The Development of a New Kinetic Spectrophotometric Method for the Determination of Vanadium(V) Based on its Catalytic Effect on the Oxidation of Malachite Green Oxalate by Bromate in Acidic and Micellar Medium

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Received 4 February 2010; Accepted 1 April 2010

Abstract: A new, simple, sensitive and selective kinetic spectrophotometric method was developed for the determination of ultra trace amounts of vanadium(V). The method is based on the catalytic effect of vanadium(V) on the oxidation of malachite green oxalate (MG) by bromate in acidic and micellar medium. The reaction was monitored spectrophotometrically by measuring the decrease in the absorbance of malachite green oxalate (MG) at 625 nm with a fixed-time method. The decrease in the absorbance of MG is proportional to the concentration of vanadium(V) in the range of 1-100 ng/mL with a fixed time of 0.5-2 min from the initiation of the reaction. The limit of detection is 0.71 ng/mL of vanadium(V). The relative standard deviation for the determination of 5, 30, 50 ng/mL of vanadium(V) was 2.5%, 2.6%, 2.4% and respectively. The method was applied to the determination of vanadium(V) in water samples.

Keywords: Vanadium(V), Malachite green oxalate (MG), Spectrophotometric, Micellar media.

Introduction

Vanadium is a biologically essential element¹. Its inclusion in enzymes such as bromoperoxidase and nitrogenase reveals the importance of its redox chemistry. A number of model complex systems have been investigated in order to elucidate vanadium redox mechanisms. Some tunicate fish and marine animals selectively accumulate vanadium species

from the ocean. Vanadium complexes, including organovanadium, compound, exist in a variety of configurations depending on their oxidation states and coordination numbers².

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 $\mu\text{g dm}^{-3}$ levels, but can be toxic at higher concentrations⁵. The toxicity of vanadium is dependent on its oxidation state⁶, 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 determination of vanadium has received extensive attention because of its increasing importance in biological and environmental studies. This metal is widely distributed in the earth's crust but in low abundance. Major sources for the emission of vanadium in the environment include combustion of fuel oils, dyeing, ceramics, ink, catalyst and steel manufacturing. Vanadium in trace amounts represents an essential element for normal cell growth, but it can be toxic when present in higher concentrations⁷. A variety of methods have been used for determination of vanadium; these include fluorometry⁸, gas chromatography⁹, neutron activation analysis^{10,11}, x-ray fluorescence spectrometry¹², emission spectroscopy¹³ and atomic absorption spectroscopy¹⁴ kinetic method¹⁵. These methods either lack sufficient sensitivity or are time consuming. In order to overcome these problems, we developed and validated a rapid, sensitive and selective kinetic spectrophotometric method for the determination of vanadium(V). This method is described based on the catalytic effect of V(V) on oxidation of Malachite green oxalate by bromate in acidic and micellar medium. The reaction was monitored spectrophotometrically at 625 nm by measuring for the first 0.5-2 min from initiation of the reaction.

Experimental

Analytical reagent grade and doubly distilled water were used. A 100 $\mu\text{g/mL}$ stock standard solution of vanadium(V) was prepared by dissolving 0.023 g of NH_4VO_3 (Merck, $\text{W}=116.94 \text{ g/mol}$) in distilled water and diluted to 100 mL in a 100 mL volumetric flask. Working solutions were prepared by appropriately diluting the stock standard solution. A 100 mL 0.1 M potassium bromate solution was prepared by dissolving 1.67 g of KBrO_3 (Merck, $\text{MW}=167 \text{ g/mol}$) in distilled water and diluting it to mark in a 100 mL volumetric flask. A 1.079×10^{-4} M malachite green oxalate solution was directly prepared by dissolving 0.01 g of malachite green oxalate (Merck, $\text{MW}=927.02 \text{ g/mol}$) diluting it with distilled water in a 100 mL volumetric flask. Triton-x-100 solution (0.066 M) was prepared by dissolving 2 mL Triton-x-100 (Merck) in distilled water and diluting to 100 mL in a 100 mL volumetric flask. The other surfactants tested, namely cetyltrimethyl ammonium bromide (CTAB), cetylpyridinium chloride (CPC), sodiumdodecyl sulphate (SDS), dodecyltrimethyl ammonium bromide (DTAB), hexadecyltrimethyl ammonium bromide (HTAB), hexadecylpyridinium bromide (HDPB), tetrabutyl ammonium bromide (TBAB) and hexadecylpyridinium chloride (HCPC) were prepared in a similar way. Phosphoric acid solution (5.0 M) was prepared by diluting a known volume of its concentrated solution (Merck).

