lustre. It is sometimes identified as refractory metal, because it has a very high melting point, 2468°C.

It is strongly inert and resistant to acids except hydrofluoric and fuming sulphuric acids, however, it is also attacked by mixtures of fuming nitric and hot concentrated hydrochloric and sulphuric and phosphoric acids. It can also be dissolved in fluoride in acid media, with vigor in a mixture of nitric and hydrofluoric acid, and very slowly in fused alkalis.

The chemistry of niobium strongly resembles to that of tantalum, but less so to vanadium. This similarity arises from their identical atomic (1.47Å) and ionic (0.69Å for the +5 state) radii (consequences of the lanthanide contraction) which are appreciably larger than the corresponding values for vanadium, 1.34Å and 0.59Å, respectively. One consequence of the size difference is that the lower oxidation states of niobium (as well as tantalum) are of relatively minor importance. Thus, apart from the halide chemistry, the vast majority of characterized niobium compounds are pentavalent and although compounds with

formal oxidation states of +4,+3,+2,+1,0 and -1 have been reported, these oxidation states, in particular the first three, are less well characterized.

Though there are strong similarities between the chemistries of niobium and tantalum, there are some differences as well. Thus, it is well established that niobium (V) is more readily reduced than tantalum(V) and is less readily hydrolyzed in aqueous hydrochloric acid solutions.

The metal reacts with oxygen at elevated temperatures and gives white, relatively inert pentoxide, Nb_2O_5. The pentoxide is hardly attacked by acids, except HF, which forms fluoro-complexes. It can be dissolved by fusion with an alkali hydrogen sulphate, pyrosulphate, carbonate or hydroxide.

Niobates are obtained by fusing the oxides in an excess of alkali hydroxide or carbonate and dissolving the melts in water. The solution is stable only at higher pH ; precipitation occurs below pH 7 . The only species that appear to be present in solution are the $[H_xNb_6O_{19}]^{(8-x)-}$ ions, x=0,1 or 2.

The element forms compounds with the elements of Groups IVB,VB and VIB, but relatively little is known. Binary alloys are formed with many metals, exceptions being the alkali metals, alkaline earth metals, cadmium, copper, lead, mercury,silver, yttrium, and the lanthanides.

The pentavalent niobmum forms various complex compounds with halogen, oxygen, selenium, sulphur, nitrogen, etc., donor ligands with coordination numbers 4 to 8. However, structural information is absent for most of them. With the exception of a few insoluble lanthanide niobates, e.g. $ScNbO_4$, which contains discrete tetrahedral NbO_4^{3-} ions, the coordination number of niobium(V) with oxygen is essentilly 6. The niobium(V) pentakisdialkylamides, $Nb(NR_2)_5$, are known to have trigonal bipyramidal geometry. The pentafluoride reacts with fluoride ions forming octahedral, NbF_6^-, complex. It can also form complexes with higher coordination number, and with higher concentrations of fluoride ion the complexes $[NbOF_5]^{2-}$ and $[NbF_7]^{2-}$ are formed. The latter has a structure related to a trigonal prism with one extra atom in a rectangular face. Hydrated oxytris (oxalato) niobates(V) are also known and structural studies have shown that niobium in $(NH_4)_3 - NbO(C_2O_4)_3 \cdot H_2O$ is seven coordinate, the oxygen atoms being arranged as a pentagonal bipyramid. Pentavalent niobium reacts with tropolone to give an eight coordinated complex compound, $[Nb(trop)_4]^+$, which is bicapped trigonal prism (9). It is also known that certain α-hydroxycarboxylic acids (tartaric, citric, lactic, trihydroxy-glutaric) react with niobium(V) to form complex compounds (2,5).

1.3. Reagents Used for the Spectrophotometric Determination of Niobium

A large number of reagents have been reported in the literature for the spectrophotometric determination of niobium in various samples during the last five years. No trial will be made here to provide the complete coverage of the reagents. However, some of the most sensitive and selective reagents that may find wide analytical applications are reviewed below.

A method for the detrmination of Nb(V) (up to 20 ug) after its extraction as ethylene-bis-(tetraphenylphosphonium) thiocyanatoniobate(V) into chloroform has been developed (10). The molar absorptivity is 31,000 $M^{-1}cm^{-1}$ at 393 nm. The complex remains stable for only 8 h .Furthermore, the technique requires prior extraction of Fe(III), Mo(VI), and W(VI) to overcome their interference.

Niobium(V) forms a complex with promazine hydrochloride extractable into trichloroetylene from 3 M hydrochloric acid medium which absorbs strongly at 400 nm (= 25,000 $M^{-1}cm^{-1}$). Beer's law is obeyed for 0.2-3.2ug/ml of Nb(V) and the Sandell sensitivity for the system is 4 ng/cm^2. On the basis of these studies, Nb(V) has been determined in presence of several metal ions(11).

Aznarez et al.(12) have developed a method for the determination of niobium(V) with N-phenylbenzohydroxamic acid and 4-(2-pyridylazo) resorcinol in non-aqueous medium (dimethyl-

formamide-pyridine, 9:1). The absorbance is measured at 547 nm (ϵ =33,500 $M^{-1}cm^{-1}$). The method is claimed to enable the determination of traces of Nb(V) in presence of high concentration of other ions.

A simple, rapid, and selective method for extraction and spectrophotometric determination of micro-amounts of niobium(V) has been described (13). It is based on extraction of Nb(V) in the presence of thiocyanate with a benzene solution of N,N'-diphenylbenzamidine(HA) as a yellow coloured $NbO(SCN)_3 \cdot 2HA$ complex over a wide range of acidity (1.5-4.0 M HCl). The molar absorptivity of the complex is 34,000$M^{-1}cm^{-1}$ at 400 nm and the limit of detection is 0.04 µg Nb/ml. Interference by molybdenum is removed by prior extraction.

Diaz Garcia and Sanz-Medel (14) have studied the analytical potentiality of complexation of Nb(V) with bromopyrogallol red in micellar media and showed that trace amounts of Nb(V) can be determined by formation of a 1:2:2 complex(λ_{max}=645 nm and ϵ_{max} =40,000 $M^{-1}cm^{-1}$) of Nb with bromopyrogallol and hexadecyl pyridinium bromide in 15 % dimethylofrmamide solution in 1 M HCl. The colour reaction of Nb(V) with pyrogallol red is even enhanced when hexadecylpyridinium bromide is present in amounts above its critical micellar concentration (15). The complex, at pH_6, has absorption maxima at 615nm and ϵ =46,700 $M^{-1}cm^{-1}$, and obeys Beer's law up to 2µg/ml of Nb.

A method has been reported (16) for the determination of Nb(V) based on the formation of a 1:2:1 complex between Nb(V), pyrogallol, and 2,3,5-triphenyltetrazolium chloride. The complex is extractable into chloroform or dichloroethane from 1 M H_2SO_4 medium which enables the determination of 0.1 to 8.4 µg/ml Nb when absorbance of the extract is measured at 390 nm. Though, the determination suffers from the interference of Mo(VI) and W(VI), it is claimed that this effect can be corrected.

Niobium in alloy steel and superalloy has been determined spectrophotometrically with 2-(5-bromo-2-pyridylazo) -5-diethylaminophenol in H_3PO_4 medium (17). Citric acid and EDTA are used to mask interference from foreign ions. To obtain a blank, a reference solution is prepared by decolourizing the complex with fluoride ions. The absorbance is measured at 610 nm (ϵ =51,000 $M^{-1}cm^{-1}$) and the system obeys Beer's law up to 0.6 µg/ml. The coefficient of variation is less than 4.6%.

Agrawal and John (18) have reported a sensitive method for the determination of Nb(V) based on the reaction of N-4-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid (PTCHA) with niobium(V) to form a yellow complex extractable into chloroform from 8-10M HCl medium. The complex exhibits absorption maximum at 380 nm (ϵ =63,000 M^{-1} cm^{-1}) and is stable for 24h. The system obyes Beer's law

in the concentration range 0.1-1.25 µg/ml of Nb(V). It is claimed that the interference imposed by Ti(IV) and Zr(IV) is masked with EDTA. However, it is very unlikely to mask the cited interferents with EDTA in such a highly acidic medium.

A method has been reported (19) in which quinquevalent Nb forms an intensely blue complex in presence of bromopyrogallol red, hexadecylpyridinium bromide and emulsifier polyoxyethylene glycol octylphenylether. The complex is stable within the pH range 6.5 to 7.0 and exhibits an absorption maximum at 635 nm (ϵ =141,000$M^{-1}cm^{-1}$). Beer's law is obeyed for upto 22 µg Nb(V) in 50 ml.. EDTA is used to mask the interference of several metal ions.

Niobium(V) has been determined based on the formation of a coloured Nb(V)-salicylfluorone-hexadecyltrimethylammonium complex in 0.1M H_2SO_4(20). The complex exhibits maximum absorption at 525 nm (ϵ =184,000$M^{-1}cm^{-1}$) and Beer's law is obeyed for 8 to 40µg/ml of Nb, when absorbance is measured 20 min after mixing of the reactants. Ta(V) in greater than 5µg interferes when determining 0.1 to 1 µg of Nb.

Multiplication reactions between molybdoniobic heteropolyacid and di-or tri-methylthionine have been used for the determination of niobium (21). The precipitate obtained by the reaction of molybdoniobic acid and di-or trimethylthionine is dissolved in a mixture of acetone-nitric

acid, 9:1. The absorbance of this solution is measured at 660 nm (ϵ = 270,000$M^{-1}cm^{-1}$). Beer's law is obeyed for 3 to 140 ng/ml of Nb. However, Si, Ge, and Ta interfere in the determination.

Aforegoing discussion reveals that, a large number of spectrophotometric reagents have been employed for the quantification of niobium in different samples. However, it is evident that most of the reagents, though good in one aspect they are defficient in another. For example, a highly sensitive reagent may not be available commercially, or its synthesis may not be simple, or it may not at all be selective enough.

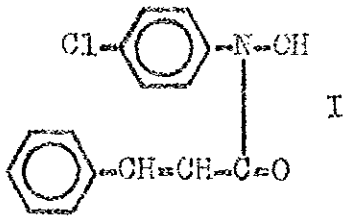
As a matter of fact, search for more sensitive, selective, and cheap reagents, and simple, rapid, and precise methods of determination is still going on.

1.4. Aim and Scope of Present Investigation

N-Arylhydroxamic acids have a number of desirable properties as potential analytical reagents for the determination of metal ions: (i) they contain an acid group with a replaceable hydrogen atom and a basic co-ordinating group in such a position so as to form a five membered ring on reaction with metal ions, (ii) they are available commercially at cheap coast, or even simple to synthesize in simple laboratories, (iii) they are stable towards heat, light, and air. As a result of these properties, these reagents have been used as analytical reagents for several

metal ions (22,27) as well as for the gravimetric (24,25) and spectrophotometric determination of niobium(V) (25,26). When the niobium(V) hydroxamates are complexed with either thiocyanate or a chromogenic reagent, the sensitivity of determination is further improved, coupled with bathochromic shift (27,28) due to mixed ligand complex formation.

One of analytical useful hydroxamic acid analogues is N-4-chlorophenylcinnamohydroxamic acid, I, which is abbreviated as Cl-CHA.



I

This potentially active reagent could be suited to solvent extraction and spectrophotometric determination of metal ions because of two factors:-

(i) the presence of chromophoric cinnamo-group in conjugation to the carbonyl carbon can increase its sensitivity, and (ii) substitution of chloro-group on the Para position of the N-phenyl ring of hydroxamic acid can increase both the sensitivity and the selectivity of the reagent.

Inspite of all these desirable characteristics, the reagent has not been widely applied to spectrophotometric investigation of metal ions since its synthesis for the first time in 1969 (29). CPCHA has been tested for the determination of Vanadium (30) and used for the determination of cerium (31). Except these trials, no attempt has been made to exploit the analytical potentiality of CPCHA in general, and no report appeared in the literature on the use of this reagent for niobium, in particular. Therefore, it is reasonable to study the reaction of CPCHA with niobium(V) and to apply it to the determination of niobium(V) by solvent extraction-spectrophotometry.

