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Shahid Abbas Abbasi[a]; Jameel Ahmed[b]
[a] WATER QUALITY AND ENVIRONMENT DIVISION, CENTRE FOR WATER RESOURCES DEVELOPMENT AND MANAGEMENT, KERALA, INDIA [b] JK STRAW PRODUCTS, BHOPAL, INDIA

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NOTE

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SHAHID ABBAS ABBASI

WATER QUALITY AND ENVIRONMENT DIVISION
CENTRE FOR WATER RESOURCES DEVELOPMENT AND MANAGEMENT
KUNNAMAGALAM P.O., CALICUT 673571, KERALA, INDIA

JAMEEL AHMED

JK STRAW PRODUCTS
BHOPAL, INDIA

Abstract

A highly sensitive, selective, and rapid method for the spectrophotometric determination of trace amounts of vanadium(V) is described. Vanadium(V) is extracted from 4–8 *M* hydrochloric acid solutions as its violet complex with *N*-*p*-methoxyphenyl-2-furohydroxamic acid (MFHA) in chloroform. The extract shows maximum absorbance at 545 nm ($E = 7.3 \times 10^3$ L·mole^{-1} cm^{-1}) and obeys Beer's law over the range 0–12 ppm of vanadium; Sandell's sensitivity being 0.007 μg/cm^2. The method has been applied for the analysis of vanadium in pond water, rock phosphates, and steels.

INTRODUCTION

N-Phenyl-benzohydroxamic acid (PBHA) and its analogs containing benzenoid systems have been extensively studied and employed as analytical reagents (*1*) but there is a paucity of information on the hydroxamic acids derived from heteroaromatic compounds. The reported studies, although they are few and far between, on *N*-phenyl-2-thenohydroxamic acid (PTHA) (*2*) and *N*-phenyl-2-furohydroxamic acid (PFHA) (*3*), have shown that both of these compounds are more sensitive reagents than PBHA. Now the *N*-*p*-methoxyphenyl-2-furohydroxamic acid (MFHA) has been studied for liquid–liquid extraction and spectrophotometric determination of vanadium(V). A report of these studies, which reveals MFHA as a more sensitive and selective reagent for vanadium than PBHA, PTHA, or PFHA, is presented here. The method is suitable for the simple and rapid determination of vanadium in the presence of high concentrations of several cations and complexing anions. The applicability of the method was tested by analysis of vanadium in standard steel samples supplied by the National Bureau of Standards (U.S.), in rock phosphates, and in pond water.

EXPERIMENTAL

The reagent MFHA was synthesized by coupling *p*-methoxyhydroxylamine and furan-2-carboxylic acid by the general method of Tandon and Bhattacharyya (*2*). It was crystallized several times from benzene to a sharp, constant melting point and it was characterized by elemental analysis, UV, and IR spectroscopy. A 0.1 *M* reagent solution in ethanol-free chloroform was used for extraction work. Chloroform was freed from ethanol by washing it several times with water and then distilling it after drying it over fused calcium chloride.

A standard vanadium(V) solution was prepared by dissolving 0.1 g of analytical grade ammonium metavanadate in a liter of deionized water. The solution was standardized volumetrically for vanadium(V) in the presence of $KMnO_4$ (*4*).

EXTRACTION OF VANADIUM

A 5-mL aliquot solution of vanadium(V) (5.0×10^{-4} *M*) was transferred into a 100-mL separatory funnel. To ensure that all the vanadium was present as vanadium(V), a dilute $KMnO_4$ solution was added dropwise until a faint pink color persisted. This was followed by 5 mL of hydrochloric acid (8–12 *M*) and 5 mL of reagent solution (0.1 *M*) in chloroform. The contents were equilibrated for about 5 min and the phases allowed to separate. The violet-colored extract was removed from the separatory funnel, dried over anhydrous sodium sulfate, and collected in a 25-mL volumetric flask. To ensure complete recovery of vanadium, the aqueous layer was extracted once more with 5mL of reagent solution. After drying and adding it to the first extract, the sodium sulfate was washed twice with 2 mL portions of reagent solution to remove the last traces of the violet color. Finally the extracts were diluted to the mark and the absorbance of the violet solution was measured at 545 nm against the reagent solution as blank. The results were reproducible within ±0.2%.

RESULTS AND DISCUSSION

Choice of Extracting Solvent

Chloroform, benzene, carbon tetrachloride, hexanol, isoamyl alcohol, and methyl isobutyl ketone were tried as extracting solvents for the vanadium(V)–MFHA complex. Of these, chloroform was found to be the most suitable because it is convenient to handle and the extracts show maximum sensitivity. The absorbance of the extract in oxygenated solvents was low and the color tended to fade within a few hours.

