Catalytic Determination of Vanadium Using the Perphenazine–Bromate Redox Reaction and a Citric Acid Activator

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Citric acid was found to have a highly activating effect on the vanadium-catalysed oxidation of perphenazine (PP) with bromate. An extremely sensitive, selective and simple method was developed for the determination of vanadium based on this effect. The reaction rate was followed spectrophotometrically by monitoring the formation of the red oxidation product of PP at 526 nm within 1 min of mixing. Using the recommended procedure, vanadium can be determined up to 6.5 ng ml^{-1} with a linear calibration graph and a detection limit of 0.08 ng ml^{-1}. A suggested mechanism of the reaction and the activating mechanism of citric acid is presented. The method surpassed the standard Fishman–Skougstad catalytic method in sensitivity, selectivity and speed and was successfully applied to the determination of vanadium in polluted river waters.

Keywords: *Catalytic analysis; vanadium determination; perphenazine–bromate redox reaction; citric acid; activator; river water*

Introduction

Vanadium is a pollutant the determination of which in the sub-ng ml^{-1} level is of increasing importance in biochemical and environmental studies.[1] Current techniques for the trace determination of vanadium include catalytic analysis,[1,2] neutron activation analysis (NAA),[3] AAS,[4] ICP-AES[5] and ICP-MS.[6] However, NAA, AAS and ICP-AES have high detection limits and require laborious procedures for preconcentration. Disadvantages of ICP-MS and NAA include the high cost of the instruments.

The catalytic methods for vanadium determination were recently reviewed.[1,2] Of these methods, the Fishman–Skougstad method[7] was considered as a standard method for the determination of vanadium in natural waters.[8] Two modifications were suggested to improve the reproducibility[9] and sensitivity[10] of the original method. However, the increase in sensitivity was compensated for by a large volume increase in the blank readings, which greatly affected the precision of the method. In spite of such modifications, the application of the method to a wide variety of waters (especially polluted waters) may be unreliable.[8,11]

In the presence of oxidizing agents, perphenazine (2-{4-[3-(2-chlorophenothiazin-10-yl)propyl]piperazin-1-yl}ethanol) (PP), one of the phenothiazines, was first oxidized to give a red radical cation, PP$^{\cdot}$, and may be further oxidized to a colourless sulfoxide derivative.[12] The application of PP to catalytic analysis was recently introduced and applied to the determination of vanadium, (LOD, 10 ng ml^{-1}) based on the perphenazine–bromate reaction.[13] However, the method[13] lacked the required sensitivity and selectivity when applied to river waters. The present paper describes the enhancement of the sensitivity of the former method by a factor of 27 using the activating effect of citric acid and overcoming the serious interferences of nitrite, iodide and iodate (which are common pollutants in natural waters). The method was conveniently applied to the determination of vanadium in polluted river waters. The mechanism of the reaction and also the activating mechanism of citric acid are suggested.

Experimental

Reagents and Apparatus

All glassware and storage bottles were soaked in 0.17 mol l^{-1} HNO_3 overnight and thoroughly rinsed with freshly distilled, de-ionized water prior to use. All chemicals were of analytical-reagent grade. Distilled, de-ionized water was used in the preparation of all solutions. A stock standard solution of 40 mmol l^{-1} perphenazine (shelf life $\approx$ 1 month) was prepared by dissolving perphenazine (Sigma, St. Louis, MO, USA) in 0.10 mol l^{-1} H_3PO_4 and storing in the dark at 4 °C. Two stock standard vanadium solutions[14] [1000 μg ml^{-1} vanadium(IV) or (V)] were prepared from NH_4VO_3 or $VOSO_4$, respectively. Dilute working standard solutions were prepared daily from their respective stock solutions. The following working solutions were used: 4 mmol l^{-1} PP (prepared in 0.05 mol l^{-1} H_3PO_4); 50 ng ml^{-1} vanadium(V) (prepared in 0.01 mol l^{-1} H_2SO_4); 250 mmol l^{-1} sodium bromate; an acid mixture of 1.0 mol l^{-1} H_3PO_4 and 1.0 mol l^{-1} citric acid; 0.2 mol l^{-1} sulfamic acid solution (prepared daily); and 0.1 mmol l^{-1} mercury chloride solution.

