CHEMISTRY LETTERS, pp. 597-600, 1981.

A KINETIC DETERMINATION OF NANOGRAM AMOUNTS OF VANADIUM BY ITS CATALYTIC EFFECT

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A new method is proposed for the determination of vanadium(IV) and vanadium(V). The method is based on their catalytic effect on the reaction of N-phenyl-p-phenylenediamine with N,N-dimethylaniline to form a green compound (λ_{max}= 735 nm) in the presence of bromate. The method is highly sensitive with a Sandell sensitivity of 1.3 x 10^{-3} ng cm^{-2} and useful for the analysis of vanadium in sea water.

Kinetic methods of analysis based on catalytic reactions are especially sensitive and thus applied to the trace analysis of various elements.1) Several catalytic methods have been reported for the determination of submicrogram amounts of vanadium by its catalytic effect.2) - 7)

In the present paper, a new sensitive catalytic method is described for the determination of vanadium(IV) and vanadium(V). When an oxidant is present, N-phenyl-p-phenylenediamine (PPD) couples with N,N-dimethylaniline (DMA) to form a green compound (λ_{max}= 735 nm). The present authors found that vanadium(V) catalyzed the oxidative coupling reaction in the presence of bromate and tartrate acted as an activator on the same reaction. As little as 10^{-9} mol dm^{-3} of vanadium(V) can be determined easily by its catalytic effect at a fixed time after the initiation of the reaction. Vanadium(IV) being oxidized by bromate could also be determined.

DMA was purified by vacuum distillation. All other chemicals used were of analytical grade and deionized distilled water was used to prepare the solutions of the reagents. The recommended procedure is as follows: To 20 - 25 ml of a sample solution containing vanadium no more than 50 ng in a beaker, add 3 ml of sodium tartrate solution (1.0 mol dm^{-3}), 5 ml of PPD solution (5.0 x 10^{-4} mol dm^{-3}) and 2 ml of DMA solution (4.0 x 10^{-2} mol dm^{-3}). Adjust the pH of the solution to 2.2 - 2.4 by adding hydrochloric acid (1.0 mol dm^{-3}) using a pH meter. After keeping the solution in a thermostat at 50.0 ± 0.1°C to attain thermal equilibrium (about 10 min), start the reaction by mixing 1 ml of potassium bromate solution (0.1 mol dm^{-3}) and diluting to the mark with water of 50°C. Exactly 20 min after the addition of bromate, pipette about 4 ml of the reaction mixture into a 10-mm glass cell and measure the absorbance at 735 nm against a distilled water reference. Obtain the net absorbance by subtracting a blank absorbance.

The green comound formed during the reaction with or without vanadium(V) has an absorption maximum at 735 nm at pH lower than 2.5. The shift of the maximum to shorter wavelength was observed at pH higher than 2.5. Thus the compound is thought to be N-diphenylamine-N',N'-dimethyl-p-benzoquinone diimine-N'-ium. The effect of pH on the color development was examined at a reaction time of 20 min at 50°C. The results are shown in Fig. 1; the rate of color formation is faster at lower pH. However, the reagent blanks are very high at pH lower than 2.1. Thus the reaction was carried out in the pH range of 2.2 - 2.4.

The reaction proceeded faster at higher temperatures. However, an increase in temperature also increased the blank absorbance at temperatures higher than 55°C. The reaction temperature was fixed at 50°C and a reaction time of 20 min was chosen for the sake of high sensitivity and reproducibility.

