Asian Journal of Chemistry Vol. 21, No. 9 (2009), 6741-6746

Spectrophotometric Kinetic Determination of Ultra Trace Amounts of Vanadium(V) Based on The Oxidation of Rhodamine B by Bromate in Sulfuric Acid Medium

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A new, simple, sensitive and selective catalytic spectrophotometric method was developed for the determination of trace amounts of V(V). The method is based on the catalytic effect of vanadium(V) on the oxidation of rhodamine B by bromate in acidic medium. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of rhodamine B at 554 nm with a fixed-time method. The decrease in the absorbance of rhodamine B is proportional to the concentration of V(V) in concentration range 0.02-20 ng/mL, with a fixed time of 0.5-2.0 min from initiation of the reaction.The limit of detection of V(V) is 0.011 ng/mL. The relative standard deviation of 2.0 and 10.0 ng/mL V(V) was 2.6 and 2.8 %, respectively. The method was applied to the determination of vanadium(V) in natural water.

Key Words: Vanadium(V), Catalytic, Rhodamine B, Bromate.

INTRODUCTION

Vanadium is a biologically essential element[1]. Its inclusion in enzymes such as bromoperoxide and nitrogenase reveals the importace of its redox chemistry. A number of model complex systems have been investigated in order to elucidate vanadium redox mechanisms. Some tunicate fish and marin animals selectivity accumulate vanadium species from the ocean. Vanadium complexes, including organovanadium exist in a variety of configureations depending on their oxidation states and coordination numbers[2].

Vanadium in the hyposphere was believed to be a conservative element due to its almost uniform distribution in both oceanic and limnetic areas. However, slight seasonal variations with the depth of water might be encountered due to biological processes and/or the geochemical cycles of particulate vanadium and phosphorus[3,4].

Vanadium in trace amounts is an essential element for cell growth at mg dm^{-3} levels, but can be toxic at higher concentrations[5]. The toxicity of vanadium is dependent on its oxidation state[6], with vanadium(V) being more toxic than vanadium(IV). Vanadium pentoxide dust and fumes are strong respiratory irritants, owing to their capacity to lessen the viability of alveolar macrophages, which play an important role in the lung defense against environmental contaminations. The threshold limit values (TLV) for V_2O_5 dust and fumes are 0.5 and 0.05 mg cm^{-3}, respectively[7].

Vanadium is widely distributed in nature in ores, clays, hard coal, igneous rock, limestones, sandstones and fossil fuel, but not in appreciable amount in high silicon rocks. It is emitted into the the environment through the combustion of fossil fuels. A variety of methods have been used for determination of vanadium, which include colorimetry[7-9], fluorometry[10,11], voltammetry[12], potentiometry[13], gas chromatography[14], neutron activation analysis[15,16], X-ray fluorescence spectrometry[17], emission spectroscopy[18] and atomic absorption spectroscopy[19].

In this paper a rapid, selective, sensitive and simple method is described, which is based on the catalytic effect of V(V) on oxidation of rhodamine B by bromate in acidic medium. The reaction was monitored spectrophotometrically at 554 nm by measuring the decrease in absorbance of the reaction mixture for the first 0.5-2.0 min from initiation of the reaction.

EXPERIMENTAL

Doubly distilled water and analytical reagent grade chemicals were used during all of the experimental studies. Rhodamine B solution 1×10^{-3} M was prepared by dissolving 0.0479 g of the compound (Merck, MW = 479.02) in water and solution was diluted to the mark in a 100 mL volumetric flask. Bromate stock solution 0.10 M, was prepared by dissolving 1.67 g of potassium bromate (M = 167) in water and diluting to 100 mL in a 100 mL volumetric flask. Standard stock V(V) solution (100 μg/mL) was prepared by dissolving 0.0179 g of V_2O_5 (Merck) in conc. sulfuric acid and diluted to 100 mL in a 100 mL volumetric flask. Stock solution (1000 μg/mL) of interfering ions were prepared by dissolving suitable salts in water, hydrocloric acid or sodium hydroxide solution.

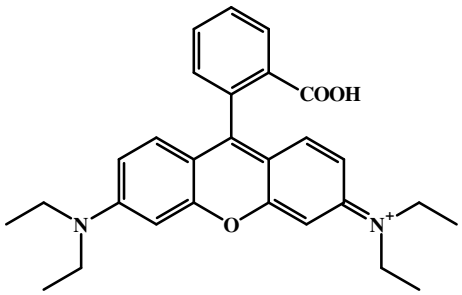
All glassware were cleaned with detergent solution, rinsed with tap water, soaked in dilute HNO_3 solution (2 % v/v), rinsed with water and dried.

Absorption spectra were recorded with a CECIL model 7500 spectrophotometer with a 1.0 cm quartz cell. A model 2501 CECIL spectrophotometer with 1.0 cm glass cuvettes was used to measure the absorbance at a fixed wavelength of 521 nm. A thermostat water batch was used to keep the reaction temperature at 25 ºC.