Hence, in the present investigation, the reaction of niobium(V) with CPCHA in presence of thiocyanate from concentrated hydrochloric acid medium has been studied. Therefore, the objectives of the present investigation are: (i) to study the complex formation reaction between Nb(V), CPCHA, and SCN^- and spectral properties of the reaction products in the UV-Visible region; (ii) to investigate and establish the optimum experimental conditions for the solvent extraction of the reaction products; (iii) to determine the stoichiometric composition of the reaction products; and (iv) to apply the system to the analysis of diverse samples.

The investigation has led to the development of a new,

simple, precise, sensitive and highly selective method for the determination of niobium(V) with CPCHA and thiocyanate from hydrochloric acid solutions by solvent extraction-spectrophotometry.

2. THEORETICAL BACKGROUND

2.1. Fundamentals of Solvent Extraction (32-39)

Solvent extraction (or liquid-liquid extraction) is a technique in which a solution (usually aqueous) is brought into contact with a second solvent (usually organic), essentially immiscible with the first, inorder to bring about a transfer of one or more solutes into the second solvent. The separations that can be performed are simple, clean, rapid, and convenient.

To understand the fundamental principles of extraction, the various terms used for expressing the effectiveness of a separation must first be considered.

For a solute A distributed between two practically immiscible phases a and b, the Nernst distribution law states that, provided its molecular state is the same in both liquids and that the temperature is constant:

$$\frac{\text{concentration of solute in solvent a}}{\text{concentration of solute in solvent b}} = \frac{[A]_a}{[A]_b} = K_{D,A} \quad (1)$$

where $K_{D,A}$ is known as the distribution constant. In the practical applications of solvent extraction interest lies primarily in the fraction of the total solute in one or other phase, quite regardless of its mode of dissociation, association, or interaction with other dissolved species. It is, therefore, convenient to introduce the term distribution ratio, D:

$$D_A = \frac{(C_A)_a}{(C_A)_b} \quad (2)$$

where the symbol C_A denotes the concentration of A in all its forms as determined analytically.

If attention is confined to the distribution of a solute A between aqueous and an organic solvent, the percentage extraction, E (or the degree of extraction in percent) can be written as:

$$E = \frac{100\,[A]_{org}V_{org}}{[A]_{org}V_{org} + [A]_{aq}V_{aq}} = \frac{1000D_A}{D_A + \frac{V_{aq}}{V_{org}}} \qquad (3)$$

where V_{org} and V_{aq} represent the volumes of the organic and aqueous phases, respectively and the square brackets represent the molar concentrations. Thus, the degree of extraction varies with the volume ratio of the two phases and the distribution ratio.

2.2. Quantitative Treatment of Extraction Equilibria of Metal Ions (32-37)

Ionic compounds would not be expected to extract into organic solvents from aqueous solutions, because of the large loss in electrostatic solvation energy which would occur. The most obvious way to make an aqueous ionic species extractable is to neutralize its charge. This can be done by formation of a neutral metal chelate complex or ion association; the larger and more hydrophobic the resulting molecular species, the better will be its extraction.

Organic reagents play an eminent role in extraction and separations of metal ions, because they can react with metal ions to give products favouring solvent extraction; i.e., electroneutral chelate complexes or ion-association complexes. Here, attempt will be made to derive quantitative relationships for chelate extraction systems from a consideration of the combined equilibria involved. The main equilibria included in the extraction of a metal ion with a weakly acidic chelating agent from an aqueous solution into an organic solvent are:

(i) distribution of the chelating anent, HL, between the two phases.

$$HL_{aq} \rightleftharpoons HL_{org} \; ; \; K_{D,L} = \frac{[HL]_{org}}{[HL]_{aq}} \qquad (4)$$

(ii) dissociation of the chelating agent in the aqueous phases,

$$HL \rightleftharpoons H^+ + L^- ; \; \beta_{HL}^{-1} = \frac{[H^+][L^-]}{[HL]} \qquad (5)$$

(iii) reaction of L^- and the metal ion M^{n+} in the aqueous phase (formation of the extractable chelate, ML_n),

$$M^{n+} + nL^- \rightleftharpoons ML_n \; ; \; \beta_n = \frac{[ML_n]}{[M^{n+}][L^-]^n} \qquad (6)$$

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

$$ML_{n,aq} \rightleftharpoons ML_{n,org}; \; K_{D,M} = \frac{[ML_n]_{org}}{[ML_n]_{aq}} \qquad (7)$$

Assuming that the metal chelate, ML_n, is the only metal-containing species in the organic phase and the metal ion, M^{n+}, is essentially the only metal containing species in the aqueous phase, the following equation can be obtained, from the combination of equations 4 to 7, for the distribution ratio, D_M,

$$D_M = \frac{[ML_n]_{org}}{[M^{n+}]_{aq}} = \frac{K_{D,M}\,\beta_n}{(K_{D,L}\,\beta_{HL})^n} \left(\frac{[HL]_{org}}{[H^+]_{aq}}\right)^n \qquad (8)$$

By introducing the extraction constant, K_{ex}, equation 8 can be reduced to,

$$D_M = K_{ex} \frac{[HL]_{org}}{[H^+]_{aq}}$$

By taking the logarithm, equation 9 can be written as

$$\log D_M = \log K_{ex} + n\log[HL]_{org} + npH \qquad (10)$$

Thus, the distribution ratio, D_M, of the metal depends on the pH of the solution and the concentration of the extracting reagent in the organic phase.

The distribution ratio, 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 10.

A change in the temperature changes the value of the equilibrium constant, but it is not possible to predict how it affects the value of K_{ex}.

A change in the ionic strength affects the value of the relative permitivity and so the value of K_{ex}, which in turn 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.

Kinetic masking can be utilized if the rate of extraction of one species is much faster than that of another. Otherwise, there is no kinetic effect involved in the value of D_M, provided that D_M has been determined for an equilibrium state.

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.

An additional advantage of solvent extraction is that the solution of the separated species in a given

organic solvent usually has some properties, e.g. change in colour, volatility, luminescence, etc., on which the determination of the isolated constituent can be based on. Thus, the extract can be utilized directly for the determination of isolated component by spectrophotomentry, fluorimetry, gas chromatography, atomic absorption, radiochemical, or other suitable methods.

The fundamental principles governing one of these techniques, i.e., spectrophotometry, which has been used in the present investigation, are briefly described below.

2.3. Spectrophotometry (32,33,36,40-43)

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

When a monochromatic beam of light passes through a homogeneous absorbing medium of length, l, the radiant power will diminish in proportion to the amount or concentration, C, of the absorbing substance in the light path. Beer's law is the quantitative statement of this phenomenon, which can be written mathematically as,

$$A = \epsilon Cl \qquad (11)$$

Where A is the absorbance and ϵ is the proportionality constant known as molar absorptivity or molar absorption coefficient, which is measure of the extent of interaction between the molecule of a substance and radiation.

When the values of and l are known, the concentration of the unknown solution can be evaluated using equation 11.

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.

2.3.1. Spectrophotometric Determination of Metal Ions (32,33,36,40,41,44)

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. Coloured metal complexes, with the reagent, are formed only when the organic reagent has II-electron chromophoric groups in the molecule; the cyclo group should also form a part of the II-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. Colourless species can also be investigated,

since the usable range of spectrophotometric determinations extends to the UV region.

2.3.2. Characteristic Terms in Photometric Analysis (32,42,45)

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 the instrument used and on the chemical reaction chosen.

Deviations 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 coefficients) 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 the change of the 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 minimum, was introduced by Ringbom (46). 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 minimum is obtained by constructing tangents to the steepest portion of the curve.

Sensitivity and the 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 (47), where C is the concentration of the substance to be determined, and A the absorbance of the solution. The initial linear portion of the calibration curve can be expressed as:

$$C = (A-A_o)\ (\frac{dA}{dC})^{-1} \qquad (12)$$

where A_o 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 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 (e.g. µg) or as the lowest molar concentration, M, or in any other convenient way, e.g. as µg/ml, percentage, ppm, which shows a statistically significant difference from zero or the average value of the blank.

Of the several methods of evaluating the limit of determination, two of the most commonly used methods are described below. According to Kaiser (48) C_{min} is evaluated as:

$$C_{min} = (A_{min} - A_o)\left(\frac{dA}{dC}\right)^{-1} = 3S_o\left(\frac{dA}{dC}\right)^{-1} = \frac{3S_o}{\epsilon \cdot 1} \qquad (13)$$

where S_o is the standard deviation for the blank determination. Sandell(40) defines the limit of determination (or "Sensitivity" according to him) as the weight in ug per ml 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 dimensions are $\mu g.cm^{-2}$. In accordance to this definition, the limit of determination, C_s, is given by

$$C_s = \frac{M}{\epsilon} \left(\mu g/ml\right) \qquad (14)$$

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

2.3.3. Spectrophotometric Methods for Determination of Compostion of Metal Complexes (36, 43, 49)

Several methods are available for the spectrophotometric determination of the stoichiometry of metal complexes. However, the most commonly used techniques include: the method of continuous variations (50,51), the mole ratio (52), and the extraction (36) methods.

Method of continuous variations. The principle of this method is that the mole fraction of ligand, $X_L = C_L/(C_M + C_L)$, and that of the metal, $X_M = C_M/(C_M + C_L)$, 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:

$$m\,M + nL \rightleftharpoons M_mL_n \qquad (15)$$

if the absorbance is measured at a 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:

$$\frac{n}{m} = \frac{X_{L(max)}}{1-X_{L(max)}} \cdot \frac{1-x_{M(max)}}{x_{M(max)}} \qquad (16)$$

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

$$M^{n+}_{aq} + nHL_{org} \rightleftharpoons ML_{n,org} + nH^{+}_{aq} \qquad (17)$$

$$ML_{n,org} + mX_{aq} \rightleftharpoons ML_nX_{m,org} \qquad (18)$$

The extraction constant, K_{ex}, for the complex ML_nX_m is given by

$$K_{ex} = \frac{[ML_nX_m]_{org}}{[ML_n]_{org}[X]^m_{aq}} \qquad (19)$$

Rearrangement of equation 19 yields

$$\frac{[ML_nX_m]_{org}}{[ML_n]_{org}} = K_{ex}[X]^m_{aq} \qquad (20)$$

since

$$[ML_n]_{org} = C_M - [ML_nX_m]_{org}$$

equation 20 can be written as

$$\frac{[ML_nX_m]_{org}}{C_m - ML_nX_{m\ org}} = K_{ex}[X]^m_{aq} \qquad (21)$$

Where C_M is the total concentration of metal ion. If only one stable complex, ML_nX_m, is formed, which has selective light absorption at the selected wavelength, then it follows from Beer's law (equation 1) that

$$[ML_nX_m] = A/\epsilon \text{ and } C_M = A_{max}/\epsilon$$

(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 (21),

$$\frac{A/\epsilon}{A_{max}/\epsilon - A/\epsilon} = \frac{A}{A_{max} - A} = K_{ex}[X]^m_{aq} \qquad (22)$$

Equation (22) can be expressed in logarithmic form as

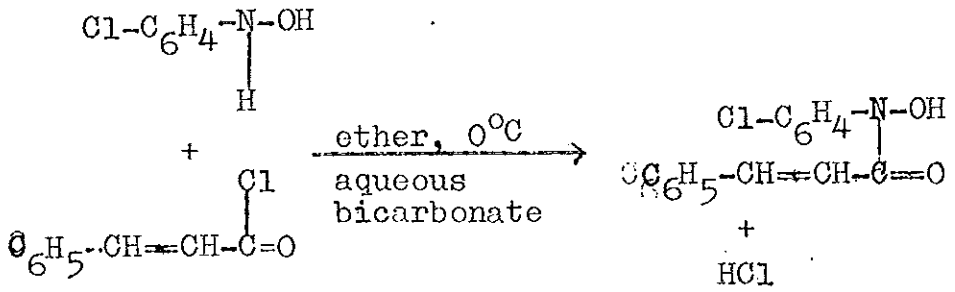
$$\log\left(\frac{A}{A_{max} - A}\right) = \log K_{ex} + m\log[X]_{aq} \qquad (23)$$

Thus, the slope of the plot $\log\left(\frac{A}{A_{max} - A}\right)$ against $\log[X]$ gives the number of the auxiliary ligand, X, in the mixed ligand complex, ML_nX_m.

