APPLICATION OF SEQUENTIAL INJECTION - WETTING FILM EXTRACTION TO THE PHOTOMETRIC DETERMINATION OF VANADIUM(IV) AND VANADIUM(V)

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ABSTRACT

A sequential injection photometric method for the determination of V(IV) and V(V) using wetting film extraction is presented. The chelate of V(V) with N-cinnamoyl-N-(2,3-xylyl)hydroxylamine was extracted into benzene film formed on the inner wall of a Teflon tubing. After being washed with hydrochloric acid, the wetting film was eluted to a flow-through cell by 50 µl of benzene. Absorbance of the benzene segment was continuously monitored at 546 nm. Vanadium(IV) was oxidized to V(V) and then determined. The V(IV) content was obtained by subtracting the concentration of V(V) from that of total V. Vanadium(IV) and (V) as little as 10^{-6} mol l^{-1} can be determined with sampling rates of up to 15 samples h^{-1}.

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INTRODUCTION

Organic wetting film extraction, a new approach to on-line preconcentration and separation, was recently developed in our laboratory[1], and applied to the separation and determination of chromium(III) and (VI)[2], and of molybdenum(VI).[3] When an organic solvent is introduced into a Teflon tube, a wetting film of the solvent is formed on the inner wall of the tube. Subsequently, an aqueous solution containing extractable analytes is aspirated into the tube; the extraction takes place at the interface of the film. After its elution with microliter volumes of a suitable solvent, the absorbance of the extract segment is monitored. Thus, the wetting film is injected and removed during each analysis cycle so that its recovery is not necessary. This extraction system does not require a segmentor and a phase separator which are used for mixing and separation of two immiscible liquids in traditional flow-injection extraction.

Vanadium has several oxidation states; tetravalent and pentavalent forms are usually encountered in environmental and biological samples. The significance of vanadium speciation is that the two oxidation states have different nutritional and toxic properties.[4] It is worthwhile differentiating between the two oxidation states of vanadium.

N-Cinnamoyl-N-(2,3-xylyl)hydroxylamine (CXA) was used for the determination of V(V) after the extraction of the V(V)-CXA chelate into an organic solvent.[5-9] The reagent allowed the catalytic determination of the two oxidation states by extraction of their chelates formed at different pH values into toluene followed by back-extraction into an alkaline medium.[9] However,

this procedure was tedious and time-consuming because separation and detection steps were independent. This paper describes a sequential injection - wetting film extraction method including continuous separation and detection steps for the photometric determination of V(IV) and V(V) in each other's presence, based on complex formation of V with CXA.

EXPERIMENTAL

Reagents

Deionized water obtained from a Nanopure II system (Sybron Barnstead, Dubuque, IA) was used for preparation of the solutions. All chemicals were of analytical reagent grade unless stated otherwise.

Standard stock solutions of V(VI) and V(V) (500 μg ml^{-1}) were prepared by dissolving appropriate amounts of vanadyl sulfate trihydrate and ammonium metavanadate (J. T. Baker), respectively, in 5×10^{-2} mol l^{-1} sulfuric acid. These stock solutions were standardized volumetrically with EDTA. Each working standard solution was prepared daily by diluting the stock solutions with water and adjusting sulfuric acid to 1×10^{-2} mol l^{-1}.

N-Cinnamoyl-N-(2,3-xylyl)hydroxylamine (CXA) was obtained from Wako Junyaku Co., Japan and a CXA-benzene solution (0.4%w/v) was prepared. A potassium periodate solution (1.5×10^{-2} mol l^{-1}) was also prepared.

Apparatus

The manifold as shown in Fig. 1 was constructed from the

following components; a VICI six-port selection rotary valve (V1, Valco Instrument Co. Ins., Houston, TX) connected with reservoirs (R1 - R5) and an injection valve (V2, Valco Instrument Co. Ins., Houston, TX) attached to a reservoir (R6), an extraction coil (EC, 0.8-mm i. d., 3.5 m long), a fiber-optic spectrophotometer (D, PC-701, Brinkmann Analytical,
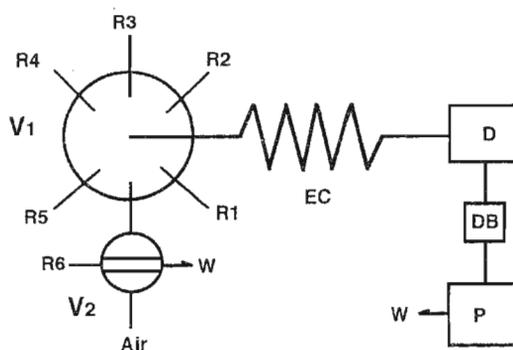

Fig. 1 Schematic diagram of the sequential injection - wetting film extraction manifold. V1, selection valve; V2, injection valve; R1, water; R2, CXA-benzene; R3, air; R4, sample solution; R5, hydrochloric acid; R6, benzene; EC, extraction coil; D, detector; DB, displacement bottle; P, pump; W, waste.

