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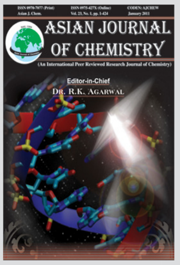

Dual-Wavelength Catalytic Spectrophotometry Determination of Trace Vanadium(V) in Tap Water and Rice

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A new dual-wavelength catalytic kinetic spectrophotometric method is applied for the determination of trace amounts of vanadium(V). The method is based on the catalytic effect of vanadium(V) on the redox reaction between alizarin green and potassium bromate in the citric acid- H_2SO_4 medium. The probably mechanism of catalytic reaction was proposed. The absorbance's decrease of the reagent at 413 nm and 641 nm was proportional to the concentration of vanadium in the solution. Under the optimum conditions, the linear range of the determination was 0.150-40.0 ng mL^{-1} with the detection limit of 6.4×10^{-11} g mL^{-1}. The method was applied to the determination of trace vanadium in rice and tap water with satisfactory results.

Key Words: Vanadium(V), Dual-wavelength, Spectrophotometry.

INTRODUCTION

Vanadium is biologically essential element[1] to people and has the effect of anticarcinogen[2] and reducing the level of insulinoid para-insulin of the diabetes blood[3]. Whereas, vanadium(V) is more toxic than vanadium(IV). If people contact with V_2O_5 for a long time, their memory will become worse and the rate of their movement will become slower[4]. People have paid more attention to the pollution in environment from vanadium. Therefore, the determination of vanadium in tap water and food is becoming more and more important in assessing its toxicity in environmental and biological samples.

There are many methods which have been used for the determination of vanadium, including photometry[5-7], voltammetry[8], potentiometry[9], liquid chromatography[10,11] and atomic spectrometric techniques[12-15]. Nevertheless, these methods lack the necessary sensitivity and/or selectivity. Atomic emission spectrometry and absorption spectrometry have been applied to the determination of total vanadium with nanogram or lower amounts, these methods can only be used after preliminary isolation and preconcentration, which need costly instrument. Kinetic methods[16-19] afforded spectrophotometric detection. Based on the catalytic action of vanadium are more sensitive and due to their selectivity no preconcentration steps are necessary. Furthermore, these methods are relatively simple and easy to perform. The method are based on the catalytic effect of vanadium(V) on oxidation of organic compounds by an inorganic oxidation. But all the methods above lack sensitivity or satisfactory selectivity or have a limit dynamic range as they implement the determination of vanadium at a single-wavelength. Therefore, developing new catalytic-kinetic spectrophotometric methods for the determination of vanadium is still necessary.

In this paper, we found that alizarin green (AG) can be oxidated by potassium bromate in a dilute H_2SO_4 medium and trace amount of vanadium(V) can catalyze this reaction. Citric acid was found to have a highly activating effect on the vanadium-catalyzed oxidation of alizarin green with bromate at the same time. A single-reagent and double-wavelength catalytic-kinetic spectrophotometric method was applied for the determination of vanadium based on the absorption spectrum showing two maximums in 380-700 nm region. The present method was successfully applied to the analysis of real samples of rice and water with satisfactory results. The effect of some interference is easily removed by a suitable procedure. In addition, the elementary discussion on the reaction mechanism is proposed.

EXPERIMENTAL

All reagents were of analytical grade or the highest purity available. All aqueous solutions were prepared using doubly distilled deionized water.

A 1000 μg mL^{-1} stock solution of vanadium(V) was prepared by dissolving 0.2297 g of ammonium vanadate in water and diluted to 100 mL in a volumetric flask. Working solution of vanadium(V) were prepared by appropriate dilution of stock solution of vanadium(V). A stock solution of alizarin green was prepared by dissolving 0.2000 g of alizarin green in water and diluted to 500 mL in a volumetric flask. Potassium bromate solution (0.02 M) was prepared by dissolving 0.3340 g of potassium bromate with water in a 100 mL volumetric flask. Citric acid solution (0.40 M) was prepared by dissolving 0.3340 g of citric acid in water diluted to 250 mL. 0.010 M Sulfuric acid solution was used in this study. Stock solutions (1000 µg mL^{-1}) of interfering ions were prepared by dissolving appropriate amounts of their suitable salts in water.

All absorption measurements were made on a UV-2102PC spectrophotometer (Shanghai Younike Instrument Co. Ltd., China) with 10 mm cells. The HH-6 digital display constant temperature water-bath boiler (Changzhou Guohua Electrical Instruments Co. Ltd., China). A stopwatch was used to record the reaction time.