3. EXPERIMENTAL

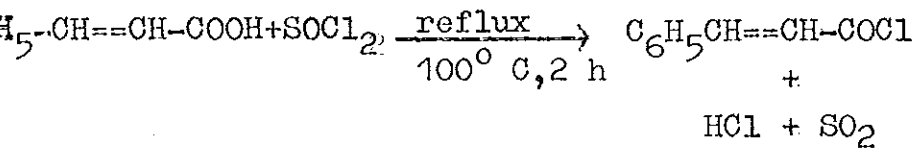
3.1. Synthesis of N-4-Chlorophenylcinnamohydroxamic Acid (CPCHA)

CPCHA was prepared by the condensation of N-4-chlorophenylhydroxylamine with cinnamoyl chloride at 0°C in diethylether made alkaline with an aqueous suspension of sodium bicarbonate (29).



Thus the preparation of N-4-chlorophenylcinnamohydroxamic acid required the synthesis of cinnamoyl chloride and N-4-chlorophenylhydroxylamine.

Preparation of cinnamoyl chloride. It was prepared by chlorination of cinnamic acid with thionyl chloride (53).



A 40 % excess of thionyl chloride (10 ml, 0.14 mol) was mixed with cinnamic acid (14.8g, 0.1 mol) in a 150 ml round bottom flask and refluxed over an oil bath at 100°C for 2 h. The excess thionyl chloride was driven off by heating the reaction mixture over hot oil bath at 100° C for an additional 2 h. On cooling a golden orange pasty solid of the

acid chloride was obtained. It was used as such for the synthesis of CPCHA.

Preparation of N-4-chlorophenylhydroxylamine. N-4-Chlorophenylhydroxylamine was prepared by the reduction of 4-chloronitrobenzene with zinc dust in aqueous alcoholic medium buffered with ammonium chloride(54),

$$Cl\text{-}C_6H_4\text{-}NO_2 \xrightarrow[60\ \%\ \text{ethanol}]{Zn/NH_4Cl,\ 60\text{-}65^{\circ}\ C} Cl\text{-}C_6H_4\text{-}NHOH$$

4-Chloronitrobenzene (25 g, 0.16 mol) was dissolved in 60 ml of hot alcohol in a 250 ml conical flask. Water was added dropwise until precipitation begun. The precipitated compound was dissolved by shaking, heating and if necessary, by the addition of few ml of alcohol. Ammonium chloride (4 g, 0.075 mol) was added, the mixture was vigorously shaken for a while, and temperature was kept at 60- 65° C. Purified (55) zinc dust (32 g, 0.48 mol) was added at the rate of about 1 g/min, so that the temperature of the reaction medium did not rise beyond 60-65° C due to the exothermicity of the reaction. After the completion of the reaction, which was indicated by the fact that the temperature commenced to fall, zinc oxide and unreacted zinc dust were filtered off by suction. The residue was washed with 30 ml of 60 % (v/v) hot alcohol. The filtrate was diluted to 150 ml with cold distilled water and placed in an ice bath for 1 h to ensure maximum crystallization.

The yellow crystals of N-4-chlorophenylhydroxylamine were filtered through a buchner funnel under suction. The product was recrystalized from a mixture of petroleum ether (60 - 80° C) and benzene (2:1). The substance deteriorates upon storage and was therefore used immediately for the synthesis of CPCHA.

Preparation of N-4-chlorophenylcinnamohydroxamic acid. A freshly crystallized N-4-chlorophenylhydroxylamine (13.0 g, 0.091 mol) was dissolved in 100 ml of diethyl ether and transferred to a 500 ml conical flask. A fine suspension of sodium bicarbonate (12.6 g, 0.15 mol) in 20 ml of water was added to it. The flask was kept in a freezing mixture and the contents were stirred with a magnetic stirrer. To this a solution of cinnamoyl chloride (15.08 g, 0.091 mol) in 100 ml of diethyl ether was added dropwise during the course of 1 h. Stirring was continued for an additional 15 min. The yellowish white precipitate of hydroxamic acid was transferred to a mortar containing cold saturated solution of sodium bicarbonate. The mixture was triturated with a pestle to remove acidic impurities, which was signaled by disappearance of CO_2 bubbles. The product was filtered under suction, washed with cold water to remove sodium bicarbonate and dried in air. The crude product was recrystallized from ethanol. The yield was 20 g, (71 %), m.p. 193° C, reported (31) 188° C; UV: $\lambda_{max(ethanol)}$ = 297 nm, ϵ_{max} 2.44×10^4 M^{-1} cm^{-1},

reported (56) for N-phenylcinnamohydroxamic acid, λ_{max} (ethanol) = 292 nm, ϵ_{max} = $2.26 \times 10^4 M^{-1}$ cm^{-1}.

3.2. Equipment and Reagents

Equipment. A Beckman Model 24 UV-Visible spectrophotometer equipped with a Beckman recorder and 1-cm matched quartz cells was used for recording the absorption spectra and absorbance measurements.

Standard niobium(V) solution. A stock solution of niobium(V) was prepared by fusing 0.1439 g of niobium pentoxide (Johnson & Mathy, 99 %) with 3.6312 g of potassium pyrosulphate (Riedel-de Hean) in silica crucible (57). The cooled melt was dissolved in 100 ml of 20 % (W/v) tartaric acid (BDH, Analar) solution by heating over sand bath. The solution was cooled, transferred to a 1 litre volumetric flask, and diluted to volume with water. The solution was standardized spectrophotometrically (28).

Standard thiocyanate solution. 5 M standard solutions of ammonium thiocyanate (Hopkin & Williams) and potassium thiocyanate (Riedel-de Haen) were prepared by dissolving the appropriate amounts of the salts in distilled water, respectively. The solutions were standardized by the Volhard method (58).

Stannous chloride solution. A 40 % (W/v) stannous chloride solution was prepared by dissolving 40 g of $SnCl_2 \cdot 2H_2O$ (BDH, Analar) in 75 ml of concentrated hydrochloric acid by heating. After cooling, the solution was made to 100 ml

with concentrated hydrochloric acid. Fresh solutions of stannous chloride were used every week.

Magnesium chloride. Solid $MgCl_2 \cdot 6H_2O$ (BDH, Analar) was used to adjust the concentration of chloride ions in the aqueous phase.

Hydrochloric acid. Concentrated hydrochloric acid (37 % $^w/_w$) (Riedel-de Haen) was used to adjust the acidity of the solutions.

Solutions of diverse ions. Solution of Ta(V), 1 mg ml^{-1}, was prepared by fusing 0.1221 g Ta_2O_5 (Johnson & Mathey) with 5 g $K_2S_2O_7$, leaching the cool melt with 20 ml of 10 % ($^w/_v$) tartaric acid and diluting the solution to 100 ml with 15 N H_2SO_4.

Solution of Ti(IV), 2.4 mg ml^{-1}, was prepared by fusing 0.4 g TiO_2 (BDH) with 4 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.

Rhenium(VII) solution was prepared by dissolving the metal (SPEX) in cold concentrated nitric acid. The solution was evaporated almost to dryness and the residue was dissolved in distilled water to yield 1 mg/ml Re(VII).

Solution of Ga(III), 2.5 mg ml^{-1}, Zr(IV), 10 mg ml^{-1}, and Pd(II), 1 mg ml^{-1}, were prepared by dissolving Ga metal (BDH), $ZrCl_4$ (BDH), and $PdCl_2$ (SPEX) in cold conc. HCl, respectively; while solution of Er(III), 2.5 mg ml^{-1}, was

prepared by dissolving Er_2O_3 (May & Baker) in hot conc. HCl.

Solutions of Hg(II), 5 mg ml^{-1}, Cu(II), 5 mg ml^{-1} and Mn(II), 10 mg ml^{-1}, were prepared by dissolving the respective chloride salts (Riedel-de Haen or BDH) in distilled water. Solution of Pt(IV), 1 mg/ml, was prepared by diluting 5 % ($^{w}/_{w}$) solution of $PtCl_4$ (SPEX) with 3 M HCl.

Solutions of Ca(II), Ba(II), Cd(II), Mg(II), Zn(II), Pb(II), Ni(II), Co(II), Sr(II), Y(III), UO_2(II), La(III), Fe(III), Al(III), Bi(III), Cr(III), Th(IV), Be(II), Tl(I), Ag(I), Li(I), Na(I), Ce(IV) and Rh(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, Vanadate, molybdate, acetate, borate, citrate, antimonytartrate, arsenate, nitrate, sulphate, fluoride, EDTA, and dichromate solutions were prepared by dissolving sodium,potassium or ammonium salts (BDH or Riedel-de Haen) in distilled water to give 1, 5, 10 or 20 mg ml^{-1} of the ion in solution.

Solutions of tartaric acid (BDH), 100 mg/ml, oxalic acid (Riedel-de Haen), 10 mg/ml, ascorbic acid (BDH), 100 mg/ml, boric acid (May & Baker) 20 mg/ml and Thiourea ((Hopkin and Williams), 50 mg/ml, were prepared by dissolving the solid compounds in distilled water.

Phosphoric acid, 85 % ($^{W}/_{w}$) (BDH), and fluoroboric acid, 42 % ($^{W}/_{w}$) (Hopkin & Williams) were used as received.

Sample Solutions. Stock solutions of synthetic samples of desired composition were prepared by mixing known quantities of the solution of different ions. The solutions were diluted to known volumes (50 ml each) with sufficient quantities of 20 % ($^{W}/_{w}$) tartaric acid and concentrated hydrochloric acid to give the final solutions that were 2 % ($^{W}/_{w}$) with respect to tartaric acid and 1 M with respect to hydrochloric acid.

Solvents. Chloroform was purified (59) every two days and distilled twice before use. All other solvents were used after a single distillation.

Reagent (CPCHA) solution. A 0.005 M stock solution of CPCHA was prepared by dissolving a weighed amount of CPCHA in chloroform by gentle heating and diluting to volume with chloroform.

A 0.005 M solution of CPCHA in ethanol (Riedel-de Haen) was used for studying the effects of other solvents.

Drying agents. Anhydrous sodium sulphate (BDH) and anhydrous calcium chloride (Riedel-de Haen) where used for drying the coloured extracts and chloroform, respectively.

3.3. Procedures

3.3.1. Standardization of Nb(V) Solution A 0.5 ml aliquot of the stock niobium(V) solution was transferred to a 100 ml separatory funnel. To this were added 20 ml of concentrated hydrochloric acid and 1 ml of 40 % ($^{w}/_{v}$) stannous chloride solution and the contents were mixed thoroughly. The solution was mixed thoroughly after addition of 1 ml of 1 % ($^{w}/v$) N-benzoyl-N-phenylhydroxylamine (BPHA) in ethanol and allowed to stand for 1 min. The Nb-BPHA complex was extracted into 10 ml of toluene by shaking for 1 min. After the phases were separated completely, the aqueous phase was drained off and discarded. To the Nb-BPHA extract, 20 ml of 4 M HCl and 5 ml of 3.28 M ammonium thiocyanate were added and the mixture was shaken vigorously for 1 min. The toluene layer was transferred into a 25 ml volumetric flask after drying over anhydrous sodium sulphate. The separatory funnel and the sodium sulphate crystals were washed with fresh portions of toluene and the washings were transferred into the volumetric flask. The coloured extract was diluted to volume with toluence and absorbance of the solution was measured against reagent blank at 365 nm (ε= 32000 $M^{-1}cm^{-1}$) in a 1-cm cell. The concentration of the niobium(V) solution was calculated from Beer's law and found to be 1.05×10^{-3} M.