A Shimadzu (Kyoto, Japan) UV-160A double-beam spectrophotometer with 10 mm cells was used for recording the absorbance *versus* time graphs. The temperature of the cell compartment was kept constant (within ± 0.01 °C) by circulating the water from a thermostated water-bath regulated at the reaction temperature. Eppendorf (Westbury, NY, USA) micropipettes (10–100 and 100–1000 μl) were used to deliver accurate volumes.

Recommended Procedure

The reagent solutions, test-sample solutions, water and 20 ml stoppered glass test-tubes are kept at 25 °C in the thermostated water-bath. Transfer 3.90 ml or less of the test sample into a test-tube and make up with water to 3.90 ml. Add 0.05 ml of the Hg^{II} solution, 0.10 ml of the sulfamic acid solution and 0.50 ml of the acid mixture, shake and stand for 5 min to decompose the nitrite. Add 0.20 ml of the bromate working standard solution, shake and stand for another 5 min. Start the reaction by adding 0.25 ml of the PP working standard

solution, shake and immediately transfer a portion of the reacting solution into the cell of the spectrophotometer to record the absorbance *versus* time graph at 526 nm against water. The rate (tan α) can be calculated from the slope of the initial linear part of the graph (linear for 1 min after the start of the reaction). The vanadium concentration of the test sample is determined from a calibration graph similarly prepared with the vanadium working standard solution.

Results and Discussion

Effect of Phosphoric Acid Concentration

The rates of both the catalysed (k_c) and uncatalysed (k_u) reactions increased with H_3PO_4 concentration. However, the effect was more pronounced for the latter, as shown in Fig. 1(*a*). The lowering effect of H_3PO_4 on the catalysed reaction might be attributed to a complex formation with vanadium.[14] However, 0.10 mol l^{-1} H_3PO_4 was adopted in the recommended procedure, in order to provide a suitable selectivity for the method.

Effect of PP Concentration

The reaction rates, k_c and k_u, increased with PP concentration as shown in Fig. 1(*b*). However, the increase in PP concentration above 0.2 mmol l^{-1} slightly enhanced the sensitivity ($k_c - k_u$) and gave a sharp increase in the blank values. Therefore, a PP concentration of 0.2 mmol l^{-1} was chosen for the recommended procedure.

