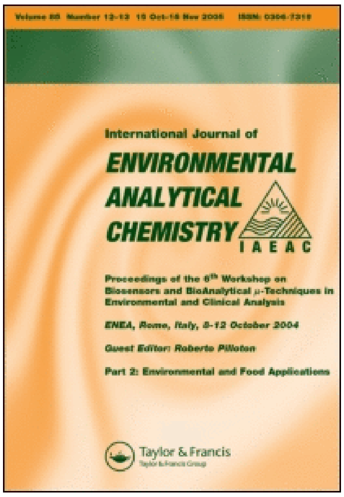

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Microdetermination of Vanadium in Water Samples

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The proposed method incorporates preconcentration of vanadium in water samples by its coprecipitation on ferric hydroxide at pH 8.0–9.6 which is redissolved in sulphuric acid; this is followed by extraction with *N*-phenylbenzohydroxamic acid (PBHA). The precision and accuracy of the newly developed method was ascertained by analysing EPA (Environmental Protection Agency, U.S.A.) standard water samples.

INTRODUCTION

Vanadium has been recognised as a potentially dangerous pollutant[1] in the class of lead, cadmium and mercury.[2] It plays a vital role in enzyme reactions and nitrogen fixation.[3] The determination of vanadium receives increasing attention in pollution studies as it has attracted considerable attention as a public health hazard.[4]

Several methods have been reported for the determination of vanadium in water samples.[5–12] Fishman and Skougstad[5] reported a method, which is based on the catalytic effect of vanadium on the rate of oxidation of gallic acid by persulfate in acid solution. The method severely suffers from chloride interference. Fukasawa and Yamane[6] reported a kinetic method based on the oxidation of gallic acid by bromate. The modified method[7] also suffers from the interferences of oxidising substances. A modified catalytic photometric procedure has been reported by Qiang.[8] Shijo *et al.*[9] proposed vanadium extraction with capriquat. Cole *et al.*[10] coprecipitated vanadium from seawater by tris-(pyrrolidinedithiocarbamate cobalt(III)) at pH 4.0 with final determination using X-ray fluorescence. Abdullah *et al.*[11] and Ogawa *et al.*[12] have employed thiophene-2-hydrazide and 2-2′-dipyridyl-2-quinolylhydrazone, respectively, for the microdetermination of vanadium.

EXPERIMENTAL

Apparatus

A Carl-Zeiss Jena UV-VIS spectrophotometer, SPECORD, with 10-mm matched cell was employed for scanning absorption spectra of extracts. An Electronic Corporation of India (Hyderabad) spectrophotometer GS 685 was used for absorption measurements at fixed wavelength. A Systronics pH meter 325 was employed for pH measurements.

Graduated apparatus of standard calibration was used for measurements. Contamination from glassware, stoppers and pipette tips was scrupulously prevented. All glassware was washed with nitric acid (5% v/v); new glassware was allowed to stand for several hours in acid. After three rinses with deionized water and three rinses with further purified water, the glassware was stored under dust-free conditions.

Reagents and samples

All reagents used were of analytical grade of B.D.H. or S.M. Triple-glass-distilled water and double-distilled solvent was used for solution preparation and other purposes.

Ammonium metavanadate A stock solution was prepared by dissolving 1 g of ammonium metavanadate (H&W; AnalaR) in triple-glass-distilled water and diluted to 1 l. Working solutions for trace analysis were prepared daily by further appropriate dilutions. The vanadium content of the solution was determined by the potassium permanganate method.[13]

PBHA *N*-phenylbenzohydroxamic acid was prepared as described in the literature.[14] An approximately 0.005 M (0.1% w/v) solution of the reagent in *o*-dichlorobenzene was used. The solutions, if stored in amber bottles, were stable for several days.

Ammonia solution A 20% (v/v) solution.

Ferric nitrate solution 3.1 g ferric nitrate ($Fe(NO_3)_3 . 6H_2O$) was dissolved in 100 cm^3 water.

Sampling

Seawater samples

Seawater samples from the Arabian Sea (71.2° longitude and 21.5° latitude) were procured by the Salt and Marine Research Institute, Bhavnagar, India. The Samples were transferred in polyethylene sample bottles, with the addition of 1 ml of nitric acid (AnalaR). The polyethylene bottles were cleaned by soaking them in nitric acid (5% v/v) overnight, followed by thorough washing with deionized and glass-distilled water.

