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Selective Determination of Vanadium(V) Using its Catalytic Effect on the Bromate Oxidation of Nuclear Fast Red

N. POURREZA * and H. ZAVVAR MOUSAVI
Chemistry Department, College of Sciences, Shahid Chamran University, Ahvaz, Iran
E-mail: pourrezan@yahoo.co.in

A highly selective and sensitive catalytic method is described for the determination of trace amount of vanadium(V) based on its catalytic effect on the oxidation of nuclear fast red with bromate. The reaction was followed spectrophotometrically by measuring the change in absorbance of nuclear fast red at 517 nm, 4 min after the initiation of the reaction. In this study experimental parameters were optimized and the effect of other cations and anions on the determination of vanadium(V) was examined. The calibration graph was linear in the range of 5–100 ng ml^{-1} of vanadium(V) and $3S_b$ detection limit was 3.4 ng mL^{-1}. The method was successfully applied to the determination of vanadium(V) in water and steel samples.

Keywords: Determination, Catalytic, Vanadium(V), Bromate oxidation, Spectrophotometric, Nuclear fast red.

INTRODUCTION

Vanadium occurs at parts per billion levels in many natural systems, alloys and geochemical minerals[1]. Wet analysis and spectrophotometric methods[2] can perform determination of vanadium in geological samples. Preconcentation with solvent extraction has also been followed for the trace analysis of vanadiurn[3]. Vanadium is also a pollutant, the determination of which has become of great importance in biochemical and environmental studies[4].

Several kinetic methods for the determination of vanadium based on its catalytic action on the oxidation of various organic compounds have been reported[5–11]. Most of these methods use bromate as an oxidant followed by photometric monitoring. Kinetic methods can be implemented on very simple, inexpensive equipment and provide low level determination comparable to those typically offered by much more expensive techniques such as inductively coupled plasma, atomic emission spectrometry (ICP-AES)[12] or electrothermal atomic absorption spectrometry (ETAAS)[13]. In this paper we have described a simple, sensitive and highly selective catalytic method for the determination of vanadium(V) based on its catalytic effect on the oxidation reaction of nuclear fast red by bromate.

EXPERIMENTAL

All chemicals were of analytical reagent grade. Distilled, de-ionized water was used for the preparation of all the solutions. A stock standard vanadium solution

(1000 μg mL^{-1}) was prepared by dissolving 2.297 g NH_4VO_3 (Merck) in water and diluting to 1000 mL in a volumetric flask. Dilute working standard solutions were prepared daily from this stock solution. Bromate solution 0.1 mol L^{-1} was prepared by dissolving 8.350 g of $KBrO_3$ (Merck) in water and diluting to 500 mL. A 7×10^{-4} mol L^{-1} solution of nuclear fast red (Merck) was prepared by dissolving 0.125 g of the reagent in water and diluting to 500 mL. A 2.5 mol L^{-1} solution of H_2SO_4 (Merck) was used.

A Jasco UV-Vis spectrophotometer model 7850 was used for recording the spectra and a Perkin-Elmer UV-Vis spectrophotometer model 550S was used tor absorbance measurements. A Colora C-1668 thermostat in which temperature could be fixed within ±0.10°C was used for maintaining the temperature.

Recommended Procedure: In a 10 mL volumetric flask were added 2 mL of nuclear fast red (7×10^{-4} mol L^{-1}), 1 mL of H_2SO_4 solution (2.5 mol L^{-1}) and appropriate amount of vanadium(V) stock solution, 2 mL of 0.1 mol L^{-1} bromate and made up to the mark with water. The absorbance was measured at 517 nm after 4 min. The time was measured immediately after the addition of the last drop of bromate solution. A blank solution was also prepared in the same way using distilled water instead of vanadium(V) solution.