Apparatus

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 625 nm. A thermostat water bath was used to keep the reaction temperature at 20 °C. A stopwatch was used for recording the reaction times.

Recommended procedure

All the solutions and distilled water kept in thermostated water bath at 20 °C for 30 min before starting the experiment. The reaction monitored spectrophotometrically at 625 nm for the first 0.5-2 min from initiation of the reaction. An aliquot of the solution containing 1-100 ng/mL vanadium(V) was transferred into a 10 mL volumetric flask and then 1.6 mL of 5.0 M phosphoric acid, 1.6 mL of 1.079×10^{-4} M MG and 2.8 mL Triton x-100 solution were added to the flask. The solution was diluted to 8 mL with water, then 1.2 mL 0.1 M potassium bromate solution 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 spectrophotometric cell. The reaction was followed by measuring the decrease in absorbance of the solution against water at 625 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. The calibration graph was constructed by plotting of ΔA_s versus vanadium(V) concentration at a fixed-time of 0.5-2.0 min from initiation of the reaction.

Results and Discussion

Malachite green oxalate undergoes a oxidation reaction with bromate in acidic medium at very slow rate. We found that in the presence of Triton x-100 as a micellar medium, the analytical signal is sharply increased by addition of trace amounts of vanadium(V). The rate equation of the catalyzed reaction is:

$$\begin{aligned} \text{Rate} &= -d[\text{Malachite green oxalate}]/dt \\ &= k[\text{Vanadium(V)}][\text{Malachite green oxalate}]^m[\text{BrO}_3^-]^n \end{aligned} \quad (1)$$

Where k is the rate constant. Because $[\text{BrO}_3^-]$, $[\text{Malachite green oxalate}]$, BrO_3^- can be considered to be constant and m was found to be 1. By integration of Eq[1] and by incorporating Beer's law, we obtain the final expression:

$$\Delta A = k[\text{Vanadium(V)}]t \quad (2)$$

Where, t is the reaction time Figure 1. There are many methods, such as fixed-time, initial rate, rate constant and variable time methods for measuring the catalytic species, the fixed-time method is the most conventional and simplest, involving the measurement of ΔA at 625 nm. Figure 1 shows the relationship between A and reaction time. It was found that the rate of reaction is proportional to the vanadium (V) concentration. The reaction rate was monitored spectrophotometrically by measuring the decrease in absorbance of the characteristic band of malachite green oxalate at 625 nm. Therefore, by measuring the decrease in absorbance of MG for a fixed time of 0.5-2.0 min from initiation of the reaction, the vanadium (V) contents in the sample can be measured. Malachite green oxalate has the following structure (Figure 2).

Figure 1. Absorption spectrum for the vanadium(V) -MG- BrO_3^- system with time. Conditions: 0.8 M H_3PO_4 ; 100 g/mL V(V); 2.8×10^{-2} M Triton-x-100; 1.72×10^{-5} M MG; 1.2×10^{-2} M BrO_3^- ; temperature, 20 °C; interval time for each scan, 0.5, 1.0, 1.5, 2, 2.5 and 3.5 min from initiation of the reaction

Figure 2. Structure of malachite green oxalate

Optimization of variables

The influence of phosphoric acid concentration, malachite green oxalate concentration, bromate concentration, the effect of different kinds of surfactants, surfactant concentration and temperature on the analytical signal was studied, to find the optimum conditions.

The effect of H_3PO_4 concentration on the sensitivity was studied in the range of 0.6 M to 1 M in the presence of 100 ng/mL V(V) (Figure 3). The results show that the analytical signal increases with increasing phosphoric acid concentration up to 0.8 M and decreases at higher concentrations. This means that the rate of uncatalyzed reaction increases with phosphoric acid concentration (>0.8 M) to a greater extent than the catalyzed reaction and the difference between the rates of catalyzed and uncatalyzed reactions $\Delta A_s - \Delta A_b$ diminishes at higher phosphoric acid concentrations. Therefore, a phosphoric acid concentration of 0.8 M was selected for further study.

Figure 4 shows the influence of MG concentration on the analytical signal in the range of 1.07×10^{-5} M to 2.15×10^{-5} M. The results show that by increasing MG concentration up to 1.72×10^{-5} M, the analytical signal increases, whereas greater amounts of the dye decrease the analytical signal. This may be due to the aggregation of the dye in higher concentration. Therefore, a MG concentration of 1.72×10^{-5} M was selected for further study.

