CHAPTER IV

ANALYTICAL APPLICATIONS OF N-ARYLHYDROXAMIC ACIDS

RESUME

A rapid selective and sensitive spectrophotometric method for the trace determination of cerium(IV), Niobium(V), Tantalum(V), Titanium(IV), Vanadium(V) and Zirconium(IV) is described with synthesised high molecular weight N-arylhydroxamic acids. A comparative study for the sensitivity of different hydroxamic acids towards these metal ions has been made. A detailed study of various parameters for the optimum extraction of these metals have been undertaken with N-p-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid (PTCHA). The ternary complexes with suitable chromogenic reagents were also studied and applied for the enhancement of the sensitivity of the method. These metal ions have been determined in presence of several diverse ions and in standard samples.

ANALYTICAL APPLICATIONS OF N-ARYLHYDROXAMIC ACIDS

Advances in modern instrumentation have resulted in the development of several new simple, rapid, selective and sensitive techniques for the determination of ppm to sub ppm quantities of the constituents. A number of methods for determining metals in the environmental and biological samples have been prescribed. However, because of the cost, sensitivity and the nature of the sample, the choice have to be narrowed down depending upon the existing facilities. Hence the organic analytical reagents play an important role for the determination of several metal ions (1-3).

Various analytical methods have been utilized for the determination of trace metals viz. colorimetry, spectrophotometry, optical spectrography, atomic absorption spectrography, radioactivation, mass spectrophotometry, polarography, etc. But, amongst all these, colorimetric and spectrophotometric methods are most simple, easy to handle and are largely sufficiently sensitive. Further, the link between extraction and photometry is so close that they are often called extraction photometry. Extraction-photometric analysis owes its broad development to its practically unlimited scope both for controlling chemical processes, in geochemistry, biochemistry, soil science, metallurgy and many other fields. Hydroxamic acids because of their stability and strong complexing ability have become an important tool in inorganic analysis (1-20).

A review of literature work reveals (CHAPTER I) that still there is a continuous demand for the simple, selective and sensitive methods of analysis for the determination of heavy metals in view of the biological importance, metal, steel and oil industries and nuclear energy programme. With this view in the present investigation the extraction and spectrophotometric determination of Ce(IV), Nb(V), Ta(V), Ti(IV), V(V) and Zr(IV) have been studied with newly synthesised high molecular weight N-arylhydroxamic acids.

These metal ions are extracted with the proper choice of solvent and judicious adjustment of pH. The various parameters such as effect of pH or acidity, reagent concentration, diverse ions and addition of other reagent in the process of extraction are studied.

1. EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF CERIUM(IV)

1.1 SUMMARY

A sensitive and selective method for the solvent extraction and spectrophotometric determination of cerium(IV) with N-p-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid (PTCHA) has been described. It forms a reddish brown coloured complex with cerium(IV) which can be extracted into chloroform at pH 9-10 and the molar absorptivity is 8.5×10^3 l mol^{-1} cm^{-1} at 465 nm. The effects of pH, reagent concentration, extraction time and stability of the complex are discussed.

1.2 INTRODUCTION

Substituted hydroxamic acids have received a great deal of attention as colorimetric and gravimetric reagents for metals (21-29). Among the rare earths, it has been found that cerium(IV) forms stable complexes with N-arylhydroxamic acids which are quantitatively extractable into different organic solvents in pH 8-10 range (30-32). Substituted cinnamohydroxamic acids have elicited special interest in the extraction and spectrophotometric determination of Ce(IV) due to its high sensitivity and selectivity (33). On the basis of this a number of substituted N-arylhydroxamic acids were synthesized and complexation has been studied for Ce(IV). A comparison of the selectivity and sensitivity with other reported hydroxamic acids is shown in Table 1. N-p-Chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid (PTCHA) has been studied in detail since it proved to be the best reagent for the rapid, sensitive and selective determination of cerium(IV).

1.3 EXPERIMENTAL

All chemicals used were of A.R. and E. Merck quality.

The hydroxamic acids used were synthesised as described in CHAPTER II. Reagent solution of the N-arylhydroxamic acids 0.2% (w/v) in ethanol were used for complexation.

The standard buffer solutions in the pH ranges 6.0-7.4 and 10.0-11.6 were prepared with 0.1 M KH_2PO_4 + 0.5 M borax and 0.025 M borax + 0.1 M NaOH (also 0.05 M $NaHCO_3$ + 0.1 M NaOH) respectively, as described elsewhere (34).

A standard solution of cerium(IV) was prepared by dissolving required amount of cerium(IV) ammonium sulphate in redistilled water and its final concentration

TABLE 1

COMPARISON OF SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF CERIUM

Hydroxamic acid	λ max	Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$)	Reference
N-Phenylbenzo-	460	3740	30
N-p-Tolylbenzo-	465	4600	37
N-p-Tolyl-p-chlorobenzo-	460	4500	20
N-p-Tolylcroteno-	460	3700	33a
N-Phenyl-p-chlorocinnamo-	470	5500	33
N-p-Tolyl-p-chlorocinnamo-	470	5300	33
N-p-Chlorophenyl-p-chlorocinnamo-	470	5300	33
N-p-Chlorophenyl-3,4,5-trimethoxycinnamo-	465	8500	Present work

(1.2×10^{-3} M) was determined by spectrophotometry (30) and titrimetry (35).

Absorbance measurements were made in C.Z. Jena VSU2-P with 1 cm quartz cells.

1.3.1 General Procedure

One ml of cerium(IV) solution (1.2×10^{-3} M) and 3 ml of 0.2% (w/v) reagent solution in ethanol were transferred to a 60-ml separatory funnel. The pH was adjusted to 9.0 with borax buffer (34) and the volume of the aqueous phase to 25 ml, and the complex was extracted into 10 ml chloroform. The chloroform layer was separated after shaking for 3-5 min, dried over anhydrous sodium sulphate and transferred to a 25-ml volumetric flask. To ensure the complete recovery of cerium, the aqueous layer was treated with 2 ml of reagent solution and extracted with 2 x 5 ml of chloroform. The extracts were diluted to 25 ml with chloroform and the absorbance was measured against the reagent blank.

1.4 RESULTS AND DISCUSSION

Cerium-N-p-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid complex gives a reddish brown coloured extract at pH 9-10, having a maximum absorbance at 465 nm with a molar absorptivity 8.5×10^{3} l mol^{-1} cm^{-1}. The characteristics of the cerium(IV) complexes of the several N-arylhydroxamic acids studied are recorded in Table 2. The enhanced sensitivity of the reagent as reflected by an increased molar absorptivity is due to the increased conjugation and presence of the alkoxy groups in the C-phenyl ring. It is noted that the molar absorptivity of the complex is increased with the introduction of chlorine to the para position of N-phenyl (Table 2) presumably due to the resonance stabilization of the conjugate base anion by the electron withdrawing ability of the chlorine atom. This allows positive charge built upon N and thereby stabilize the anion by induction. Separation of C-phenyl ring from the functional carbonyl group by a tertiary carbon yields a decreased sensitivity in the reagent towards cerium(IV), due to the decreased conjugation in the reagent.

1.4.1 Effect of pH

The extraction behaviour of cerium(IV) complex was studied in the pH range 6-11 (Table 3). The results given in Table 3 shows that the extraction commences from pH 7.0 and it is quantitative around pH 8.0. The extraction curve remains almost constant in the pH range 8-11. The extraction at higher pH (> 11) gives the turbidity. The optimum pH range for quantitative extraction is 9-10.

TABLE 2

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF CERIUM(IV) WITH HYDROXAMIC ACIDS

Cerium : 6.7 μg/ml

pH : 8-10

Solvent : Chloroform

Reagent : 3 ml of 0.2% alcoholic solution

Compd. No.	Hydroxamic acid	Colour of chloroform extract	Wavelength of maximum absorption (nm)	Molar absorptivity (l mol^{-1} cm^{-1})	Sandell sensitivity (μg/cm^2)
I	N-p-Chlorophenyl-3,4,5-trimethoxycinnamo-	RB	465	8.5×10^3	0.016
II	N-Phenyl-2,3-dimethoxycinnamo-	RB	460	7.5×10^3	0.018
III	N-p-Chlorophenyl-p-butoxybenzo-	RB	460	6.5×10^3	0.021
IV	N-Phenyl-p-butoxybenzo-	RB	460	5.9×10^3	0.024
V	N-p-Chlorophenyl-p-chlorophenoxyisobutyro-	YO	440	4.25×10^3	0.033
VI	N-Phenyl-p-chlorophenoxyisobutyro-	YO	440	3.9×10^3	0.036

RB = Reddish brown, YO = Yellowish orange

TABLE 3

EFFECT OF pH ON THE EXTRACTION OF CERIUM(IV)-N-p-CHLOROPHENYL-3,4,5-TRIMETHOXYCINNAMOHYDROXAMIC ACID COMPLEX

Cerium = 6.7 μg/ml   Reagent = 3 ml of 0.2% alcoholic solution

pH	Absorbance at 465 nm	% Extraction
6.0	0.073	17
6.3	0.145	35
7.0	0.220	52
7.4	0.350	85
8.0	0.410	100
8.5	0.410	100
9.0	0.410	100
9.5	0.410	100
10.0	0.410	100
11.0	0.410	100
11.6	0.400	97

1.4.2 Beer's Law

Beer's law is obeyed in the concentration range of 0.3 to 13 μg/ml of cerium(IV) (in the extract) at 465 nm, and Sandell sensitivity is 0.016 μg/cm^2.

