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SHORT COMMUNICATION

CATALYTIC KINETIC SPECTROPHOTOMETRIC DETERMINATION OF TRACE TITANIUM BASED ON TITANIUM(IV)-(DBS-ARSENAZO)-POTASSIUM BROMATE SYSTEM

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ABSTRACT. Based on the property that in 0.12 M sulfuric acid medium titanium(IV) catalyzes the discoloring reaction of DBS-arsenazo oxidized by potassium bromate, a new catalytic kinetic spectrophotometric method for the determination of trace titanium (IV) was developed. The linear range of the determination of titanium is 0-2.4 μg/25 mL. The detection limit of the method is 0.47 ng/mL. The effects of fifty coexisting substances were studied and most of common substances do not interfere with the determination of titanium. The method has good selectivity. The present method was used in the determination of trace amount of titanium in cabbage and potato samples with satisfactory results. The relative standard deviations of ten replicate determinations of the method are 1.4-1.5 % and the recoveries of standard addition are 97.6-98.0 %, respectively.

KEY WORDS: Titanium(IV), Catalytic kinetic spectrophotometry, DBS-Arsenazo, Potassium bromate, Cabbage, Potato

INTRODUCTION

Titanium is one of necessary microamount of elements for the health of human body. Mocroamount of titanium in human body has the function of strengthening the immunity ability and titanium may participate in physiological and biochemical reaction as the active centers of some enzymes. People absorb titanium by food and drink. The development of new methods for the determination of trace amount of titanium has important significance in life science. Catalytic kinetic spectrophotometry has the advantages of high sensitivity and simplicity of operation [1]. The catalytic kinetic spectrophotometric method is especially suitable for the determination of trace component. Most of the indicator reaction of the catalytic kinetic spectrophotometric determination of titanium used base dyes such as indirubin [2], neutral red [3] and nile blue hydrochloride [4]. However, the determination of titanium based on an unsymmetric bis-arylazo derivatives reagent of chromotropic acid as an indicator reaction is few. Also, there is no commonly accepted catalytic kinetic spectrophotometric method for titanium due to the limit of selectivity. Thus, the development of a new system of the determination of titanium is still of interest. DBS-Arsenazo(DBS-ASA), 3-(2,6-dibromo-4-sulfo-phenylazo)-6-(2-arsenophenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid, dibromo-*p*-sulfonic acid-arsenazo, is an unsymmetric bis-arylazo derivative of chromotropic acid and has been used for the spectrophotometric determination of rare earths [5]. It was found that in 0.12 M sulfuric acid potassium bromate can oxidize DBS-arsenazo to fade using DBS-arsenazo as an indicator and trace titanium(IV) has the catalytic effect on this reaction. Based on this property, the optimum conditions of the catalytic reaction were studied in detail in this paper and a novel method for the determination of trace titanium was developed by catalytic

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*Corresponding author. E-mail: Zhaiqingzhou@sohu.com, zhaiqingzhou@hotmail.com kinetic spectrophotometry. For the present method, the operation is simple and rapid. Its sensitivity is high and the selectivity is good. It has been used in the determination of trace titanium in cabbage and potato samples with satisfactory results.

EXPERIMENTAL

Apparatus

A 722S spectrophotometer (Shanghai Linggunag Technique Co., Ltd., China) with a 1.0 cm cell was used for measuring the absorbance. A HH-2 constant temperature water bath kettle (Jiangsu Jintan Ronghua Instrument Manufacture Co., Ltd, China) was employed to control the reaction temperature.

