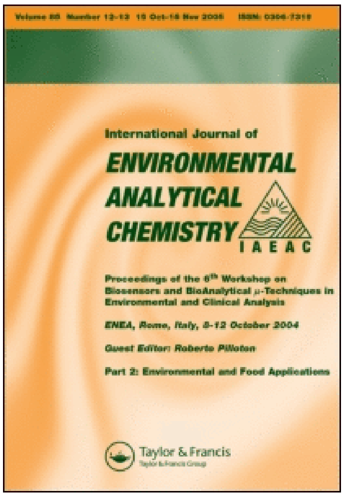

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Determination of Vanadium with Chlorosubstituted Hydroxamic Acids for Photometric and Atomic Absorption Spectrophotometric Determination

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The eight newly synthesized chlorosubstituted hydroxamic acids are described for the extraction and spectrophotometric determination of vanadium. The sensitive and selective reagent, N-m-Chlorophenylpalmito hydroxamic acid, (m-CPPHA), which gives violet coloured vanadium complex was extracted with chloroform from 6M HCl. The violet coloured complex thus obtained has a maximum absorbance at 520 nm and molar absorptivity 4.9 $\times 10^3$ l mol^{-1} cm^{-1}. The Beer's law obeyed in the region 0.50–12.0 ppm. Effects of acidity, reagent concentration, diverse ions have also been investigated. A comparison has been made with atomic absorption spectrophotometric method. Vanadium has been determined in the environment, e.g. plant, soil, rock, etc.

KEY WORDS: Vanadium, hydroxamic acids, extraction, photometric, atomic absorption spectrophotometry (AAS), environment.

INTRODUCTION

Hydroxamic acids are selective and sensitive reagents for the determination of trace metals.[1-9] They give violet colour complexes with vanadium(V) in the chloroform solution from 6–8 M HCl. Eight new chlorosubstituted hydroxamic acids were synthesized[10] and studied for the extraction and spectrophotometric determination of vanadium(V) with a view to develop a selective and sensitive method for the determination of vanadium(V). Generally, Ti, Zr, Nb, Ta and Mo are interfering in the determination of vanadium.[7] In the present investigation the studies have been made such that the interference of the Ti, Mo and Zr is eliminated. The various parameters for the stability of the method, viz. acidity, reagent concentration and diverse ions have been studied. All these acids give violet or reddish violet coloured complexes with vanadium(V) in strongly acid solution from chloroform. A method combining extraction and atomic absorption has been developed for the determination of vanadium in lake water and natural resources.

EXPERIMENTAL

The spectral determinations were made on a Spekol (Carl Zeiss, Jena) using 1 cm path length cells. A Varian Techtron Model AA-6 atomic absorption spectrophotometer equipped with HCN-V hallow cathode lamp was used. The 3184 A° vanadium line and nitrous oxide and acetylene gas was used.

The synthesis and properties of all the acids were described elsewhere.[10] 0.1 % solutions of the hydroxamic acids in ethanol free chloroform were prepared. The vanadium solution was prepared by dissolving the required amount of ammonium metavanadate in double distilled water and its final concentration (0.8871×10^{-3} M) was measured volumetrically.[11]

Extraction and Spectrophotometric Determination of Vanadium(V):

Into a 100 ml separatory funnel was transferred 2 ml of vanadium solution (0.8871×10^{-3} M). Adjustment of the aqueous phase of 25 ml of 6–8 M hydrochloric acid with concentrated hydrochloric acid and water was carried out. 5 ml of 0.1 % chloroform solution of the hydroxamic acid was added and the contents were shaken for 2–3 min. The chloroform layer was allowed to separate, dried over anhydrous sodium sulphate to remove the moisture and transferred into 25 ml volumetric flask. To ensure the complete recovery of vanadium the aqueous layer was extracted twice with 2 ml of the reagent solution. Finally the extract was diluted to 25 ml with chloroform. The maximum absorbance of the coloured complex was measured against the reagent blank.

The extracts were aspirated directly into the flame.

RESULTS AND DISCUSSION

The spectral characteristic of vanadium(V) complexes of the various hydroxamic acids studied are recorded in Table I. Their absorbance bands are generally broad and the maxima between 510–535 nm (Table I).

TABLE I

Extraction and spectrophotometric determination of vanadium(V) at 6 M HCl

S. No.	Hydroxamic acid	Colour of V extract	λ-max (nm)	Molar absorptivity[a] $l\,mol^{-1}\,cm^{-1}$
I	N-o-chlorophenyl-o-chloro Benzo-	V	530	4.4×10^3
II	N-m-chlorophenyl-myristo-	RV	515	4.9×10^3
III	N-m-chlorophenyl-palmito-	RV	520	4.9×10^3
IV	N-m-chlorophenyl stearo-	RV	515	4.7×10^3
V	N-o-chlorophenyl myristo-	RV	510	4.5×10^3
VI	N-o-chlorophenyl palmito-	RV	515	4.6×10^3
VII	N-o-chlorophenyl stearo-	RV	515	4.6×10^3
VIII	N-m-chlorophenyl-o-chloro Benzo-	V	535	3.9×10^3

V = violet, RV = Reddish violet
[a]Average of three determinations.

For the determination of vanadium(V) with N-m-chlorophenyl palmito hydroxamic acid (m-CPPHA), the effects of the following variables were investigated.

