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Spectrophotometric Reaction Rate Method for the Determination of Ultra Trace Amounts of Vanadium(V) by its Catalytic Effect on the Oxidation of Naphthol Green B by Bromate in Micellar Medium

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A simple, sensitive and selective catalytic spectrophotometric method was developed for the determination of ultra trace amounts of V(V).The method is based on the catalytic effect of vanadium(V) on the oxidation of Naphthol green B by bromate at acidic medium. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of Naphthol green B at 710 nm with a fixed-time method. The decrease in the absorbance of Naphthol green B is proportional to the concentration of V(V) in concentration range 0.10-40.0 ng/mL, with a fixed time of 0.5-4.0 min from initiation of the reaction.The limit of detection is 0.068 ng/mL V(V).The relative standard deviation of 10.0 and 40.0 ng/mL V(V) was 1.69 and 2.3 %, respectively. The method was applied to the determination of vanadium(V) in water.

Key Words: Vanadium(V), Catalytic, Naphthol green B, Bromate, Micelle.

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, compound, 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 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; 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 based on the catalytic effect of V(V) on oxidation of Naphthol green B by bromate in micellar medium. The reaction was monitored spectrophotometrically at 710 nm by measuring the decrease in absorbance of the reaction mixture for the first 0.5-4.0 min from initiation of the reaction.

EXPERIMENTAL

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. Double distilled water and analytical reagent grade chemicals were used during all of the experimental studies.

Naphthol green B solution 1.15×10^{-3} M was prepared by dissolving 1.01 g of the compound (Merck) 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 sulfuric acid (Conc.) and diluted to 100 mL in a 100 mL volumetric flask. Triton X-100 (Merck) stock solution 0.066 M was prepared by dissolving 2.0 mL Triton X-100 in water and diluted to the mark with in a 100 mL volumetric flask. The other surfactants tested, namely, sodium dodecyl sulfate (SDS), Triton X-100 and cetyl pyridinium chloride (Serva), were prepared in a similar way. Stock solution (1000 µg/mL) of interfering ions were prepared by dissolving suitable salts in water, hydrochloric acid or sodium hydroxide solution.

Absorption spectra were recorded with a Cary model 100 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 710 nm. A thermostate water batch was used to keep the reaction temperature at 30°C.

Recommended procedure: All the solutions and distilled water were kept in a thermostated water batch at 30°C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 1.0-400.0 ng/mL V(V) was transferred into a 10 mL of volumetric flask and then 0.5 mL of sulfuric acid 0.120 M, 1.0 mL 0.042 M Triton x-100 solution and 2.0 mL 1.15×10^{-3} M Naphthol green B were added to the flask. The solution was diluted to *ca.* 8 mL with water. Then, 0.40 mL solution 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 710 nm for 0.5-4.0 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

Naphthol green B undergoes a oxidation reaction with bromate in acidic medium to form a colourless product at very slow rate. It is noted that this reaction rate is sharply increased by addition of trace amount of V(V), especially in the presence of Triton X-100 as a micellar medium. This process was monitored spectrophotometrically by measuring the decrease in absorbance of the characteristic band of Naphthol green B (710 nm) (Fig. 1). Therefore, by measuring the decrease in absorbance of Naphthol green B for a fixed time of 0.5-4.0 min initiation of the reaction, the V(V) contents in the sample can be measured.

Influence of variables

In order to take full advantage of the procedure, the reagent concentrations must be optimized. The effect of acid concentration, Naphthol green B and bromate concentration, type and concentration of surfactants and temperature on the rate of catalyzed and uncatalyzed reaction was studied.

The accelerating effect of micelles arises essentially from electrostatic and hydrophobic interactions between the reactants and micellar surface[20]. Cationic (CPC, CTAB), anionic (SDS) and nonionic (Triton X-100) micelles were tested at a concentration greater than that critical micelle concentration (CMC). The results are shown in Table-1. The results show that the Triton X-100 enhance the rate of Naphthol green B-V(V)-bromate reaction, thus Triton X-100 was chosen for the study.