The effect of bromate concentration on the analytical signal was studied in the range of 0.8×10^{-2} M to 1.6×10^{-2} M. The results show that the analytical signal increases with bromate concentration up to 1.2×10^{-2} M, whereas the analytical signal decreases with increasing bromate concentration from 1.2×10^{-2} M to greater values. This means that the rate

of uncatalyzed reaction increases with bromate concentration ($>1.2 \times 10^{-2}$ M) to a greater extent than the catalyzed reaction and the difference between the rates of catalyzed and uncatalyzed reaction ($\Delta A_s - \Delta A_b$) diminishes at higher bromate concentration. Thus, a bromate concentration of 1.2×10^{-2} M was selected for further study.

Figure 3. Effect of H₃PO₄ concentration on the sensitivity. Conditions: 100 ng/mL vanadium(V); Triton-x-100 0.01 M; MG 1.07×10^{-5} M; BrO₃⁻, 8×10^{-3} M; temperature, 23 °C and time of .5-2.0 min from initiation of the reaction

Figure 4. Effect of MG concentration on the sensitivity. Conditions: 100 ng/mL V(V); H₃PO₄, 0.8 M; Triton-x-100, 0.01 M; BrO₃⁻, 8×10^{-3} M; temperature, 23 °C and time of 2.0 min from initiation of the reaction

In many reactions, Suitable micelles can affect the rate of reactions¹⁶⁻²³. A micelle usually can be formed by aggregation of charged organic molecules. These micelles have the same charge at the outer sphere. For those reactions which have charged species, these micelles can affect the rate of reaction by increasing the effective collisions. In order to choose an appropriate micellar system to enhance the rate of reaction, one should take into account the type of charge of the reactants, because the accelerating effect of micelles arises essentially due to electrostatic and hydrophobic interactions between the reaction and micellar surfaces²⁴. Cationic (CTAB, CPC, DTAB, HDPB, HTAB, TBAB, HCPC), anionic (SDS) and nonionic (Triton-x-100) micelles were tested at a concentration greater than the critical micelle concentration (C.M.C). The results are shown in Table 1. In fact, Triton-x-100, DTAB, TBAB and HDPC increased sensitivity, but Triton-x-100 increased sensitivity more than DTAB, TBAB and HDPC; thus, Triton-x-100 was chosen for further study. Table 1.

Figure 5. Influence of BrO_3^- on the sensitivity. Conditions: 100 ng/mL V(V); H_3PO_4 , 0.8 M; Triton-x-100, 0.01 M; MG, 1.72×10^{-5} M; temperature, 23 °C and time of 2.0 min from initiation of the reaction

Table 1. Surfactant tested as a potential micellar catalyst for the enhanced rate of MG- BrO_3^- -V(V) reaction

Surfactant	Type	CMC, M	Micellar catalysis
Tritonx100	Nonionic	3.0×10^{-4}	Positive
DTAB	Cationic	1.5×10^{-2}	Positive
HDPC	Cationic	2.4×10^{-4}	Positive
TBAB	Cationic	7.5×10^{-5}	Positive
CPC	Cationic	1.2×10^{-4}	Positive
CTAB	Cationic	1.3×10^{-4}	Positive
HDPB	Cationic	6.5×10^{-4}	Negative
HTAB	Cationic	9.2×10^{-4}	Negative
SDS	Anionic	8.1×10^{-4}	Negative

The effect of the Triton-x-100 concentration on the analytical signal was studied in the range of 0 M to 3.6×10^{-2} M (Figure 6). the analytical signal increases with increasing Triton-x-100 concentration up to 2.8×10^{-2} M and decreases at higher concentrations. Therefore a final concentration of 2.8×10^{-2} M was selected as the optimum concentration of Triton-x-100 for further study. The effect of the temperature on the sensitivity was studied in the range 10-30 °C with the optimum of the reagents concentrations. The results showed that, as the temperature increases up to 20 °C, the analytical signal increases, whereas higher temperature values decrease the analytical signal ($\Delta A = \Delta A_s - \Delta A_b$). Therefore, 20 °C was selected for further study.