Westbury, NY) equipped with a 546 nm interference filter and a sandwich flow-through cell[10], a displacement bottle (DB) and an Alitea XV peristaltic pump (P, Alitea U. S. A. Medina, WA). All these components were connected by Teflon tubing, having a 0.8-mm i. d. Control of pump and valve V1 and collection of signals were performed with Atlantis software (Lakeshore Tech. Inc., Chicago IL). A more detailed description has been given previously.[1-3]

The absorption spectra were recorded on a Hewlett Packard Model 8452A photodiodearray spectrophotometer.

Preparation of sample solutions

Into a 10-ml calibration flask, appropriate volumes of V(V) solution to provide a final concentration of below 0.3 μg ml^{-1} and the volume of hydrochloric acid (0.5 mol l^{-1}) required to obtain a

final pH of *ca.* 1.5 were added and the solution was diluted to the mark with water. For the determination of total V, 1 ml of 1.5×10^{-2} mol l^{-1} periodate solution was added to the flask after placing the V solution and hydrochloric acid.

Procedure

The transmittance was firstly adjusted to 100% after the flow cell was filled with benzene. When the system was started up at a flow rate of 1.0 ml min^{-1}, water was provided to the flow line from R1 for 15 sec in order to rinse the system. Then valve V_1 was switched to R2 and a CXA-benzene solution (0.4 %w/v) was aspirated into the extraction coil to coat the inner wall of the tubing for 10 sec. Next, valve V_1 was shifted to R3; house air was aspirated into the extraction coil EC for 5 sec to stabilize the wetting film formed. A sample solution was introduced into the reaction coil for 3 min by switching valve V_1 to R4; extraction of V(V) with the wetting film occurred. Benzene as an eluting solvent (50 µl) was loaded into the injection loop with valve V_2 in the position of load during the sample aspiration. After that, valve V_1 was switched to R5 and hydrochloric acid (6 mol l^{-1}) was aspirated into the coil for 10 sec. Then valve V_1 was switched to V_2 and valve V_2 to injection position. The wetting film was eluted to the flow cell by an air-segmented benzene from the injection loop. The flow signals were collected at 2 Hz for 30 sec and were saved in Atlantis for further processing.

RESULTS AND DISCUSSION

Preliminary experiment

Manual extraction was carried out by using CXA (0.1 %w/v) in chloroform and 2 μg ml^{-1} of V(IV) and V(V) solutions at different acidities or pH values. Preliminary experiments indicated that CXA reacts with V(V), yielding extracts the color of which depends on the acidity of the aqueous phase (Fig. 2). The color intensity of the violet chelate on extraction from 6 mol l^{-1} hydrochloric acid was higher than that of the chelates extracted from the weakly acidic media. Their color could be changed to violet by adding concentrated hydrochloric acid to the organic phase. Vanadium(IV) was also extracted with CXA and pH dependency on the V(IV)-CXA chelate was different from that of V(V)-CXA chelate.[9] The V(IV)-CXA chelate did not form at below pH 2, but it was extracted from an aqueous solution at pH 5; the extract was almost colorless. Its color could be also converted to violet by being oxidized with periodate and then being acidified with hydrochloric acid.

The violet chelate which have an absorption maximum at 520 to 540 nm has been employed in order to optimize the wetting film extraction and detection of V.
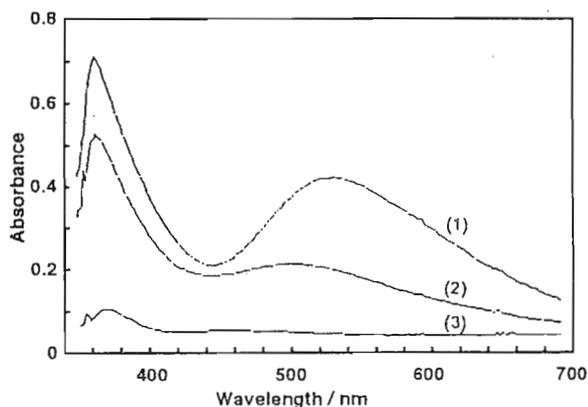

Fig. 2. Absorption spectra of V(V)-CXA chelates in chloroform against the reagent blank. The acidity or pH of aqueous phase: (1), 6 mol l^{-1} HCl; (2), pH 1.4; (3) pH 5.0. $C_{V(V)}$, 2.0 μg ml^{-1}. C_{CXA}, 0.1 %w/v. Volume ratio of the aqueous to the organic phase was 1.

