



Study of the Catalytic Kinetic Spectrophotometry of Iron(III)-(Dibromo-*p*-methyl-arsenazo)-Potassium Bromate

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Trace amount of iron is a necessary element for human body. The iron content in some foods is not only high, but also the absorption rate is high. To the anemia patient of lacking iron, it is of great benefit. It can also prevent heart disease and lower the role of cholesterol. Therefore, the research of new method for the determination of trace amount of iron has applied value. In a sulfuric acid medium of $5 \times 10^{-3} \text{ mol L}^{-1}$, the maximum absorption wavelength of Fe(III)-(dibromo-*p*-methyl-arsenazo)-KBrO₃-ascorbic acid system is at 530 nm. The amount of iron(III) over the range of 0.5-7.0 ng/mL and the difference of absorbance present a good linear relationship. The detection limit of the method is 0.26 ng mL⁻¹. The present method was satisfactorily applied to the determination of trace iron in peanut.

Key Words: Iron, Dibromo-*p*-methyl-arsenazo, Potassium bromate, Kinetic spectrophotometry.

INTRODUCTION

In our life, iron can be regarded as the most useful and the most inexpensive, the most abundant and the most important metal. In the industrial and agriculture production, iron is the very important material for basic structure and the uses of ferroalloy are wide. For the human body, iron is an indispensable trace element. For more ten essential trace element to human bodies, iron is in the first place regardless of importance or quality. A normal adult body contains more than 3 g of iron in all over the body, equivalent to a small nail quality. Hemoglobin in human blood is iron complexes and it has the function of fixing oxygen and of delivering oxygen. That a human body lacks iron can cause anemia. The iron contented in the peanut of food is higher, which has the big benefit towards anemic sufferer lacking of iron. It also has a function to prevent heart attack and cut down cholesterol. Therefore, research and the establishment of highly sensitive method for determination of iron has a certain practical significance. The methods of determining iron include atomic absorption spectrometry (AAS), polarography, differential stripping voltammetry, *etc.*, but they all need an expensive instrument and are not easy to be operated and have other shortcomings¹. As spectrophotometry is easy to be operated and the instrument is cheap, for the determination of iron, it is more suitable and has higher practical value. Phenanthroline spectrophotometric method²⁻¹³ is commonly used to determine iron, but the sensitivity of

method is low. In recent years, although some spectrophotometric method of determination of iron was proposed¹⁴⁻¹⁶, the determination method of iron is not ideal on sensitivity. Kinetic spectrophotometric method for the determination of trace material has the advantages that has high sensitivity, low detection limit, *etc.* and has been applied to the determination of some trace materials¹⁷⁻²⁰.

Dibromo-*p*-methyl arsenazo, abbreviated as DBM-ASA, is a chromogenic agent. Its molecular formula is C₂₃H₁₇N₄O₁₁S₂AsBr₂, the molecular structure formula (Fig. 1).

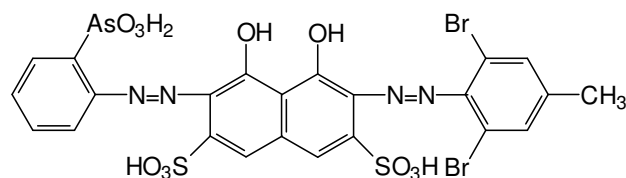


Fig. 1. Molecular structure of DBM-ASA

From Fig. 1, it can be known that there are some chemical groups on the aromatic ring of DBM-ASA, such as -OH, -SO₃H, -AsO₃H₂ and -N=N- and many groups contain the ligand of N,O. It can produce colour by itself. When it is oxidize or deoxidize and the -N=N- group is damaged, it will make solution colour become shallow or even colourless. Dibromo-*p*-methyl arsenazo has been used for kinetic spectrophotometric determination of Ti(IV)²¹. Although the catalytic

kinetic spectrophotometric method for determination of iron has been reported¹, the determination method of iron through potassium bromate oxidation dibromo-*p*-methyl arsenazo fading as the indicator reaction, has not been reported. This study found that in the sulfuric acid medium whose concentration is $5.0 \times 10^{-3} \text{ mol L}^{-1}$, Fe^{3+} can catalyze the fading reaction of dibromo-*p*-methyl arsenazo oxidized by potassium bromate and a new method for the determination of iron has been established. The method has high sensitivity and is easy to be operated. When it was applied to the determination of iron in peanuts, the results were satisfactory.