River water samples

Water samples of the Kharun river (Kumhari, India) and Chipra river (Ujjain, India) were collected.

Municipal water from Raipur City, India was collected from taps.

Analytical procedure

The water sample (200–250 ml) was poured into a beaker and acidified by the addition of 2 ml of hydrochloric acid (AR, Basynth). We added 5 ml of a ferric nitrate solution and, then, 20% v/v ammonia with constant shaking (pH = 8.0 to 9.6) and allowed the mixture to stand for about 10 min. After siphoning off the water, we transferred the precipitate to a centrifuge tube, centrifuged and dissolved the precipitate in a minimum volume (1–2 ml) of 2 N sulphuric acid. In order to oxidise all the vanadium to the quinquevalent state 2–3 drops of a ca. 0.05 N potassium permanganate solution were added. We transferred the solution to a 60 ml separatory funnel and added concentrated hydrochloric acid so that the final acidity was between 3.0 and 8.2 M. We added 5 ml of reagent and, after shaking vigorously, allowed the phases to separate. We collected the extract and directly read the absorbance at 530 nm, using 0.1% w/v PBHA in *o*-dichlorobenzene as a reference. The completeness of the extraction was verified by adding and shaking with an aliquot of the reagent.

Normal precautions for trace analysis were taken throughout.

RESULT AND DISCUSSION

Choice of extraction solvent

The extraction of the vanadium(V)-PBHA violet complex could be accomplished by a variety of solvents such as benzene, carbontetrachloride, chloroform, diethylether and ethyl acetate with varying extraction efficiencies.

In the present procedure the organic solvent employed was *o*-dichlorobenzene. *o*-Dichlorobenzene was found to be superior to chloroform[15,16] due to its high boiling point, smaller aqueous solubility and less volatility. The boiling points and aqueous solubilities of *o*-dichlorobenzene and chloroform are 180 and 61°C, and 0.815% and 0.026%, respectively. The vanadium (V)-PBHA complex reacts with ethanol and other alcohols and gives a golden yellow or red product. The small amounts of ethanol, added to chloroform as preservative adversely affect the absorption spectrum of the violet complex. *o*-Dichlorobenzene is a stable solvent and free from such complications. Hence, it is highly suitable for the extraction procedure. This extraction technique has been successfully employed for the spectrophotometric determination of vanadium in plant samples.[17]

Choice of acid

Shome[18] determined vanadium at pH 2.4–2.6 and Depool[19] reported its quantitative extraction between pH 2.4 and 4.4 using PBHA. The methods have poor selectivity and the results depend upon the rigid control of pH. Donaldson[20] and others[21] extracted a red vanadium(V)-PBHA complex using 2 M H_2SO_4–4 M HF media. However, the choice of acid mixture did not appear to offer any special practical advantage. Besides, the trace amounts of hydrofluoric acid present in the extract, turned the optical cells foggy due to their etching action. The method is slightly less sensitive ($\varepsilon = 4280$ at 475 nm) than the present method ($\varepsilon = 4950$ at 530 nm) in which the violet complex of vanadium was extracted from hydrochloric acid media. It has been observed that for the maximum colour development the hydrochloric acid concentration of the aqueous phase should be between 3.0 and 8.2 M.

Effect of pH on coprecipitation

The optimum pH value for coprecipitation of vanadium was found to be between 8.0 and 9.6. The percentage recoveries of vanadium were 25.4, 58.6, 89.8, 94.8, 99.5, 101.4, 100.0, 100.6, 101.2, 99.8, 100.0, 98.4, 97.9, 92.6 and 87.4 at pH values of 7.2, 7.5, 7.8, 7.9, 8.0, 8.2, 8.6, 8.9, 9.2, 9.5, 9.6, 9.8, 10.0, 10.2 and 10.4, respectively.

Beer's law

The system obeyed Beer's law. The molar absorptivity is 4950 ± 25 litre $\text{mole}^{-1}\,\text{cm}^{-1}$ and the sensitivity of the system as defined by Sandell[22] is 0.010 μg of vanadium cm^{-2} at 530 nm.

Effect of coprecipitant on recovery of vanadium

The data in Table I indicate that 20 mg of iron must be precipitated to obtain complete recovery of 30 μg of vanadium. However, higher concentration of iron did not interfere in the spectro-photometric determination of vanadium.

