Asian Journal of Chemistry Vol. 22, No. 3 (2010), 1729-1735

Determination of Vanadium(V) by Kinetic-Catalytic Spectrophotometric Method Using the Oxidation of Commassive Violet R 150 by Bromate

MOHSEN KEYVANFARD
Faculty of Science, Islamic Azad University, Majlesi Branch, Isfahan, Iran
E-mail: keyvan45638@yahoo.com

A new, simple, sensitive and selective catalytic spectrophotometric method was developed for the determination of trace amounts of vanadium(V). The method is based on the catalytic effect of vanadium(V) on the oxidation of commassive violet R150 by bromate in acidic medium. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of commassive violet R150 at 632 nm with a fixed-time method. The decrease in the absorbance of commassive violet R150 is proportional to the concentration of vanadium(V) in concentration range 20-300 ng/mL, with a fixed time of 0.5-2.0 min from initiation of the reaction. The limit of detection is 8 ng/mL vanadium(V). The relative standard deviation of 100 and 200 ng/mL vanadium(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, Commassive Violet R150, 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, inclouding organovanadium, compound, exist in a variety of configurations 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 μg 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 0.5-0.05 μg 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.

The determination of vanadium has received considerable attention because of its industrial importance in recent years. A variety of methods have been used for determination of vanadium such as 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 for based on the catalytic effect of vanadium(V) on oxidation of commassive violet R150 by bromate in acidic medium. The reaction was monitored spectrophotometrically at 632 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. Commassive violet R150 solution 2.53×10^{-4} M was prepared by dissolving 0.02 g of the compound (MW = 791.93) 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 of vanadium(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, hydrochloric 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 632 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 bath at 25 °C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 200-3000 ng/mL vanadium(V) was transferred into a 10 mL volumetric flask and then 0.4 mL of sulfuric acid 2 M, 2 mL of 2.53×10^{-4} M commassive violet R150 were added to the flask. The solution was diluted to *ca*. 8 mL with water. Then, 0.80 mL of 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 632 nm for 0.5-2 min from initiation of the reaction. This signal (sample signal) was labeled as ΔA_s. The same procedure was repeated without addition of vanadium(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

Commasive violet R150 undergoes a oxidation reaction with bromate in acidic medium at slow rate. It is found that this reaction rate is sharply increased by addition of trace amount of vanadium(V). This process was monitored spectrophotometrically by measuring the decrease in absorbance of the characteristic band of commasive violet (632 nm) (Fig. 1). Therefore, by measuring the decrease in absorbance of commasive violet for a fixed time of 0.5-2 min initiation of the reaction, the vanadium(V) contents in the sample can be measured.

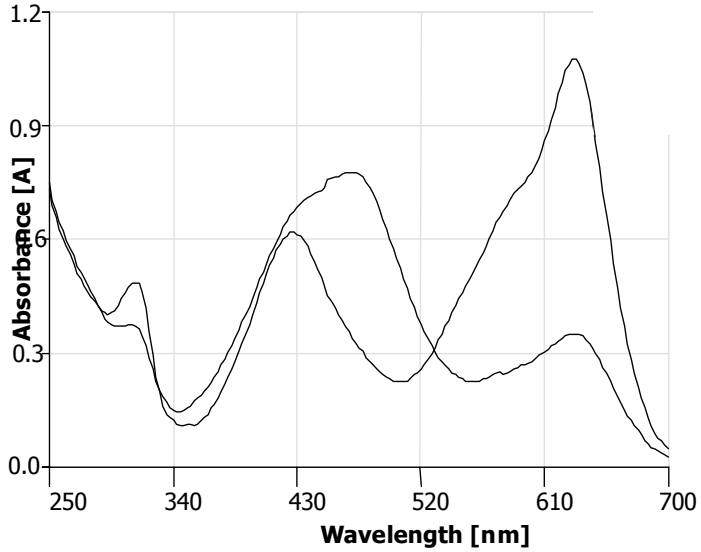

Fig. 1. Variation of the comasive violet-bromate-vanadium(V) with time. Conditions:0.08 M H_2SO_4, 5×10^{-5} M commasive violet; 8.0×10^{-3} M BrO_3, 100 ng/mL vanadium(V); temperature, 25 ºC. Time for each scan after initiation of the reaction: 30-180 S