EXPERIMENTAL

Fe^{3+} solution: $1.16 \times 10^{-4} \text{ mol L}^{-1}$ working solution prepared by $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; H_2SO_4 solution: 0.10 mol L^{-1} ; ascorbic acid (Vc) solution: $5.68 \times 10^{-4} \text{ mol L}^{-1}$ working solution stored in a refrigerator at 2°C ; dibromo-*p*-methyl arsenazo (DBM-ASA) solution: $6.07 \times 10^{-4} \text{ mol L}^{-1}$ solution; KBrO_3 solution: 0.10 mol L^{-1} solution. Unless specially indicated, all reagents were of analytical grade. The water used was deionized water.

A 722S spectrophotometer (Shanghai Lingguang Technique Co., Ltd., China) with 1 cm cells was used for absorbance measurements. A HH-2 thermostat water bath kettle (Jiangsu Jintan Ronghua Apparatus Manufacture Co., Ltd, China) was used for temperature control. A stopwatch was used for recording the reaction time.

Procedure: In two 10 mL comparison tubes, 20 ng Fe(III) of standard solution (catalytic system) was added to the one comparison tube and no Fe(III) was added to another comparison tube (non-catalytic system). Then, 0.50 mL H_2SO_4 solution, 0.50 mL Vc solution and 1 mL of DBM-ASA solution were added to both comparison tubes in turn respectively and shaken up. The solutions were placed in a boiling bath for 2 min, taken out and cooled by running water for 10 min. 1 mL KBrO_3 solution was added and then the solution was diluted with water to the mark and shaken well. The solutions were heated in a boiling water for 12 min, taken out, and rapidly cooled by running water for 10 min. The absorbance of non-catalytic reaction solution (A_0) and the absorbance of catalytic reaction solution (A) were respectively measured at 520 nm using 1 cm cells against water and then $\Delta A = A_0 - A$ was calculated.

RESULTS AND DISCUSSION

Absorption spectra: The absorption curves of different reaction systems are shown in Fig. 2. It can be seen from curves (a), (b) that the addition of KBrO_3 can make the absorbance of DBM-arsenazo decrease, showing that KBrO_3 can slowly oxidize DBM-arsenazo for fading under acidic conditions, but the peak value change is not great and the fading reaction rate is slower. It can be seen from curves (b), (c) that Vc plays a role of activation in the system. Curves (c), (d) showed that trace $\text{Fe}(\text{III})$ has a catalytic effect on the fading reaction of DBM-arsenazo by potassium bromate. Compared with curve (d), the absorbance of curve (e) decreased. The amount of Fe^{3+} used in curve (e) was 2 times of that used in curve (d). This showed that the fading degree increased as the $\text{Fe}(\text{III})$

amount added increased. Fig. 3 indicated that the maximum absorption wavelengths of both catalytic and non-catalytic reactions are 530 nm under the test conditions. At this wavelength, the catalytic action of Fe^{3+} has a maximum absorbance difference ΔA and 550 nm was selected as the measurement wavelength.