Recommended procedure: All the solutions and distilled water were kept in a thermostated water batch at 25 °C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 0.2-2.0 ng/mL V(V) was transferred into a 10 mL volumetric flask and then 0.4 mL of sulfuric acid 6 M, 0.3 mL 1.0×10^{-3} M rhodamine B were added to the flask. The solution was diluted to *ca.* 8 mL with water. Then, 0.40 mL 0.10 M bromate was added and the solution was diluted to the mark with water. The solution was mixed and a portion of the solution was transferred to the spectrophotometer cell. The reaction was followed by measuring the decrease in absorbance of the solution against water at 554 nm for 0.5-2.0 min from initiation of the reaction. This signal (sample signal) was labeled as ΔA_s.The same procedure was repeated without addition of V(V) solution and the signal (blank signal) was labeled as ΔA_b.Time was measured just after the addition of last drop of bromate solution.

RESULTS AND DISCUSSION

Rhodamine B undergoes a oxidation reaction with bromate in acidic medium to form a colourless product at very slow rate. It is found that this reaction rate is sharply increased by addition of trace amount of V(V).This process was monitored spectrophotometrically by measuring the decrease in absorbance of the characteristic band of rhodamine B (554 nm). Therefore, by measuring the decrease in absorbance of rhodamine B for a fixed time of 0.5-2.0 min initiation of the reaction, the V(V) contents in the sample can be measured.



Structure of rhodamine B

Influence of variables: In order to take full advantage of the procedure, the reagent concentrations must be optimized. The effect of acid concentration, rhodamine B and bromate concentration and temperature on the rate of catalyzed and uncatalyzed reaction was studied.

The effect of the sulfuric acid concentration on the rate of reaction was studied in the range of 0.12-0.6 M (Fig. 1). The results show that the net reaction rate

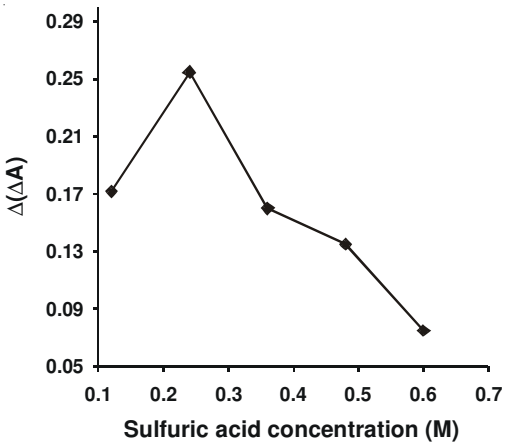


Fig. 1. Influence of sulfuric acid coccentration on the sensitivity, conditions: 10.0 ng/mL V(V), 6.0×10^{-5} M rhodamine B and 4.0×10^{-3} M bromate at 25 °C, in fixed time of 0.5-2.0 min from initiation of reaction

increases with increasing sulfuric acid concentration up to 0.24 M and decreases at higher concentrations.This mean that the rate of uncatalyzed reaction increases with phosphoric acid concentration (> 0.24 M) to a greater extent than the catalyzed reaction and the difference between the rates of catalyzed and uncatalyzed reactions (ΔA_s-ΔA_b) diminishes at higher phosphoric acid concentrations. Therefore, a phosphoric acid concentration of 0.24 M was selected for further study.

Fig. 2 shows the effect of the rhodamine B concentration on the sensitivity for the range 2×10^{-5} to 8×10^{-5} M. This sensitivity (net reaction rate) increases with increasing rhodamine B concentration up to 3×10^{-5} M and decreases at higher concentrations. This may be due to the aggregation of the dye at higher concentrations. Therefore, a final concentration of 3×10^{-5} M of rhodamine B was selected at the optimum concentration.

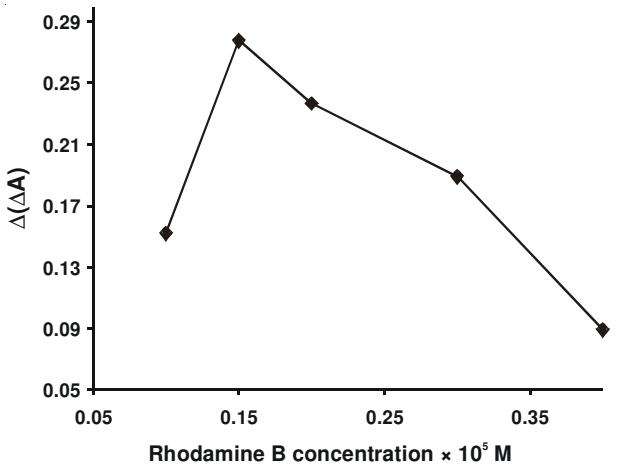


Fig. 2. Effect of rhodamine B concentration on the sensitivity. Conditions: 0.24 M H_2SO_4, 10.0 ng/mL V(V) and 4.0×10^{-3} M bromate at 25 °C, in fixed time of 0.5-2.0 min from initiation of reaction

The effect of the bromate concentration on the rate of reaction was studied in the range of 2.0×10^{-3}-1.0×10^{-2} M (Fig. 3). The results show that the net reaction rate increases with increasing bromate concentration up to 4.0×10^{-3} M and decreases at higher concentrations. Therefore, a bromate concentration of 4.0×10^{-3} M was selected for further study.