Procedure: In a 25 mL test tube, 0.500 µg working solution of vanadium(V), 4.00 mL 0.40 M citric acid, 6.0 mL 0.010 M H_2SO_4 solution, 4.00 mL 6.44×10^{-4} M alizarin green solution and 0.25 mL 0.020 M $KBrO_3$ solution were added in turn. The mixture was finally diluted to the mark with water. The mixture was placed in a boiling water bath to heat for 20 min and then was rapidly taken out and cooled it for 5 min in running water. Afterward, the solution was transferred into 1 cm cell of spectrophotometer. The absorbance(A) was measured against water at λ_{max1} = 413 nm, λ_{max2} = 610 nm and λ_{max3} = 641 nm, respectively. The measurement in the absence of vanadium(V) was repeated to obtain the values A_o for the uncatalyzed reaction. We can see the variation in absorbance of A_o and A from Fig. 1. $\Delta A_{413} = A_{0413} - A_{413}$, $\Delta A_{610} = A_{0610} - A_{610}$, $\Delta A_{641} = A_{0641} - A_{641}$, $\Delta A = \Delta A_{413} + \Delta A_{641}$ (or ΔA_{610}). The values ΔA were calculated. From the previous values of standard vanadium solution, a calibration graph of the change of absorbance *versus* vanadium concentration was constructed.

RESULTS AND DISCUSSION

Absorption spectra: Under the optimum conditions, the absorption spectra of the catalytic and noncatalytic systems in the absence and presence of citric acid were monitored by the absorbance change at 360-700 nm against water. The results were shown in Fig. 1. The maximum absorptions of all systems located at 413, 610 and 641 nm. The absorbance of 641 nm vanished with the addition of vanadium concentration, the value of $\Delta A = \Delta A_{413} + \Delta A_{641}$ was larger than $\Delta A = \Delta A_{413} + \Delta A_{610}$ and the linear relationship between $\Delta A = \Delta A_{413} + \Delta A_{641}$ and the concentration of vanadium(V) was found over the range from 0.150-40.0 ng mL^{-1}. Therefore, in the experiments 413 nm and 641 nm were selected to be measurement wavelength.

Effect of sulfuric acid concentration: The effect of H_2SO_4 concentration on the reaction rate was studied. Fig. 2 shows the dependence of the absorbance on different concentration of H_2SO_4. The value of ΔA_{413} increased more rapidly than the ΔA_{641} with the added of H_2SO_4 before the concentration reaching 2.4×10^{-3} M. Therefore, 2.4×10^{-3} M was chosen as the optimum concentration of H_2SO_4 for the values of ΔA_{413} and ΔA_{641} both reaching their maximum at the same time and the system had a good sensitivity under this condition.

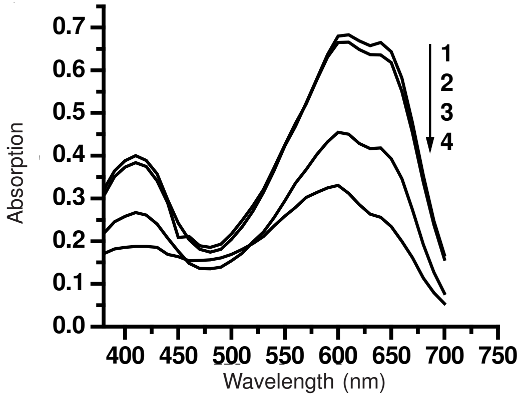


Fig. 1. Absorption spectra of (1) citric acid + H_2SO_4 + alizarin green + potassium bromate; (2) H_2SO_4 + alizarin green + potassium bromate; (3) vanadium(V) + H_2SO_4 + alizarin green + potassium bromate; (4) vanadium(V) + citric acid + H_2SO_4 + alizarin green + potassium bromate

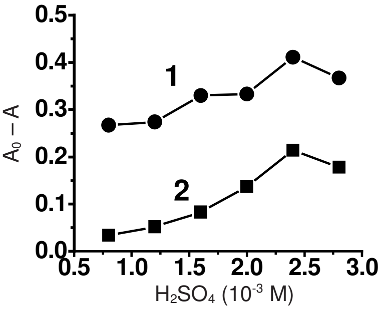


Fig. 2. Effect of conc. H_2SO_4 on determination of V: 0.020 µg mL^{-1} V(V), 0.064 M of citric acid, 1.0×10^{-4} M alizarin green, 2.0×10^{-4} M of $KBrO_3$. (1) $A_{0641} - A_{641}$; (2) $A_{0413} - A_{413}$

Effect of citric acid concentration: From Fig. 1, it is found that the citric acid could greatly enhance the sensitivity of analysis since its perfect activator effect. The appropriate citric acid can enhance and accelerate the rate of alizarin green with potassium bromate (curve 1, 4).