Influence of variables: In order to take full advantage of the procedure, the reagent concentrations must be optimized. The effect of acid concentration, commassive violet R150 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 0.04-0.12 M (Fig. 2). The results show that the net reaction rate increases with increasing sulfuric acid concentration upto 0.08 M and decreases at higher concentrations. This mean that the rate of uncatalyzed reaction increases

with sulfuric acid concentration (> 0.08 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 sulfuric acid concentration of 0.08 M was selected for further study.

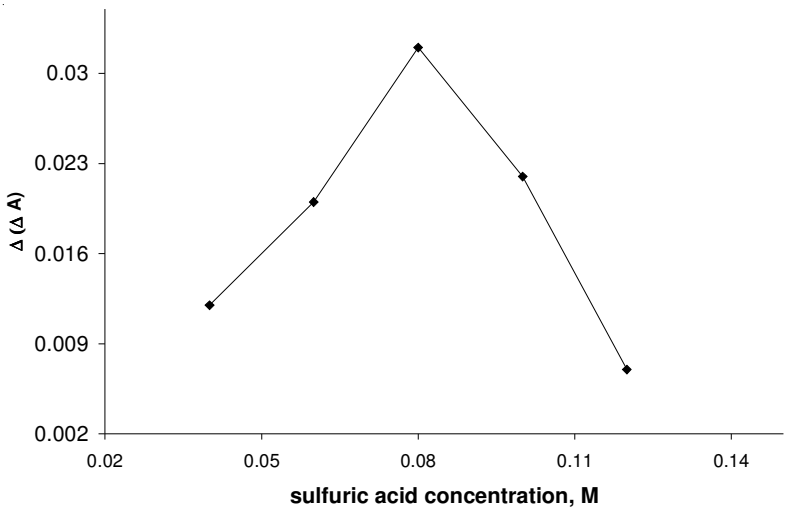

Fig. 2. Influence of sulfuric acid concentration on the sensitivity. Conditions: 100 ng/mL vanadium(V), 3.5×10^{-5} M commasive violet, 2.0×10^{-3} M bromate at 25 ºC, in fixed time of 0.5-20 min from initiation of reaction

Fig. 3 shows the effect of the commasive violet R150 concentration on the sensitivity for the range 3×10^{-5}-6×10^{-5} M. This sensitivity (net reaction rate) increases with increasing commasive violet R150 concentration up to 5×10^{-5} M and decreases at higher concentrations. This may be due to the aggregration of the dye at higher concentrations. Therefore, a final concentration of 5×10^{-5} M of commasive violet R150 was selected as the optimum concentration.

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. 4). The results show that the net reaction rate increases with increasing bromate concentration upto 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 temperature 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 the uncatalyzed reaction occurred at a suitable rate. Therefore, 25 °C was selected for further study.

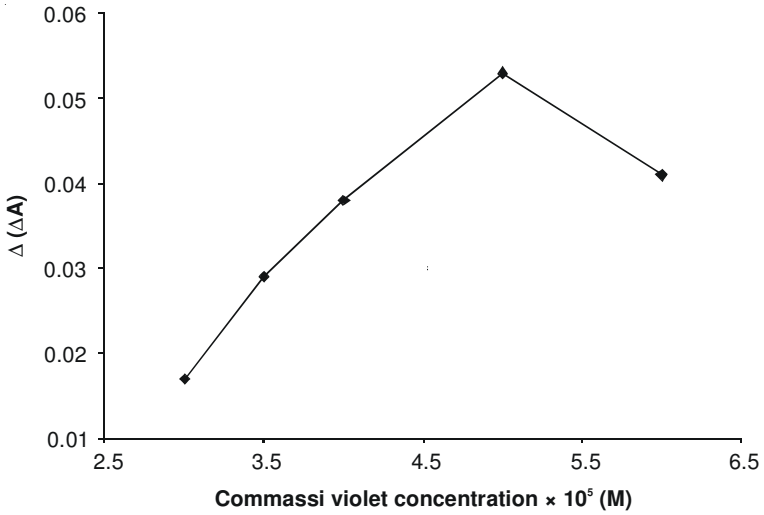

Fig. 3. Effect of commasive violet concentration on the sensitivity. Conditions: 0.08 M H_2SO_4, 100.0 ng/mL vanadium(V) and 2.0×10^{-3} M bromate at 25 °C, in fixed time of 0.5-2.0 min from initiation of reaction