The effect of the temperature on the sensitivity was studied in the range 20-45 °C with the optimum of the reagents concentrations. The results showed that, as the temerature increases up to 25 °C, the net reaction rate increases, whereas higher temperature values decrease the sensitivity ($\Delta A = \Delta A_s$-ΔA_b). This means that the rate of uncatalyzed reaction increases with temperature to a greater extent and occurred at a sutable rate. Therefore, 25 °C was selected for further study.

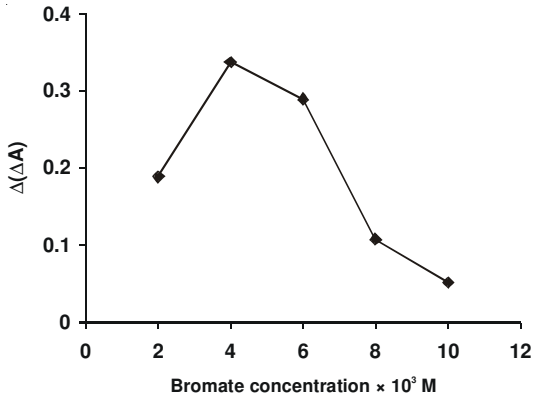


Fig. 3. Effect of bromate concentration on the reaction rate. Conditions: 0.24 M H_2SO_4, 10.0 ng/mL V(V), 3×10^{-5} M rhodamine B, at 25 °C, in fixed time of 0.5-2.0 min from initiation of reaction

Calibration graph, precision and limit of detection: Calibration graphs were obtained using the fixed-time method. This method was applied to the change in absorbance over an interval of 0.5-2.0 min from intiation of the reaction because it provided the best regresion and sensitivity. Under the optimum conditions described above, a linear calibration range 0.02-20.0 ng/mL of V(V) was found.

The equation of the calibration graph is $\Delta A = 0.0737 + 0.0338C$ (n = 6, r = 0.9998), where ΔA is change in absorbance for the sample reaction for 0.5-2.0 min from initiation of the reaction (catalytic reaction) and C is V(V) concentration in ng/mL. The limit of detection from $Y_{LOD} = Y_b + 3\ S_b$ is 0.011 ng/mL, where, Y_{LOD} is signal for limit of detection, Y_b is average blank signal (n = 10) and S_b is standard deviation of blank signal (n = 10, uncatalyzed reaction). The relative standard deviation for six replicate determination of 2.0 and 10.0 ng/mL V(V) was 2.6 and 2.8 %, respectively.

Interference study: In order to assess the application of the proposed method to synthetic samples, the efffect of various ions on the determination of 10.0 ng/mL V(V) was studied. The tolerance limit was defined as the concentration of a added ions causing a relative error less than 3 % the results are summarized in Table-1. Many ions did not interfere, even when they were present in 500 fold excess over V(V). The results show that method is relatively selective for V(V) determination.

TABLE-1
EFFECT OF FOREIGN IONS ON THE DETERMINATION OF 10 ng/mL V(V)

Species	Tolerance limit ($w_{ion}/w_{Ru(III)}$)
Na^+, K^+,Ca^{2+}, Mg^{2+}, Rb^+, Pb^{2+}, Zn^{2+} , Ba^{2+}, Cu^{2+}, Te^{4+}, Se^{4+}, $C_2O_4^{2-}$, $S_2O_8^{2-}$, HSO_4^-, ClO_3^-,CO_3^{2-},NO_3^-, Tatarate, BO_3^{3-}, Cl^-	1000
Ni^{2+}, Rh^{3+}	400
Ag^+, Br^-	100
I^-	10

Sample analysis: In order to evaluate the applicability of the proposed method, water samples and synthetic water, samples were analyzed to determine V(V) contents. The results are presented in Table-2. Good recoveries with precise results show good reproducibility and accuracy of the method.

TABLE-2
DETERMINATION OF V(V) IN SYNTHETIC SAMPLES

Sample	V(V) added (ng/mL)	V(V) found (ng/mL)	Recovery (%)	RSD (%) (n = 5)
River water	-	Less than detection limit	-	-
River water	5.0	5.2	104	1.8
Drinking water	5.0	4.8	96	2.6
Drinking water + Ni(II) (4.0 μg/mL) + Rh(III) (4.0 μg/mL)	10.0	10.5	105	2.9

Conclusion

The catalytic-spectrophotometric method developed for the determination of V(V) is inexpensive, uses readily available reagents, allows rapid determination at low operating costs and shows simplicity, adequate selectivity, low limit of detection and good precision and accuracy compared to other catalytic procedures. With this method, it is possible to determine vanadium(V) at levels as low as 0.011 ng/mL without the need for any preconcentration step.

ACKNOWLEDGEMENT

The author is thankful to the Islamic Azad University, Majlesi Branch for the support of this work.

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(*Received*: 23 August 2008; *Accepted*: 30 July 2009) AJC-7688