The effect of the concentration of citric acid (in the range of 0.02-0.12 M) on the determination of 0.500 µg 25 mL^{-1} vanadium was investigated. The results are showed in Fig. 3, which indicates that a concentration of 0.064 M could be selected as the optimum concentration for the system studied.

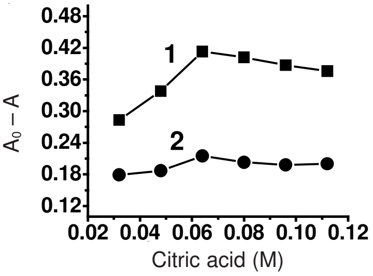


Fig. 3. Effect of citric acid concentration on determination of V: 0.020 µg mL^{-1} V(V), 2.4×10^{-3} M H_2SO_4, 1.03×10^{-4} M alizarin green, 2.0×10^{-4} M $KBrO_3$. (1) $A_{0641} - A_{641}$; (2) $A_{0413} - A_{413}$

Effect of alizarin green: The effect of alizarin green on the catalytic and uncatalytic reactions was investigated. The effects of varying concentrations of alizarin green on the kinetic determination of vanadium(V) at a constant concentration of vanadium(V) and acidity and other reactants concentrations were examined by measuring the absorbance difference at 413 and 641 nm. The result was illustrated in Fig. 4. The result reveals that the rates of the uncatalyzed and catalyzed reaction both increase with increasing of alizarin green concentration. On the basis of selecting the concentration that offered a satisfactory difference between the absorbances of the catalyzed and uncatalyzed reactions, 4.0 mL 6.44 × 10^{-4} M of alizarin green was finally selected.

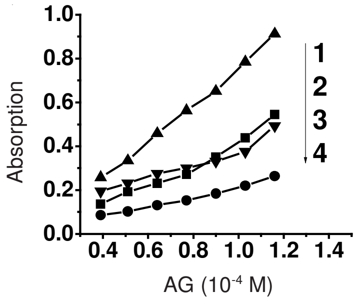


Fig. 4. Effect of alizarin green concentration on determination of V: 0.020 µg mL^{-1} V(V), 2.4 × 10^{-3} M H_2SO_4, 0.064 M citric acid, 2.0 × 10^{-4} M $KBrO_3$ (1) A_{0641}; (2) A_{0413}; (3) A_{641}; (4) A_{413}

Effect of potassium bromate: The dependence of the absorbance on the concentration of potassium bromate showed that with the increase of the amount of potassium bromate the absorbance differences increased and the precision and sensitivity of determination vanadium(V) improved. The result is illustrated in Fig. 5. From the graph we can find that the ΔA was maximum with the concentration of potassium bromate being 2.0 × 10^{-4} M and the precision and sensitivity of determination vanadium(V) improved. Therefore 2.0 × 10^{-4} M potassium bromate solution were selected as the optimum concentration.

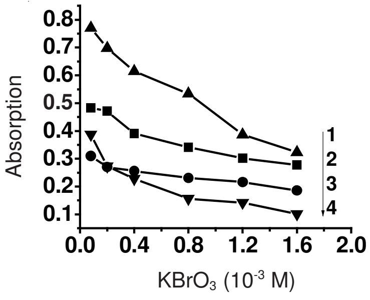


Fig. 5. Effect of $KBrO_3$ concentration on determination of V: 0.020 µg mL^{-1} V (V), 2.4 × 10^{-3} M H_2SO_4, 0.064 M citric acid, 1.03 × 10^{-4} M AG. (1) A_{0641}; (2) A_{0413}; (3) A_{413}; (4) A_{641}

Effect of heat temperature and time: The investigation shows that there was no catalytic reaction at 30 ºC; at 60 ºC, there was catalytic action, at temperature higher than 60 ºC reaction speed accelerated; up to 90 ºC catalytic effect was good and at 100 ºC reaction speed reached the maximum. A reaction temperature of 100 ºC was adopted as the optimum one since it provided a good reaction rate and satisfactory sensitivity. Reaction can be easily controlled and operated.

The effect of time in the experiments is revealed in Fig. 6. Results indicate that the absorbances of catalyzed and uncatalyzed reactions both reduce with the time extending and the value of ΔA was on the increase in the range of 5-20 min at 100 ºC. After 20 min the ΔA value is becoming a constant. Therefore, the heat time is chosen as 20 min as the experiments having a good sensitivity under this condition.