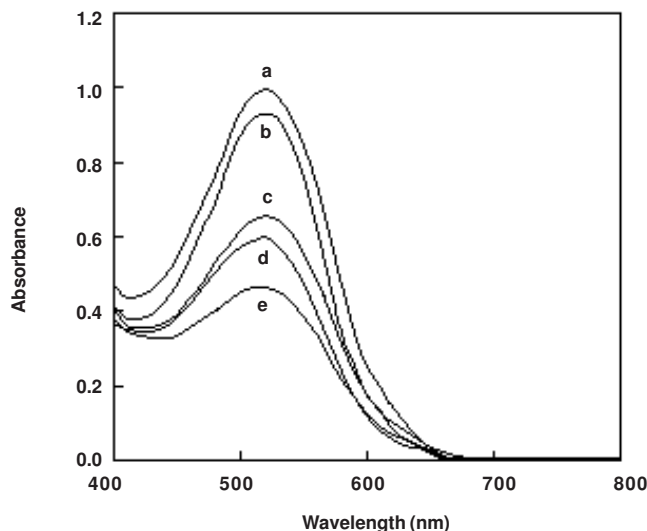


Fig. 2. Absorption spectra: (a) DBM-ASA; (b) (DBM-ASA) + KBrO_3 ; (c) (DBM-ASA) + KBrO_3 + Vc; (d) (DBM-ASA) + KBrO_3 + Vc + 10 ng Fe^{3+} ; (e) (DBM-ASA) + KBrO_3 + Vc + 20 ng Fe^{3+} ; [DBM-ASA] = $6.07 \times 10^{-5} \text{ mol L}^{-1}$; [KBrO_3] = $1.0 \times 10^{-2} \text{ mol L}^{-1}$; [Vc] = $2.84 \times 10^{-5} \text{ mol L}^{-1}$; [H_2SO_4] = $5.0 \times 10^{-3} \text{ mol L}^{-1}$; heating temperature: $T = 100^\circ\text{C}$; before and after addition of KBrO_3 , heating time was respectively: 2 min, 12 min

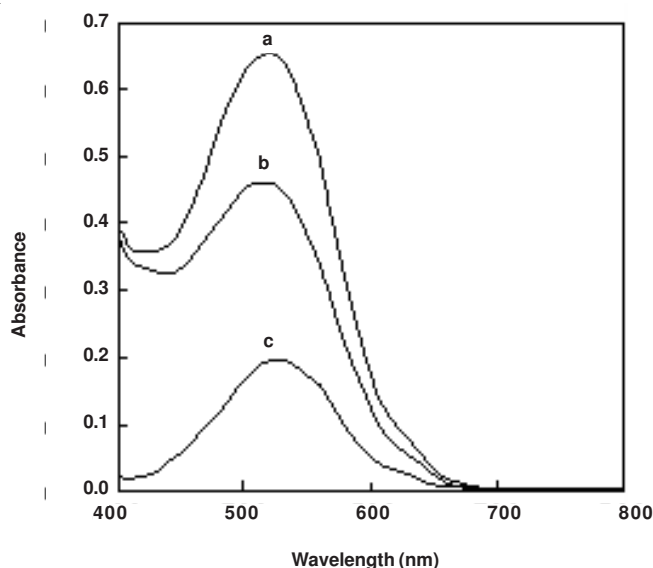


Fig. 3. Absorption spectra: (a) non-catalytic reaction (A_0)-(DBM-ASA) + KBrO_3 + Vc; (b) catalytic reaction (A)-(DBM-ASA) + KBrO_3 + Vc + Fe^{3+} ; (c) net catalytic reaction (ΔA); [Fe^{3+}] = $2.32 \times 10^{-5} \text{ mol L}^{-1}$; [DBM-ASA] = $6.07 \times 10^{-5} \text{ mol L}^{-1}$; [KBrO_3] = $1.0 \times 10^{-2} \text{ mol L}^{-1}$; [Vc] = $2.84 \times 10^{-5} \text{ mol L}^{-1}$; [H_2SO_4] = $5.0 \times 10^{-3} \text{ mol L}^{-1}$; heating temperature: $T = 100^\circ\text{C}$; before and after addition of KBrO_3 , heating time was respectively: 2 min, 12 min

Sulfuric acid dosage: Keeping other experimental variables optimum, effects of the sulfuric acid amounts of 0.1,

0.2, 0.5, 0.8, 1.0 mL on the reaction were respectively reviewed. The results showed that under the test conditions in range of 0.1-0.5 mL the sensitivity of the catalytic reaction increased as H₂SO₄ dosage increased. When the dosage was at 0.5 mL, ΔA value was maximum and the reaction sensitivity was the highest. When the amount of H₂SO₄ solution was greater than 0.5 mL, the reaction sensitivity reduced. Therefore, the test selected 0.5 mL as the appropriate acidity. At this time the system acidity was [H₂SO₄] = 5.0 × 10⁻³ mol L⁻¹.