Absorption Spectra

The complex showed a maximum absorbance at 540–550 nm. The reagent blank does not absorb in this region. All the measurements were made at 545 nm.

Effect of Varying Reaction Conditions

Maximum color intensity was obtained when extractions were done from 4–8 *M* HCl. A 0.1 *M* solution of MFHA in chloroform was adequate for complete extraction within 5–12 min of equilibration. Higher reagent concentrations reduced the optimum time of equilibration by 0.5 to 1 min and did not affect the sensitivity of the color system. The effect of pH on the extraction of vanadium(V)–MFHA system is recorded in Table 1. The extraction was quantitative between $0 < \mathrm{pH} < 1.0$, but the color system was less sensitive and stable when compared to extractions from 4–8 *M* HCl solutions. There was no effect on the extraction of 50 μg of vanadium when the aqueous volume was varied from 5 to 100 mL.

Beer's Law, Sensitivity, Molar Absorptivity, and Reproducibility

Beer's law was obeyed over the range 0–12 μg/mL of vanadium(V). The sensitivity of the method, as per Sandell's definition (*5*), was 0.007 $\mu g/cm^2$ of vanadium and the molar absorptivity was 7.3×10^3 $L \cdot mole^{-1} cm^{-1}$. The reproducibility of the method was checked by replicate analysis of standard vanadium solutions. Results are shown in Table 2.

Effect of Diverse Ions

The vanadium was extracted in the presence of 50 diverse ions. The tolerance limit was set at the amount required to cause a ±2.0% error in

TABLE 1

Extraction of Vanadium–MFHA System as a Function of pH

pH	Extraction percent, *E*	Distribution ratio, *D*
0 to 0.6	100	0.0
0.8	99	99.0
1.0	96	24.0
1.2	92	11.5
1.5	80	4.0

TABLE 2

Analytical Data on Reproducibility of Method

Vanadium(V) μg/25 mL of extract	Average vandium(V) found (μg)	No. of determinations	Range	Standard deviation
5.00	4.98	6	±	0.02
75.00	75.01	6	±	0.02

TABLE 3

Effect of Foreign Ions (Vanadium(V) = 50 μg/25 mL, *N*-*p*-methoxyphenyl-2-furohydroxamic acid = 0.1 *M*)

Tolerance limit (μg/25 mL)	Ions
100,000[a]	Ag(I), Na(I), K(I), Be(II), Mg(II), Ca(II), Ba(II), Li(I), Sr(II), Hg(II), Zn(II), Pb(II), U(II)O_2, La(III), Sc(III), Y(III), Ga(III), fluoride, chloride, bromide, iodide, ascorbate, acetate, cyanide, phosphate
80,000	Cu(II), Ni(II), Co(II), Cd(II), Pb(II), Pd(II), As(III), Sb(III), Bi(III), In(III), Al(III), Th(IV), citrate, tartrate, sulfate
60,000	Fe(III), Cr(III), Ti(III), Hf(IV), Sn(IV)
20,000	Ti(IV),[a] Zr(IV), Mo(VI), W(VI)

[a] In presence of fluoride.

vanadium recovery. The results (Table 3) show that a great number of ions are tolerated in the ratios 1:2000 to 1:1000. Iron(III), uranium(VI), lanthanum(III), calcium, fluoride, phosphate, etc., which are normally associated with vanadium in natural or synthetic mixtures, are tolerated to a higher degree. Titanium(IV), when present in ratios higher than 1:2 with vanadium, interfered as it was coextracted with vanadium(V) but fluoride could mask the titanium interference.

TABLE 4

Analysis of Rock Phosphate, Standard Steel Samples, and Pond Water

Sample	Reported value, % vanadium	Vanadium added	Vanadium found[a]
Steel (N.B.S., No. 132)	1.67	—	1.68
Ferrotitanium (N.B.S., No. 117)	0.06	—	0.08
Manganese steel (N.B.S., No. 67)	0.18	—	0.18
Mussorrie rock phosphate	—	—	0.05
Pond water, I	—	0.0 ppm	0.03
Pond water, II	—	5.0 ppm	5.05
Pond water, III	—	10.0 ppm	10.03

[a] Average of six determinations.

Stoichiometry of the Complex

Job's method of continuous variation (*6*) and the molar ratio method (*7*) were applied with extractions from solutions of varying acidities and determinations at various wavelengths. All results point toward the existence of a complex with vanadium and MFHA in a molar ratio 1:2.

Determination of Vanadium in Steels and Rock Phosphates

Vanadium was determined in pond water by the standard addition technique. Mussoorie Phosphate Deposits (India) and three National Bureau of Standards (U.S.) steel samples were also analyzed for vanadium to test the reliability of the proposed method. The results are shown in Table 4.

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