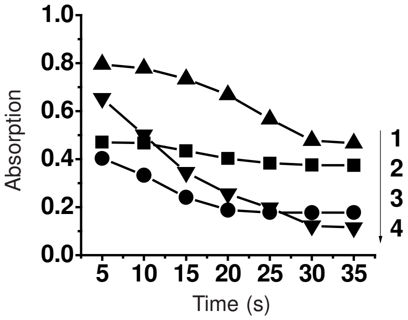


Fig. 6. Effect of time on determination of V: 0.020 µg mL^{-1} V (V), 2.4 × 10^{-3} M H_2SO_4, 0.064 M citric acid, 1.03 × 10^{-4} M alizarin green , 2 × 10^{-4} M $KBrO_3$. (1) A_{0641}; (2) A_{0413}; (3) A_{413}; (4) A_{641}

Characteristics of the method: A calibration curve for vanadium was constructed under the optimum conditions. A solution containing 0.00375, 0.125, 0.250, 0.500, 0.750, 1.0 µg of vanadium(V) was transferred into a series of 25 mL calibrated flasks. Then, the operation was made according to the analytical procedure. The calibration graph was linear in the range of 0.150-40.0 ng mL^{-1} of vanadium(V). Regression analysis with an equation ΔA = 30.09C (µg mL^{-1}) + 0.0247 (R = 0.9988) was used in order to fit the best line to the points of the graph. C is the concentration of vanadium(V) in solution and R is the correlation coefficient, respectively. The relative standard deviation for a vanadium(V) standard solution of 10 ng mL^{-1} was 0.39 % (n = 11). The relative standard deviation for the reagent blank was 0.064 %, respectively. The detection limit of the vanadium was found to be 6.4 × 10^{-11} g mL^{-1} which was calculated by multiplying the standard deviation of eleven replicate measurements of absorbance for the reagent blank by three and dividing by the slope of the linear calibration curve.

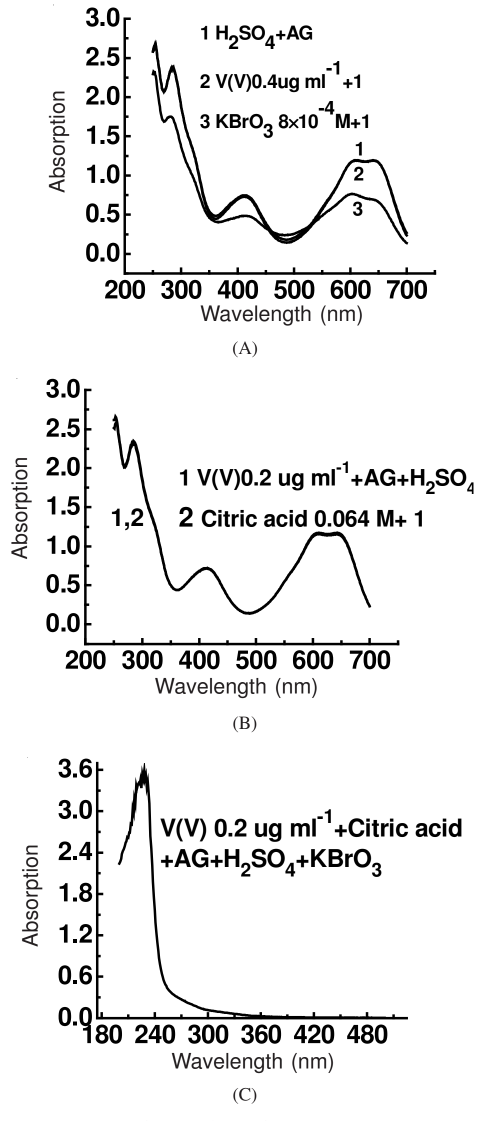
Interference study: To study the selectivity of the method, we undertook a systematic investigation of the effect of foreign ions on the catalytic determination of 0.50 µg of vanadium(V) in 25 mL calibrated flasks. The tolerance limits were taken for a maximum error of ± 5 %. The results were summarized in Table-1. Table-1 shows that the metal cations which seriously interfere with the determination of vanadium(V) were Fe^{3+}

TABLE-1
TOLERANCE LIMITS OF INTERFERING
IONS IN 2.0 × 10^{-3} µg mL^{-1} VANADIUM(V)