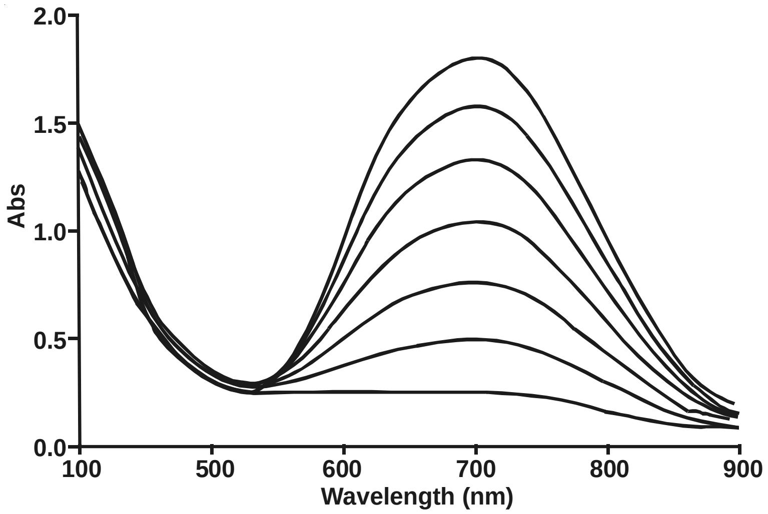


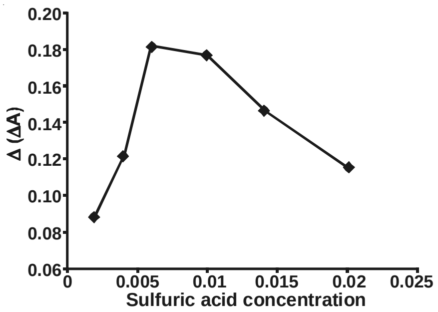
Fig. 1. Variation of the Naphthol green B-BrO$_3^-$ -V(V) system with time. Condition: 0.006 M H_2SO_4; 2.3 × 10^{-4} M Naphthol green B; 4.0 × 10^{-3} M BrO$_3^-$; 4.2 × 10^{-3} M Triton X-100; 20 ng/mL vanadiumV(V); temperature, 30ºC

TABLE-1
SURFACTANT TESTED AS A POTENTIAL MICELLAR CATALYST FOR THE ENHANCED RATE OF NAPHTHOL GREEN B - BrO$_3^-$ - V(V) REACTION

Surfactant	Type	CMC (M)	Micellar catalysis
Trition X-100	Non-ionic	3.0×10^{-4}	Positive
SDS	Anionic	8.1×10^{-4}	Negative
CTAB	Cationic	1.3×10^{-4}	Negative
CPC	Cationic	1.2×10^{-4}	Negative

The effect of the sulfuric acid concentration on the rate of reaction was studied in the range of 0.002-0.020 M (Fig. 2). The results show that the net reaction rate increases with increasing sulfuric acid concentration up to 0.006 M and decreases at higher concentrations.This mean that the rate of uncatalyzed reaction increases with sulfuric acid concentration (> 0.006 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 sulfuric acid concentrations. Therefore, a sulfuric acid concentration of 0.006 M was selected for further study.

The influence of bromate concentrations on the reaction rate was studied in the concentration range of 0.001 to 0.010 M (Fig. 3). The results show that the net reaction rate increases with increasing bromate



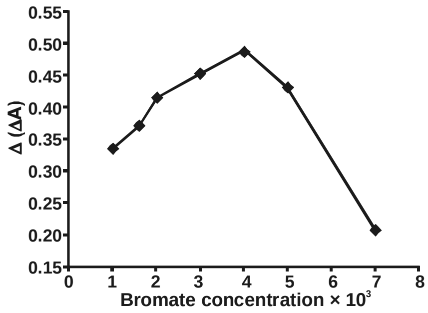


Fig. 2. Influence of sulphuric acid coccentration on the sensitivity, conditions: 10.0 ng/mL V(V), 1.84 × 10^{-4} M Naphthol green B, 3 × 10^{-3} M Triton X-100 and 4.0 × 10^{-4} M bromate at 30°C, in fixed time of 0.5-2.0 min from initiation of reaction

Fig. 3. Effect of bromate concentration on the sensitivity. Conditions: 0.006 M H_2SO_4 and 10.0 ng/mL V(V), 1.84 × 10^{-4} M Naphthol green B, 3 × 10^{-3} M Triton X-100 at 30°C, in fixed time of 0.5-2.0 min from initiation of reaction

concentration up to 0.004 M and decreases at higher concentrations.This mean that the rate of uncatalyzed reaction increases with bromate concentration (> 0.004 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 bromate concentrations. Therefore, a bromate concentration of 0.004 M was selected for further study.