1.4.3 Effect of Reagent Concentration

Extractions of cerium were studied with varying concentrations of the reagent. The results showed that a single extraction with 2 ml of 0.2% w/v reagent solution in ethanol (the absorbance of the reagent solution vs $CHCl_3$ at 465 nm is 0.001) was enough for the complete recovery of 16.75 μg of cerium. Although the excess reagent has no adverse effect on the extraction of cerium, lower concentration of the reagent gave incomplete extraction. The increased amount of the alcohol (> 16%) tends to reduce the extraction percentage.

1.4.4 Extraction Time and Stability

Extraction of cerium complex is very rapid under the conditions recommended in the analytical procedure. Shaking for 2-3 min was enough to attain equilibrium when the reagent was added to the aqueous phase. The cerium complex is stable for several days. The absorbance remains unchanged for at least 10 days.

1.4.5 Effect of Diverse Ions

The recommended procedure was followed to study the interference due to various diverse ions in the direct spectrophotometric determination of cerium(IV) with [illegible]-PTCHA.

Cerium (6.7 ppm in the extract) can be determined (standard deviation 0.005, n = 6) in the presence of the following ions:

Ag^{+}(100 mg); Be^{2+}(100 mg); Mg^{2+}(100 mg); Mo^{6+}(40 mg); Ca^{2+}(100 mg); Sr^{2+}(100 mg); Cu^{2+}(100 mg); Cd^{2+}(100 mg); Zn^{2+}(100 mg); Ni^{2+}(100 mg); Pb^{2+}(100 mg); Ga^{3+}(60 mg); UO_2^{2+}(60 mg); Ta^{5+}(80 mg); Nb^{5+}(80 mg); Co^{2+}(100 mg); Ba^{2+}(100 mg); Hg^{2+}(100 mg); Mn^{2+}(100 mg); La^{3+}(100 mg); Sc^{3+}(80 mg); Sb^{3+}(100 mg); As^{3+}(80 mg); Fe^{3+}(100 mg); In^{3+}(80 mg); Cr^{3+}(80 mg); Ti^{4+}(30 mg); Zr^{4+}(30 mg); Th^{4+}(80 mg); V^{5+}(30 mg); and rare earths (Gd, Pr, Nd, Sm, etc.) (100 mg).

NO_3^{-}(80 mg); NO_2^{-}(80 mg); F^{-}(80 mg); Cl^{-}(80 mg); Br^{-}(80 mg); I^{-}(80 mg); SO_4^{2-}(80 mg) and PO_4^{3-}(40 mg).

The complexing ions such as citrate and tartrate had no effect on the extraction and determination of cerium(IV).

TABLE 4

DETERMINATION OF CERIUM IN STANDARD SAMPLES AND SEA WATER

Cerium sample	Recommended value(37,39) (ppm)	Cerium found (ppm) present method	Standard deviation (n=7)	Coefficient of variation
Cerium standard sample	2.5	2.5	± 0.005	0.002
Monazite Ore	43%	42.8%	± 0.1%	0.002
Seawater, near Bombay				
Thana (Bridge)	0.005	0.004	± 0.001	0.250
Appolo Bunder	0.003	0.004	± 0.001	0.250
Marine lines	0.003	0.003	± 0.001	0.333
Mahim	0.004	0.005	± 0.001	0.200
Belapur	0.003	0.003	± 0.001	0.333

1.4.6 Precision and Accuracy

To test the reliability of the present method, standard cerium samples were analysed. The results represented in Table 4 show that cerium can be determined accurately.

The cerium standard and monazite ore samples were obtained from Indian Rare Earths. The sea water samples were collected from Bombay and used (one litre) as such for the determination of cerium(37). Values for standard cerium analysis were obtained by emission spectrographic and radioactive tracer technique. Analysis was carried at Radiochemistry Division, B.A.R.C., Bombay (38,39).

The cerium samples were dissolved in 12 M HCl, oxidised with HNO_3 and evaporated to dryness. The residue was redissolved in 1 M H_2SO_4. Then 0.1 M potassium permanganate solution was added drop by drop until a pink colour persisted for 5 min. The solution was finally diluted to 100 ml with 0.05 M H_2SO_4.

1.4.7 Stoichiometry of the Complex

Job's continuous variation method (40) and molar ratio method (41) were used to determine the ratio of cerium(IV) to PTCHA in the extracted species at pH 9.0 which showed that cerium to ligand ratio is 1:4.

2. EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM(V)

2.1 SUMMARY

A simple rapid and selective method for the solvent extraction and spectrophotometric determination of microgram amount of niobium(V) has been described. The niobium is quantitatively extracted with N-p-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid (PTCHA) into chloroform from 8-10 M HCl, exhibits a maximum absorbance at 380 nm with a molar absorptivity 6.3×10^4 l mol^{-1} cm^{-1}. The system obeys Beer's law in the range of 0.1-1.25 μg/ml of niobium(V). The various parameters for the optimum extraction conditions are discussed. The separation of niobium(V) from tantalum(V) is described and the niobium is determined in standard samples of high purity steel and alloys.

2.2 INTRODUCTION

Various methods are reported in literature for the determination of niobium(V), but many of them lack in sensitivity and exhibits poor selectivity due to the interference of several commonly associated metal ions (42). Hydroxamic acids have been extensively used as a potential analytical reagent for several metal ions (5-6) and also used for the gravimetric (14,43,44) and spectrophotometric (45-48) determination of niobium(V). In most of the cases the niobium(V)-hydroxamates are colourless which are complexed with either thiocyanate or with some chromogenic reagents for the estimation of niobium in the visible region. Recently, the N-substituted cinnamohydroxamic acids were found to form coloured complexes with niobium(V), which are extractable into organic solvents from strongly acidic media (46).

The present work is concerned with the exploration of several newly synthesised N-arylhydroxamic acids as the reagents for microgram determination of niobium(V). The niobium is extracted with the chloroform solution of the reagent from the higher acidic media. Optimum conditions for its analytical determinations were established. Many cations and anions do not interfere in the estimation of niobium, are described in this paper. The present method is used for the determination of niobium in high purity steel and alloy samples.

2.3 EXPERIMENTAL

2.3.1 Chemicals and Reagents

All the chemicals used were of AnalaR grades of B.D.H. unless otherwise specified.

2.3.2 N-Arylhydroxamic Acids

The N-arylhydroxamic acids used were synthesised as described in CHAPTER II. Their 0.05% (w/v) chloroform solutions were used for the extraction purposes.

2.3.3 Niobium(V) Solution

It was prepared by fusing Nb_2O_5 with potassium bisulphate and dissolving the fused mass in 1 M tartaric acid. The final concentration of the metal solution was estimated gravimetrically (44) and spectrophotometrically (45).

2.3.4 Stannous Chloride

40% (w/v) solution was prepared in concentrated hydrochloric acid.

2.3.5 Procedure

To a separatory funnel, transfer an aliquot containing 6.26 μg/ml of niobium solution, 1 ml of $SnCl_2$ solution and conc HCl and distilled water to get a final acidity of 9.0 M HCl in a total volume of 15 ml. Add 10 ml of reagent solution in chloroform and shake for 5 min. Separate the organic layer and collect it in a 25-ml volumetric flask after drying by passing through a cotton plug. Repeat the extraction with 5 ml more of the reagent to ensure the complete recovery of the metal ion. Collect the extract in the same flask after drying and make up to the mark with chloroform. Measure the absorbance of the complex at 380 nm against a reagent blank.

2.4 RESULTS AND DISCUSSION

The spectral characteristics of the niobium-hydroxamic acids complexes are summarized in Table 5. From the preliminary studies, it is observed that PTCHA is the most sensitive reagent amongst the N-arylhydroxamic acids studied here. Hence the optimum conditions for the extraction of niobium with PTCHA has been further investigated. Compounds II-V form almost colourless complexes with niobium(V) having a maximum absorbance at 355-360 nm except PTCHA which forms yellow coloured complex with niobium(V). The shift to higher wavelength may be due to the presence of the conjugated double bond in the reagent. While in the compounds IV-V, the functional carbonyl group is separated from the phenyl group by a neocarbon nucleus, which breaks the conjugation in the reagent causes the lower shift in the absorbance maximum of the complex.

TABLE 5

SPECTRAL CHARACTERISTICS OF Nb-HYDROXAMIC ACIDS COMPLEXES

Niobium = 12.52 μg/25 ml   Solvent = Chloroform
HCl = 9.0 M

Compd. No.	Hydroxamic acid	λ max	Colour	Molar absorptivity (l mol^{-1} cm^{-1})
I	N-p-Chlorophenyl-3,4,5-trimethoxy-cinnamo-	380	Yellow	6.3×10^4
II	N-p-Chlorophenyl-p-butoxybenzo-	360	Light yellow	2.2×10^4
III	N-Phenyl-p-butoxybenzo-	360	Light yellow	2.0×10^4
IV	N-p-Chlorophenyl-p-chlorophenoxy-isobutyro-	355	Yellowish	7.4×10^3
V	N-Phenyl-p-chlorophenoxy-isobutyro-	355	Yellowish	6.0×10^3

2.4.1 Absorption Spectra and Beer's Law

The niobium(V)-PTCHA yellow complex has a maximum absorbance at 380 nm while the reagent absorbs at 326 nm. The molar absorption coefficient of the complex is 6.3×10^4 l mol^{-1} cm^{-1}. Sandell's sensitivity is 0.0015 $\mu g/cm^2$. The system obeys Beer's law within the range of 0.1-1.25 $\mu g/ml$ of chloroform. The colour of the complex is stable for 24 hr.