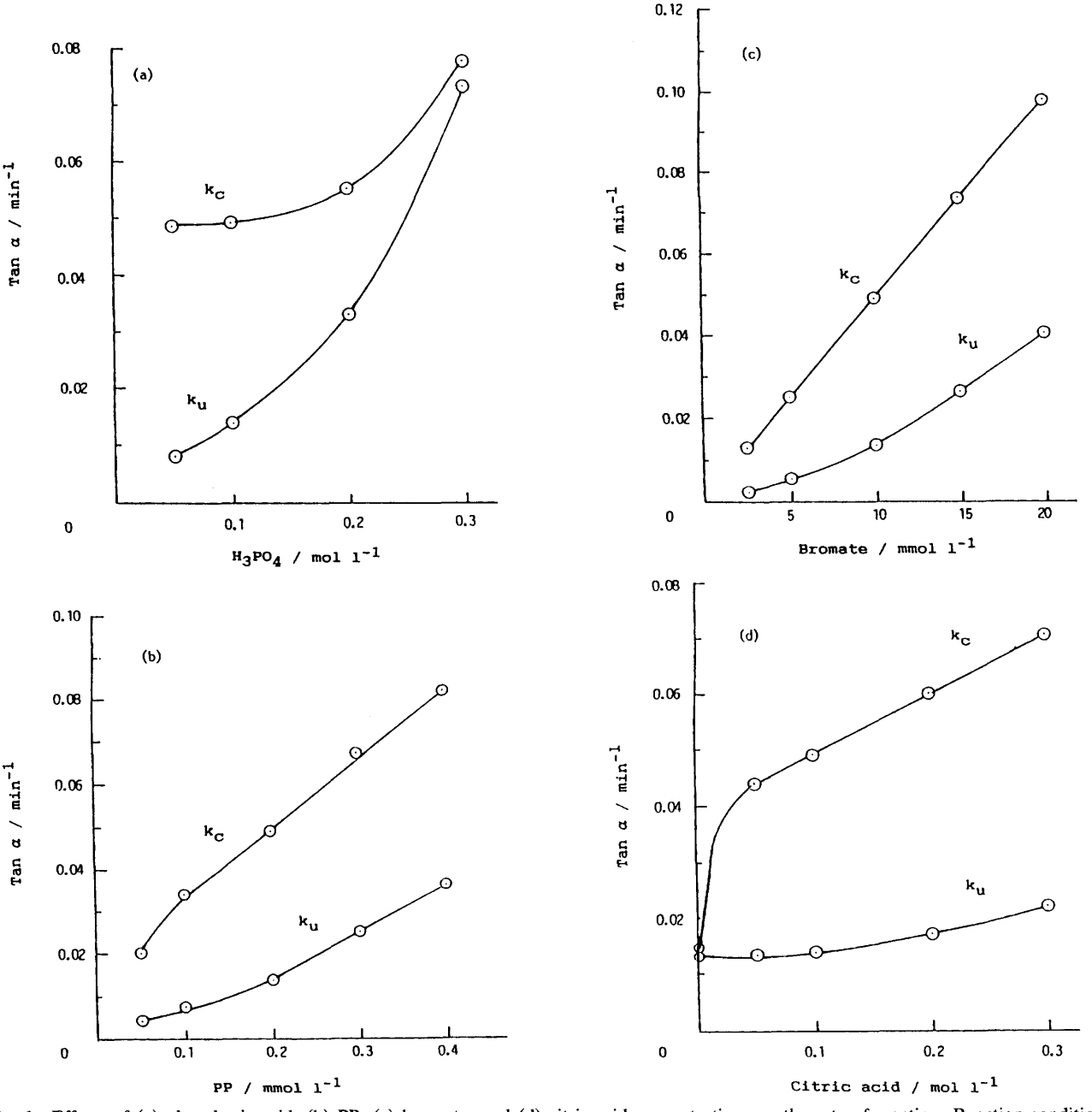

Fig. 1 Effects of (a) phosphoric acid; (b) PP; (c) bromate; and (d) citric acid concentrations on the rate of reaction. Reaction conditions were as given in the recommended procedure (except for the abscissa variable); k_u, reagent blank; k_c, 4 ng ml^{-1} vanadium(v).

Effect of Bromate Concentration

The reaction rates, k_c and k_u, and sensitivity gradually increased with the bromate concentration, as shown in Fig. 1(*c*). Therefore, a bromate concentration of 10 mmol l^{-1} was adopted in the procedure because it gave a moderate sensitivity and a low reagent blank.

Effects of Citric Acid and Other Activators

The choice of a proper activator may greatly enhance the sensitivity of a catalytic method and increase its selectivity.[15] The use of the activating and masking effects of citric acid in catalytic analysis was first proposed and applied by Bontchev[16] to the vanadium-catalysed *p*-phenetidine–chlorate reaction. In that reaction,[16] citric acid enhanced the selectivity towards Fe^{II} and Cu^{II} and increased the sensitivity by a factor of 15. Therefore, the effects of citric acid and other activators were tested for the vanadium-catalysed perphenazine–bromate reaction. Table 1 shows that the best activator for the reaction was citric acid, which gave the highest sensitivity and the lowest blank value.

Fig. 1(*d*) shows that an increase in citric acid concentration, up to 0.05 mol l^{-1}, caused a sharp increase in k_c, whereas it only had a slight effect on k_u. Further increase in the acid concentration resulted in a gradual increase of both k_c and k_u, but had a small effect on the sensitivity. Therefore, a citric acid concentration of 0.10 mol l^{-1} was adopted in the procedure.

Effect of Temperature

As shown in Fig. 2, the reaction rates, k_c and k_u, increased with temperature. However, a temperature of 25 °C was adopted in the procedure because of convenience of operation and the low blank values obtained.