Choice of coating and eluting solvents

Various organic solvents such as benzene, carbon tetrachloride, chloroform, 1,2-dichloroethane, methylene chloride, 3-methyl-1-butanol, 3-methyl-2-pentane and toluene were tested as extractants for the V(V)-CXA chelate under the reaction condition described in the procedure. Absorbance with benzene was the highest of all because of solubility of the V(V)-CXA chelate; benzene was chosen as a coating solvent.

Acetone, acetonitrile and the organic solvents described above were tested as eluting solvents. Of these, benzene was selected for further studies owing to its highest absorbance. The smaller volumes of benzene, the higher absorbances. Taking account of reproducibility and sensitivity, a 50 μl of benzene was used for the procedure.

Effect of chemical and flow variables

The effect of pH on the wetting film extraction of 0.2 μg ml^{-1} V with and without periodate was investigated over the pH range 0.5 - 9 by using acetate (1.0 mol l^{-1}) and phosphate (1.0 mol l^{-1}) buffers, and aspirating 2 ml of the V solution. Maximum absorbances for V(V) were observed at pH 0.5 - 2.0 in the absence of the oxidant as shown in Fig. 3. On the other hand, the absorbances were almost constant in the pH range 0.5 - 5.5 in the presence of periodate. It seemed that V(V) was reduced to V(IV) during the preparation of V(V) solutions at pH 2.5 or above. In order to detect V(IV), a 1.5 x 10^{-2} mol l^{-1} periodate solution and 6 mol l^{-1} hydrochloric acid were successively introduced into the extraction coil after aspiration of V(IV) solutions, and then the

film was eluted with benzene. The highest absorbance for the V(IV)-CXA chelate was observed at pH 5.5 (Fig. 3). There are two ways to determine the amounts of V(IV). One is to oxidize V(IV) to V(V) with periodate followed by extraction at pH 1.5. Another is to adjust the pH of the sample solution to 5.5 so that V(IV)-CXA
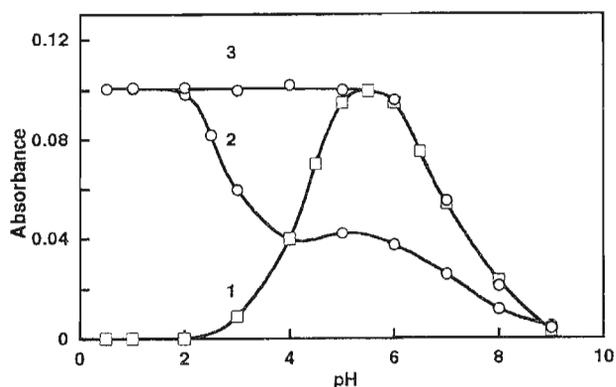

Fig. 3. Effect of pH on the wetting film extraction of V(IV) and V(V).
1, 0.2 μg ml^{-1} V(IV); 2, 0.2 μg ml^{-1} V(V) without periodate; 3, 0.2 μg ml^{-1} V(V) with periodate. Aspirating time of the V solution was 2 min. Other conditions as in the procedure.

chelate is extracted. Although both procedures could be used to quantify V(IV), the former was chosen because of its simplicity. The pH of sample solutions with and without periodate was therefore adjusted to about pH 1.5.

The CXA concentration in benzene was varied from 0 to 0.6 %w/v. Maximal and constant absorbances were obtained at CXA concentrations above 0.15 %w/v. The CXA concentration was fixed at 0.4%w/v. In order to change the color of V(V)-CXA chelate extracted with the film, 0.5 - 9 mol l^{-1} hydrochloric acids were introduced into the extraction after aspiration of V(V) solutions. The absorbances were constant over the concentration range 4 - 9 mol l^{-1}; 6 mol l^{-1} hydrochloric acid was used for the procedure.

The effect of flow rate on the absorbance was investigated by varying it from 0.5 to 2 ml min^{-1}. Absorbances decreased as the flow rate increased presumably because of its slow extraction

rate. Thus, a 1.0 ml min^{-1} of flow rate was adopted for the procedure. Extraction coil length was changed from 0.5 - 5 m; absorbances increased with length of extraction coil. A 3.5 m long extraction tubing was used by considering sampling frequency. The sample volumes were changed by varying the aspirating time from 0.5 to 6 min. Absorbances increased with increasing the sample volume; 3 ml of the sample solution (aspirating time for 3 min) was a convenient compromise between sensitivity and sample throughput.