RESULT AND DISCUSSION

The absorption spectrum of nuclear fast red shows that maximum absorption occurs at 517 nm. This reagent is oxidized by bromate and its absorbance is decreased. However, the reaction between nuclear fast red and bromate is mild but when traces ot vanadium(V) are present the reaction proceeds faster. The catalytic effect of vanadium on the reaction was monitored spectrophotometrically by measuring the change in absorbance (ΔA) of nuclear fast red at 517 nm with time. A fixed time of 4 min was applied because highest ΔA was obtained.

Effect of Variables: The optimum conditions were established by investigating the effect of different variables influencing the reaction.

Fig. 1 shows the effect of sulfuric acid concentration on the reaction. Highest

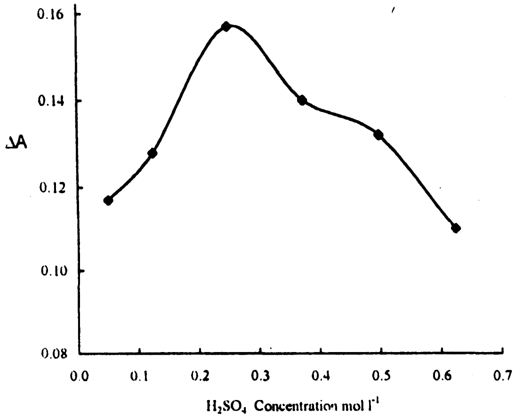

Fig. 1. Effect of H_2SO_4 concentration on oxidation of nuclear fast red (Conditions: V(V) 40 ng mL^{-1}, bromate 0.02 mol L^{-1}, nuclear fast red 1.4×10^{-4} mol L^{-1})

change in absorbance (ΔA) was obtained when H_2SO_4 concentration was 0.25 mol L^{-1} in the final solution; therefore it was chosen as the optimum.

The influence of nuclear fast red concentration on the change in absorbance was studied. From Fig. 2 we can see that highest ΔA is obtained when nuclear fast red concentration is 1.4×10^{-4} molL^{-1} in the final solution. As a result 0.4×10^{-4} mol L^{-1} was selected as optimum concentration.

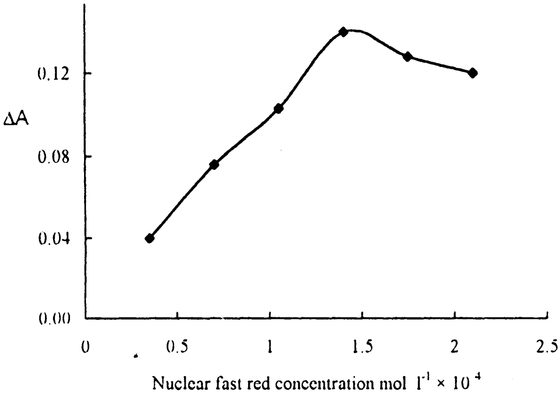

Fig. 2. Effect of concentration of nuclear fast red on reaction rate (Conditions: V(V) 40 ng mL^{-1}, bromate 0.02 mol L^{-1}, H_2SO_4 0.25 mol L^{-1})

The reaction rate was gradually increased by increasing bromate concentration up to 0.02 mol L^{-1} and hence highest ΔA was observed (Fig. 3). Therefore a bromate concentration of 0.02 mol L^{-1} was chosen for further work.

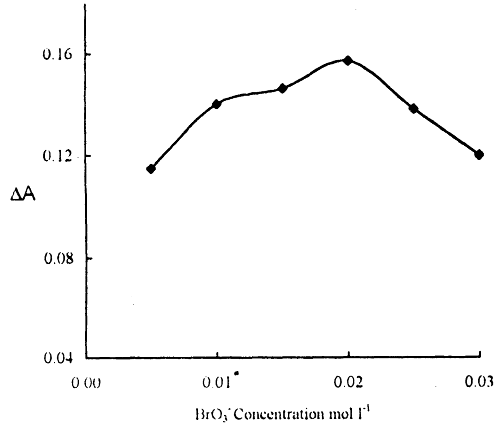

Fig. 3. Effect of bromate concentration on reaction rate (Conditions: V(V) 40 ng mL^{-1}, nuclear fast red 1.4×10^{-4} mol L^{-1}), H_2SO_4 0.25 mol L^{-1})

The effect of temperature was also studied in the range 25–45°C under the conditions given in the recommended procedure. It was observed that the change in absorbance was decreased at higher temperatures. Although the rate of both catalyzed and uncatalyzed reaction was increased at higher temperatures, the rate of uncatalyzed reaction became considerably higher and ΔA was decreased. Therefore a temperature of 25°C was selected as the working temperature.