The effect of concentrations of the reactants on the color formation was

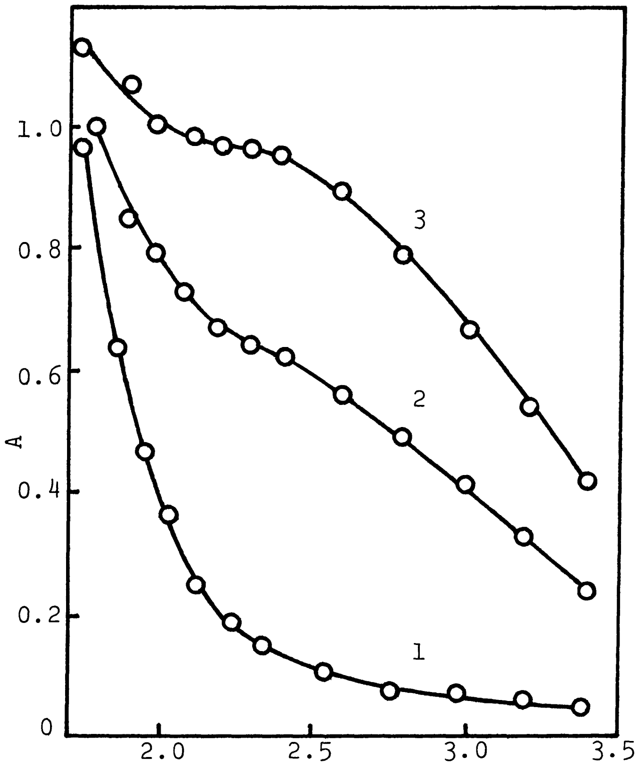

Fig. 1. Effect of pH
1: reagent blank 2: 0.6 ng of vanadium (V) per ml 3: 1.0 ng of vanadium(V) per ml

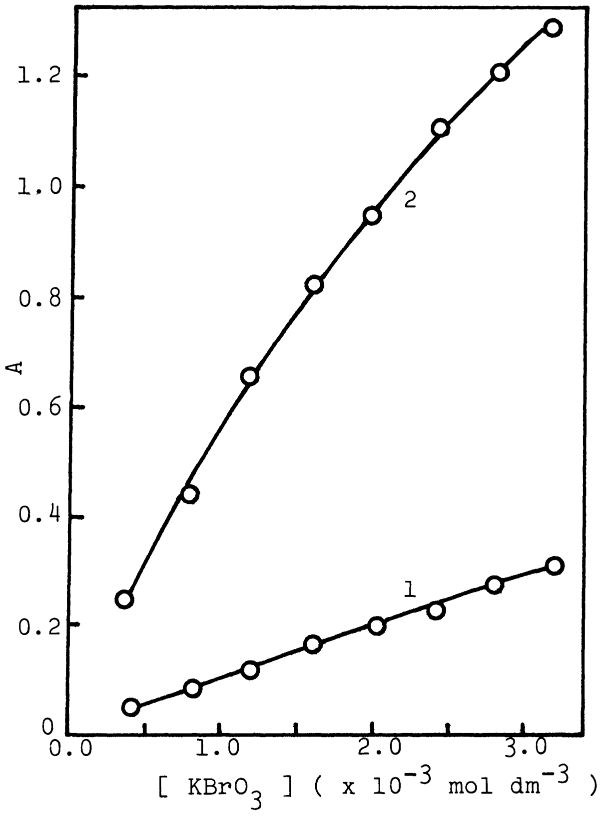

Fig. 2. Effect of potassium bromate concentration
1: reagent blank
2: 1.0 ng of vanadium(V) per ml

examined. The reaction proceeded faster with increase in the concentrations of PPD and DMA, but the blank absorbances also increased. The concentrations of PPD and DMA were selected as 5.0×10^{-5} mol dm^{-3} and 1.6×10^{-3} mol dm^{-3}, respectively. As the concentration of bromate increased, the rate of color formation proceeded faster as shown in Fig. 2. A concentration of bromate was selected as 2.0×10^{-3} mol dm^{-3} in the procedure. The rate of color formation also increased with increase in the tartrate concentration as shown in Fig. 3. Tartrate seems to act as an activator in the color reaction.[7),8)] A concentration of tartrate was selected as 6.0×10^{-2} mol dm^{-3}.

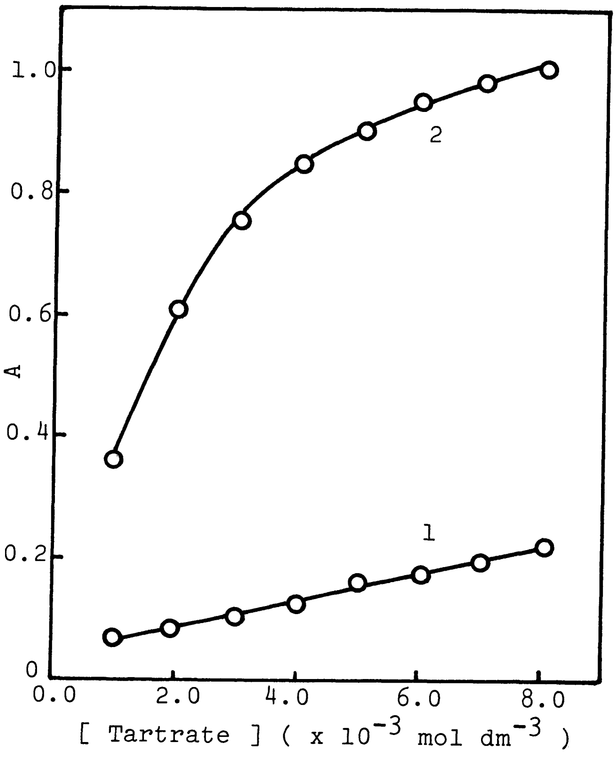

Fig. 3. Effect of sodium tartrate concentration
1: reagent blank
2: 1.0 ng of vanadium(V) per ml