Effects of the Order of Addition of Reagents and of Foreign Ions

The order of addition of reagents had no effect on k_c or k_u values. However, when bromate was added as the last reagent (addition order A), the method was subject to severe interferences from SCN^-, S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, NO_2^-, I^- and Fe^{II}. Therefore, the order of addition had to be changed so that in the presence of the acid mixture, bromate was added to the test solution and the resulting mixture was allowed to stand for 5 min. In this way, bromate oxidized these species to their higher oxidation states where they did not interfere. This order of addition (addition order B) enhanced the selectivity of the method with respect to these species and was adopted in the recommended procedure. However, NO_2^- and I^- remained as serious interferents, the effects of which were successfully eliminated by the addition of sulfamic acid and Hg^{II}, respectively, (as given in the recommended procedure). The presence of 1 μmol l^{-1} Hg^{II} in the reacting solution had no effect on k_c because it was below its tolerance limit, however, it was added to the test solutions and the working standards.

The effects of foreign ions were investigated on the determination of 2 ng ml^{-1} vanadium(v), using the recommended procedure. The tolerance limit was defined as the maximum concentration of the foreign ion that produced a determination error of less than 5%. Table 2 shows the high selectivity of the method. A comparison of Table 2 with that of one corresponding to it in ref. 8 clearly showed the advantages

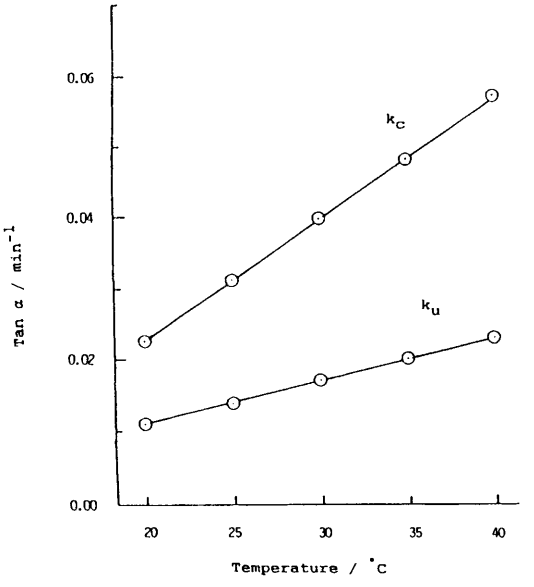

Fig. 2 Effect of temperature on the rate of reaction. Reaction conditions and symbols as in Fig. 1, except for k_c, 2 ng ml^{-1} vanadium(v).

Table 1 Sensitivities and reaction rates of reagent blank for the perphenazine–bromate reaction in the presence of different activators. Reaction conditions are PP, 0.2 mmol l^{-1}; $NaBrO_3$, 10 mmol l^{-1}; H_3PO_4, 0.1 mol l^{-1} and vanadium(v), 0 or 4 ng ml^{-1} at 25 °C

Experiment No.	Activator/mmol l^{-1}		Reaction rate of reagent blank k_u/min^{-1}	Sensitivity $(k_c-k_u)/10^{-3}$ min^{-1} ng^{-1} ml
1*			0.0312	0.33
2			0.0133	0.04
3	Citric acid	100	0.0136	8.85
4	Citric acid	200	0.0173	10.50
5	Tartaric acid	100	0.0211	6.68
6	Tartaric acid	200	0.0261	9.05
7	8-Hydroxyquinoline	2	0.0148	5.00
8	8-Hydroxyquinoline	9	0.0162	6.30
9	8-Hydroxyquinoline-5-sulfonic acid	2	0.0267	6.08
10	1,10-Phenanthroline	1	0.0138	0.53
11	1,10-Phenanthroline	0.2	0.0136	0.75
12	2,2′-Bipyridyl	0.3	0.0136	0.60

* Reaction conditions similar to those in ref. 13: PP, 0.2 mmol l^{-1}; $KBrO_3$, 0.5 mmol l^{-1} and 1.5 mol l^{-1} H_3PO_4 at 25 °C.