Interference Studies: The interference effects of various cations and anions on the determination of 40 ng mL^{-1} of vanadium were examined. The tolerance ratio of each foreign ion was taken as the largest amount yielding an error of less than 4%. The results are presented in Table-1.

TABLE 1
TOLERANCE LIMIT OF FOREIGN IONS IN THE DETERMINATION OF 40 ng mL^{-1} VANADIUM(V).

Foreign ion	Tolerance ratio
K^+, Ni^{2+}, CH_3COO^-, Mn^{2+}	2000
$SO_4{}^{2-}$, Cr^{3+}, IO_3^-, Cd^{2+},NO_3^-, PO_4^{3-}, ClO_4^-, F^-	1000
Co^{2+}, Li^+, Sn^{2+}, Al^{3+}, $S_2O_5{}^{2-}$, Cl^-, Cu^{2+}	500
Ca^{2+}, Fe^{2+}, Sr^{2+}, Fe^{3+}, Na^+	300
Mo(VI), Ag^+, I^-, Hg^{2+}	50
NO_2^-	5

Calibration Graph and Detection Limit: A calibration graph was prepared for the determination of vanadium(V) using the recommended procedure under the optimum conditions. There was a linear relationship between ΔA and vanadium concentration in the range of 5–100 ng mL^{-1}. The linear regression equation for calibration graph is $\Delta A = 0.042 + 0.0028C$, where C is the concentration of vanadium in ng mL^{-1} with correlation coefficient $r = 0.9992$. Eight replicate determinations of 40 ng mL^{-1} of vanadium(V) gave a relative standard deviation of 1.3%. The detection limit calculated by $3S_b$ was 3.4 ng mL^{-1}.

Application

In order to test the reliability of the present method, it was applied to the determination of vanadium(V) in steel. 0.11 g of steel was dissolved in 10 mL nitric acid by heating on a hot plate. The solution was cooled and then 10 mL of ammonia solution and 10 mL water were added. The solution was filtered and diluted to 100 mL in a volumetric flask. An aliquot of this solution was treated under the recommended procedure. The samples were also analyzed by spark emission spectrometry. The results presented in Table-2 show a good agreement between the two methods.

TABLE-2
DETERMINATION OF VANADIUM(V) IN STEEL

Sample No.	Spark emission method (%) found	Purposed kinetic method (%) found	Relative Error (%)
1.	0.0190	0.0197	3.68
2.	0.0300	0.0310	3.33
3.	0.0400	0.0410	2.50

The proposed method was also successfully applied to the determination of vanadium in tap water sample (Table-3). The data obtained for water samples spiked with vanadium showed very good recoveries.

TABLE-3
DETERMINATION OF VANADIUM IN TAP WATER

Sample No.	V(V) added (ng mL^{-1})	Total V(V) found (ng mL^{-1})	Recovery (%)
1.	0	8.5	—
2.	20	28.8	101.05
3.	40	49.1	101.20

Conclusion

Although numerous kinetic-spectrophotometric methods have been developed for vanadium determination, the enhanced selectivity of this method compared to some of the other methods[8] is its great advantage. Fe^{2+} and Fe^{3+} are tolerated up to 300 fold. It also has a wider linear range (5–100 ng mL^{-1})[9] and is more sensitive than some of the other methods reported[11]. The method can be directly applied to the determination of vanadium in tap water, because interfering ions in water are tolerable.

Compared to the ICP-AES and ETTAAS techniques, the proposed method uses less expensive instrumentation but provides equally good result. This method is very simple and useful for determination of vanadium in real samples.

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