Fig. 4 shows the effect of the Naphthol green B concentration on the sensitivity for the range of 4.6 × 10^{-5} - 2.76 × 10^{-4} M . This sensitivity (net reaction rate) increases with increasing Naphthol green B concentration up to 2.3 × 10^{-4} M and decreases at higher concentrations. This may be due to the aggreagration of the dye at higher concentrations. Therefore, a final concentration of 2.3 × 10^{-4} M of Naphthol green B was selected as the optimum concentration.

The effect of the Triton X-100 concentration on the rate of reaction was studied in the range of 0.0-7.2 × 10^{-3} M (Fig. 5). This sensitivity increases with increasing Triton X-100 concentration up to 4.2 × 10^{-3} M and decreases at higher concentrations. This is due to the high aggregation of the surfactant and change in the molar absorptivity of the Naphthol green B in the solution. Therefore, a final concentration of 4.2 × 10^{-3} M was selected as the optimum concentration of Triton X-100.

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 30°C, the net reaction rate increases, whereas higher temperature values decrease the sensitivity ($\Delta A = \Delta A_s - \Delta A_b$). This means that the rate of uncatalyzed reaction increases with temperature to a greater extent and the uncatalyzed reaction occurred at a sutable rate. Therefore, 30°C was selected for further study.

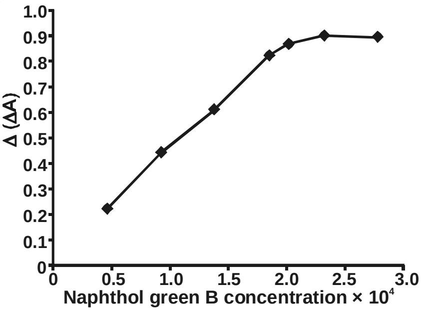


Fig. 4. Effect of Naphthol green B concentration on the reaction rate. Conditions: 0.006 M H_2SO_4 and 10.0 ng/mL V(V), 4.0 × 10^{-3} M bromate, 3 × 10^{-3} M Triton X-100 at 30°C, in fixed time time of 0.5-2.0 min from initiation of reaction

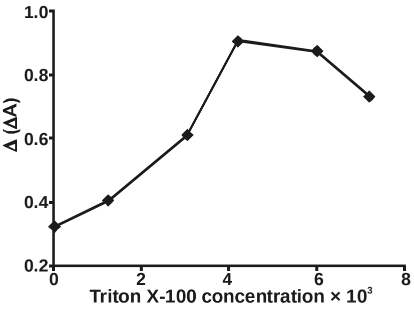


Fig. 5. Effect of Triton X-100 concentration on the reaction rate. Conditions: 0.006 M H_2SO_4 and 10.0 ng/mL V(V), 4.0 × 10^{-3} M bromate, 2.3 × 10^{-4} Naphthol green B at 30°C, in fixed time of 0.5-2.0 min from initiation of reaction

Calibreation 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 0.5-4.0 min from intiation of the reaction because it provided the best regresion and sensitivity. Under the optimum conditions described above, a linear calibration range 0.10-40.00 ng/mL of V(V).

The equation of the calibration graph is $\Delta A = 0.6195 + 0.0219\ C$ (n = 6, r = 0.9998), where ΔA is change in absorbance for the sample reaction for 0.5-4.0 min from initiation of the reaction (catalytic reaction) and C is V(V) concentration in ng/mL. The limit of detection from $Y_{LOD} = Yb + 3\ S_b$ is 0.068 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 10 and 40 ng/mL V(V) was 1.69 and 2.3 %, respectively.

Interference study: In order to assess the application of the proposed method to synthetic samples, the effect of various ions on the determination of 10.0 ng/mL V(V) was studied. The tolerance limit was defined as the concentration of added ions causing a relative error less than 3 %, the results are summarized in Table-2. Many ions did not interfere, even when they were present in 100 fold excess over V(V). The results show that method is relatively selective for vanadium(V) determination.

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-3. Good recoveries with precise results show good reproducibility and accuracy of the method.

TABLE-2
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+}, Co^{2+}, Mn^{2+}, Ni^{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-}, SCN^-, Cl^-	1000
Ag^+, Rh^{3+}	500
I^-, Br^-	100
Hg^{2+}	50
Fe^{2+}	5

TABLE-3
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	20.0	19.0	95	2.1
Drinking water	20.0	21.0	105	1.9
Drinking water + Ag^+ (5.0 μg/mL) + Co^{2+} (8.0 μg/mL) + Ni^{2+} (8.0 μg/mL)	20.0	21.0	105	2.1

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 0.068 ng/mL without the need for any preconcentration step.

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