Reagents and chemicals

Doubly distilled water and analytical reagent-grade chemicals were used. A stock titanium(IV) solution containing 1.000 mg/mL Ti(IV) was prepared as follows: 0.1668 g of TiO_2 (The First Reagent Plant of Shanghai, China) and 2 g of potassium pyrosulfate were mixed and then fused for 30 min at 700 ^oC. The mixed substance cooled and then it was dissolved in 0.5 M sulfuric acid. It was diluted to 100 mL with 0.5 M of sulfuric acid and 1.000 mg/mL Ti(IV) of stock solution was obtained. Then, an appropriate amount of the stock solution was diluted with 0.5 M of sulfuric acid; 0.3 μg/mL of standard solution was obtained. A 1.85 x 10^{-4} M DBS-arsenazo (DBS-ASA, $C_{22}H_{15}AsBr_2N_4O_{14}S_3$, Shanghai Changke Research Institute for Reagents, China) was prepared by dissolving 0.0165 g of DBS-ASA in water and diluting to the mark in a 100-mL volumetric flask. A 0.020 M of potassium bromate solution was used. 1.0 M sulfuric acid was prepared by appropriate dilution from concentrated solution.

Analytical procedure

A sample solution was prepared by pouring a suitable amount of the standard titanium(IV) solution, 0.9 μg, into a 25 mL comparison tube; then the solution was diluted to about 10 mL with water. 1.5 mL of 1.0 M sulfuric acid solution, 2.5 mL of a 1.85 x 10^{-4} M DBS-arsenazo solution and 2.0 mL of a 0.020 M potassium bromate solution were added. The solution was diluted to the mark with water; shaked well and placed into a boiling water bath at 100 ^oC to heat for 10 min. The comparison tube was rapidly taken out, and cooled for 10 min in running water to terminate the reaction. The absorbance (catalytic reaction), A, was measured at 510 nm against water using 1 cm cells. The measurement of non-catalytic reaction was carried out in the absence of Ti(IV). The net analytical signal (ΔA) was obtained from the difference of absorbance between the non-catalytic reaction (A_0) and the catalytic reaction (A), $\Delta A = A_0 - A$.

Procedure for the determination of titanium in cabbage or potato sample

10.000 g of fresh cabbage or potato, which was washed and dried by air, was weighed and placed in a beaker. To it 10 mL of concentrated nitric acid was added and evaporated to dryness. Then, 2 mL of nitric acid (1 + 1, v/v) was added drop by drop and then evaporated to dryness. Under a heating condition concentrated hydrogen peroxide was added drop by drop until the solution became clear. The above solution was evaporated to dryness; then water was added and the solution was heated to remove hydrogen peroxide. After cooling, it was transferred to a 50 mL volumetric flask with water. 0.50 mL of the test solution was taken and then the determination of titanium was carried out according to the procedure described above.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of various systems are shown in Figure 1. From the curves 1 and 2 it can be seen that bromate can decrease the absorbance of DBS-arsenazo solution at 510 nm. This suggests that bromate can oxidize DBS-arsenazo under the acidic condition. However, the change in peak value is not significant and the speed of decolorizing reaction of DBS-arsenazo is slow. Curves 3 and 4 show that when Ti(IV) was added to the (DBS-arsenazo)-potassium bromate system, the absorbance rapidly decreased along with the increase in the concentration of titanium(IV). This indicates that trace Ti(IV) has a strong catalytic effect on the oxidation of DBS-arsenazo by potassium bromate and discoloring extent is proportional to the amount of Ti(IV) added over a specified range. The maximum absorption wavelengths of catalytic and non-catalytic reaction solutions are both at 510 nm. Thus, the measurement wavelength was selected to be 510 nm.

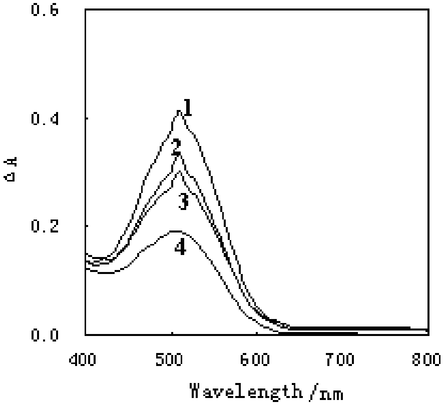

Figure 1. Absorption spectra. 1- H_2SO_4 + DBS-ASA, 2- 1 + $KBrO_3$, 3- 2 + 0.30 μg Ti(IV), 4- 3 + 0.90 μg Ti(IV). Experimental conditions: [H_2SO_4] = 0.12 M; [DBS-ASA] = 1.85×10^{-5} M; [$KBrO_3$] = 1.6×10^{-2} M; reaction temperature: 100 °C; reaction time: 10 min.