Vc amount: The results of effect of Vc amount indicated that as Vc amount increased over the range of 0-0.5 mL, the sensitivity of catalytic reaction increased. When the amount of Vc was 0.5 mL, ΔA was maximum. When the amount of Vc was more than 0.5 mL, the reaction sensitivity reduced. Therefore, the Vc amount selected was 0.5 mL of 5.68 × 10⁻⁴ mol L⁻¹ solution.

DBM-ASA amount: The experimental results indicated that over the range of 0-1.0 mL DBM-ASA amount the sensitivity of catalytic reaction increased along with DBM-ASA increased. When DBM-ASA amount used was 1 mL, ΔA was a maximum and the reaction sensitivity was the highest. When it was more than 1 mL, the reaction sensitivity reduced. Therefore, 1 mL of 6.07 × 10⁻⁴ mol L⁻¹ solution was used.

KBrO₃ amount: The experimental results of effect of KBrO₃ amount indicated that as KBrO₃ amount increased over the range of 0-1 mL, the sensitivity of catalytic reaction increased. When the amount of Vc was 1.0 mL, ΔA was maximum. When the amount of KBrO₃ was more than 1 mL, the reaction sensitivity reduced. Therefore, 1 mL of 0.10 mol L⁻¹ KBrO₃ solution was further used.

Effect of heating temperature: The sensitivity of the system at different temperature before the addition of KBrO₃ was tested. The results found that the sensitivity was the highest over the range of temperature 90-100 °C. For the convenience of control of the experiment, 100 °C bath was selected.

After the addition of KBrO₃ and under the other conditions keeping optimum, in the water baths of 60, 65, 70, 75, 80, 85, 90, 95 and 100 °C was made and contrasted with blank reagent. The results indicated that below 80 °C the catalytic reaction at a temperature lower than 80 °C went slowly. At a higher temperature more than 80 °C, the reaction rate was accelerated. At 100 °C, the reaction rate reached maximum (ΔA was maximum) and the sensitivity of reaction was the highest. Thus, the water bath of 100 °C was selected for heat and the reaction was terminated by running water. ΔA with the temperature over the range of 80-100 °C presented a linear relationship and a linear regression equation was obtained: $\log(A_0/A) = -647.63 / T(K) + 1.8652$, with a correlation coefficient $\gamma = 0.9970$. According to slope of the equation, the activation energy of the catalytic reaction was obtained to be $E_a = 33.805$ KJ/mol.

Effect of heating time: Before adding KBrO₃, heating was respectively made for 0, 0.5, 1, 1.5, 2, 2.5, 3, 5 min under the situation where other conditions were kept optimum and compared with the blank reagent. The results indicated that

ΔA over the range 0.5-2.0 min and time presented a linear relationship. The reaction rate continuously increased. At 2 min, reaction rate achieved a maximum. After 2 min, it gradually decreased. Thus, heating time was recommended to be 2 min.

After adding KBrO₃, heating was respectively made for 0, 1, 3, 5, 7, 9, 10, 11, 12, 13, 13.5, 14 min under the situation where other conditions were kept optimum and compared with the blank reagent. The results indicated that ΔA over the range 9-12 min and time presented a linear relationship. The reaction rate continuously increased. At 12 min, reaction rate achieved a maximum. After 12 min, it gradually decreased. Therefore, reaction time was selected to be 12 min. By calculation, its linear regression equation obtained was $\Delta A = 0.0401 t(\text{min}) - 0.2675$, with a correlation coefficient $\gamma = 0.9954$. The reaction rate constant was $K = 1.00 \times 10^{-3} \text{ s}^{-1}$ and the half-life period was 11.55 min.

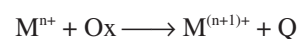
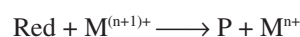
Stability of system: Under the optimum conditions, for the determination of 2 ng/mL Fe³⁺, a change of ΔA was less than 5 % within 2.5 h and the system maintained stable.