2.4.2 Acidity and Extraction Time

Extraction of niobium from 1-11 M HCl concentration has been carried out with PTCHA (Table 6). It is observed that as the concentration of the HCl increases the percentage extraction of the metal ion also increases relatively and becomes quantitative (100% E) arround 8.0 M HCl. The 100% extraction is attainable from 8-11 M HCl while higher acidity ($>$ 10 M) tends to make the reagent blank slightly coloured which practically decrease the absorbance of the complex. Hence all the extractions were carried out at 9.0 M HCl. Moreover the extraction of Nb(V) is very fast at 9.0 M HCl and the system attains the equilibrium within 2-3 min.

TABLE 6

EFFECT OF HCl MOLARITY ON THE EXTRACTION OF Nb-PTCHA COMPLEX IN CHLOROFORM

Nb = 12.52 μg/25 ml λ max = 380 nm

HCl (M)	% Extraction	Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$)
5.5	44	2.7×10^4
7.0	67	4.3×10^4
7.5	82	5.2×10^4
8.0	100	6.3×10^4
9.0	100	6.3×10^4
10.0	100	6.3×10^4
10.5	91	5.7×10^4

2.4.3 Effect of Reagent Concentration

Extraction of niobium(12.52 μg/25 ml) was carried out with varying amounts of 0.05% reagent solution in chloroform (Table 7). From the result it is concluded that 4 ml of 0.05% reagent is enough for the quantitative extraction of Nb(V) from 9.0 M HCl. Even though slight excess of the reagent has no adverse effect on the extraction but the large excess of the reagent tends to decrease the absorbance of the complex, due to the high absorbance of the reagent blank.

2.4.4 Effect of Diverse Ions

12.52 μg/25 ml of niobium in the extract was quantitatively determined by the recommended procedure in the presence of following ions (mg): Ni^{2+}(45), Cd^{2+}(20), Ba^{2+}(50), Al^{3+}(40), Be^{2+}(40), Cu^{2+}(45), Fe^{2+}(50), Mn^{2+}(20), Co^{2+}(35), Pb^{2+}(20), Fe^{3+}(50), VO^{2+}(25), VO$_2^+$(8), UO$_2^{2+}$(30), W^{6+}(50), Mo^{6+}(25); citrate, oxalate, acetate and EDTA can be tolerated in more than 100 times excess while interference due to Zr^{4+} and Ti^{4+} can be masked with NaF. The niobium is extracted in presence of tantalum quantitatively from the oxalate solution.

TABLE 7

EFFECT OF REAGENT CONCENTRATION ON THE EXTRACTION OF Nb(V)

Nb(V) = 12.52 μg/25 ml Reagent = 0.05% PTCHA

Solvent = Chloroform λmax = 380 nm

HCl = 9.0 M

Volume of reagent (ml)	Absorbance	Molar absorptivity (l mol^{-1} cm^{-1})
1	0.12	2.2×10^4
2	0.22	4.1×10^4
3	0.29	5.4×10^4
4	0.34	6.3×10^4
6	0.34	6.3×10^4
10	0.34	6.3×10^4
15	0.34	6.3×10^4
20	0.33	6.1×10^4
25	0.32	5.9×10^4

2.4.5 Stoichiometry of the Complex

The composition of the niobium complexes were studied by slope ratio method (40,41) i.e. by plotting the graph between the log of distribution of metal (log $D_{(M)}$ vs log of ligand (PTCHA) concentration [log (ligand)]. The extraction was carried out by taking a fixed amount of niobium and varying the concentration of PTCHA. The plot of log $D_{(M)}$ and -log (ligand) gave a straight line of slope 2 which indicate that the composition of the complex as niobium : PTCHA :: 1 : 2.

The possible reaction is as under

$$NbOCl_3 + 2HA \longrightarrow NbOCl\,A_2 + 2HCl$$

2.4.6 Analysis of the Standard Samples

The niobium was determined in the standard samples of high purity steel and low alloy steel ~~samples.~~ The results are given in Table 8.

TABLE 8

DETERMINATION OF NIOBIUM IN ALLOYS AND STEEL SAMPLES

Standard Sample	Niobium certified value (μg)	Niobium found (μg)	Relative standard* deviation %	Relative error %
NBS 123b (Stainless steel)	0.700	0.705	5.0	0.71
NBS 345 (Cr, Ni Steel)	0.210	0.208	1.0	0.95
32E low-alloy Steel	15.0	15.01	1.0	0.06
33d low-alloy Steel	15.0	14.98	2.0	0.13

* Average of six determination

3. EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF TANTALUM(V) WITH SUBSTITUTED N-ARYLHYDROXAMIC ACIDS

3.1 SUMMARY

A sensitive and rapid method for the extraction and spectrophotometric determination of tantalum(V) in trace amounts with the newly synthesised N-arylhydroxamic acids have been described. The tantalum-N-p-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid (Ta-PTCHA) complex is extractable into benzene from a strongly acidic medium with a molar absorptivity 2.9×10^4 l mol^{-1} cm^{-1} at 385 nm. The effects of brilliant green (BG) and ammonium thiocyanate on the binary complex are evaluated.

3.2 INTRODUCTION

Hydroxamic acids have received a great deal of attention as gravimetric and spectrophotometric reagents for several metal ions (5-6). A few hydroxamic acids were reported as analytical reagents for tantalum(V) (44,47,48). Hydroxamic acids form the stable colourless complexes with tantalum(V) in highly acidic media which are extractable into organic solvents, and hence a direct colorimetric method is lacking. But the sensitivity of the method can be increased with ternary complexes by the addition of ammonium thiocyanate or some chromogenic reagents.

The present investigation comprises of exploring the applicability of the newly synthesised substituted N-arylhydroxamic acids as reagents for tantalum(V). Out of the five hydroxamic acids studied here, N-p-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid (PTCHA) has been found to form yellow coloured complex with tantalum while other hydroxamic acids form colourless complexes. The ternary systems of Ta-hydroxamic acids with thiocyanate and brilliant green have been studied.

3.3 EXPERIMENTAL

3.3.1 Reagents

All the chemicals used were of AnalaR Grade of B.D.H.

Hydroxamic acids used for the extraction purposes were synthesised as described in CHAPTER II. A 1% (w/v) solution of the reagent was prepared in 95% ethanol.

3.3.2 Brilliant Green

0.01% (w/v) solution was prepared in chloroform.

3.3.3 Ammonium Thiocyanate

25% (w/v) solution was prepared in distilled water.

3.3.4 Stannous Chloride

40% (w/v) solution in conc HCl was prepared by dissolving it with gentle heating.

3.3.5 Tantalum Solution

Tantalum(V) stock solution was prepared by fusing Ta_2O_5 with potassium bisulphate for 24 hr and the fused mass was extracted with 4% (w/v) ammonium oxalate solution. Filtered the solution and diluted the filtrate with 4% ammonium oxalate solution. The final concentration of the tantalum was determined gravimetrically (44) and spectrophotometrically (49).

3.3.2 Apparatus

All the absorbance measurements were made in 1.0 cm quartz cells on VSU2-P spectrophotometer.

3.3.3 Procedure

A. Determination of Ta with PTCHA

Take an aliquot of Ta solution (27.8 μg) in a 60 ml separatory funnel, add 1 ml of $SnCl_2$ and adjust the acidity to 9.0 M with conc HCl and distilled water to get a final volume of 20 ml. Add 1 ml of the reagent in alcohol, allow to stand for 1 min and extract the complex with 10 ml of benzene. Transfer a portion of the organic phase through a cotton plug into a 1.0 cm cell and measure the absorbance of the complex at 385 nm against the reagent blank.

3.3.4 B. Determination of Ta with PTCHA and BG

Follow the procedure as above. The organic layer is collected in a 25-ml volumetric flask, after drying by passing through a cotton plug. Wash the cotton with 5 ml of benzene and collect the washing in the same flask. Add 2 ml of 0.01% BG in chloroform to the flask and diluted with benzene. Measure the absorbance of the complex at 635 nm against a reagent blank.

3.3.5 Determination of Ta with PTCHA and NH_4SCN

To the Ta solution (27.8 μg) add 1 ml of $SnCl_2$ and adjust the acidity to 9.0 M with con HCl and distilled water to a final volume of 20 ml. Add 1 ml of the reagent, allow the solution to stand for a min and extract with 10 ml of benzene. Separate and discard the aqueous phase. Add 5 ml of ammonium thiocyanate solution and adjust the acidity of the aqueous phase with conc HCl and distilled water to 5 M HCl. Shake for 2 min and drain off a portion of the benzene layer after drying by passing through a cotton plug. Measure the absorbance at 405 nm against the reagent blank.

3.4 RESULTS AND DISCUSSION

The spectral characteristics of the tantalum complexes with the hydroxamic acids studied here are summarized in Tables 9 and 10. The preliminary studies showed that except PTCHA, all other acids form colourless complexes with tantalum. Tantalum forms an yellow coloured complex with PTCHA, extractable from 9.0 M HCl with benzene. The addition of brilliant green or thiocyanate has shown to impart a bathochromic shift and thereby the ternary complex have the maximum absorbance in the visible region.

3.4.1 Absorption Spectra and Beer's Law

The yellow complex of Ta-PTCHA has a molar absorptivity 2.9 x 10^4 l mol^{-1} cm^{-1} at 385 nm. The reagent has a maximum absorption at 326 nm. The Sandell sensitivity of the method is 0.006 $\mu g\ cm^{-2}$. The system obeys Beer's law in the range 0.3 to 5.0 $\mu g\ ml^{-1}$ at 385 nm.