Foreign ion	Tolerance limit, foreign ion/V(V)
Ba^{2+}, Na^{+}, La^{3+}, Sr^{2+}, Ga^{6+}, NO_3^-, Cl^-	800
Ca^{2+}	600
Bi^{3+}	500
Nd^{3+}	400
Cd^{2+}	300
Mg^{2+}, I^-, Co^{2+}	200
Pb^{2+}, Zr^{4+}, Tl^{3+}	100
Zn^{2+}	80
Ag^{+}, Mo^{6+}	40
Al^{3+}, Mn^{2+}	20
Cu^{2+}	5
Fe^{3+}	0.5

and Cu^{2+}. The interferences can be greatly diminished by cation resin. From the results it can be seen that a series of various cations and anions can be tolerated in a satisfactory level of their limiting concentration ratio. The method has good selectivity.

Mechanism of the reaction: It is well known that most indicator reactions used for kinetic-catalytic determination of trace elements are based on oxidation-reduction reactions. Under the optimum condition, the operation was made according to the procedure with increasing the concentration of vanadium(V). From Fig. 7A, we could find that curve 1 almost coincided with curve 2, which indicates that vanadium(V) did not undergo the oxidization for the alizarin green under the acid condition and at the same time curve 3 showed that potassium bromate is the oxidant. Fig. 7B illustrated that citric acid didn't have the catalysis and from Fig. 1 we could find that citric acid had an effect of activator on the catalytic reaction. The intermediate product (1) of vanadium(V) and citric acid could change the charge distribution of AG molecule and facilitate and accelerate the intermediate product (2) oxidation and the product is anthraquinone (3) (Fig. 7C has a strong absorption at 230 nm).



(A)

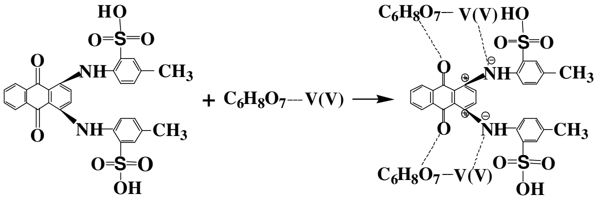
(B)

(C)

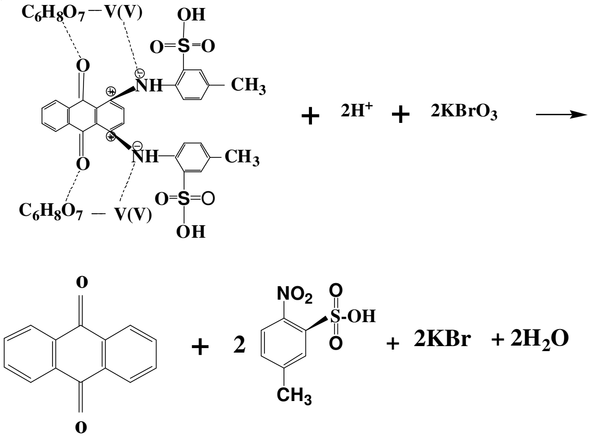
Fig. 7. Absorption spectra

According to the results of present experiment, the probably reaction mechanism of the reactions could be proposed as follows:

$$C_6H_8O_7 + V(V) \longrightarrow C_6H_8O_7\text{-}V(V) \qquad (1)$$



(2)



(3)

Determination of vanadium(V) in rice and tap water: 2.0 g of rice sample was accurately weighed and placed into 50 mL-calibrated flask. One drop of nitric acid was added to dissolve the sample. After the dissolution of the sample, the solution was evaporated gently by fire heating in a ventilated cabinet. Under heating condition perchloric acid was added by drop to diminish the colour of nitration product till the becomes colourless clearness and evaporated. The sample solution was cooled and diluted to the mark of 250 mL calibrated flask with water. An aliquot of this sample solution was taken for the determination of vanadium content by following the general procedure. Sample of tap water could be analyzed directly without pretreatment. The results obtained are shown in Table-2.

TABLE-2
DETERMINATION RESULTS OF VANADIUM IN SAMPLES

Sample	Found	RSD (%)	Added (μg)	Found (μg)	Recovery (%)
Rice (μg g^{-1})	0.025	4.3	0.030	0.0291	97.0
Tap water (μg mL^{-1})	0.003	3.9	0.030	0.0303	101

The results of the analysis of samples were excellent agreement with those of standard reference results. The recoveries and relative standard deviations (n = 8) of the proposed method were between 97.00-101 and 3.9-4.3 %, respectively. The analytical results were quite satisfactory.

ACKNOWLEDGEMENTS

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