3.3.2. Standardization of Thiocyanate Solution

A 25 ml aliquot of the standard 0.1 M silver nitrate solution was transferred into a 250 ml conical flask and

5 ml of 6 M nitric acid and 1 ml of 40 % ($^{W}/v$) ferric ammonium sulphate (BDH) were added to it. The solution was titrated with ammonium thiocyanate solution until a faint brownish red colour was produced which no longer disappeared on shaking.

3.3.3. Purification of Chloroform

A litre of chloroform was treated with 200 ml of concentrated sulphuric acid (BDH) and kept over night. A 500 ml portion of the treated chloroform was transferred into a 1 litre separatory funnel and washed four times with equal volume of distilled water. The chloroform was further washed twice with 200 ml of 1 % ($^{W}/v$) sodium hydroxide (BDH) solution and twice with 400 ml portions of distilled water (until clear chloroform layer was observed). The washed chloroform was dried over fused anhydrous calcium chloride and distilled twice discrding the low boiling and the high boiling fractions. The purified chloroform was stored in a coloured bottle and used within two days.

3.3.4. Extraction and Determination of Niobium(V)

An aliquot of the solution containing 2 to 60 µg of Nb(V) was transferred into a 100 ml separatory funnel. Solutions of conc. HCl, 40 % ($^{W}/v$) $SnCl_2$, and 5 M KSCN or NH_4SCN (5, 1 and 1.2 ml, respectively) were added and the volume of the aqueous phase was made 12 ml with distilled water. The aqueous phase was extracted with 10 ml of

5×10^{-4} M chloroform solution of CPCHA for 4-5 min. The funnel was allowed to stand to separate the two phases. The chloroform layer was collected in a 50 ml beaker containing about 2 g of anhydrous sodium sulphate and stirred with a glass rod. The aqueous layer was washed twice with 5 ml portions of chloroform. The extracts were dried and transferred into a 25 ml volumetric flask and diluted to volume with chloroform. The absorbance of the coloured solution was measured at 368 nm against the reagent blank.

For calibration 0.2, 0.4, 0.6, 0.8 and 1.0 ml samples of the standard solution containing 50 µg Nb(V) ml^{-1} were used.

3.3.5. Selection of Solvents by Two Step Extraction

An aliquot of the solution containing 24.4 µg of Nb(V) was transferred into a 100 ml separatory funnel. Solutions of conc. HCl and 40 % ($^{w}/_{v}$) $SnCl_2$ (5 and 1 ml, respectivery) were added and the aqueous phase was diluted to 11 ml with distilled water. A 10 ml aliquot of a particular solvent and 1 ml of 0.005 M CPCHA in ethanol were added to the funnel and the mixture was shaken vigorously for 4-5 min. The funnel was allowed to stand to separate the two phases. The aqueous phase was discarded while keeping the organic phase in the funnel. Solutions of 12 M HCl and 5 M ammonium thiocyanate and water (5,12, and 5.8 ml, respectively) were added to the funnel and

the mixture was shaken vigorously for 4-5 min. The funnel was allowed to stand to separate the two phases and then proceeded as in section 3.3.4.

3.3.6. Examination of Experimental Variables

The effect of a particular variable was studied by measuring the absorbance of the system following the general procedure described in section 3.3.4 for the extraction and determination of Nb(V), keeping all the experimental variables constant except the one under investigation.

The effect of chloride ion concentration (added as $MgCl_2$) in the aqueous phase at constant concentration of HCl and vice versa were also studied by following the procedure described in section 3.3.4.

The quantitative extraction of Nb(V) from the aqueous phase was examined by changing each variable to its optimum condition and following the general procedure. The extraction was considered incomplete when Nb(V) was detected in the aqueous phase.

The aqueous phase left after extraction was transferred into a 100 ml separatory funnel and sufficient quantities of 40 % ($^{w}/v$) $SnCl_2$, 5 M KSCN, and distilled water were added to it so that the final solution was at the optimum condition with respect to each parameter (5 M HCl, 0.5 M KSCN, 0.15 M $SnCl_2$, aqueous volume of 24 ml). The extraction and determination of Nb(V) was made according to the

procedure discribed in section 3.3.4.

3.3.7. Investigation of the Influence of Diverse Ions

The effects of diverse ions were studied by adding known quantities of the desired ion to a solution containing 20 µg of Nb(V). The extraction and determination of the metal ions were made according to the general procedure described earlier in section 3.3.4.

3.3.8. Determination of the Stoichiometry of the Complex

Continuous variations method. To determine the ratio of niobium(V) to CPCHA a series of solutions was prepared in which the mole fractions of Nb(V) and CPCHA were varied between 0 and 1 with constant total concentration (C_t = 2.1×10^{-4} M). The concentrations of HCl, KSCN, and $SnCl_2$ (5 M, 0.5 M, and 0.15 M, respectively) and the volumes of the aqueous and organic phases (10 ml each) were also kept constant throughout the series. The complex was extracted by the procedure described in section 3.3.4. The absorbance of the coloured extract was measured at 368 nm against the reagent blank and plotted against the mole fraction of the metal.

Mole ratio method. To determine the ratio of Nb(V) to CPCHA a series of solutions was prepared in which the concentrations of Nb(V) (2.1×10^{-5} M), HCl (5 M), KSCN (0.5 M) and $SnCl_2$ (0.15 M) were kept constant and the concentration of CPCHA was varied over a wide range (1:1 to 1:100,Nb(V): CPCHA). The volumes of the aqueous

phase and the organic phase (10 ml each) were also kept constant. The complex was extracted and the absorbance was measured by the procedure described in section 3.3.4. The absorbance was plotted versus the mole ratio of Nb(V) to CPCHA. Two straight lines were drawn from the two parts of the curve which intersected each other at the ratio of Nb(V) to CPCHA in the complex.

Extraction method. To determine the niobium(V) to thiocyanate ratio, a series of solutions was prepared in which the concentrations of Nb(V), CPCHA, $SnCl_2$, and HCl were kept constant at 2.1×10^{-5} M, 5×10^{-4} M, 0.15 M and 5 M respectively and the concentration of thiocyanate was varied over a wide range (up to 0.5 M). The volumes of aqueous and organic phases (10 ml each) were also kept constant. The complex was extracted by the general procedure described in section 3.3.4 and absorbance was measured against the Nb(V)-CPCHA complex as blank (because Nb(V)-CPCHA complex absorbs strongly at 368 nm, the reagent blank was replaced by it). The quantity $\log \frac{A}{A_{max}-A}$ was plotted against $\log [SCN^-]$.

4. RESULTS AND DISCUSSION

4.1. Colour Reaction and Absorption Spectra

The absorption spectrum of the CPCHA in chloroform exhibited practically no absorption between 700 and 400 nm and strong absorption below 400 nm. The absorption spectrum of the CPCHA in ethanol has also been recorded in the UV region. The spectrum showed an intense absorption band at 297 nm with molar absorptivity of 2.44×10^4 M^{-1} cm^{-1} (Fig. 1) which is due to $\pi \rightarrow \pi^*$ electronic transition. Therefore every measurement has been made against reagent blank.

Niobium(V) was found to react with CPCHA to give a pale yellow complex extractable into chloroform. The absorption spectrum of the Nb(V)-CPCHA complex exhibited an intense absorption band at 353 nm with molar extinction coefficient of 3.67×10^4 M^{-1} cm^{-1} (Fig. 2).

When Nb(V) was extracted with the chloroform solution of CPCHA from thiocyanate solution in presence of stannous chloride, a golden yellow complex was obtained indicating the formation of a mixed ligand complex. The absorption spectrum of the Nb(V)-SCN-CPCHA complex exhibited an intense absorption band at 368 nm with molar absorption coefficient of 4.75×10^4 M^{-1} cm^{-1} (Fig. 2). Thus, the formation of mixed ligand complex is accompanied by red shift with increase in intensity. This colour reaction formed the basis for the development of a new spectrophotometric method for the determination of niobium(V).

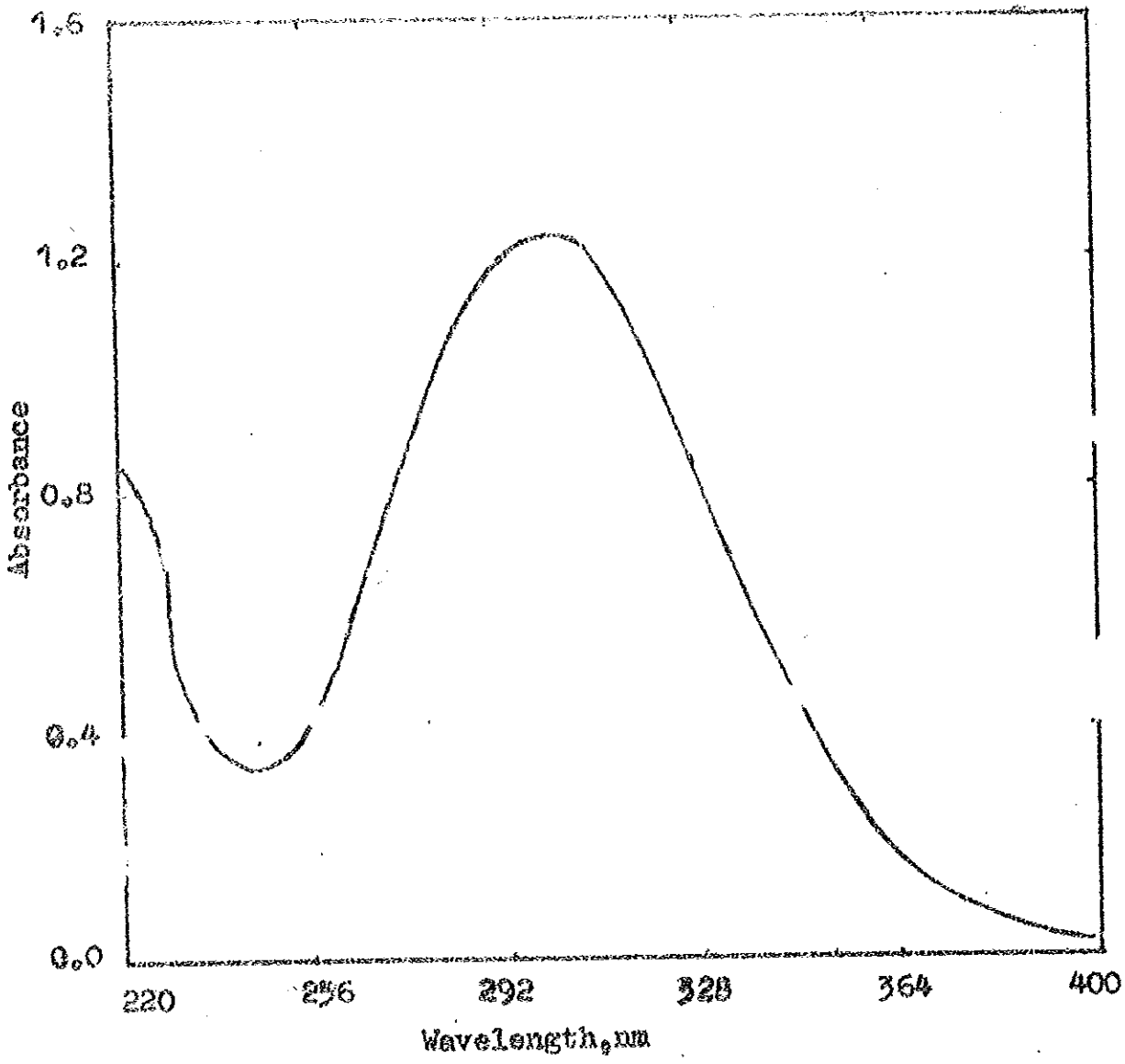


Fig.1 Absorption spectrum of 5×10^{-5}M CPCHA in ethanol.