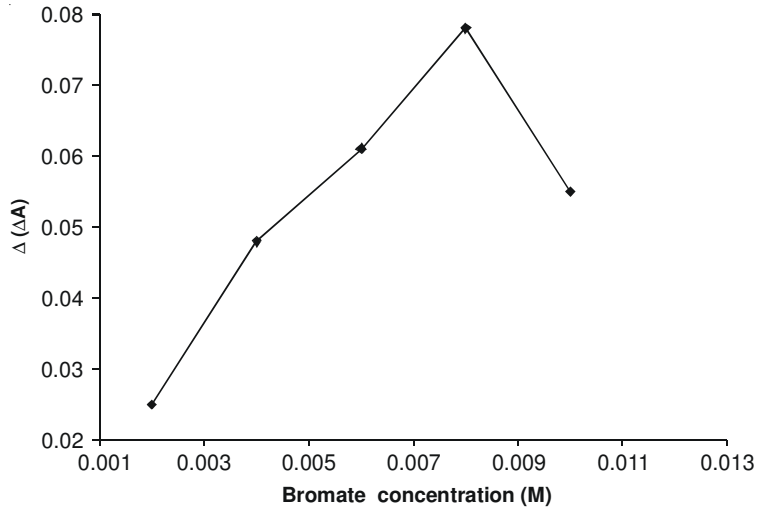

Fig. 4. Effect of bromate concentration on the reaction rate. Conditions: 0.08 M H_2SO_4, 100 ng/mL vanadium(V), 5×10^{-5} M commasive violet, at 25 °C, in fixed time of 0.5-2.0 min from initiation of reaction

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 regression and sensitivity. Under the optimum conditions described above, a linear calibration range 20-300 ng/mL of vanadium(V).

The equation of the calibration graph is $\Delta A = 0.244 + 6 \times 10^{-4}$ C (n = 8, 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 vanadium(V) concentration in ng/mL. The limit of detection from $Y_{LOD} = Y_b + 3S_b$ is 8 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 100 and 200 ng/mL of vanadium(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 100.0 ng/mL vanadium(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 400 fold excess over vanadium(V). The results (Table-1) show that the method is relatively selective for vanadium(V) determination.

TABLE-1
EFFECT OF FOREIGN IONS ON THE
DETERMINATION OF 100 ng/mL VANADIUM(V)

Species	Tolerance limit ($w_{ion}/w_{V(V)}$)
Na^+, K^+, Ca^{2+}, Mg^{2+}, Rb^+, 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, borate, Cl^-	1000
Ni^{2+}, Co^{2+}, Mn^{2+}, Rh^{3+}, Pd^{2+}	400
Ag^+, Pb^{2+}, SCN^-, Br^-	200
Ru^{3+}, I^-	20

Sample analysis: In order to evaluate the applicability of the proposed method, water samples and synthetic water, samples were analyzed to determine vanadium(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 VANADIUM(V) IN SYNTHETIC SAMPLES

Sample	Vanadium(V) (ng/mL)		Recovery (%)	RSD % n = 5
	Added	Found		
River water	–	Less than detection limit	–	–
River water	50	52	104	2.7
Drinking water	100	96	96	1.9
Drinking water + Ni^{2+} (50 µg/mL) + Mn^{2+} (50 µg/mL) + Co^{2+} (50 µg/mL)	100	106	106	2.9

Conclusion

The catalytic-spectrophotometric method developed for the determination of vanadium(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 8 ng/mL without the need for any preconcentration step.

ACKNOWLEDGEMENT

The authors are thankful to the Campus of Islamic Azad University of Majlesi for the support of this work.

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(*Received*: 6 February 2009; *Accepted*: 16 November 2009) AJC-8049