Optimization of experimental variables

Effect of acidity

The effect of acidity on the reaction rate was studied with a titanium concentration of 36 ng/mL and 1.85×10^{-5} M DBS-arsenazo and 1.6×10^{-3} M bromate. The effect of acidity on ΔA was studied over the range of 0.10-4.0 mL of 1.0 M sulfuric acid added. The results showed that as the amount of sulfuric acid increased, ΔA value increased. When the amount of 1.0 M sulfuric acid reached 1.5 mL, ΔA was a maximum. Then, ΔA value gradually decreased as the amount of sulfuric acid further increased. When the amount of the sulfuric acid was 4.0 mL, $\Delta A \approx 0$. The optimum amount of 1.0 M sulfuric acid was selected to be 1.5 mL. Under this condition, the acidity of the system was 0.12 M.

Effect of the amount of DBS-arsenazo

The effect of DBS-arsenazo concentration on the reaction rate was studied at 0.12 M of sulfuric acid with a titanium concentration of 36 ng/mL and 1.6×10^{-3} M of potassium bromate. The results showed that as the amount of DBS-arsenazo increased, the reaction rate increased and ΔA is also increased. When the amount of DBS-arsenazo was 2.4 mL, ΔA reached a maximum. When the amount of DBS-arsenazo was 2.4-3.0 mL, ΔA was maximum and stable. Thus, the amount of 1.85×10^{-4} M DBS-arsenazo was selected to be 2.5 mL.

Effect of potassium bromate

The effect of potassium bromate concentration on the reaction rate was studied at 0.12 M of sulfuric acid with a titanium concentration of 36 ng/mL and 1.85×10^{-5} M of DBS-arsenazo. The experimental results showed that as the amount of the added potassium bromate increased, the net reaction rate and the sensitivity increased. When the amount of potassium bromate was 1.8-2.2 mL, ΔA was maximum and basically constant. Thus, 2.0 mL of 0.020 M $KBrO_3$ solution was selected for further studies.

Effect of temperature on reaction

The effect of temperature over 30-100 °C on the sensitivity was studied at 0.12 M of sulfuric acid with a titanium concentration of 36 ng/mL and under the optimum conditions of other reagents. The results showed that below 45 °C the catalytic reaction nearly could not occur. Over the range of 50-100 °C the sensitivity of reaction increased as the temperature increase. In order to obtain high sensitivity, 100 °C was selected in the experiments.

Effect of reaction time

The experimental results showed that over the range of 4-10 min ΔA increased and good linearity was observed as reaction time increased. The linear regression equation is: $\Delta A = 0.022t - 0.0323$, correlation coefficient $\gamma = 0.9991$. The rate constant of the reaction is $k = 2.57 \times 10^{-4}$/s, and a half life period is $t_{1/2} = 49.9$ min. In the experiment, a heating time of 10 min was selected. After the reaction, the solution was cooled by running water for 10 min in order to terminate the reaction and the absorbance of the system could keep stable for 3.5 h at least.

Calibration curve and detection limit

Under the selected optimum experimental conditions, the difference between blank and sample solutions is proportional to the concentration range over 0-2.4 μg/25 mL of Ti(IV) with the linear regression equation $\Delta A = 0.2029C$ (C = μg/25 mL) + 0.0093, $\gamma = 0.9990$, where ΔA is the difference in the absorbance change between the blank and sample solution, C is the Ti(IV) amount in μg in 25 mL of solution, and γ is the correlation coefficient, respectively.