Calibration graphs and analysis of synthetic mixtures

Under the optimum conditions obtained, calibration curves for V(IV) and V(V) were prepared. Figure 4 shows detector response signals for V(V). Both calibration graphs were linear over the concentration range 0.05 - 0.3 μg ml^{-1}. The least squares lines are A = 0.85 C + 0.006, R^2 = 0.996, where A and C are absorbance and concentration of V in μg ml^{-1}, respectively. A relative standard deviation was 2.4 % (n = 8) for 0.2 μg ml^{-1} of V(V) at a rate of 15 samples h^{-1} and the detection limit (3 x baseline noise) was 12 ng ml^{-1}. The sensitivity of the proposed method is approximately 10 times
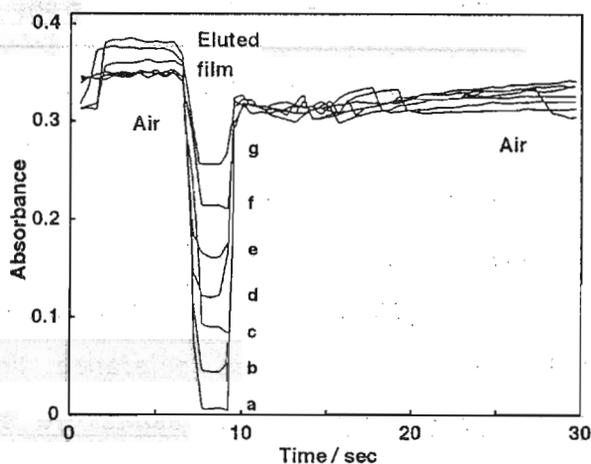

Fig. 4 Detector response signals of V(V) standard solutions.
$C_{V(V)}$/μg ml^{-1}: a, o; b, 0.05; c, 0,10; d, 0.15; e, 0.20; f, 0.25; g, 0.30. Conditions as in the procedure.

higher than manual extraction - spectrophotometric methods.[7,8]

When sample solutions containing different concentrations of V(IV) and V(V) with and without periodate were processed by the present procedure, good correlation between the added and found amounts was obtained as shown in Table 1.

Table 1 Determination of vanadium(IV) and vanadium(V) in synthetic mixtures.

| Sample No. | Concentration of vanadium $/ \mu g\ ml^{-1}$ | | | | |
| | Added | | | Found | |
	V(V)	V(IV)	Total V [a]	V(V) [b]	V(IV)[c]
1	0.05	0.05	0.10_0	0.04_6	0.05_4
2	0.05	0.10	0.14_6	0.04_3	0.10_3
3	0.05	0.15	0.19_2	0.04_3	0.14_9
4	0.10	0.05	0.14_2	0.10_0	0.04_2
5	0.10	0.10	0.19_1	0.10_2	0.08_9
6	0.10	0.15	0.24_9	0.10_4	0.14_5
7	0.15	0.05	0.20_4	0.15_5	0.04_9

[a] with periodate, [b] without periodate, [c] $C_{Total\ V} - C_{V(V)}$.

Interference studies

The effect of diverse ions on the determination of V(V) was examined by adding various amounts of diverse ions to a 0.15 μg ml^{-1} V(V) solution. The tolerance limit was estimated with a relative error of 5%. The results are summarized in Table 2.

Almost diverse ions tested did not interfere with the determination of V(V) at their amounts of 10 μg ml^{-1}. Iron(III), Mo(VI), W(VI) and Sn(II) at this amount caused negative

interferences. However, these ions up to 30-fold excess over V(V) did not interfere except for Sn(II).

Table 2 Tolerance limits of diverse ions on the determination of 0.15 μg ml^{-1} of vanadium(V).

Tolerance limit /μg ml^{-1}	Ion added
1000	Ca(II), Mg(II), Br$^-$, Cl$^-$, ClO$_4^-$, NO$_3^-$, PO$_4^{3-}$, Citrate, Tartrate
100	Al(III), As(III), As(V), Cd(II), Ce(III), Cu(II), Hg(II), Mn(II), Ni(II), Pb(II), Se(IV), Zn(II), Oxalate
10	Bi(III), Ce(IV), Cr(III), Cr(VI)
5	Fe(III), Mo(VI), W(VI)
1	Sn(II)

In conclusion, the proposed method is simple, selective and rapid, and should be feasible in routine work. The wetting film extraction system is characterized by a low consumption of organic solvent, 50 μl sample^{-1}. It should be emphasized that the present system is a very effective means for improving the sensitivity of solvent extraction - spectrophotometry without the need for any complicated step.

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