The Ta-PTCHA-BG complex has a maximum absorbance at 635 nm, while the Ta-PTCHA-SCN complex absorbs at 405 nm and the molar absorptivities are 2.3 x 10^4 l mol^{-1} cm^{-1}, 1.5 x 10^4 l mol^{-1} cm^{-1}, respectively.

TABLE 9

SPECTRAL CHARACTERISTICS OF THE TERNARY SYSTEM OF Ta-HYDROXAMIC ACID-SCN IN BENZENE

Ta = 27.8 μg/25 ml Acidity = 5.0 M HCl

NH_4SCN = 5 ml [25% (w/v) in H_2O]

Compd. No.	Hydroxamic acid	λ max	Molar absorptivity (l mol^{-1} cm^{-1})
I	N-p-Chlorophenyl-3,4,5-trimethoxy-cinnamo-	405	1.5×10^4
II	N-p-Chlorophenyl-p-butoxybenzo-	355	1.7×10^4
III	N-Phenyl-p-butoxybenzo-	355	1.5×10^4
IV	N-p-Chlorophenyl-p-chlorophenoxy-isobutyro-	345	7.1×10^3
V	N-Phenyl-p-chlorophenoxy-isobutyro-	345	6.5×10^3

TABLE 10

SPECTRAL CHARACTERISTICS OF THE TERNARY SYSTEMS OF Ta-HYDROXAMIC ACID-BG IN BENZENE

Ta = 27.8 μg/25 ml Acidity = 9.0 M HCl

BG = 2 ml 0.01% (w/v) in $CHCl_3$

Compd. No.	Hydroxamic acid	λmax (nm)	Molar absorptivity (l mol^{-1} cm^{-1})
I	N-p-Chlorophenyl-3,4,5-trimethoxycinnamo-	635	2.3×10^4
II	N-p-Chlorophenyl-p-butoxybenzo-	635	6.8×10^3
III	N-Phenyl-p-butoxybenzo-	635	6.2×10^3
IV	N-p-Chlorophenyl-p-chlorophenoxy-isobutyro-	635	4.5×10^3
V	N-Phenyl-p-chlorophenoxyisobutyro-	635	4.0×10^3

Beer's law obeys in the 0.5-6.0 $\mu g\ ml^{-1}$ and 1.0-10.0 $\mu g\ ml^{-1}$, respectively. The spectral characteristics studied here are summarized in Tables 9 and 10.

3.4.2 Effect of HCl Molarity

Maximum colour intensities for Ta-TMCHA and Ta-TMCHA-BG complexes were observed at 8-10 M HCl while the optimum condition for Ta-TMCHA-SCN complex is 5.0-6.0 M HCl. Deviation from the above acidities found to give incomplete extraction (Table 11).

3.4.3 Effect of Solvents

Amongst the several solvents studied for extraction viz. carbon tetrachloride, chloroform, iso-butylmethyl ketone, iso-amyl alcohol, benzene and toluene, the benzene and toluene were found to be most suitable for the extraction of Ta complexes (Table 12). Benzene has been selected for the studies as the solubility of PTCHA was found more than that in toluene.

3.4.4 Effect of Reagent Concentration

Extraction of tantalum was studied with varying amounts of the reagent at the optimum conditions. It has been observed that 1 ml of 1% (w/v) reagent was enough for the complete extraction of tantalum. Excess

TABLE 11

EFFECT OF HCl MOLARITY ON THE EXTRACTION OF Ta-PTCHA-SCN AND Ta-PTCHA-BG COMPLEXES

Ta = 55.6 μg/25 ml   PTCHA = 1 ml of 1% (w/v) in Ethanol

HCl (M)	Absorbance	Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$)
	Ta-PTCHA-SCN (λmax 405 nm)	
1.0	0.04	0.3×10^4
2.0	0.10	0.7×10^4
3.0	0.15	1.2×10^4
4.0	0.18	1.4×10^4
5.0	0.19	1.5×10^4
6.0	0.19	1.5×10^4
7.0	0.17	1.3×10^4
	Ta-PTCHA-BG (λmax 635 nm)	
4.0	0.14	1.1×10^4
6.0	0.21	1.7×10^4
7.0	0.26	2.1×10^4
8.0	0.29	2.3×10^4
9.0	0.29	2.3×10^4
10.0	0.29	2.3×10^4
10.5	0.27	2.2×10^4

TABLE 12

EFFECT OF SOLVENTS ON THE EXTRACTION OF Ta-PTCHA-SCN AND Ta-PTCHA-BG COMPLEXES

A	B
Ta = 27.8 μg/10 ml	Ta = 55.6 μg/25 ml
HCl = 5.0 M	HCl = 9.0 M
max = 405 nm	λmax = 635 nm

	Solvent	Colour of the complex	Absorbance	Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$)
A.	Ta-PTCHA-SCN			
	Benzene	Y	0.24	1.5×10^4
	Toluene	Y	0.24	1.5×10^4
	Chloroform	Y	0.20	1.3×10^4
	Carbon tetrachloride	Y	0.12	0.8×10^4
	Iso-butyl methyl ketone	LY	0.08	0.5×10^4
	Iso-amyl alcohol	LY	0.06	0.4×10^4
B.	Ta-PTCHA-BG			
	Benzene	G	0.29	2.3×10^4
	Toluene	G	0.26	2.1×10^4
	Chloroform	LG	0.18	1.5×10^4
	Carbon tetrachloride	LG	0.17	1.4×10^4
	Iso-butyl methyl ketone	LG	0.10	0.8×10^4
	Iso-amyl alcohol	LG	0.08	0.6×10^4

Y = Yellow; LG = Light yellow

G = Green; LG = Light green

reagent can be used without any difficulty for the ternary complexes (Ta-PTCHA-BG) but a large excess of reagent in the binary complex (Ta-PTCHA) tends to increase the absorbance of the blank.

3.4.5 Effect of Ammonium Thiocyanate

The maximum colour intensity of the Ta-PTCHA-SCN complex was found in the presence of 5-6 ml of 25% NH_4SCN. Further the increase of the ammonium thiocyanate found to decrease the absorbance of the complex.

3.4.6 Effect of Brilliant Green

2.0 ml of 0.01% (w/v) solution of BG in chloroform was enough for complexing 6 μg/ml of Ta. Excess addition of BG tends to increase the absorbance of the blank.

Separation of Tantalum in Presence of Niobium

Generally Nb(V) interfers in the determination of tantalum. Tantalum can be estimated quantitatively in presence of Nb(V) by marking niobium with ammonium oxalate and extracting Ta(V) as Ta-PTCHA-BG complex into benzene. 35 μg/ml of Nb(V) can be easily separated by the present method (Table 13). Higher amounts of Nb was found to interfere in the determination of tantalum.

TABLE 13

DETERMINATION OF TANTALUM IN PRESENCE OF NIOBIUM

Acidity = 9.0 M HCl BG = 2 ml of 0.1% (w/v) in $CHCl_3$

λ max = 635 nm

Tantalum (μg/25 ml)	Niobium added (μg/25 ml)	Tantalum found (μg/25 ml)	Relative error (%)
27.8	10.0	27.7	0.4
	20.0	27.8	0.4
	25.0	27.9	0.5
	30.0	28.1	1.0
	35.0	28.0	0.7
55.6	10.0	55.6	0.2
	20.0	55.4	0.4
	30.0	55.7	0.3
111.2	10.0	111.1	0.1
	20.0	111.4	0.2
	30.0	111.3	0.1

3.4.7 Effect of Diverse Ions

Tantalum (27.8 μg) was determined by the procedure B in the presence of 40 mg each of the following ions:- Li^+, B^{3+}, Na^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, Y^{3+}, Mo^{6+}, Sn^{4+}, Ba^{2+}, La^{3+}, Rare Earths, Th^{4+}, U^{6+}, Pb^{2+}, V^{5+}, W^{6+}, Co^{2+}, Cu^{2+}, Cr^{6+}, Be^{2+}, Sr^{2+}, Zr^{4+}, Bi^{3+}, Ni^{2+}, Zn^{2+}, Pd^{2+}, Ag^+. Amongst them Zr^{4+}, Bi^{3+} and Ag^+ were found interfering; which can be eliminated by masking with H_3PO_4, thioglycolic acid and thiourea, respectively. Interference due to many reduceable metal ions have been eliminated using $SnCl_2$ in the recommended procedure.

3.4.8 Stoichiometry of the Complex

The composition of the tantalum complexes were studied by slope ratio method (40,41) i.e. by plotting the graph between the log of distribution of metal log $D_{(M)}$vs log of ligand (PTCHA) concentration, log (ligand). The extraction was carried out by taking a fixed amount of niobium and varying the concentration of PTCHA. The plot of log $D_{(M)}$ and -log (ligand) gave a straight line of slope 2 which indicate that the composition of the complex as tantalum : PTCHA :: 1 : 2.

TABLE 14

DETERMINATION OF TANTALUM IN STANDARD SAMPLES*

Samples	Tantalum (%)	Tantalum found (%)	Relative error (%)
BCR-1 (52/19)	0.80	0.82	2.5
G 2 (108/15)	0.75	0.76	1.3
PCC-1 (2/1)	0.10	0.10	1.0
AGV-1 (74/19)	0.90	0.91	1.1

* Geological (USGS) samples

3.4.9 Analysis of the Standard Samples

The tantalum was determined in the standard samples of high purity alloy and steel samples. The results are given in Table 14.

4. EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM(IV)

4.1 SUMMARY

Extraction spectrophotometric method for the determination of titanium(IV), based on the formation of Ti-N-p-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid (Ti-PTCHA) chelate extractable into chloroform, from strongly acidic media is described. The complex exhibits maximum absorbance at 380 nm with a molar absorptivity 1.7×10^4 l mol^{-1} cm^{-1}. Comparison of the sensitivity with the several synthesised hydroxamic acids for the extraction photometric determination of titanium(IV) has been made. Various parameters for the optimum extraction condition including the effect of thiocyanate, have been discussed.

4.2 INTRODUCTION

Several hydroxamic acids have been reported for the extraction as well as photometric determination of various metal ions (5-7). But only a few hydroxamic acids were studied for the quantitative estimation of titanium(IV). Titanium forms a yellow coloured complex with hydroxamic acids, which can be extracted into organic solvents at higher acidities. It has been observed that change in the substitution in the N- and C- phenyl ring of the hydroxamic acids, alter the sensitivity and selectivity of the reagent towards metal ions. N-phenylbenzohydroxamic acid has been reported for the determination of titanium. The complexes have the maximum absorbance at 380 and 420 nm, with a molar absorptivities 6.7×10^3 and 3.8×10^3 l mol^{-1} cm^{-1} respectively (50,51). Addition of thiocyanate was found to enhance the sensitivity of the method by the formation of a ternary complex. The sensitivity of the reagent has been observed to increase in the case of N-phenylcinnamohydroxamic acids due to the increase in conjugation in the C-phenyl ring (52-54). But the interference of the diverse ions are found to be the same. With this view five new hydroxamic acids were synthesised and their sensitivity and selectivity towards the extraction photometric estimation of titanium have been explored. Among the acids studied, N-p-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid (PTCHA) is found to be the most sensitive reagent for titanium. The effect of thiocyanate, acidity, reagent concentration, on the extraction and spectrophotometric determination of titanium is reported.

4.3 EXPERIMENTAL

4.3.1 Reagents and Chemicals

All the chemicals used were of AnalaR grades of B.D.H. The preparation of the hydroxamic acids is described in CHAPTER II. A 0.1% (w/v) of the reagent solution in chloroform has been used for extraction purposes.

Titanium solution is prepared by heating 0.20 g of TiO_2 in a pyrex flask with 8.0 g of ammonium sulphate and 25 ml of conc sulphuric acid for 4 hrs. After cooling the resulting solution was transferred into a 250-ml volumetric flask containing 150 ml of water. The pyrex flask was washed with 5% sulphuric acid and finally diluted with 5% sulphuric acid. The final concentration (1.46×10^{-2} M) was determined volumetrically (35) and colorimetrically (50,51).

Thiocyanate solution (0.6 M) is prepared by dissolving required amount of ammonium thiocyanate in distilled water and standardised by Volhard's method (55).

Spectral measurements were made on VSU2-P spectrophotometer with 1.0 cm cells.

4.3.3 Procedure

Transfer an aliquot of Ti(IV) solution containing 28 μg of metal into a separatory funnel and adjust the acidity of the aqueous phase to 9 M with conc HCl and distilled water to final volume of 15 ml. Add 8 ml of 0.1% reagent in chloroform and shake the contents for 10 min. Collect the organic layer in a 25-ml volumetric flask after drying over anhydrous sodium sulphate. Repeat the extraction with 2 ml of the reagent to ensure the complete recovery of the titanium. Collect the extract in the same flask and dilute the extracts upto the mark with chloroform. Measure the absorbance of the yellow complex at 380 nm against the reagent blank prepared in the same manner.

To study the ternary complex of Ti-hydroxamate with thiocyanate, add 10 ml of (6 M) ammonium thiocyanate solution to the mixture prior to the acidity adjustment and extract the complex as mentioned above.

4.4 RESULTS AND DISCUSSION

4.4.1 Absorption Spectra and Beer's Law

The spectral characteristics of the titanium-hydroxamate complexes are summarized in the Table 15. The N-p-Cl-phenyl-3,4,5-trimethoxycinnamohydroxamic acid (PTCHA) solution in chloroform extracts Ti(IV) from 8-11 M HCl. The extracted complex exhibits a maximum absorbance at 380 nm with a molar absorptivity 1.7×10^4 $l\ mol^{-1}\ cm^{-1}$; and the reagent has an absorbance maxima at 326 nm in ethanol. While in case of other hydroxamic acids a general absorbance curve is obtained in between 400 and 420 nm and hence all the measurements were made at 410 nm and the absorbance was found to be reproduceable in all the cases.

Beer's law is obeyed in the range of 0.1-3.3 μg/ml titanium as Ti-PTCHA complex at 380 nm.

4.4.2 Effects of Acidity

There is no noticeable colour observed in the chloroform extract upto 5 M HCl but the complex is found extractable from 6 M HCl with an appearence of yellow colour. The extraction increases with increase of HCl

TABLE 15

SPECTRAL CHARACTERISTICS OF Ti-HYDROXAMIC ACID COMPLEXES IN CHLOROFORM

Titanium = 28 μg/25 ml Acidity = 9 M HCl
Reagent = 10 ml (0.1% in Chloroform)

Compd. No.	Hydroxamic acids	λ_{max} (nm)	Molar absorptivity (l mol^{-1} cm^{-1})
I	N-p-Chlorophenyl-3,4,5-trimethoxycinnamo-	380	1.7×10^4
II	N-p-Chlorophenyl-p-butoxybenzo-	410	6.5×10^3
III	N-Phenyl-p-butoxybenzo-	410	6.3×10^3
IV	N-p-Chlorophenyl-p-chlorophenoxyisobutyro-	410	1.4×10^3
V	N-Phenyl-p-chlorophenoxy-isobutyro-	410	1.3×10^3

molarity upto 9.5 M HCl (Table 16). But at higher acidities beyond 9.5 M, the chloroform extract is found to be turbid, and difficult to dry on sodium sulphate. Optimum molarity is taken as 9.0 M HCl and all the studies were carried out at this molarity.

4.4.3 Effect of Reagent and Time

The 28 μg of the titanium was extracted with varying amount of reagent concentration. It has been observed from the Table 17 that 2 ml of 0.1% of the reagent is enough for the complete extraction of the titanium. A slight excess of the reagent can also be used without any difficulty, but the large excess of the reagent increases the blank absorbance.

Shaking time of 5 min is enough for quantitative extraction of the titanium. The chloroform extracts of the complex are stable for 2 days.

4.4.4 Effect of Ammonium thiocyanate

The sensitivity of the method is enhanced by the use of thiocyanate for the extraction of titanium with hydroxamic acid as Ti-PTCHA-SCN ternary complex. The results indicate that a maximum of 1.0 ml ammonium thiocyanate (6 M) is sufficient for the ternary

TABLE 16

EFFECT OF HCl MOLARITY ON THE EXTRACTION OF TITANIUM WITH N-p-CHLOROPHENYL-3,4,5-TRIMETHOXYCINNAMOHYDROXAMIC ACID

Titanium = 28 μg/25 ml λ_{max} = 380 nm

HCl Molarity	% E	Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$)
2	45	0.4×10^4
4	51	0.8×10^4
6	61	1.0×10^4
7	86	1.4×10^4
8	100	1.7×10^4
9	100	1.7×10^4
10*	100	1.7×10^4
11*	100	1.7×10^4

* The extract becomes turbid

TABLE 17

EFFECT OF REAGENT CONCENTRATION IN THE EXTRACTION OF TITANIUM

Reagent = 0.1% TMCHA in $CHCl_3$; Titanium = 28 μg/ml
λ max = 380 nm Acidity = 9 M HCl

Volume of reagent (ml)	Absorbance	Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$)
0.1	0.050	0.2×10^4
0.2	0.095	0.4×10^4
0.4	0.250	1.0×10^4
1.0	0.350	1.5×10^4
2.0	0.400	1.7×10^4
4.0	0.400	1.7×10^4
10.0	0.400	1.7×10^4
15.0	0.400	1.7×10^4
20.0	0.395	1.7×10^4

complex formation and the molar absorptivity of Ti-PTCHA-SCN complex was found to be 2.7 x 10^4 l mol^{-1} cm^{-1} at 380 nm.

4.4.5 Stoichiometry

The composition of extracted species has been studied by Job's continuous variation method (40) and slope ratio method (41). In both the cases the metal to ligand ratio is 1:2 for the binary Ti-PTCHA complex and slope ratio method gives 1:2:1 for the ternary Ti-PTCHA-SCN complex as follows:

$$\mathrm{TiOCl_2 + 2\ HA \xrightarrow{HCl} (TiOCl\ A_2)^- + 2H^+ + Cl^-}$$

$$\mathrm{(TiOCl\ A_2)^- + SCN^- \xrightarrow{HCl} (TiOA_2\ SCN)^- H^+ + 2Cl^-}$$

4.4.6 Effect of Diverse Ions

Titanium (28 μg/25 ml) was determined in the presence of a large number of diverse ions (Table 18). Moderate amounts of various metal ions and anions commonly associated with titanium were tolerated except chromium, vanadium, molybdenum, zirconium and fluoride which are interfering. The interferences of vanadium was checked by adding $FeSO_4$ while the molybdenum was removed by precipitation with sulphide, prior to extraction.