Table 2 Tolerance limits of foreign ions in the determination of 2 ng ml^{-1} vanadium. Reaction conditions were: 0.1 mol l^{-1} citric acid, 1 μmol l^{-1} Hg^{II} and 0.4 mmol l^{-1} sulfamic acid. Other conditions as in Table 1

Tolerance limit/ μg ml^{-1}	Foreign ion
≥ 100	Acetate, tartarate, sulfamic acid, CyDTA, Na^+, K^+, NH_4^+, Mg^{II}, Ca^{II}, Ba^{II}, Ni^{II}, Pb^{II}, Zn^{II}, NO_3^-, Cl^-, ClO_4^-, SO_4^{2-}
20	EDTA,* oxalate,* 1,10-phenanthroline,* F^-,* Al^{III}
5	Cd^{II}, Co^{II}, Cu^{II}, Fe^{III}, Fe^{II},* Mn^{II}
1	Cr^{III}, Mo^{VI}, W^{VI}, Zr^{IV}, Br^-, NO_2^-,* SCN^-,* S^{2-}, SO_3^{2-},* $S_2O_3^{2-}$
0.5	Ag^I,* Hg^{II}*
0.2	I^-, IO_3^-
0.005	I^-,† IO_3^-,† NO_2^-*‡

* Species which decreased the rate of reaction.
† In the absence of Hg^{II}.
‡ In the absence of sulfamic acid.

of the present method over the Fishman–Skougstad method, especially with respect to SCN^-, S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, NO_2^-, Fe^{II}, Fe^{III} and Cu^{II}.

Calibration Graph and Detection Limit

A linear calibration graph of up to 6.5 ng ml^{-1} vanadium was obtained using the recommended procedure. Statistical treatments of the results were performed as recommended by Miller and Miller.[17] The equation of the calibration graph was $\tan \alpha\ (A\ \text{min}^{-1}) = 1.36 \times 10^{-2} + 8.85 \times 10^{-3}$ [V], where [V] is the vanadium concentration expressed in ng ml^{-1}. The correlation coefficient was $r = 0.9999$ and the detection limit calculated from three times the standard deviation of the blank ($3s_b$ criterion) was 0.08 ng ml^{-1}. The relative standard deviation, s_r (%), for the determination of 2, 4 and 6 ng ml^{-1} vanadium(v) were 1.8, 0.9 and 0.7%, respectively ($n = 7$). Moreover, the values of the Student's t-test were $\leqslant 0.87$, showing that the t-test could not detect any systematic error in the method (the tabulated t-value for the 95% confidence level is 2.45). Vanadium(IV) gave the same equation for the calibration graph as vanadium(v).

Table 3 compares the sensitivities of the present method, the standard Fishman–Skougstad method and the other methods utilizing related phenothiazine derivatives.[13,18–20]

Mechanism of the Reaction and the Activating Effects of Citric Acid

In acidic media, the oxidation reactions with bromate usually involve Br_2 rather than Br^-.[20,21] However, Br^- might be involved at very low acidities, or in the presence of species which form stable complexes or precipitates with Br^-.[21]

The vanadium-catalysed perphenazine–bromate reaction in an acid medium might be represented by the following equations:

$$5\ PP + BrO_3^- + 6\ H^+ \rightarrow 5\ PP^{\cdot} + 1/2\ Br_2 + 3\ H_2O \quad (1)$$

$$PP + VO_2^+ + 2\ H^+ \rightleftharpoons PP^{\cdot} + VO^{2+} + H_2O \quad (2)$$

$$BrO_3^- + 5\ VO^{2+} + 2\ H_2O \rightarrow 5\ VO_2^+ + 1/2\ Br_2 + 4\ H^+ \quad (3)$$

The uncatalysed reaction is represented by eqn. (1) and the catalytic cycle of vanadium(v)–vanadium(IV) by eqns. (2) and (3), respectively.

The mechanism of the activator's action in the process may differ considerably depending on: the role of the catalyst in the reaction; the character of the catalyst–activator interaction; and the stage(s) of the reaction directly affected by the presence of the activator.[15] Therefore, in order to elucidate the mechanism of the activating effects of citric acid, the rate of reaction in eqns. (2) and (3), in the presence and absence of 0.1 mol l^{-1} citric acid, were compared spectrophotometrically. Namely, the absorbance change of PP$^{\cdot}$ at 526 nm for reaction (2) and that of vanadium(IV) at 800 nm for reaction (3) were measured, where higher concentrations of vanadium were required for the detection of PP$^{\cdot}$ and vanadium(IV).

In mechanistic studies, all solutions were rapidly mixed in the cell of the spectrophotometer, to avoid time-lag. Moreover, bromate was added as the last reagent (addition order A), to minimize the direct oxidation of vanadium(IV).

