CHAPTER X

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V)

RESUME

Nine newly synthesised substituted α-phenyl cinnamohydroxamic acids have been reported for the extraction and spectrophotometric determination of vanadium(V) in trace amount. The N-p-tolyl-α-phenyl-p-methoxycinnamohydroxamic acid (PTPMCHA) is found the most sensitive reagent amongst the substituted hydroxamic acids. The vanadium(V) is extracted with PTPMCHA from 2-5 M HCl. The bluish violet extract has a maximum absorbance at 550 nm and molar absorptivity 6.4×10^3 l $mol^{-1} cm^{-1}$. The various parameters viz. effect of acidity, reagent concentration, diverse ions and stoichiometry of the complex have been discussed. A comparison has been made with atomic absorption spectrophotometric method.

INTRODUCTION

The hydroxamic acids are the potential analytical reagents. The parent acid N-phenylbenzohydroxamic acid (PBHA) is used for the extraction and spectrophotometric determination of vanadium (ϵ=4.3 x 10^3 l $mol^{-1}cm^{-1}$). Later N-phenyl cinnamohydroxamic acid has been synthesised and reported for vanadium (ϵ=6.3 l $mol^{-1}cm^{-1}$).

In literature several substituted hydroxamic acids have been reported for the extraction and spectrophotometric determination of vanadium (1). However, generally, Ti, Zr, Nb and Mo are interfering in the determination of vanadium. In the present investigation the series of cinnamo substituted hydroxamic acids are synthesised with a view to have a better selective and sensitive reagent for vanadium(V). and the interference of Ti, Zr, Nb and Mo is eliminated. A method combining extraction and atomic absorption spectrophotometry has been developed for the determination of vanadium.

EXPERIMENTAL

CHEMICALS AND REAGENTS

All the chemicals used were of AnalaR or G.R. grade of B.D.H. or E. Merck, respectively, unless otherwise specified.

Hydroxamic acids

These are synthesised as described in Chapter II. 0.1% reagent solution of hydroxamic acids in chloroform were used for extraction purposes.

The standard vanadium solution was prepared by dissolving requisite amount of ammonium meta vanadate into water along with a few drops of hydrochloric acid. The final concentration was determined by spectrophotometrically (2).

APPARATUS

The spectral measurements were made on Shimadzu UV-VIS 240 spectrophotometer.

A GBC 901 atomic absorption spectrophotometer equipped with GBC HG 900 Vapour Generation Assembly and vanadium hollow cathode lamp was operated at current of 18.0 mA with a band pass 0.2 nm. The 318.4 nm vanadium line and nitrous oxide acetylene flame were used for direct AAS measurements.

EXTRACTION PROCEDURE

Transfer 1.0 ml vanadium(V) solution (2×10^{-3} M) into a 60-ml separatory funnel. Adjust the acidity of the aqueous phase to 2-5 M HCl with conc. Hydrochloric acid and distilled water to a final volume of 25 ml. Add 10 ml of 0.1% reagent solution of hydroxamic acid in chloroform and shake vigorously for 2-5 min. Allow the phases to separate, dry the chloroform extract over anhydrous sodium sulphate and transfer 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 dilute the extract to 25 ml with chloroform. Measure the absorbance of the bluish violet chloroform extract at 550 nm against the reagent blank.

Atomic absorption measurements

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 EPF method (3).

RESULTS AND DISCUSSION

The spectral characteristics of vanadium complexes with substituted α-phenyl cinnamohydroxamic acids are summarized in Table 1. From the preliminary studies, it is observed that N-p-tolyl-α-phenyl-p-methoxycinnamohydroxamic acid (PTPMCHA) is the most sensitive reagent amongst the hydroxamic acids studied here. Hence the optimum conditions for the extraction of vanadium with PTPMCHA has been investigated.

Effect of acidity

The extraction of vanadium was studied in different hydrochloric acid media. The results show that the extraction of the metal is very poor less than 1 M HCl and higher than 8 M HCl but steadily increases and becomes quantitative at 1 to 7 M with respect to hydrochloric acid concentration. The extraction curve remains constant at 2 to 5 M of hydrochloric acid. (Table 2).

Effect of reagent concentration

Extraction of vanadium(V) were studied with varying the concentration of N-p-tolyl-α-phenyl-p-methoxycinnamohydroxamic acid (PTPMCHA). A single extraction with 10 ml of 0.1% (w/v) reagent solution in chloroform was sufficient for the quantitative extraction of the vanadium(V). The higher

TABLE 1

Spectral characteristic of Vanadium-cinnamohydroxamic acid complexes

V(V) : 4.08 ppm

Molarity : 4 M HCl

Hydroxamic acid : 0.1%, 10 ml in $CHCl_3$

Solvent : $CHCl_3$

Shaking time : 5 min

Compd No.	Cinnamohydroxamic acid	λmax nm	Colour of complex	Molar absorptivity $l\ mol^{-1}\ cm^{-1}$	Sandell's sensitivity $\mu g\ cm^{-2}$
I	N-Phenyl-α-phenyl-p-methoxy-	550	BV	6.2×10^3	0.0082
II	N-p-Tolyl-α-phenyl-p-methoxy-	550	BV	6.4×10^3	0.0080
III	N-m-Tolyl-α-phenyl-p-methoxy-	550	BV	6.3×10^3	0.00810
IV	N-p-Chlorophenyl-α-phenyl-p-methoxy-	550	BV	6.0×10^3	0.0085
V	N-Phenyl-α-phenyl-	550	BV	6.0×10^3	0.0085
VI	N-p-Tolyl-α-phenyl-	550	BV	6.2×10^3	0.0082
VII	N-m-Tolyl-α-phenyl-	550	BV	6.1×10^3	0.0083
VIII	N-p-Chlorophenyl-α-phenyl-	550	BV	5.7×10^3	0.0089
IX	N-Phenyl-α-phenyl-3,4,5 trimethoxy-	550	BV	6.2×10^3	0.0082