TABLE 18

EFFECT OF DIVERSE IONS

(Ti = 28 μg per 25 ml)

Foreign ion	Added as	Tolerance limit (mg)
Ag^{+}	$AgNO_3$	25
Cd^{2+}	$CdSO_4$	30
Pb^{2+}	$Pb(NO_3)_2$	30
Be^{2+}	$BeSO_4$	30
Mg^{2+}	$MgSO_4$	30
Ca^{2+}	$Ca(NO_3)_2$	30
Ba^{2+}	$BaCl_2$	25
Sn^{2+}	$SnCl_2$	25
Co^{2+}	$CoCl_2$	25
Cu^{2+}	$CuSO_4$	30
Hg^{2+}	$HgCl_2$	25
Ni^{2+}	$NiCl_2$	20
Zn^{2+}	$ZnSO_4$	35
Mn^{2+}	$MnCl_2$	20
Cr^{3+}	$CrCl_3$	20*
Al^{3+}	$AlCl_3$	35
V^{5+}	NH_3VO_3	25*
$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24}$	10*
Zr^{4+}	$Zr(NO_3)_4$	5*
Cl^{-}	NaCl	40
Br^{-}	NaBr	15
I^{-}	NaI	20
CH_3COO^{-}	CH_3COONa	40
Cit^{3-}	Citric acid	40

* Masking agents used

TABLE 19

DETERMINATION OF TITANIUM IN STANDARD SAMPLES

No.	Sample (BCS)	Certified value (%)	Obtained by* present method (%)	Obtained by AAS (%)
243	Ferrotitanium (Ti,Al,C,Cu,Si,Mn)	40.00	39.80	40.10
236	Cast iron (Si,S,P,Mn,Ti)	0.102	0.10	0.10
182	Silicon-aluminium alloy (Si,Fe,Cu,Mn,Mg, Ti,Zn,Ni)	0.210	0.20	0.21

* The values are averages of 8 determinations

Moderate amounts of zirconium and chromium were tolerate in presence of tin(II) chloride.

4.4.7 Analysis of the Standard Samples

The results for the determination of titanium in steel are given in Table 19.

5. EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V)

5.1 SUMMARY

Five new substituted hydroxamic acids were synthesised and used for extraction and spectrophotometric determination of vanadium(V) in trace amount. The binary complex of vanadium(V) with N-p-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid (PTCHA) and the mixed ligand complex of vanadium(V) with N-p-chlorophenyl-p-chlorophenoxyisobutyrohydroxamic acid (PPBHA) and thiocyanate were studied. The molar absorptivities of the bluish violet vanadium(V) hydroxamate and mixed ligand complexes are 6.9×10^3 and 1.1×10^4 l mol^{-1} cm^{-1} respectively. The vanadium is also determined with AAS and the method is applied for its determination in steel, alloy, rock and environmental samples.

5.2 INTRODUCTION

The hydroxamic acids are the versatile reagent used in organic, inorganic and pharmaceutical analysis (5-7). N-phenylbenzohydroxamic acid(PBHA) is extensively used for the spectrophotometric and colorimetric determination of several metal ions (5-7). Several substituted N-arylhydroxamic acids were synthesized in view of having a better sensitivity and selectivity for metal ions. It has been found that increase in the length of conjugation by the introduction of a side chain double bond, (-CH = CH-) between the carbonyl carbon atom and phenyl group caused a conspicuous increase in the molar absorptivity as in the case of N-phenylcinnamohydroxamic acid (56,57). The selectivity and sensitivity of the reagent is also increased by the introduction of an electrophilic group or substituent in the benzene ring. In the present investigation, five new substituted hydroxamic acids were synthesized and their complexing capacity for vanadium(V) including mixed ligand complex with thiocyanate is studied. The several parameters for the optimum extraction are discussed. The developed spectrophotometric method is compared with AAS and can be applied for the trace determination of vanadium in alloy, steel, rock and environmental samples.

5.3 EXPERIMENTAL

5.3.1 Reagents

All the chemicals used were of G.R. or AnalaR grades of E. Merck and B.D.H. respectively.

Vanadium(V) solution was prepared by dissolving 0.0585 g of ammonium metavanadate in 500 ml redistilled water and its final concentration (1.0 x 10^{-2} M) was determined spectrophotometrically (5-7).

Hydroxamic acids were synthesised as described in CHAPTER II. A 0.1% (w/v) reagent solution of N-arylhydroxamic acids were prepared in ethanol free chloroform and methyl isobutyl ketone (MIBK), for binary and mixed-ligand complexes respectively.

Ammonium thiocyanate solution (026 M) was prepared in doubly distilled water and standardised by Volhard's method (55).

Buffer solution was prepared from potassium chloride and hydrochloric acid (34,35).

5.3.2 Apparatus

The spectral measurements were made on VSU2-P (C.Z. Jena) Spectrophotometer.

A Varian Techtron Model AA-6 atomic absorption spectrophotometer (AAS) equipped with HCN-V hollow cathod lamp was used. The 318.4 nm vanadium line and nitrous oxide and acetylene gas were used.

5.3.3 Procedure

5.3.3.1 Binary Complex

Transfer 2 ml of vanadium(V) solution (1.0×10^{-3} M) into a 60-ml separatory funnel. Adjust the acidity of the aqueous phase 6-8 M HCl with conc hydrochloric acid and distilled water to a final volume of 25 ml. Add 10 ml of 0.1% reagent (PTCHA) solution (in chloroform) and shake vigorously for 2-5 min. Allow the phases to separate, dry the chloroform extract over anhydrous sodium sulphate and transfer it into a 25-ml volumetric flask. To ensure the complete recovery of vanadium, repeat the extraction with 2 x 2 ml of the reagent solution, wash the sodium sulphate with chloroform and finally dilute the extracts with chloroform to 25 ml. Measure the absorbance of the bluish violet chloroform extract at 570 nm against the reagent blank.

For AAS measurements, the extracts either directly or after back extraction of vanadium into 0.01 M HNO_3 were aspirated into the flame as per EPA method (58).

5.3.3.2 Mixed-Ligand Complex

Transfer 1 ml of vanadium(V) solution (1.0×10^{-3} M) into a 60-ml separatory funnel and adjust the pH 2-3 with (KCl + HCl) buffer. Add 10 ml of 0.1% reagent (PPBHA) solution in MIBK. Shake for 5 min and add 5 ml of ammonium thiocyanate (0.26 M) solution. Continue shaking for 5 min, separate the bluish violet extract, dry over anhydrous sodium sulphate and transfer into a 25 ml volumetric flask. Wash the sodium sulphate with MIBK, collect into the same flask and finally dilute the extract with MIBK upto the mark. Measure the absorbance of the mixed complex at 540 nm against the reagent blank.

The sample solutions for the determination of vanadium(V) in rock, steel and environment were prepared as below.

5.3.4 Rock Samples

The solutions for the rock samples were prepared as B solutions of Shapiro and Brannock (59).

5.3.5 Steel Samples

A weighed steel sample was dissolved in conc hydrochloric acid, oxidized with nitric acid and evaporated to dryness. The residue was redissolved in conc hydrochloric acid and oxidized with ammonium persulfate, filtered and finally diluted to 100 ml with 0.1 M hydrochloric acid.

5.3.6 Natural Resources and Plant Samples

The plants were dried in the oven and then heated to ash. Depending on the concentration of metal ion, 5-10 g samples were digested with an excess of hydrochloric and nitric acids. The hot solution was filtered or centrifuged off any siliceous residue. The filtrate was evaporated to dryness and finally diluted to 100 ml with 0.1 M hydrochloric acid.

5.3.7 Soil Samples

Dried and weighed amount of soil sample was digested with conc hydrochloric and nitric acids for 2-3 hr. Residue was boiled with 0.1 M hydrochloric acid, centrifuged, filtered and the filtrate was evaporated to dryness. Finally, the solution was prepared in 0.1 M hydrochloric acid.

5.3.8 Blood Samples

2 ml blood sample was digested with conc hydrochloric acid for 2-3 hr, centrifuged and filtered. The filtrate was evaporated to dryness and finally the solution was diluted to 25 ml with 0.1 M hydrochloric acid.

Aliquots from the above prepared samples were taken and the vanadium content was determined with AAS and PPBHA using the procedure described for the mixed-ligand complex. The results are given in Tables 23 and 24.

5.4. RESULT AND DISCUSSION

The spectral data of vanadium complexes with the synthesised N-arylhydroxamic acids are given in Table 20. All the compounds except IV and V are more sensitive for vanadium(V) comparedto N-phenylbenzohydroxamic acid (PBHA). The spectra of these complexes show the strong bathochromic and hyperchromic effect with respect to PBHA. The effects of $\pi - \pi$ and n- π system present in conjugation with the functional group and substituents in the ligand molecule is transmitted in the spectra of PTCHA-vanadium complex. The complexes of compounds IV and V with vanadium show a decreased molar absorptivity than PBHA. The reddish violet complex formed from 4-8 M HCl shows maximum absorbance at 500-510 nm. It is observed that the presence of tertiary carbon group between the functional carbonyl group and the C-phenyl ring reduces the sensitivity of the reagent (compound IV and V) can be due to the decreased conjugation in the reagent. Similarly, the introduction of lower alkoxy groups in the para position of the C-phenyl ring usually increases the

TABLE 20

SPECTRAL CHARACTERISTICS OF VANADIUM-HYDROXAMIC ACIDS COLOURED SYSTEM IN CHLOROFORM

Compd. No.	Hydroxamic acid	Colour of the complex in chloroform	Wavelength of maximum absorbance (nm)	Optimum HCl Molarity	Beer's law ppm	Molar absorptivity ($1\ mol^{-1}\ cm^{-1}$)	Sandell's sensitivity ($\mu g/cm^2$)	Reference
I	N-p-Chlorophenyl-3,4,5-trimethoxycinnamo-	BV	570	6-8	0.1-9.0	6.9×10^3	0.0074	None
II	N-p-Chlorophenyl-p-butoxybenzo-	V	540	6-8	0.4-16.0	5.0×10^3	0.0102	None
III	N-Phenyl-p-butoxybenzo-	V	535	6-8	0.4-16.0	4.5×10^3	0.0113	Nine
IV	N-p-Chlorophenyl-p-chlorophenoxyisobutyro-	RV	510	4-8	0.5-18.0	4.3×10^3	0.0118	Nine
V	N-Phenyl-p-chlorophenoxyisobutyro-	RV	505	4-8	0.5-18.0	4.2×10^3	0.0121	Nine
VI	N-Phenylbenzo-	V	530	4	0.7-12.0	4.6×10^3	0.0111	5

V = Violet; BV = Bluish violet; RV = Reddish violet.

sensitivity of the reagent compared to PBHA but bulky alkoxy group substitution in the C-phenyl ring reduces the sensitivity as well as the solubility of the reagent as in the case of compounds II and III.