The relative standard deviation for eleven replicate determination of 1.0 μg/25 mL of Ti(IV) testing solution was 2.0 %. The standard deviation for eleven replicate determination of a reagent blank solution was 3.2×10^{-3}. The limit of detection is defined as $C_L = 3S_B/m$, where C_L, S_B and m are the limit of detection, standard deviation of the blank signal and slope of the calibration graph [6], respectively. The limit of detection for the present method is 0.47 ng/mL.

Interference study

The effect of various foreign substance on the determination of Ti(IV) in a sample solution containing 1.0 μg/25 mL of Ti(IV) was examined under the optimum conditions. When a relative error did not exceed ±5 %, the allowed amounts, mass multiple (m/m) of fifty foreign substances are as follows: K^+, Na^+, Cl^-, NO_3^- (1000); Li^+, Ag^+, Mg^{2+}, Cd^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Pb^{2+},

Al^{3+}, F^-, SiO_3^{2-} (500); Sr^{2+}, Sn^{2+}, Mn^{2+}, Cr^{3+}, Bi^{3+} (70); Ni^{2+} (60); Co^{2+}, B(III), Th(IV), urea, citric acid, glycine, serum albumin (50); Mo(VI), Br^-(40); La^{3+} (20); PO_4^{3-}, ascorbic acid, glucose, tartaric acid, phenylalanine, acetic acid (10); Fe^{3+}, I^-, VO_3^-, MnO_4^- (5); EDTA (4); Fe^{2+}, Eu^{3+} (2); Cu^{2+}, NO_2^-, $Cr_2O_7^{2-}$, $S_2O_7^{2-}$, lysine, apple acid (1). The allowable amounts of common substances are large. The present method for the determination of trace Ti(IV) has good selectivity. For the catalytic kinetic spectrophotometry of Ti(IV), Bi^{3+}, Ni^{2+} [2], Fe^{3+}[3] and Mn^{2+} [4] often interfere. However, the selectivity of the present method for these ions is much better than those of the literatures [2-4].

Determination of apparent activation energy

When the amount of each reactant is fixed, the following relationship exists for the system of the catalytic reaction:

$$\ln k_2 = \ln(-\Delta A_2/\Delta t) + E(\text{constant})$$

According to Arrhenius equation: $\ln k = -Ea_2/RT + E(\text{constant})$. It can be obtained:

$$\ln(-\Delta A_2/\Delta t) = -Ea_2/RT + \text{constant}$$

$$\text{or } \log(-\Delta A_2/\Delta t) = (-Ea_2/2.303R) \times (1/T) + \text{constant}$$

Fixing time $t_1 = 5.5$ min, $t_2 = 6.0$ min, other conditions were the optimum experimental ones and the experiments were made. The $-\Delta A_1$ value of non-catalytic reaction and $-\Delta A_2$ value of catalytic reaction were determined, respectively. Then the figures were drawn by using $\log(-\Delta A_1/\Delta t)$, $\log(-\Delta A_2/\Delta t)$ with respect to 1/T, respectively, and the straight lines were linearly regressed. The following results were obtained:

$$\log(-\Delta A_1/\Delta t) = (5.899 \text{ x } 1/T)10^3 - 7.898, \gamma = 0.9944$$

$$\log(-\Delta A_2/\Delta t) = (3.813 \text{ x } 1/T)10^3 - 4.099, \gamma = 0.9954$$

From this, the apparent activation of the catalytic reaction is obtained as follows:

$$E_{a-2} = 3.813 \text{ x } 2.303 \text{ x } 8.314 = 73.01 \text{ kJ/mol}$$

The apparent activation of the non-catalytic reaction is obtained as follows:

$$E_{a-1} = 5.899 \text{ x } 2.303 \text{ x } 8.314 = 112.95 \text{ kJ/mol.}$$

It can be conclude from the above results that the apparent activation energy of the catalytic reaction is less than that of non-catalytic reaction. Thus, under the experimental condition of the present study, in the dilute sulfuric acid medium potassium bromide oxidizes DBS-arsenazo using titanium(IV) as a catalyst and titanium(IV) can sensitively catalyze the reaction.