Figure 6. Influence of Triton-x-10 on the sensitivity. Conditions: 100 ng/mL V(V); H_3PO_4 , 0.8 M; MG, 1.72×10^{-5} M; 1.2×10^{-2} M BrO_3^- ; temperature, 23 °C and time of 2.0 min from initiation of the reaction

Calibration graph, detection limit, reproducibility and accuracy

The calibration graph was linear for Vanadium(V) concentration in the range of 0.1-10 ng/mL with the regression equation of $\Delta A = 0.007C + 0.158$ with ($r = 0.999$ $n=9$) 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 the Vanadium(V) concentration in ng/mL. The limit of detection (Defined as $CL = 3S_b / m$, where C_L , S_b and m are limit of detection, standard deviation of the blank signal and slope of the calibration graph, respectively) is equal to 0.71 ng/mL Vanadium(V). The relative standard deviations (R.S.D.) for ten replicate determination of 30, 40, 50 and 5 ng/mL Vanadium(V) is 2.6%, 2.8%, 2.4% and 2.5% respectively.

Interference study

More than 25 foreign substances in solution were studied for the possible influence on the determination of vanadium(V) by the proposed method. The maximum amount of substance causing an error of more than 3% in the determination of 100 ng/mL vanadium(V) was taken as the tolerance limit. The results are showed in Table 2. The results show that the method is relatively selective.

Figure 7. Influence of temperature on the sensitivity. Conditions: 100 ng/mL V(V); H_3PO_4 , 0.8 M; MG 1.72×10^{-5} M; 1.2×10^{-2} M BrO_3^- ; 2.8×10^{-2} M; Triton x-100 and time of 2.0 min from initiation of the reaction

Table 2. Effect of foreign ions on the determination of 100 ng/mL V(V)

Species	Tolerance Limit(w ion/w V(V))
Na^+ , K^+ , Mg^{2+} , Ni^{2+} , Cd^{2+} , Zn^{2+} , Cr^{2+} , Al^{3+} , $Cu(II)$, $Pb(II)$, $Se(IV)$, $Mn(II)$, $Co(II)$, ClO_3^- , SO_3^{2-} , IO_3^- , PO_4^{3-} , CH_3COO^- , BO_3^{2-}	1000
IO_4^-	800
Pd^{2+}	100
Rh^{3+} , $Ru(III)$, $Mo(VI)$	50
Cl^- , I^-	Inhibited

Application of the method

In order to evaluate the applicability of the proposed method, real and synthetic water samples were analyzed to determine vanadium(V) contents. The results are presented in Table 3. Good recoveries and precise results show good reproducibility and accuracy of the method. The kinetic-spectrophotometric method developed for the determination of vanadium(V) is inexpensive, employs available reagents, allows rapid determination

at low operating costs, provides simplicity, adequate selectivity, a low limit of detection compared to other kinetic procedures. Using this method, it is possible to determine vanadium(V) at levels as low as 1 ng/mL without the need for any preconcentration steps.

Table 3. Determination of V(V) added to water samples

Sample	V(V) added, ng/mL	V(V) found, ng/mL	Recovery, %	RSD, % n=5
Well water	5	4.8	96	2.5
Well water	30	28	93	2.6
Well water	40	44	110	2.8
Well water	50	48	96	2.4

Table 4. Comparison of kinetic spectrophotometry methods for determination of Vanadium(V) with proposed method

Method	DL, µg/mL	LDR, µg/mL	Reference no.
Catalytic Spectrophotometry	1	4.1-33.3	25
Catalytic Spectrophotometry	4	400-4000	26
Catalytic Spectrophotometry	0.02	0-2.5	27
Catalytic Spectrophotometry	0.5	1-240	28
Catalytic Spectrophotometry	0.01	0.05-8.0	29
Catalytic Spectrophotometry	3	4-520	30
Catalytic Spectrophotometry	.0088	0.05-50	31
Catalytic Spectrophotometry	0.01	0-0.5	32
Proposed Method	0.00071	0.001-0.1	-

Conclusion

The kinetic-spectrophotometric method developed for vanadium(V) determination in water is inexpensive and readily available and allows rapid determination at low operating costs and shows simplicity, adequate selectivity, comparison of detection limit and linear dynamic range of several kinetic spectrophotometric methods with proposed method showed in Table 4. Using this method, it is possible to determine vanadium(V) at levels as low as 1 ng/mL without the need for any preconcentration steps. Therefore, the method could be proposed for environmental analyses.

Acknowledgment

The authors express their gratitude to the Center of Excellency in Science of Islamic Azad University Majlesi and the shahreza Branch for support of this work.

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