Reaction (2) was followed for the oxidation of 0.2 mmol l^{-1}

Table 3 Sensitivities and detection limits of various catalytic methods for vanadium determination

Reducing agent	Oxidizing agent	Activator	Dynamic range and DL/ng ml^{-1}	Sensitivity $(k_c - k_u)^*/10^{-3}$ min^{-1} ng^{-1} ml	Cited reference
Gallic acid	persulfate		0.2–8(0.2)	6.90	9
Perphenazine	bromate		10–400	0.33	13
Chlorpromazine	bromate		10–400	0.12	18
Chlorpromazine	chlorate		100–800		19
Chlorpromazine	bromate	tartaric acid	0–150(0.2)	2.70	20
Perphenazine (present paper)	bromate	citric acid	0–6.5(0.08)	8.85	

* Sensitivity refers to the increase in absorbance in a 50 mm cell after 40 min of mixing.

Table 4 Determination of vanadium in water samples from polluted rivers. Reaction conditions as in Table 2

Sample no.*	Sample taken/ml	Vanadium/ng ml^{-1} Added	Found (mean)	s/ng ml^{-1}	s_r (%)	n†	Recovery (%)
1	3.80‡	—	1.45			1	
	3.70	—	2.46	0.05	2.1	5	
	2.70	—	2.48	0.04	1.7	5	
			2.47	0.06	2.6	10	
	2.00	2.00	4.51 (Total§)	0.05	2.0	5	102
2	3.80‡	—	3.17			1	
	3.75	—	4.10	0.05	1.2	5	
	2.75	—	4.11	0.06	1.3	5	
			4.11	0.08	1.9	10	
	2.00	2.00	6.15(Total§)	0.06	1.4	5	102

* Samples collected at Ai river, Kofu City, Japan. 1, pH 7.9 (February 27, 1995) and 2, pH 7.3 (February 28, 1995).
† Number of determinations.
‡ In the absence of the masking solutions of Hg^{II} and sulfamic acid.
§ Total = added + found (mean).

PP with 1.96 μmol l^{-1} vanadium(v), in the absence of bromate and the presence of 0.10 mol l^{-1} H_3PO_4. In the presence of citric acid the reaction was so rapid that the initial rate value could not be estimated. The absorbances at the reaction equilibrium (A_e) were 0.022 and 0.018 and the times required to attain the equilibrium were 2 s and 25 min in the presence and absence of citric acid, respectively. This suggests that citric acid activated reaction (2), probably *via* complex formation with vanadium.[15]

Reaction (3) was followed for the oxidation of 1 mmol l^{-1} vanadium(IV) with 10 mmol l^{-1} or 2.5 mmol l^{-1} bromate, in the presence of 0.10 mol l^{-1} H_3PO_4. The reactions with 10 mmol l^{-1} bromate were too rapid to give reliable estimates of the initial rates. However, the lower bromate concentration of 2.5 mmol l^{-1} gave initial rate values of 0.044 and 0.026 min^{-1}, in the presence and absence of citric acid, respectively. These results suggest that citric acid not only activated reaction (2), but also reaction (3).

It should be noted that the oxidation of vanadium(IV) may not be as simple as that shown by eqn. (3) and may proceed through the formation of the [BrO_3^- VO^{2+}] intermediate.[21]

Determination of Vanadium in Polluted River Waters

After collection, the test sample solution was filtered through a 0.45 μm Millipore-HA filter (Milford, MA, USA) and then acidified with 0.10 ml of 18 mol l^{-1} H_2SO_4 per 200 ml of sample. The aim of the acidification step was to prevent bacterial growth and the adsorption of vanadium on the wall of the polyethylene container and on colloidal particles.[8]

Table 4 shows the results for polluted river samples collected at Kofu City, Japan. Samples without the masking agents showed much lower vanadium contents than those with the masking agents. This might be attributed to the presence of low concentrations of nitrite, which usually constitute an appreciable fraction of the total nitrogen content of river waters.[8,22] Vanadium at low ng ml^{-1} levels was determined with an s_r of 2.6% or less, and the samples fortified with the working standard vanadium solution gave excellent recoveries showing the reliability of the proposed method.

A.A.M. thanks the Ministry of Education, Egypt, for financial support during his study in Japan.

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Paper 5/01754H
Received March 20, 1995
Accepted April 18, 1995