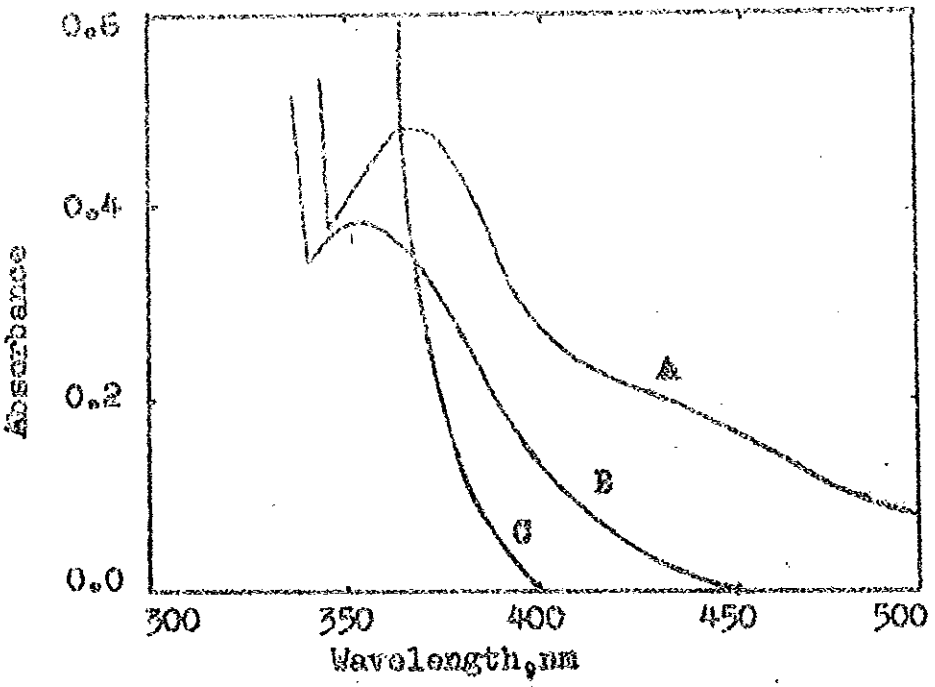


Fig.2 Absorption spectra of (A) 1.05×10^{-5}M Nb (V)-SCN-CPCHA complex against the reagent blank, (B) 1.05×10^{-5}M Nb(V)-CPCHA complex against the reagent blank, and (C) 5×10^{-4}M CPCHA, in chloroform.

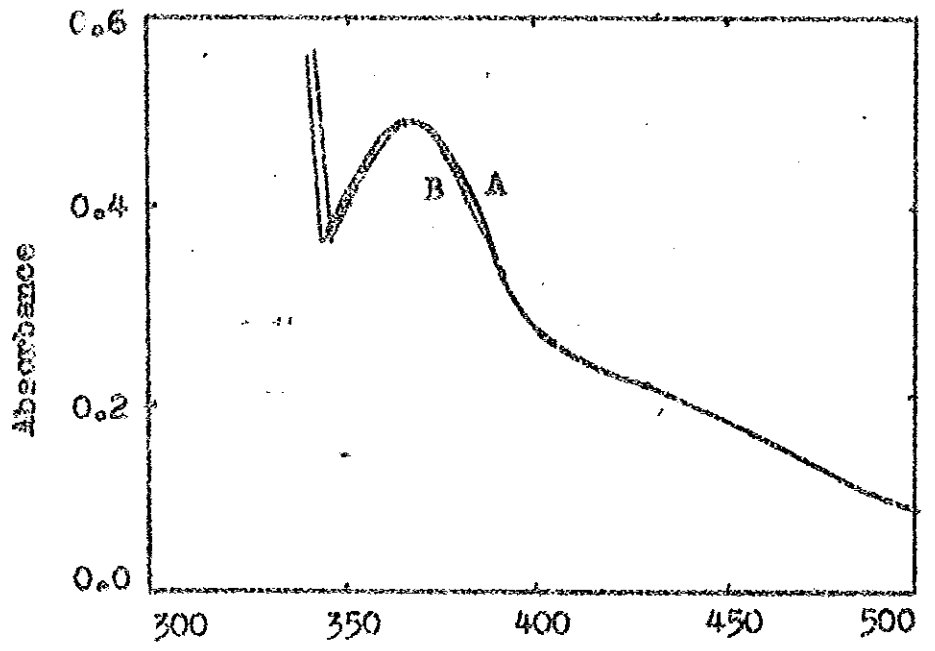


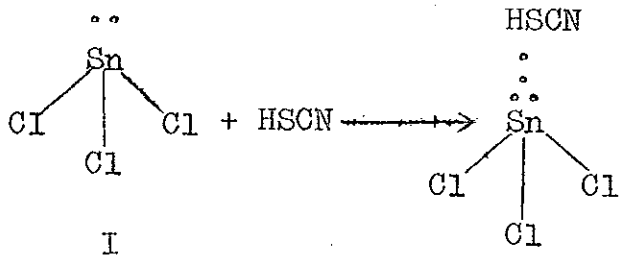
Fig.3. Absorption spectra of 1.05×10^{-5}M Nb(V)-SCN-CPCHA complex against the reagent blank in chloroform extracted in the (A) absence of $SnCl_2$ & (B) presence of 0.15M $SnCl_2$.

Niobium(V) also reacts with thiocyanate alone to form a yellow complex in acetone-water system. The complex is also extractable into ether (60,61). However, it has been found that the Nb(V)-SCN complex was not extractable into chloroform from the acidic medium used for the extraction of the mixed ligand complex.

Stannous chloride, which is added to stabilize thiocyanic acid in hydrochloric acid solutions (2) has been found to have no effect both on the position and intensity of the absorption band (Fig. 3).

The thiocyanic acid, HSCN, formed in hydrochloric acid solutions is known to undergo polymerization reaction (60) to yield parathiocyanogen, $(SCN)_n$,(62). This polymerization reaction can be hindered, i.e., the thiocyanic acid can be stabilized, by introducing a solution of stannous chloride, containing $SnCl_3^-$ species, to the HSCN solution.

The stannous chloride, in solutions containing an excess of chloride ion, exists as pyramidal, I.



I II

due to the presence of a sterically active nonbonding electrons. This electron pair makes the trichlorotin(II) anion an excellent ligand, both as a sigma-bonding donor group and as a powerful pi-acceptor ligand (63). As a result, the trichlorostannate(II) anion, I, may act as a stabilizer for the thiocyanic acid by means of a hydrogen bond, II.

The position of the absorption band of the Nb(V)-SCN-CPCHA complex was found to be unaffected by the changes in the concentrations of the constituents, HCl, and $SnCl_2$, in a wide range indicating the extraction of a single complex species under each condition.

Several organic solvents such as 1-hexanol, amylalcohol, amylacetate, ethylacetate, chloroform, carbon tetrachloride, benzene, toluene, xylene, chlorobenzene, and 1,2-dichlorobenzene were examined for the quantitative extraction of Nb(V)-SCN-CPCHA complex by following a two step extraction procedure. Esters and alcohols were found to be not suitable in that they have been found miscible with the strongly acidic aqueous phase, probably due to the hydrolysis and protonation of the solvents, respectively. Chlorobenzene was found to be not suitable solvent for extraction because it exhibited slow phase separation, perhaps due to its relatively similar density to the aqueous phase. The absorption spectra of the extracts, in the rest of the [illegible] the results [illegible] Table 1.

solvents, were recorded against reagent blank and the results are given in Table 1.

Table 1. Effect of solvents on the extraction of the Nb(V)-SCN-CPCHA complex

Solvent	λ_{max}, nm	ε_{max}, M^{-1} cm^{-1}
Carbon tetrachloride	374	39400
Benzene	370	39500
Toluene	370	39700
Xylene	370	43300
1,2-Dichlorobenzene	365	43700
Chloroform	368	45000
Chloroform	368	45500*
Chlorobenzene	-	-
Amyl alcohol	-	-
Amyl acetate	-	-
Ethyl acetate	-	-

*From one step extraction.

Benzene, toluene, and carbon tetrachloride gave low absorbance values. Chloroform, 1,2-dichlorobenzene, and xylene were found to be the most effective solvents for the extraction of the complex. Of these solvents chloroform was chosen because it allowed complete extraction with rapid phase separation in one step extraction due to the higher solubility of the reagent in it than in the other solvents.

The purity of the solvent has been found to be very crucial. Therefore, the solvents have been distilled once before use. In the case of chloroform, satisfactory results were obtained by treating the solvent with concentrated sulphuric acid for at least 12 h, washing with dilute sodium hydroxide and finally with distilled water as described in section 3.3.3. The washed solvent was dried over fused calcium chloride and distilled twice. The purified chloroform was stored in a dark bottle for not more than two days before use.

4.2. Examination of the Experimental Variables

The effect of various experimental variables on the extraction and determination of Nb(V) with CPCHA in presence of an auxiliary ligand thiocyanate from the hydrochloric acid and stannous chloride medium, has been investigated in order to establish optimum conditions.

Effect of acidity. The effect of common mineral acids such as, HNO_3, H_2SO_4, H_3PO_4, and HCl, on the extraction of the complex has been studied. Nitric acid has resulted in the decomposition of the complex whereas sulphuric acid and phosphoric acid were found to have bleaching effect (60). Only HCl was found to be adequate for rapid and complete extraction of Nb(V) as the mixed ligand complex.

The optimum acidity range of the aqueous phase for

the quantitative extraction of the complex has been found to be 3.5 — 6.5 M HCl (Fig. 4). At lower acidities low absorbance values were obtained due to incomplete extraction, while at higher acidities, again low absorbance values were observed as a result of precipitate formation. The precipitate formation is probably due to the limited solubility of KCl and/ or KSCN with high salt concentration in the aqueouse phase. The incompleteness of extraction at lower and higher acidities was confirmed by detecting the Nb(V) left in the aqueous phase which was recovered by subsequent extraction of the metal after changing the concentration of the acid to the optimum range (Table 2).

Effect of chloride ion concentration. The addition of HCl increases both the acidity and the chloride concentration. This necessitated to study the effect of chloride ion independently of HCl. The investigation was carried out by holding the HCl concentration constant while varying the chloride ion concentration up to 8.0 M by the addition of $MgCl_2$. The results are shown in Fig. 5. It was found that in the absence of HCl in the aqueous phase, the degree of extraction of the metal was incomplete even at 8 M chloride while at 1.2 M HCl, a minimum of 2.5 M chloride was required for the complete extraction of Nb(V). Excess chloride has been found to have no effect on the extraction of Nb(V) up to 7.0 M total chloride; beyond this precipitation

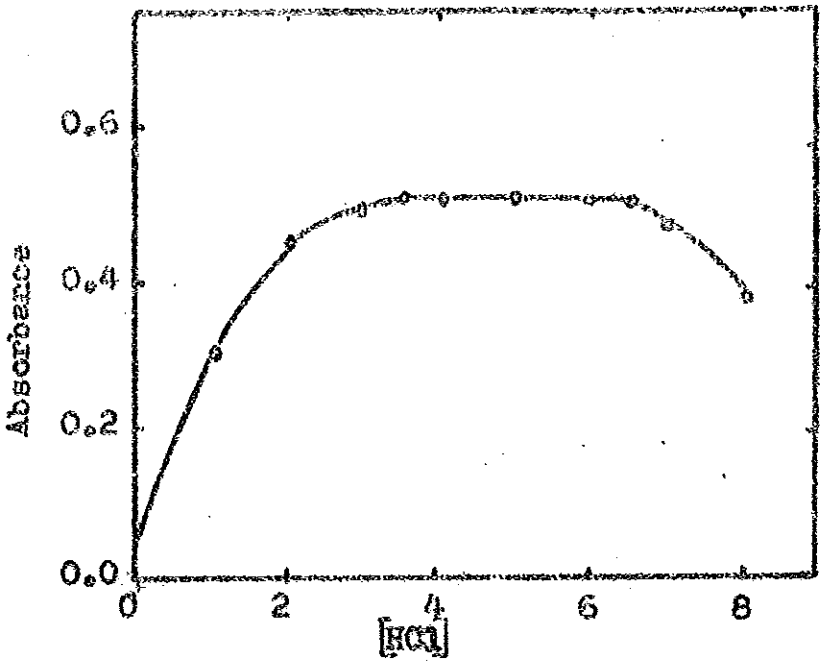


Fig.4 Effect of HCl concentration of the aqueous phase on the extraction and determination of 24.4μg Nb(V). [KSCN] = 0.5M, [$SnCl_2$] = 0.15M)