Absorption Spectra, Beer's Law and Precision

The spectra of reddish violet vanadium m-CPPHA complex has a maximum at 520 nm and at this wavelength the absorbance is reproducible. The chloroform solution of the reagent does not absorb between 350 and 600 nm. The system obeys Beer's law over the range 0.50–12.0 ppm of vanadium at 520 nm and the molar absorptivity worked out to be $4.9 \times 10^3\,l\,mol^{-1}\,cm^{-1}$.

To test the reliability of the present method, different amounts of vanadium were taken and eight determinations were made at each level. The absorbance of each extract was measured at least 3 times, averaged and the vanadium concentration was calculated. The standard deviation σ, was calculated. the values are given in Table II together with AAS determinations and show that vanadium can be determined with good precision.

Effect of Acidity, Time and Temperature

Maximum colour intensity was obtained from 4–8 M HCl but as the concentration of acid decreases, the intensity also decreases. The colour is stable up to several days and unaffected by temperature.

TABLE II

Determination of vanadium with N-m-chlorophenyl palmito hydroxamic acid
λ max = 520 nm

HCl = 6 M, Solvent = Chloroform

Vanadium taken ppm	Vanadium found, ppm			
	Photometric	σ	AAS	σ
1.00	0.99	±0.02	0.98	±0.02
2.00	2.00	±0.01	2.01	±0.02
5.00	5.00	±0.01	5.02	±0.02
10.00	9.98	±0.02	9.97	±0.03
15.00	15.00	±0.02	15.00	±0.01
20.00	19.98	±0.02	20.01	±0.01

Effect of Reagent Concentration

The excess of reagent has no effect on the absorbance of reddish violet coloured vanadium extract. The optimum concentration of the reagent solution was 0.1 w/v and the maximum colour development took place when the mole ratio of vanadium to reagent was 1:10.

Effect of Diverse Ions

The effect of diverse ions was investigated under the recommended procedure condition; the experiments were made on aqueous solutions containing a fixed amount of vanadium (5.2 ppm) in the presence of various amounts of diverse ions. The experimental results are given in Table III. Moderate amounts of common metals associated with vanadium, niobium, zirconium and titanium are not interfering. However, large amounts of tantalum, niobium and molybdenum are interfering. These interferences are removed by masking them with oxalate and tartrate.

No interference in absorption signal was observed in AAS determinations of ppm of vanadium in the presence of 40 mg of the following ions: Na, Cu, Mg, Ni, Ca, Zn, Mn, Pb, Cr, Al, Bi, Mo, Sb. The Cr(IV), Fe(III), Sn(IV) and W(VI) suppressed absorption seriously for direct determination but they do not interfere after extraction of vanadium with hydroxamic acids.

TABLE III

Effect of diverse ions in the determination of vanadium(V) with N-m-chlorophenyl palmito hydroxamic acid

Vanadium = 5.2 ppm; Absorbance = 0.50
λ max = 520 nm; HCl = 6 M
Solvent = Chloroform

Ions	Added as (mg)	Absorbance
Ba^{2+}	$BaCl_2$ (25)	0.50
Ca^{2+}	$CaCl_2$ (25)	0.50
Cd^{2+}	$CdSO_4$ (25)	0.50
Co^{2+}	$CoSO_4$ (25)	0.49
Cu^{2+}	$CuCl_2$ (30)	0.50
Hg^{2+}	$HgCl_2$ (30)	0.51
Mn^{2+}	$MnCl_2$ (30)	0.49
Zn^{2+}	$ZnCl_2$ (25)	0.50
Pb^{2+}	$Pb(NO_3)_2$ (30)	0.50
Ni^{2+}	NiCl(25)	0.49
MoO_4^{2-}	Na_2MoO_4 (20)	0.49
UO_2^{2-}	$UO_2(NO_3)_2$ (30)	0.50
WO_4^{2-}	$Na_2WO_4 \cdot 2H_2O$ (30)	0.49
Al^{3+}	$Al(NO_3)_3$ (30)	0.50
Ti^{4+}	$TiOCl_2$ (20)	0.51
Zr^{4+}	$ZrOCl_2$ (20)	0.51
Nb^{5+}	Nb_2O_5 (15)	0.49
Ta^{5+}	Ta_2O_5 (15)	0.49

TABLE IV

Vanadium in the environment

S.N.	Sample	No. of determination	Vanadium found ppm	
			Photometric[a]	AAS
1	Onion	8	6.50	6.50
2	Carrots	8	3.50	3.52
3	Rice	10	0.98	1.00
4	Peas	10	0.70	0.75
5	Cabbage	10	6.00	6.02
6	Tobacco	10	2.20	2.25
7	Lake water	10	1.05	1.00
8	Sea water	10	0.80	0.80
9	Effluents I	5	1.20	1.20
10	Effluent II	10	0.05	0.07
11	Potato	5	5.75	5.75

[a] N-m-chlorophenyl palmito hydroxamic acid.

Determination of Vanadium in Soil, Plant and Water Samples

Depending upon the concentration of vanadium in samples, 20 to 50 gm of material was digested with an excess of the perchloric and nitric acid. The hot solution was centrifuged. The filtrate was evaporated and diluted to 100 ml with 1 M HCl. The 10 ml of sample solution was used for the determination of vanadium. These data are summarised in Table IV. The vanadium content found in rat bone and kidney is almost to background (0.01 ppm).

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