Water sample analysis

Synthetic water samples were prepared by adding a known quantity of vanadium to vanadium-free triple-distilled water. Replicate analysis of each concentration level was done and the results were statistically evaluated (Table II). The method was successfully employed for the determination of vanadium in tap, river and sea water samples. No measurable amount of vanadium was detected in any of the water samples. Therefore, a standard solution of vanadium was added and, then, the analysis was repeated. The results are summarised in Table III.

TABLE I

Effect of amount of coprecipitant on recovery of vanadium. Volume of sample, 100 ml; Vanadium added, 30 μg; pH for coprecipitation, 9.0 ± 0.5. Coprecipitant concentration, 5 mg Fe(III)/ml.

Fe(III) added (mg)	Recovery (%)
5.0	40.2
10.0	78.4
15.0	90.0
17.5	94.7
20.0	98.6
25.0	99.8
30.0	99.9
35.0	101.6
40.0	101.2
50.0	99.8

TABLE II

Determination of vanadium in synthetic water samples. Volume of sample, 250 ml, pH for coprecipitation, 9.0 ± 0.5.

Vanadium conc. (μg)	No. of samples	Rel. S.D. (%)
2.0	8	6.2
3.0	5	5.8
4.0	6	5.2
5.0	9	4.6
8.0	12	3.9
15.0	7	3.5
21.0	5	2.6
25.0	10	1.5

Effect of sample volume

The proposed method was successfully employed for the microdetermination of vanadium varying the volume of sample ranging from 10 ml to 5 litres (Table IV). This demonstrates the applicability

TABLE III

Determination of vanadium in synthetic tap, river and sea water samples. Volume of sample, 250 ml; pH for coprecipitation, 9.0 ± 0.5.

Sample	Vanadium added (μg)	Vanadium found[a] (μg)	Recovery (%)
Tap water	4.3	3.7	86
	8.5	8.2	91
	20.0	19.2	96
	25.0	25.6	102
Chipra river water	4.0	4.2	105
	8.0	7.4	92
	15.0	15.6	104
	20.0	20.0	100
Kharun river water	4.0	4.4	110
	6.0	5.6	93
	10.0	9.6	96
	20.0	19.2	96
Sea water	5.0	4.6	92
	10.0	10.2	102
	12.5	12.7	102
	15.0	14.3	95
	20.0	20.5	102

[a] Average of 3 analyses.

TABLE IV

Effect of volume of sample.

Volume of sample[a] (ml)	Vanadium found[b] (μg)	Relative error (%)
10	25.63	+2.5
25	24.25	−3.0
50	25.00	0.0
100	25.25	+1.0
250	25.00	0.0
500	24.05	−3.8
1000	25.63	+2.5
2000	24.00	−4.0
2500	23.75	−5.0
5000	23.00	−8.0

[a] Vanadium added, 25 μg.
[b] Average of 3 measurements.

of the proposed method especially for the analysis of polluted water samples.

USEPA water samples analysis

Standard water samples, obtained from the U.S. Environmental Protection Agency, Environmental Support Laboratory, Cincinnati were analysed by the proposed method. The results are shown in Table V. There is an excellent agreement with the certified and obtained values.

TABLE V

Determination of vanadium in standard water samples.

USEPA water sample	Certified value ($\mu g\,l^{-1}$)	Vanadium found[a] ($\mu g\,l^{-1}$)	Composition of sample ($\mu g\,l^{-1}$)
476 E.1.	78	74.2	Al, 61; As, 24; Be, 24; Cd, 6.5; Cr, 4.4; Co, 30; Cu, 8.7; Fe, 16; Mn, 7.9; Hg, 0.4; Ni, 8.7; Se, 8.7; Zn, 6.1.
476 E.2.	848	864.6	Al, 852; As, 182; Be, 261; Cd, 59; Cr, 304; Co, 348; Cu, 374; Fe, 796; Mn, 478; Mg, 7.6; Ni, 165; Se, 48; Zn, 478.
476 E.3.	470	453.5	Al, 435; As, 61: Be, 183; Cd, 27; Cr, 65; Co, 96; Cu, 37; Fe, 378; Mn, 47; Hg, 4.4; Ni, 96; Se, 16; Zn, 26.

[a] Average value of three analyses of the sample.

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