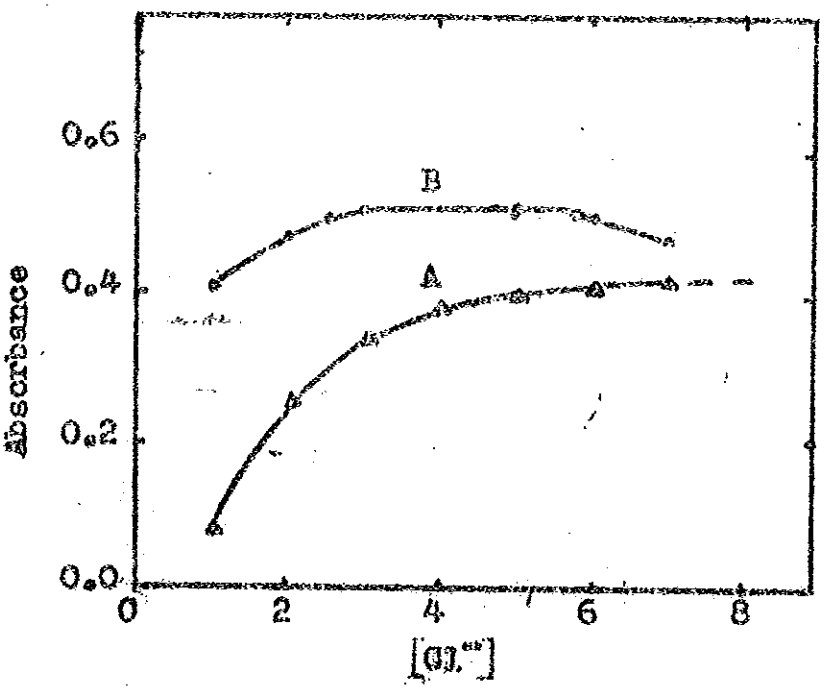


Fig.5 Effect of chloride ion concentration on the extraction of Nb(V) at (A) 0.6M HCl and (B) 1.2N HCl. (Nb(V) taken =24.4μg, [KSCN] = 0.5M, [$SnCl_2$] =0.15M)

Table 2. Effect of hydrochloric acid concentration of the aqueous phase on the extraction of Nb(V)-SCN-CPCHA complex (Nb(V) taken = 24.4 µg, $[SCN^-]$ = 0.5 M, $[SnCl_2]$ = 0.15 M)

[HCl]	Extraction of Nb (%)	Recovery of Nb from aqueous phase (%)
0.0	4.50	93.72
1.0	69.46	28.70
2.0	88.22	11.01
3.0	93.81	5.62
3.5	99.87	0.00
4.0	99.98	0.00
5.0	100.00	0.00
6.0	99.99	0.00
6.5	99.90	0.00
7.0	92.84	5.89
8.0	70.26	26.60

occurred in the aqueous phase resulting in a decrease in the degree of extraction of the metal. The precipitation is probably due to the limited solubility of KCl and/ or KSCN in the aqueous phase with high salt concentration.

A similar study was carried out to determine the minimum acid concentration at constant concentration of chloride ions. Results obtained (Fig. 6) show that at 5.0 M chloride level the minimum concentration of the acid, as HCl, for the quantitative extraction of niobium(V) was found to be 0.4 M.

Thus, it appears that both the free acid and chloride ion profoundly influence the degree of extraction of the complex and their concentrations must be controlled carefully. Hence hydrochloric acid was found to be the most effective reagent as source of both H^+ and Cl^- ions.

Effect of thiocyanate. The effect of the concentration of thiocyanate on the extraction and determination of Nb(V) has been studied over a wide range. Both potassium thiocyanate and ammonium thiocyanate have been found to give similar results. However, the stability of the Nb(V)-SCN-CPCHA complex with time was better with potassium thiocyanate (see under stability of the complex). The optimum thiocyanate concentration for the quantitative extraction of Nb(V)-SCN-CPCHA complex ranged from 0.1 - 1.5 M thiocyanate (Fig. 7). At lower thiocyanate concentrations, the absorbance decreased due to the incomplete formation of the mixed ligand complex, while at higher concentrations of thiocyanate, formation of the mixed ligand complex was retarded resulting in decreased absorbance values.

Effect of the concentration of stannous chloride. Stannous chloride required for stabilizing the thiocyanic acid in HCl medium was found to have no adverse effect up to 0.22 M, higher concentrations resulted in low absorbance values due to precipitation of salts in the aqueous phase (Table. 3).

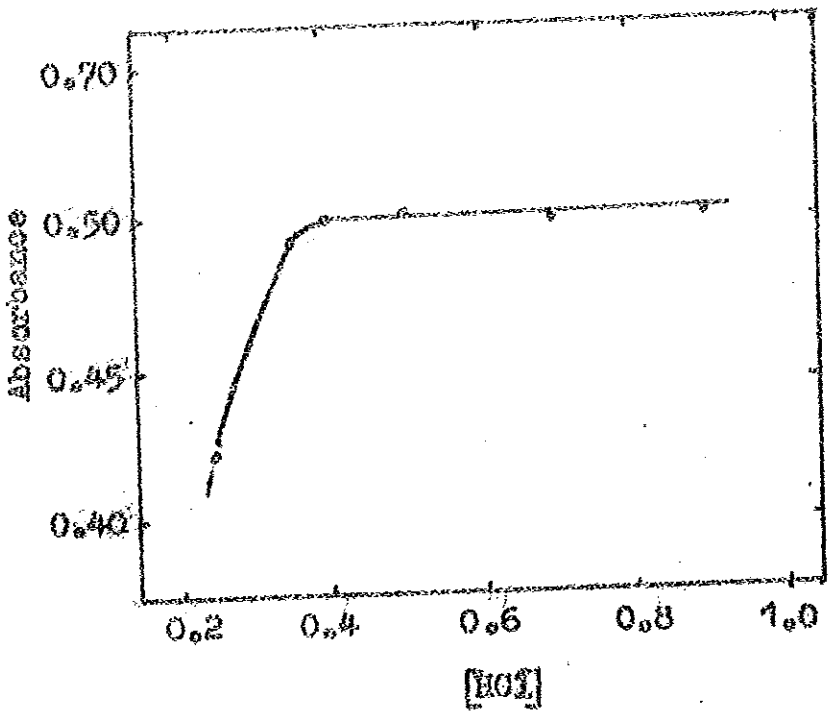


Fig.6 Determination of minimum acid concentration required for the extraction of 24.4µg Nb(V) at M chloride ion concentration. ([KSCN] = 0.5M, [$SnCl_2$] =0.15M).

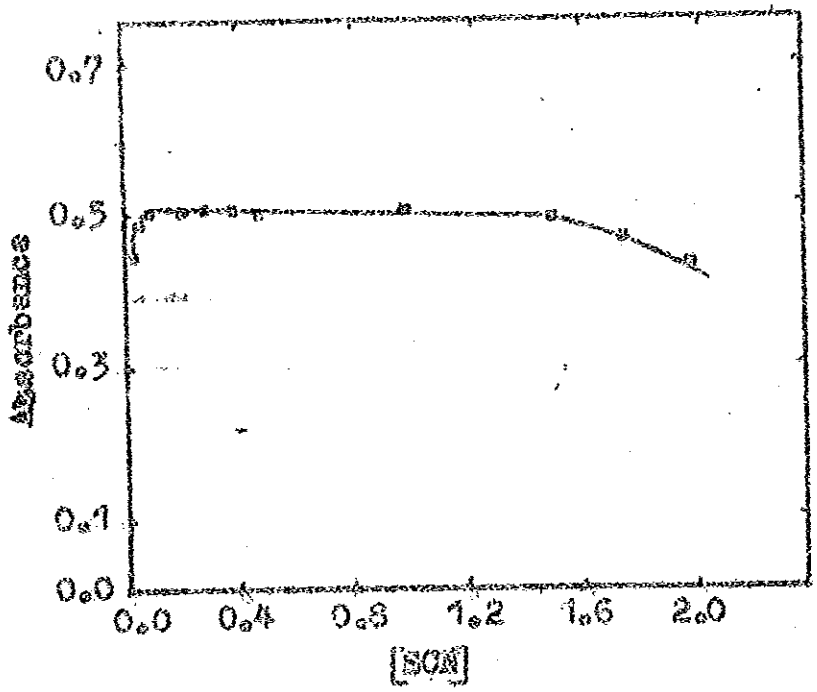


Fig.7 Effect of the concentration of thiocyanate on the extraction of 24.4 µg Nb(V). ([HCl] = 5M, [$SnCl_2$] = 0.15M).

Table 3. Effect of the concentration of stannous chloride in the aqueous phase on the extraction of 24.4 µg Nb(V) ([HCl] = 5 M, [SCN] = 0.5 M)

$[SnCl_2]$	Ansorbance at 368 nm
0.0	0.498
0.015	0.500
0.03	0.502
0.06	0.503
0.09	0.500
0.12	0.504
0.15	0.499
0.22	0.494
0.30	0.462

Effect of the amount of CPCHA. A 1 to 8 molar ratio of the metal to the ligand, CPCHA, was necessary for the complete extraction of Nb(V) as Nb(V)-SCN-CPCHA complex (Table 4). A 100-fold molar excess of the ligand, CPCHA, has been found to have no adverse effect on the extraction of the complex. Nevertheless, a large excess of the reagent resulted in an unwanted high absorbance value of the blank which caused difficulties in zero adjustment of the instrument. In practice a 20-30 fold molar excess of the CPCHA was used.

Effect of the volume of the aqueous phase. It has been found that the volume of the aqueous phase can be varied from 10-50 ml with respect to a fixed volume of 10 ml of

Table 4. Effect of the amount of CPCHA on the extraction of Nb(V) ($[Nb(V)] = 1.05 \times 10^{-5}$ M, $[HCl] = 5$ M, $[SCN^-] = 0.5$ M)

[Nb(V)] : [CPCHA]	Absorbance at 368 nm
1:0	0.000
1:1	0.199
1:2	0.354
1:3	0.419
1:4	0.469
1:5	0.484
1:6	0.492
1:8	0.500
1:10	0.501
1:12	0.503
1:15	0.503
1:20	0.502
1:50	0.502
1:100	0.496

the organic phase without any significant variation in the absorbance or extraction efficiency of Nb(V)-SCN-CPCHA complex (Table 5). However, more repetitive extractions were found to be necessary for the complete extraction of Nb(V) from larger volumes of the aqueous phase.

Table 5. Effect of the volume of the aqueous phase on the extraction of 24.4 µg Nb(V)
(V_{org} = 10 ml, [HCl] = 5 M, [SCN^-] = 0.5 M)

Volume ratio V_{org} : V_{aq}	Absorbance at 368 nm
1:1	0.500
1:2.5	0.501
1:5.0	0.496
1:6.0	0.488
1:8.0	0.470
1:10	0.456

Extraction time and the stability of the complex. The coloured Nb(V)-SCN-CPCHA complex required 4-5 min for complete extraction from the aqueous phase into chloroform based on the shaking intensity of three different people. The stability of the complex was studied by storing the solutions in a cool dark place. Exposure to laboratory fluorescent light or diffuse day light at intervals of measurement has been found to have no effect. The Nb(V)-SCN-CPCHA complex extracted from KSCN medium was stable for 52 h, while the one extracted from NH_4SCN medium was stable only for 24 h at room temperature. For both systems the absorbance values were found to decrease with time after 52 and 24 h, respectively, which may be due to the decomposition of the extracting solvent, chloroform (59), or the complex or both. The results are given in Table 6.