BV = Bluish violet

TABLE 2

Effect of acidity on the extraction of Vanadium(V)

V(V) : 4.08 ppm

PTPMCHA : 0.1%, 10 ml in $CHCl_3$

Shaking time : 5 min

Solvent : $CHCl_3$

λ_{max} : 550 nm

Colour of complex: Bluish violet

Molarity of HCl	Molar absorptivity $l\ mol^{-1} cm^{-1}$	% E
1.0	5.6×10^3	88.2
2.0	6.4×10^3	100
3.0	6.4×10^3	100
4.0	6.4×10^3	100
5.0	6.4×10^3	100
6.0	5.5×10^3	86.2

reagent concentration can be used without any difficulty.

Effect of solvents

Amongst the various organic solvent tried viz. benzene, carbontetrachloride, chloroform, isoamyl alcohol etc. chloroform was found to be the most efficient solvent. Hence all the extraction studies were carried out with chloroform. The data are given in Table 3.

Stability of the colour and extraction time

Vanadium complex is stable for several days. Extraction of the vanadium complex is very rapid under the conditions recommended in the analytical procedure. Shaking time for 2-5 min was enough to attain the equilibrium when the reagent was added to the aqueous phase.

Beer's Law

Beer's law is obeyed in the range of 0.4 to 12.22 ppm of vanadium. The molar absorptivity is 6.4×10^3 l $mol^{-1} cm^{-1}$ at 550 nm. The Sandell's sensitivity is 0.0080 $\mu g/cm^2$.

Effect of diverse ions

The interference of several ions on the extraction behaviour of vanadium was studied. The results indicate that moderate amount of many ions are tolerable in the direct spectrophotometric determination of vanadium(V) with N-p-tolyl-α-phenyl-p-methoxycinnamohydroxamic acid (Table 4).

TABLE 3

Effect of solvent on the extraction of Vanadium(V)

V(V) : 4.08 ppm

PTPMCHA : 0.1%, 10 ml in $CHCl_3$

Shaking time : 5 min

Molarity : 4 M HCl

λ_{max} : 550 nm

Colour of complex : Bluish violet

Solvents	Molar absorptivity $l\ mol^{-1} cm^{-1}$	% E
Chloroform	6.4×10^3	100
Benzene	6.3×10^3	99
Carbon tetra-chloride	2.6×10^3	40
Isoamyl alcohol	-	Nil

TABLE 4

Effect on cations and anions on the extraction of Vanadium(V)

V(V) : 4.08 ppm

PTPMCHA : 0.1%, 10 ml in chloroform

Shaking time : 5 min

Molarity : 4 M HCl

Solvent : Chloroform

λ_{max} : 550 nm

Colour of complex : Bluish violet

Ions	Added as	Amount added (mg)	Absorbance
Ba^{2+}	$BaCl_2$	(30)	0.51
Ca^{2+}	$CaCl_2$	(30)	0.51
Cd^{2+}	$CdSO_4$	(30)	0.51
Co^{2+}	$CoSO_4$	(30)	0.50
Cu^{2+}	$CuCl_2$	(30)	0.51
Hg^{2+}	$HgCl_2$	(40)	0.51
Mn^{2+}	$MnCl_2$	(40)	0.51
Zn^{2+}	$ZnCl_2$	(40)	0.50
Pb^{2+}	$Pb(NO_3)_2$	(40)	0.50
Ni^{2+}	$NiCl_2$	(30)	0.51
* MoO_4	Na_2MoO_4	(30)	0.50
UO_2^{2+}	$UO_2(NO_3)_2$	(40)	0.51
Al^{3+}	$Al(NO_3)_3$	(40)	0.51
Ti^{4+}	$TiOCl_2$	(30)	0.52
Zr^{4+}	$ZrOCl_2$	(30)	0.51
* Nb^{5+}	Nb_2O_5	(30)	0.51
* Ta^{5+}	Ta_2O_5	(30)	0.51
WO_4^{2-}	$Na_2WO_4.2H_2O$	(30)	0.51

* Masked with oxalate and tartrate.

Composition of the complex

The 1:2 (V-PTPMCHA) composition of the extractable species was determined by the molar ratio method (4,5). The V-PTPMCHA complex was determined by taking fixed amount of vanadium and gradually increasing the amount of reagent (L_1), the slope of the plot of log D_MVS - log (L_1) was found 2.0, confirms the metal to ligand (L_1) ratio is 1:2.

REFERENCES

1. Agrawal, Y.K. and Jain, R.K., Revs. Anal. Chem., 6, 49 (1982).

2. Agrawal, Y.K., Revs. Anal. Chem., 5, 3 (1980).

3. EPA-600/4-79-020, "Methods for Chemical Analysis of Water and Wastes", United States Environmental Protection Agency, and Environmental Monitoring and Support Laboratory, Cincinati, 286 (1979).

4. Joe, J.H. and Harvey, A.E., J. Am. Chem. Soc., 70, 648 (1948).

5. Harvey, A.E. and Manning, D.L., J.Am. Chem. Soc., 72, 4488 (1950).