From the spectral characteristics of the N-arylhydroxamic acids studied here, it is observed that PTCHA is the most sensitive and selective reagent for vanadium as the binary complexes. So the different parameters for an optimum analytical condition for the extraction of vanadium with PTCHA have been carried out. The chloroform solution of PTCHA forms a bluish-violet complex with vanadium(V) from 6-8 M HCl. The absorbance of the vanadium(V) PTCHA complex against the reagent blank exhibits a maximum absorbance at 570 nm with a molar absorptivity 6.9×10^{3} l mol^{-1} cm^{-1}. The system obeys Beer's law in the range of 0.1-9.0 µg/ml of vanadium and the sensitivity is 0.0074 µg of vanadium cm^{-2} for 0.001 absorbance. 10 ml of 0.1% reagent in chloroform is sufficient for the complete extraction of vanadium. Excess reagent has no adverse effect on the determination of vanadium, however, lower concentration of the reagent gives incomplete extraction. Among the solvents studied viz. benzene, n-butanol, amyl alcohol, chloroform etc., chloroform is found to be the most suitable solvent since the extraction is quicker and complete.

The spectral data for the mixed-ligand complexes of vanadium with SCN^- and N-arylhydroxamic acids studied are given in Table 21. It is observed that PPBHA shows elevated capacity in the formation of mixed-ligand complex. The bluish-violet complex has a maximum absorbance at 540 nm with a molar absorptivity 1.1×10^4 $l\ mol^{-1}\ cm^{-1}$. The extraction of ternary complex is studied at different pH and found that at pH 2-3, the extraction is 100% and the distribution coefficient is maximum (∞). 10 ml of 0.1% reagent in MIBK is sufficient for the quantitative extraction as its ternary complex and the excess reagent can be used without any difficulty. In MIBK the extraction is fast and complete (100%). The extraction with other solvents viz. chloroform, benzene, n-butanol, iso-amyl alcohol etc. show the decreased absorbance and the extraction of the ternary complex is incomplete. 5 ml of 0.26 M ammonium thiocyanate is sufficient for maximum colour intensity, while lower and higher concentrations alter the absorbance of the ternary complex. It has been noted that the mixed-ligand complexes are unstable after an hour. The ratio of vanadium to hydroxamic acid in the binary complex is 1:2 (V : PTCHA) while in the ternary complex 1:2:1 (V : PPBHA : SCN) ratio is observed. The possible

TABLE 21

SPECTRAL DATA OF MIXED LIGAND COMPLEX OF V(V) WITH SCN^- AND HYDROXAMIC ACIDS IN IBMK

Hydroxamic acid	pH	Colour of the IBMK extract	Wavelength of maximum absorbance nm	Volume of (0.26 M) NH_4SCN, ml	Molar absorptivity ($1\ mol^{-1}\ cm^{-1}$)
N-p-Chlorophenyl-p-chlorophenoxy-isobutyro-	2-3	BV	540	5	1.1×10^4
N-p-Chlorophenyl-p-butoxybenzo-	2-3	BV	540	5	6.3×10^3
N-p-Chlorophenyl-3,4,5-trimethoxy-cinnamo-	2-3	BV	555	5	8.0×10^3

reaction is

$$2(C_{18}H_{17}O_4ClNOH) + HVO_3 + HCl \longrightarrow \left(C_{18}H_{17}O_4ClNO\right)_2 VOCl + 2H_2$$

$$(C_{18}H_{17}O_4ClNO)_2 VOCl + SCN^- \longrightarrow \left(C_{18}H_{17}O_4ClNO\right)_2 VOSCN + Cl^-$$

5.4.1 Interferences

Interference studies were made for both binary and ternary complexes and the data are given in Table 22.

The effect of diverse ions was investigated under the recommended procedure; the experiments were made on aqueous solutions containing a fixed amount of vanadium (2.5 ppm) in the presence of various amounts of diverse ions. Moderate amount of common metals associated with vanadium are not interfering up to the limit given in the table. However, the metal ions Ta ($>$ 8 ppm), Nb($>$ 9 ppm) and Mo ($>$ 8 ppm) are interfering in the extraction of vanadium and their large amount could be tolerated by masking them with oxalate and tartrate (Table 22).

No interference in absorption signal was observed in AAS determination of 2.5 ppm of vanadium in presence of 40 mg of Na, Cu, Mg, Ni, Ca, Zn, Pb, Cr, Al, Bi, Mo and Sb.

TABLE 22

EFFECT OF DIVERSE IONS IN THE DETERMINATION OF VANADIUM(V) WITH N-p-CHLOROPHENYL-3,4,5-TRIMETHOXYCINNAMOHYDROXAMIC ACID

Vanadium(V) = 2.5 μg/ml
λmax = 570 nm
HCl = 6 M
Absorbance = 0.339
Solvent = Chloroform

Ions	Added as	(mg)	Absorbance
Ba^{2+}	$BaCl_2$	(40)	0.339
Ca^{2+}	$CaCl_2$	(40)	0.339
Cd^{2+}	$CdSO_4$	(40)	0.338
Co^{2+}	$CoSO_4$	(40)	0.338
Cu^{2+}	$CuCl_2$	(40)	0.338
Hg^{2+}	$HgCl_2$	(50)	0.339
Mn^{2+}	$MnCl_2$	(50)	0.340
Zn^{2+}	$ZnCl_2$	(50)	0.338
Pb^{2+}	$Pb(NO_3)_2$	(60)	0.339
Ni^{2+}	$NiCl_2$	(40)	0.339
*MoO_4^{2-}	Na_2MoO_4	(40)	0.340
UO_2^{2+}	$UO_2(NO_3)_2$	(60)	0.339
Al^{3+}	$Al(NO_3)_2$	(60)	0.339
Ti^{4+}	$TiOCl_2$	(40)	0.340
Zr^{4+}	$ZrOCl_2$	(40)	0.340
*Nb^{5+}	Nb_2O_5	(40)	0.340
*Ta^{5+}	Ta_2O_5	(40)	0.340
WO_4^{2-}	$Na_2WO_4.2H_2O$	(40)	0.339

* Masked with oxalate and tartrate

TABLE 23

ANALYSIS OF NBS AND BCS STANDARD SAMPLES

No.	Sample	Vanadium %		Standard deviation*
		Standard	New method found	(σ)
67	Manganese steel (NBS)	0.17-0.19	0.185	± 0.01
117	Ferrotitanium (NBS)	0.05-0.08	0.062	± 0.01
132	Steel (NBS)	1.60-1.68	1.69	± 0.02
224	Cr-V-Steel (BCS)	0.240	0.24	± 0.01
241/1	High speed (BCS)	1.570	1.568	± 0.01

* Six determinations

TABLE 24

VANADIUM IN THE ENVIRONMENT AND ROCK SAMPLES

Sr. No.	Sample	No. of determinations	Vanadium found ppm AAS	Vanadium found ppm Photometric present method	Standard deviation
1	Onion	8	6.50	6.50	± 0.01
2	Carrots	8	3.52	3.50	± 0.02
3	Rice	10	1.00	0.98	± 0.02
4	Peas	10	0.75	0.70	± 0.03
5	Cabbage	10	6.02	6.00	± 0.02
6	Tobacco	10	2.25	2.20	± 0.02
7	Lake water	10	1.00	1.05	± 0.03
8	Sea water	10	0.80	0.80	± 0.02
9	Effluents I	5	1.20	1.20	± 0.01
10.	Effluents II	10	0.07	0.05	± 0.02
11	Potato	5	5.75	5.75	± 0.01
12	Blood sample**	6	0.22	0.20	± 0.02
13	MS - I*	8	-	320	± 0.2
14	DV - I*	8	-	310	± 0.1
15	DV - III*	8	-	310	± 0.1

* Samples from Mussoories phosphate deposites

** Whole blood samples from adult males

5.4.2 Comparison of Present Method with AAS

The present method is compared to AAS where the reported sensitivity is 0.8 μg/ml with a detection limit of 0.2 μg/ml of vanadium (58). The Cr(VI), Fe(III), Sn(IV) and Mo(VI) suppressed the absorption seriously for the direct determination but they do not interfere after extraction of vanadium with the hydroxamic acids.

The data on steel, rock soil and blood samples were compared and are in good agreement with AAS and standard values (Tables 23-24).

6. EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM(IV)

6.1 ABSTRACT

A sensitive and selective extraction - spectrophotometric method for the determination of Zr(IV) with N-p-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid as a binary complex, extracted from 2-6 M HCl into chloroform and a ternary complex of xylenol orange in chloroform : ethanol media has been described. The binary and ternary complexes have the molar absorptivities 2.1 x 10^4 (λmax 385 nm) and 4.3 x 10^4 (λmax 540 nm) l mol^{-1} cm^{-1} respectively.