Table 6. Stability of the complex with time for the extraction and determination of 19.5 µg Nb(V)

Time h	Absorbance at 368 nm	
	KSCN (0.5 M)	NH_4SCN (0.5 M)
0	0.402	0.398
1	0.399	0.399
2	0.400	0.399
4	0.401	0.400
8	0.401	0.398
18	0.402	0.399
24	0.400	0.400
28	0.400	0.394
32	0.402	0.380
40	0.403	0.288
48	0.402	-
50	0.400	-
52	0.398	-
60	0.393	-
72	0.374	-
82	0.350	-

The optimum experimental conditions for the extraction and determination of Nb(V) are summarized in Table 7. These results show that the proposed method is free from the rigid control of experimental variables.

4.3. Stoichiometry of the Complex

The stoichiometry of the complex was determined by different spectrophotometric methods. The continuous

Table 7. Optimum experimental conditions for the extraction and determination of niobium(V)

Parameter	Condition
Aqueous phase, HCl	3.5 - 6.5 M
Aqueous phase, SCN^-	0.1 - 1.5 M
Aqueous phase, $SnCl_2$	upto 0.22 M
Organic Phase, CPCHA	$2x10^{-4}$ -$3x10^{-3}$ M
$V_{aq}:V_{org}$	1:1 - 5:1
Extraction time	4 - 5 min
Measurement time (with KSCN)	0 - 52 h
Solvent for extraction	Chloroform

variations (50, 51) and the mole ratio (52) methods were employed to determine the ratio of Nb(V) to CPCHA; while the ratio of Nb(V) to SCN^- was determined by the extraction method (36). In the continuous variations method the maximum absorbance for the complex was observed at the mole fraction of 0.33 of Nb(V), which corresponds to a 1:2 ratio of Nb(V) to CPCHA. The results of the continuous variations method are given in Table 8 and the curve is shown in Fig. 8.

The result of the continuous variations method was supported by the result of the mole ratio method which also gave a 1:2 ratio of the Nb(V) to CPCHA (Table 4 and Fig. 9).

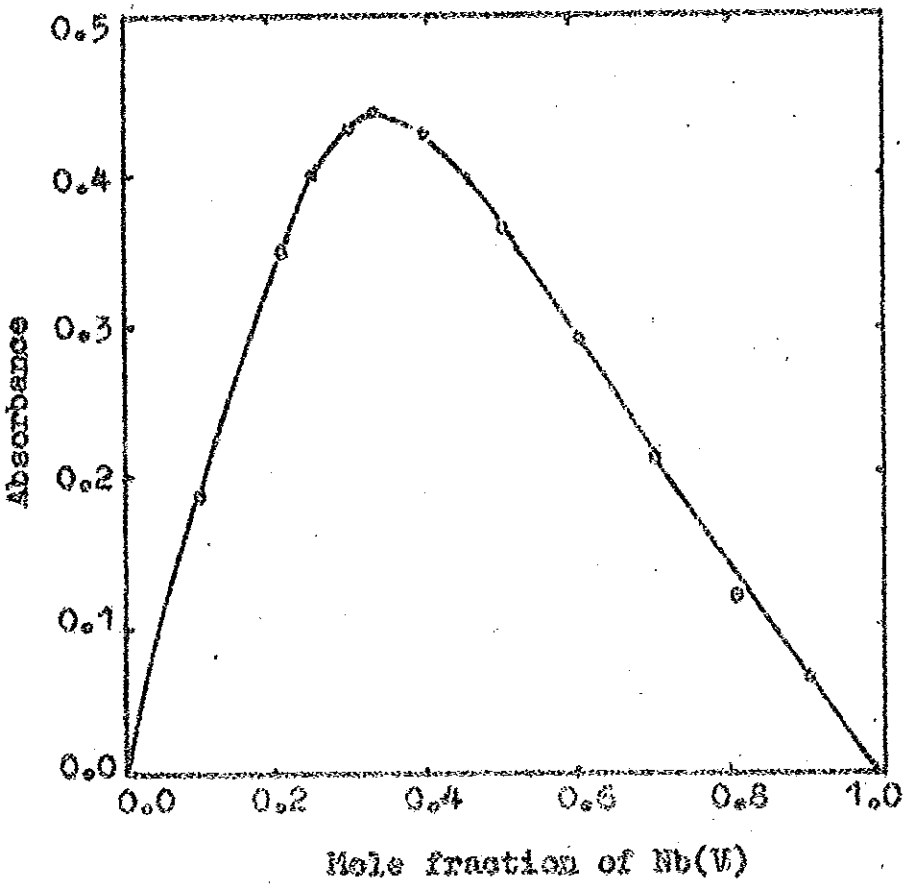


Fig.8 Curve for the determination of the ratio of Nb(V) to CPCHA by the method of the continuous variations.

Table 8. Results of the continuous variations method for the determination of the ratio of Nb(V) to CPCHA in the Nb(V)-SCN-CPCHA complex ($C_T = C_{Nb(V)} + C_{CPCHA} = 1.05 \times 10^{-3}$ M, $[HCl]$ = 5 M, $[SCN^-]$ = 0.5 M).

Mole fraction of Nb(V)	Mole fraction of CPCHA	Absorbance at 368 nm
0.00	1.00	0.000
0.10	0.90	0.186
0.20	0.80	0.346
0.25	0.75	0.400
0.30	0.70	0.428
0.33	0.67	0.440
0.40	0.60	0.429
0.50	0.50	0.363
0.60	0.40	0.291
0.70	0.30	0.212
0.80	0.20	0.112
0.90	0.10	0.062
1.00	0.00	0.000

The ratio of niobium(V) to thiocyanate was determined by the extraction method (36) in which the quantity $\log \frac{A}{A_{max}-A}$ was plotted against $\log [SCN^-]$; where A is the absorbance for a particular concentration of thiocyanate, and A_{max} is the absorbance at optimum concentration of thiocyanate. The plot yielded a slope of 1.14 which indicates the ratio of Nb(V) to SCN^- to be 1:1 in the Nb(V)-SCN-CPCHA

system. The results are given in Table 9 and the curve is shown in Fig. 10.

Table 9. Results of the extraction method for the determination of the ratio of Nb(V) to SCN^- in Nb(V)-SCN-CPCHA complex ($[Nb(V)] = 1.05 \times 10^{-5}$ M, [HCl] = 5 M $[CPCHA] = 4 \times 10^{-4}$ M)

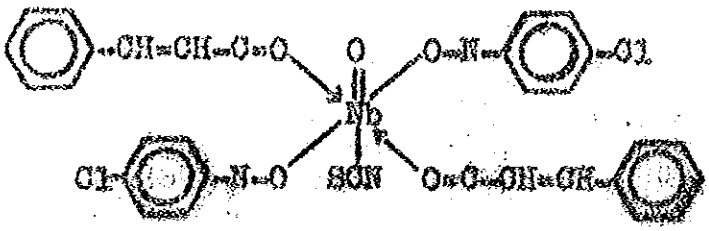
$[SCN^-]$	A at 368 nm	$A_{max}-A$	$\log \frac{A}{A_{max}-A}$	Log $[SCN^-]$
0.01	0.167	0.333	-0.300	-2.00
0.02	0.261	0.239	0.040	-1.70
0.03	0.317	0.183	0.240	-1.52
0.04	0.349	0.151	0.365	-1.40
0.05	0.376	0.124	0.481	-1.30
0.10	0.500	-	-	-
0.50	0.500	-	-	-

* $A_{max} = 0.500$.

Thus, the overall stoichiomentry of the Nb(V)-SCN-CPCHA complex has been established as 1: 1: 2 (Nb : SCN: CPCHA). This result is in agreement with the compositions reported (18, 27) for the Nb(V) complexes with some other hydroxamic acids.

Under conditions of alkali pyrosulphate or hydrogen sulphate fusion of Nb_2O_5, followed by extraction of the fused melt with tartaric acid, niobium is known to contain Nb=O group and exists in solution as NbO^{3+} (10, 18,27, 57). From the extractability of the complex into a non-

polar solvent, consideration of the presence of Nb=O group, and the stoichiometry, the following structure is proposed for the complex:



Bis-(N-4-chlorophenylcinnamohydroxamic acid) thiocyanatoniobate(V).

4.4. Evaluation of Photometric Parameters

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 the Ringbom's plot (46). The results are given in Table 10, and the graphs are shown in Figures 11 and 12.

The molar absorption coefficient, the sensitivity of the method, i.e, the concentration that corresponds to an absorbance of 0.001 (40), the limit of determination (the concentration that corresponds to an absorbance three times of the standard deviation of the blank) (48), and the precision of the method as determined from the relative standard deviation of six measurements for 24.4 µg Nb(V) are summarized in Table 11.

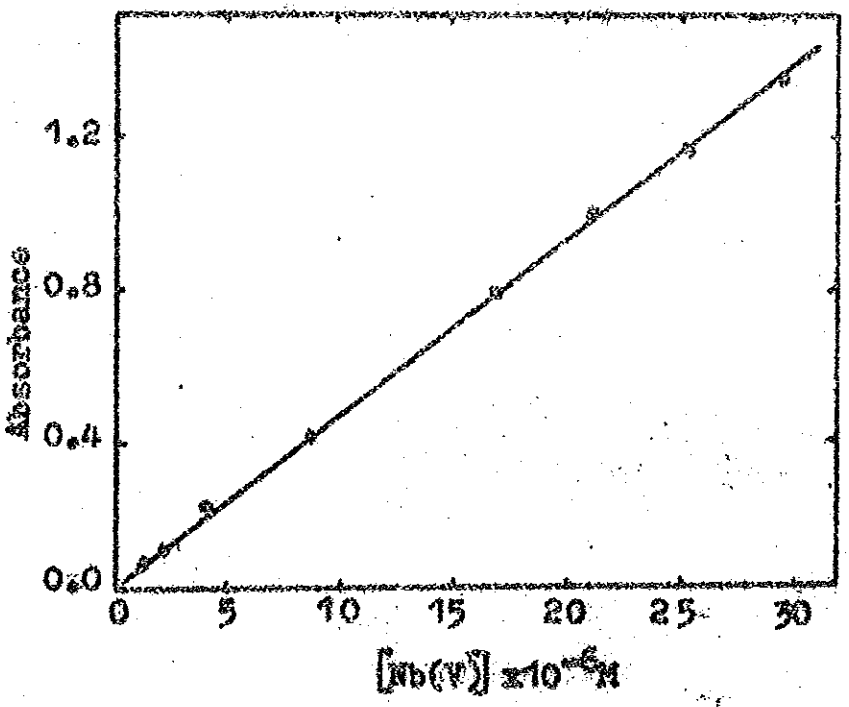


Fig.11 Calibration curve for the determination of Nb(V).

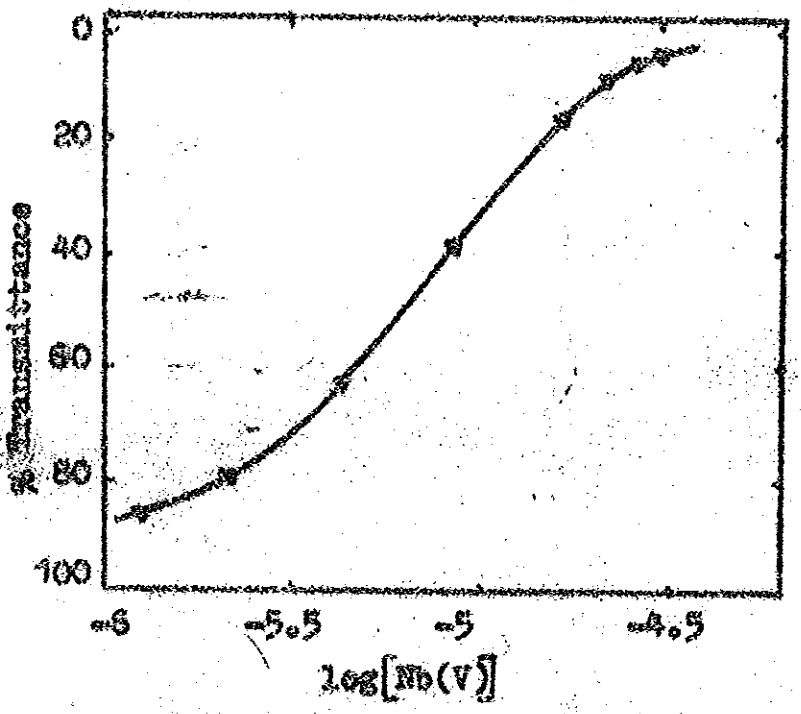


Fig. 12 Rigubem's plot for the evaluation of optimum concentration range for the determination of Nb(V).