Calibration curve for the procedure shows that Beer's law is obeyed over the range 0 - 1.0 ng of vanadium(V) per ml. Calibration curve for vanadium (IV) is almost identical to that obtained for vanadium(V) within experimental error; the mode of coloration by vanadium(IV) is the same as that of vanadium(V), presumably because vanadium(IV) is oxidized to vanadium(V) by bromate. The method is highly sensitive with a Sandell sensitivity[9)] of 1.3×10^{-3} ng cm^{-2}. The reproducibility is satisfactory with a relative standard deviation of 2.3% for ten determinations of 1.0 ng of vanadium(V) per ml.

The effect of foreign ions on the determination of 30 ng of vanadium(V) per 50 ml of the working solution was examined. The following ions and compounds caused no interference at least up to the specified amount: 10 mg of Ba(II), Ca(II), Mg(II), Sr(II); 1 mg of Cd(II), Ce(III), Co(II), Hg(II), Mo(VI), Ni(II), Pb(II), Zn(II); 100 µg of Ag(I), As(V), Bi(III), Ce(IV), Cr(III), Mn(II), Se(IV); 10 µg of Al(III), As(III), Cu(II), Sn(II), Sn(IV); 10 mg of PO_4^{3-}; 1 mg of Br^-, F^-; 10 µg of I^-, NO_2^-; 10 mg of sodium chloride, sodium sulfate, potassium chloride, potassium nitrate and ammonium chloride. Positive interferences were observed with iron(III) (>0.5 µg) or chromium(VI) (>1 µg). The interference of chromium(VI) could be suppressed by reduction to chromium(III) with ethanol. The masking agents such as fluoride and phosphate was examined to eliminate the interference of iron (III). However, a suitable masking agent for iron(III) was not found, because vanadium(V) was also masked. Thus solvent extraction technique is now in progress for the separation of vanadium(V) from iron(III). Detailed results will be published elsewhere.

The method was applied to the analysis of vanadium in sea water. The sample (5 dm^3) of freshly collected sea water was filtered through a 0.45-μm Millipore filter and then 40 ml of concentrated hydrochloric acid was added to the filtrate. After these treatments, 10 or 20 ml of the filtrate was directly uesd for the recommended procedure. As the content of iron in the same sample was found to be 2 ppb by atomic absorption spectrometry, it does not interfere in the determination of vanadium. To examine the recovery of vanadium, known amounts of vanadium (V) were added to the sample analyzed. The results are shown in Table 1. The recovery of added vanadium was found to be quantitative and the values were in good agreement with those reported by the others.10),11)

Table 1. Determination of vanadium in sea water

Sample[a] taken ml	Vanadium added ng	Vanadium found ng	Vanadium in sample ppb
10	0	23	2.3
10	0	23	2.3
10	0	22	2.2
10	10	30	2.0
10	10	30	2.0
10	10	31	2.1
20	0	45	2.3
20	0	44	2.2
20	10	53	2.2
20	10	53	2.2

[a] Seashore of Sakenotsu, Tottori (Aug. 7, 1980)

References

1) K. B. Yatsimirskii, Kinetic Methods of Analysis, Pergamon, Oxford (1966).
2) M. Tanaka and N. Awata, Anal. Chim. Acta, 39, 485 (1967).
3) M. J. Fishman and M. W. Skougstad, Anal. Chem., 36, 1643 (1964).
4) P. R. Bontchev, Mikrochim. Ichnoanal. Acta, 1962, 577, 584, 592.
5) T. Yamane and T. Fukasawa, Bunseki Kagaku, 25, 454 (1976).
6) K. Hirayama and S. Unohara, Bunseki Kagaku, 29, 733 (1980).
7) T. Kawashima, S. Karasumaru, M. Hashimoto and S. Nakano, Nippon Kagaku Kaishi, 1981, 175.
8) P. R. Bontchev, Talanta, 19, 675 (1972).
9) E. B. Sandell and H. Onishi, Photometric Determination of Traces of Metals, 4th ed., John Wiley & Sons, New York (1978) p.190.
10) S. Okabe and T. Morinaga, Nippon Kagaku Zasshi, 89, 284 (1968).
11) S. Okabe and T. Morinaga, J. Oceanograph. Soc. Japan, 25, 223 (1969).

(Received February 23, 1981)