6.2 INTRODUCTION

Extraction of metals with organic reagents as its chelate provide a preconcentration and selective method for its determination. Hydroxamic acids have been extensively used as a potential analytical reagent for the selective extraction and the simultaneous colorimetric determination of several metal ions (5-7). Amongst them N-phenylbenzo-, N-p-chlorophenylbenzo- and other hydroxamic acids have been reported for the colorimetric and gravimetric determination of zirconium(IV) (7,60-63). Apart from hydroxamic acids, several metallochromic indicators viz. pyrocatechol violet (64) xylenol orange (65), arsenazo I(66), arsenazo III (67), have also been reported for the colorimetric determination of Zr(IV). Amongst them, xylenol orange was reported as a sensitive as well as selective reagent for the quantitative estimation of zirconium in microgram quantity (65).

The present investigation include the use of some new substituted N-arylhydroxamic acids as selective chelating extractants for zirconium(IV) and the formation of ternary complex with xylenol orange. Different parameters regarding the optimum condition for the analytical method have been discussed.

6.3 EXPERIMENTAL

All the chemicals used were of AnalaR and G.R. grades of B.D.H. and E.Merck respectively. Hydroxamic acids used for the extraction were synthesised as described in CHAPTER II. A 0.1% (w/v) solution of the reagent was prepared in chloroform for the extraction purposes. Xylenol orange, 0.2% in 95% ethanol, was prepared for ternary complex study.

Zirconium stock solution was prepared by dissolving requisite amount of zirconium oxychloride in redistilled water and made upto 250 ml with 2 M HCl and water to get a final concentration 9.7×10^{-3} M in 0.1 M HCl. The concentration was checked by titrimetry (68) and spectrophotometry (63). All the absorbance measurements were made on a VSU2-P spectrophotometer with 1.0 cm quartz cells.

6.3.1 Method

Transfer 5 ml of zirconium solution (17.5 μg) to a 60-ml separatory funnel and add concentrated HCl and distilled water to get a final acidity of 5 M HCl in a total volume of 10 ml. Add 6 ml of the reagent solution in chloroform and shake for 10 min. Transfer the organic layer to a 25-ml volumetric flask after drying over anhydrous sodium sulphate. Repeat the extraction with 2 x 2 ml of the reagent solution and collect the extracts in the same flask. Dilute the extract to the mark with chloroform and measure the absorbance at 385 nm against the blank prepared in the same manner.

For the ternary complex, add 1 ml of 0.2% xylenol orange into the binary complex extract and 5 ml of 95% ethanol, before diluting to the mark with chloroform. Measure the absorbance of the red coloured complex at 540 nm against a reagent blank.

6.4 RESULTS AND DISCUSSION

The binary complexes of the zirconium with the N-arylhydroxamic acids studied here are having the maximum absorbance in the UV region except with the N-p-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid (PTCHA) which has the maximum absorbance at 385 nm. Zr(IV) forms a yellow coloured complex with PTCHA, which is extractable into $CHCl_3$ from 2-6 M HCl with an absorbance maximum at 385 nm.

To enhance the sensitivity of the method and to provide a bathochromic shift to the complex, xylenol orange was added as a chromogenic reagent. The red ternary complex has an absorbance maximum at 540-545 nm. The spectral characteristics of the ternary systems studied are reproduced in Table 25. Among the hydroxamic acids used here PTCHA was found to be the most sensitive reagent for zirconium and so the various parameters for the analytical procedure have been investigated by extracting with PTCHA.

TABLE 25

SPECTRAL CHARACTERISTICS OF Zr(IV)-HYDROXAMIC ACID XO COMPLEXES

Zr = 17.7 μg/25 ml; XO = 1 ml of 0.2% in EtOH

Compd. No.	Hydroxamic acid	Optimum HCl Molarity	λmax (nm)	Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$)
I	N-p-Chlorophenyl-3,4,5-trimethoxycinnamo-	2-6.0	540	4.3×10^4
II	N-p-Chlorophenyl-p-butoxybenzo-	1-5.0	540	3.2×10^4
III	N-Phenyl-p-butoxybenzo-	1-5.0	540	2.8×10^4
IV	N-p-Chlorophenyl-p-chlorophenoxyisobutyro-	0.8-1.2	545	2.0×10^4
V	N-Phenyl-p-Chlorophenoxyisobutyro-	0.8-1.2	545	1.8×10^4

6.4.1 Acidity and Extraction Time

The data on the effect of acidity on the extraction of Zr(IV) with PTCHA is summarized in Table 26. It has been observed that zirconium was quantitatively extracted from 2-6 M HCl. Lower and higher acidities yield incomplete extraction as shown by the decrease in absorbance of the ternary complex. Optimum time for the extraction was found to be 10 min. though more shaking time do not have any adverse effect on the extraction.

6.4.2 Validity of Beer's Law

The yellow binary complex of Zr-PTCHA has a maximum absorbance at 385 nm with a molar absorptivity 2.1×10^4 l mol^{-1} cm^{-1}. Zr-PTCHA-XO ternary complex absorbs at 540 nm having a molar absorptivity 4.3×10^4 l mol^{-1} cm^{-1}. The system obeys Beer's law for 0.2 to 2.2 μg/ml of zirconium in the extract. The binary complex is stable for 24 hrs while the ternary complexes produce turbidity after 1 hr.

6.4.3 Effect of Xylenol Orange Concentration

The various chromogenic reagents viz xylenol orange, arsenazo I, catechol violet, arsenazo III were tried for improving the sensitivity of the method and xylenol orange was found to be the most suitable for the system. Xylenol

TABLE 26

EFFECT OF HCl MOLARITY ON THE EXTRACTION OF Zr-TMCHA COMPLEX

Zr = 17.7 μg/25 ml λ_{max} = 540 nm

XO = 1 ml (0.2%) in EtOH

HCl Molarity	Absorbance	Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$)
0.1	0.070	0.9×10^4
0.5	0.130	1.6×10^4
1.0	0.190	2.4×10^4
2.0	0.335	4.3×10^4
4.0	0.335	4.3×10^4
6.0	0.335	4.3×10^4
6.5	0.310	3.9×10^4
7.0	0.290	3.7×10^4
8.0	0.260	3.3×10^4

orange addition imparts a red colour to the Zr-PTCHA complex, revealing the formation of a ternary complex. Since the ternary complex is not soluble in chloroform, shown by the formation of turbidity on addition of xylenol orange;; 5 ml of 95% ethanol was added to get a clear solution. The formation of complex has been found optimum in 4 : 1 (chloroform : ethanol) mixture. One ml of 0.2% (w/v) xylenol orange was enough for complexing 5-55 μg per 25 ml of zirconium. However the lower concentration of the reagent gave incomplete complexation while the large excess amounts increases the blank intensity.

6.4.4 Effect of Reagent Concentration

The extraction of Zr(IV) (17.7 μg/25 ml) is carried out with varying amounts of 0.1% PTCHA in chloroform. It was observed that 7 ml of reagent was sufficient for the quantitative extraction of zirconium. Excess of the reagent can be used without any difficulty in the case of the ternary complex, as the reagent does not absorbs at 540 nm. But in the case of Zr-PTCHA complex study, large excess of the reagent tends to decrease the absorbance owing to the increased absorbance of the blank,(PTCHA) λmax 326 nm). Hence 10 ml of 0.1% reagent had been used throughout the study.

TABLE 27

DETERMINATION OF ZIRCONIUM IN STANDARD USGS AND IAEA SOIL-5 SAMPLES

Sample	Zirconium, ppm		Standard deviation
	Standard value	Present method found	
BCR-1 (52/19)	170	170.2	± 0.2
W-1	100	100.1	± 0.2
GSP-1 (17/22)	10	9.8	± 0.3
PCC-1 (2/1)	7	7.1	± 0.1

6.4.5 Stoichiometry of the Complex

Slope ratio method (40) and mole ration method (41) were used to evaluate the composition of the binary and ternary complexes in chloroform. It has been observed that metal to ligand ratio in the binary complex was 1 : 2 while the ternary complex of Zr-PTCHA-XO has the ratio 1:2:1 respectively. The reaction can be as follows:

$$Zr^{4+} + 2\,HA + 2\,Cl^- \longrightarrow Zr\,Cl_2\,A_2 + 2\,H^+$$

$$Zr\,Cl_2\,A_2 + XO \longrightarrow Zr\,XOA_2 + 2\,Cl^-$$

(HA = Hydroxamic acid ; XO = Xylenol orange)

6.4.6 Effect of Diverse Ions

The interference due to diverse ions in the determination of Zr(IV) with N-p-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid was studied. 17.7 μg zirconium can be determined in presence of the following ions (mg): Ba^{2+} (30), Ca^{2+}(30), Cd^{2+}(30), Co^{2+}(20), Cu^{2+}(20), Hg^{2+}(30), Mn^{2+}(20), Zn^{2+}(20), Fe^{3+}(10), Pb^{2+}(20), Ni^{2+}(20), Al^{3+}(20), UO_2^{2+}(30), Ce^{4+}(20); Os^{6+}(40), Se^{4+}(15), Te^{4+}(20), Pt^{4+}(20), and Ge^{4+}(20). Ta and W though extracted with PTCHA under the recommended conditions, donot form coloured compounds with the xylenol orange, however Nb, V, Ti, Mo and Hf interferes in the determination of zirconium. Zirconium is determined in standard samples (Table 27).

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