Table 10. Data for calibration curve and the Ringbom's plot ($[HCl] = 5.0$ M, $[SCN^-] = 0.5$ M, $[CPCHA] = 4.2 \times 10^{-4}$ M)

$[Nb(V)] \cdot 10^6$ M	$\log [Nb(V)]$	Absorbance at 368 nm	Transmittance (%)
1.26	-5.90	0.065	86.10
2.10	-5.68	0.101	79.25
4.20	-5.38	0.201	62.95
8.40	-5.08	0.402	39.63
16.80	-4.76	0.792	16.14
21.00	-4.68	0.976	10.57
25.20	-4.60	1.166	6.82
29.40	-4.53	1.337	4.60

As can be seen clearly from the values of the relative standard deviation precise results are obtained in presence of stannous chloride.

In general the data in Table 11 show that the method is highly sensitive and reproducible and can be applied to the analysis of niobium at trace levels.

4.5. Effect of Diverse Ions

The effects of diverse ions on the extraction and determination of niobium(V) have been investigated to evaluate the selectivity of the proposed method.

In general, it has been found that the ions that react with Nb(V) (e.g. fluoride, oxalate, etc.), that form precipitate by reacting with the constituents (e.g. Ag^+,

Table 11. Photometric characteristics of the complex

λ_{max}, nm	368
ε_{max}, $M^{-1}cm^{-1}$	4.75×10^4
Sensitivity, μg cm^{-2}	1.96×10^{-3}
Concentration range from Beer's law, μg ml^{-1}	0.117 - 2.73
Optimum concentration range from Ringbom's plot, μg ml^{-1}	0.13 - 1.76
Limit of determination, μg ml^{-1}	0.021
Relative standard deviation, % (in presence of $SnCl_2$), n = 6	0.95
Relative standard deviation, % (in the absence of $SnCl_2$), n = 6	2.06

Cu^{2+}, Hg^{2+}, etc.), or that react with the reagent to deprive the niobium(V) of sufficient reagent for complete colour development (e.g. Ta(V), W(VI), etc.) affect the determination by reducing the absorbance value (negative interference); while those ions which react with the constituents and whose absorption bands overlap with the spectrum of Nb(V)-SCN-CPCHA complex interfered by increasing the absorbance value (e.g. Ti(IV), Zr(IV), etc.). Therefore these ions usually have lower tolerance limits.

The tolerance limit of diverse ions taken as concentration (mg) which cause an error less than 2 % are given in Table 12. These results indicate that most of the common ions which are normally associated with niobium in mine-

rals, ores, and alloys do not interfere up to 50 times to the weight of niobium by the proposed method. Since the amount of diverse ions that are associated with Nb(V) does not exceed the tolerance limits, in most cases, the proposed method for niobium can be applied to the analysis of minerals, ores, and alloys.

4.6. Application

Since standard or natural samples were not available, the assesment of the analytical potentiality of the new proposed method has been made on synthetic samples with compositions similar to minerals, ores, and alloys containing niobium. The composition of the samples, the amount of niobium recovered, and the relative standard deviation are given in Table 13. These results indicate that the proposed method is precise and reliable for the determination of niobium at trace levels in diverse samples.

4.7. Comparison with Other Spectrophotometric Methods

A comparative study of the proposed method for the determination of niobium with other spectrophotometric methods, in regard to sensitivity, selectivity, and stability of the complexes is made in Table 14.

The proposed method is fairly sensitive as compared to the reported methods, while the selectivity and stability of the complex is superior to most others.

Table 12. Tolarance limits of diverse ions in the determination of Nb(V) (amount of Nb(V) = 19.5 ug, [CPCHA] = 4.2×10^{-4} M, [HCl] = 5.0 M, [SCN] = 0.5 M, [$SnCl_2$] = 0.15 M)

Ion	Tolerance limit, mg	Direction of interference
Fe^{3+}	80	* *
Na^{+}, K^{+}, Li^{+}, Be^{2+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Pb^{2+}, Cr^{3+}, Ce^{4+}, Th^{4+}	20 each	*
UO_2^{2+}, La^{3+}	16 each	a
Al^{3+}	12	b
Tl^{+}	10	a
Co^{2+}	5	b
Hg^{2+}	5	a
Ca^{2+}, Y^{3+}, Er^{3+}	5 each	*
Rh^{3+}	4	b
Ag^{+}	2.5	a
Bi^{3+}	1.5	b
Pd^{2+}	1.	b
Cu^{2+}, Pt^{4+}	1 each	a
Re^{7+}	0.5	b
Ta^{5+}	0.4	a
Ti^{4+}, Zr^{4+}	0.01 each	b
$B_4O_7^{2-}$, AsO_4^{3-}, $Cr_2O_7^{2-}$, $SbOC_4H_4O_6^{-}$	20 each	*

Table 12. contd.

Ion	Tolerance limit mg	Direction of interference
MoO_4^{2-}	10	b
VO_3^-	2	a
WO_4^{2-}	1	b
Sulphate	20	*
Acetate	20	*
Nitrate	100	*
Perchlorate	200	*
EDTA	200	*
Citrate	100	*
Oxalate	10	a
Fluoride	1.5	a
Ascorbic acid	300	*
Tartaric acid	300	*
Phosphoric acid	200	a
Boric acid	60	*
Thiourea	200	*
Fluoroboric acid	30	a

* Not studied beyond the indicated level.

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

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

Table 12. contd.

Ion	Tolerance limit mg	Direction of interference
MoO_4^{2-}	10	b
VO_3^-	2	á
WO_4^{2-}	1	b
Sulphate	20	*
Acetate	20	*
Nitrate	100	*
Perchlorate	200	*
EDTA	200	*
Citrate	100	*
Oxalate	10	a
Fluoride	1.5	a
Ascorbic acid	300	*
Tartaric acid	300	*
Phosphoric acid	200	a
Boric acid	60	*
Thiourea	200	*
Fluoroboric acid	30	a

* Not studied beyond the indicated level.

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

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

Table 13. Determination of niobium in various synthetic matrices by the proposed method (with thiocyanate and CPCHA in chloroform at 5 M HCl in presence of stannous chloride)

Sample	Composition	Nb found, ug (*)	RSD (%)
Matrix A	15 µg Nb^{5+} + 15 mg Fe^{3+} + 2 mg Cr^{3+} + 2 mg Ni^{2+} + 2 mg PO_4^{3-} + 0.5 mg Co^{2+} + 0.5 mg V^{5+}	15.01	1.21
Matrix B	20 µg Nb^{5+} + 3mg Mn^{2+} + 3mg Cr^{3+} + 2mg Ni^{2+} + 1mg Al^{3+} + 2mg PO_4^{3-} + 0.4mg Ta^{5+} + 1mg Pd^{2+}	20.00	1.27
Matrix C	25µg Nb^{5+} + 10mg Fe^{3+} + 3mg Ni^{2+} + 1mg Cr^{3+} + 2mg AsO_4^{3-} + 0.75mg W^{6+} + 0.25mg Re^{7+}	25.02	1.04
Matrix D	30µg Nb^{5+} + 12mg Fe^{3+} + 2mg Ni^{2+} + 1mg Al^{3+} + 1mg Co^{2+} + 9.6µg Ti^{4+} + 0.4mg Ta^{5+}	29.96	0.84
Matrix E	19.5µg Nb^{5+} + 5mg Ca^{2+} + 0.756mg Na^{+} + 38µg Ta^{5+} + 0.625mg F^{-}	19.50	1.07

Table 13 contd.

Sample	Composition	Nn found, ug (*)	RSD (%)
Matrix F	19.5ug Nb^{5+} +mg Y^{3+} +2.5mg Er^{3+} + 5mg Ce^{4+} + 5mg La^{3+} +8mg U^{6+} + 48ug Ta^{5+}	19.46	1.18
Matrix G	24.4ug Nb^{5+} +5mg Y^{3+} + 10mg U^{6+} 15mg Fe^{3+} +10mg Th^{4+} +48ug Ta^{5+}	24.38	0.78

*Average of five determinations.

Table 14. comparison with other methods

	Reagent	λ_{max}	$\epsilon_{max,nm}$ $M^{-1}cm^{-1}$	Acidity	Interference	Stability hh		Ref.
1.	Benzohydroxamic acid	365	32000	9-12 M HCl	Ta(V), $(H_2O_2)^a$	1	1	34
2.	Ethylene-bis-(triphenyl-phosphonium) ion and thiocyanate	393	31000	1-4 M HCl	(Fe(III), Mo(VI), Cu(II), Zn(II), W(VI), Zr(VI), V(V))^b	3	8	2
3.	N,N^1-Diphenylbenzamidine and thiocyanate	400	34000	1.5-4.0 HCl	Mo, Co, Cu^c			
					Ti, Re, W		10	9
4.	N-4-Chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid	380	63000	8-10 M HCl	Ti(VI), Zr(VI))^d		24	19
5.	Bromopyrogallol red, hexadecyl pyridinium bromide and polyoxy ethylene glycol octyl-phenyl ether	635	141000	6.5-7.0 pH	Several metal ions		-	25

Table 14.contd.

Reagent	λ_{max}	$\epsilon_{max,nm}$ $M^{-1}cm^{-1}$	Acidity	Interference	Stability h	Ref.
6. Salicylfluorone and hexadecyltrimethylammonium ion	525	181000	0.1M H_2SO_4	>5 µg Ta(V)	-	26
7. Molybdoniobic heteropoly acid di-or trimethylthionine	660	270000	0.12-0.6 M HNO_3	Si, Ge, Ta	-	27
8. Bis(salicylohydrazone)	495	19000	conc. HCl	Ti(IV), (Zr(IV), Ta(V) [d]	24	64
9. N-3-Tolyl-4-methoxybenzohydroxamic acid and thiocyanate	360	31200	8.0 M HCl	Ti(IV), MoO_4^{2-}, WO_4^{2-} V(V), Sn(II), F^-	30	33
10. 1,2,4,6- Tetraphenylpyridinium perchlorate and thiocyanate	395	28200	4-6 M HCl	Fe^{3+} [e]	-	65

Table 14.contd.

Reagent	λ_{max}	ϵ_{max}, $M^{-1}cm^{-1}$	Acdity	Interference	Stability h	Ref.
11. N-4-Chlorophenylcinnamohydroxamic acid and thiocyanate	368	47500	3.5-6.5 M HCl	10 ug Ti^{4+} and Ar^{4+}	52	present

[a] Destroyed by heating the solution

[b] Removed by prior extraction.

[c] Masked with thiourea

[d] Masked with EDTA.

[e] Eliminated by prior extraction and a reducing agent.

5. C O N C L U S I O N

A new method has been developed for the determination of niobium(V) with N-4-chlorophenylcinnamohydroxamic acid and thiocyanate by solvent extraction and spectrophotometry. Though the proposed method is fairly sensitive it is highly selective. The stability of the coloured system is also better than most of the other methods reported for the determination of niobium. Furthermore the method is precise and free from rigid control of experimental variables. It is hoped that the method could be applicable to the analysis of diverse samples containing niobium.

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