Discussion on reaction mechanism

It can be seen from the literature [7] that most indicator reactions used for kinetic-catalytic determination of trace of elements are based on oxidation-reduction reactions in which the catalyst that is usually a multi-charged ion changes its oxidation state during the reaction in a cyclic way:

$$\text{Red} + M^{(n+1)+} \rightarrow P + M^{n+} \quad (1)$$

$$M^{n+} + \text{Ox} \rightarrow M^{(n+1)+} + Q \quad (2)$$

$$\text{Red} + \text{Ox} \rightarrow P + Q \quad (3)$$

Where Red and Ox are the reactants of a redox system and P and Q are the reaction products. When an ion $M^{(n+1)+}$ is a catalyst, it accelerates the formation of the product P and is then reduced to a lower oxidation state, M^{n+}. If M^{n+} is oxidized again to $M^{(n+1)+}$ by reaction (2), the oxidation of Red to P is catalysed by a minute amount of $M^{(n+1)+}$. As the concentration of the catalyst is directly proportional to the rate of reaction, the reaction rate can be used for the determination of the catalyst. In present study, the Red and the Ox are DBS-arsenazo and potassium bromate, respectively, and the catalyst is Ti(IV). The proposed catalytic reaction occurs in a cyclic manner according to equations (4) and (5):

$$6H^+ + Ti(IV) + C_{22}H_{15}AsBr_2N_4O_{14}S_3 \rightarrow Ti(III) + C_6H_7AsO_3 + C_{10}H_{10}O_8S_2 + C_6H_4Br_2SO_3 + 2N_2 \quad (4)$$

$$6H^+ + 5Ti(III) + BrO_3^- \rightarrow 5T\ i(IV) + 1/2Br_2 + 3H_2O \quad (5)$$

The proposed non-catalytic reaction occurs according to equation (6):

$$6H^+ + C_{22}H_{15}AsBr_2N_4O_{14}S_3 + BrO_3^- \rightarrow C_6H_7AsO_3 + C_{10}H_{10}O_8S_2 + C_6H_4Br_2SO_3 + 2N_2 + 1/2Br_2 \quad (6)$$

Application

To evaluate the analytical applicability of the method, it was applied to the determination of titanium in cabbage and potato samples. The analytical results are shown in Table 1. It can be seen from the Table that when the present method was used to the determination of trace titanium in cabbage and potato samples, the analytical results were in excellent agreement with those by atomic absorption spectrometry. The relative standard deviation of ten replicate determinations was 1.4-1.5 % and the recovery of addition standard was 97.6-98.0 %, respectively. The analytical results were quite satisfactory.

Table 1. Analytical results of samples.

Sample	Found ($\mu g \cdot g^{-1}$, n = 10)	Average ($\mu g \cdot g^{-1}$)	RSD (%)	Added (μg)	Found (μg)	Recovery (%)	AAS method ($\mu g \cdot g^{-1}$)
Cabbage	6.18, 6.22, 6.14, 6.29, 6.41, 6.14, 6.25, 6.16, 6.14, 6.19	6.21	1.4	0.500	0.490	98.0	6.20
Potato	9.81, 9.75, 9.86, 9.97, 9.83, 9.79, 9.64, 9.95, 9.54, 9.99	9.81	1.5	0.500	0.488	97.6	9.82

CONCLUSION

A novel catalytic kinetic spectrophotometric method for the determination of titanium was developed in this paper. The linear range of the determination of titanium is 0-2.4 μg/25 mL with the limit of detection 0.47 ng/mL. The selectivity of the system is good and common substances do not interfere in the determination of titanium. The method is suitable for the determination of some cabbage and potato biological samples.

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