Working curve: Under the optimal experimental conditions, 0, 5, 8, 10, 15, 20, 25, 30, 40, 50, 60, 70 ng of Fe³⁺ standard solution were respectively added and compared with the blank reagents. The results indicated that in 10 mL solutions Fe³⁺ content in the range of 5-70 ng with ΔA assumes a good linear relationship. The regression equation is $\Delta A = 0.078C(\text{ng/mL}) + 0.0544$, with a correlation coefficient $\gamma = 0.9957$. For 11 parallel determinations of 4.0 ng/mL Fe³⁺, the relative standard deviation was 1.1 %, which showed that the precision of the method is good. Under the optimal conditions, the standard deviation S was obtained by 11 blank experiments $S = 0.00718$. According to 3S/K method (K is the slope of working curve), detection limit of the method calculated is 0.26 ng mL⁻¹.

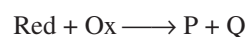
Selectivity of method: The influence of coexisting ions on the determination of 2.0 ng/mL Fe³⁺ was examined under the optimum conditions. The tolerance limits (weight ratio, m/m) of the coexisting ions tested (causing < ± 5 % relative error) are summarized as follows: PO₄³⁻ (8 × 10⁴); SO₄²⁻ (7 × 10⁴); Ca²⁺ (4000); Mg²⁺, F⁻, HAc (2000); Cl⁻ (1000); Al³⁺ (800); Cd²⁺ (600); Mn²⁺ (400); Ag⁺ (300); Zn²⁺, MnO₄⁻ (200); Bi³⁺ (150); W(VI), Mo(VI), Cr(VI), Cr³⁺, Ni²⁺, Pb²⁺ (100); B(III) (50); Y³⁺ (20); Eu³⁺ (15); La³⁺, Br⁻ (10); Zr⁴⁺ (8); Ti⁴⁺, Ce⁴⁺, Th⁴⁺, Cu²⁺, I⁻, VO₃⁻ (5); H₂C₂O₄ (3).

Mechanism of reaction: According to literature²², kinetic catalysis reaction for the determination of trace amount of element usually goes according to the following reaction:

Catalytic reaction:



Uncatalyzed reaction:

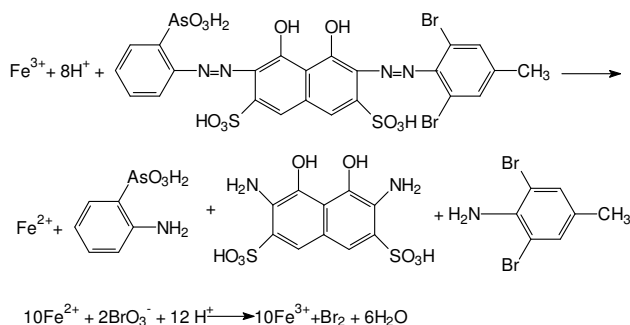


Based on this, it is speculated that the reaction mechanisms are as follows:

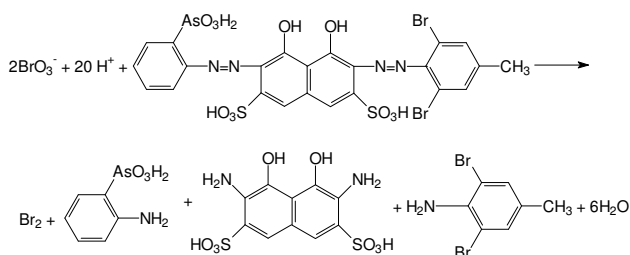
TABLE-1
 ANALYTICAL RESULTS OF SAMPLES

Sample	Found ($\mu\text{g g}^{-1}$)	Average value ($\mu\text{g g}^{-1}$)	RSD (%)	Added ($\mu\text{g g}^{-1}$)	Recovered ($\mu\text{g g}^{-1}$)	Recovery (%)	Atomic absorption spectrometric contrast method ($\mu\text{g g}^{-1}$)
1	29.44, 29.34, 29.62, 29.15, 29.02, 29.54, 29.85, 29.30, 29.44	29.41	0.85	2.000	2.011	100.6	29.41
2	31.33, 31.22, 31.11, 31.15, 31.01, 31.08, 31.41, 31.43, 31.56	31.26	0.60	2.000	1.989	99.45	31.28

Catalytic reaction:



Uncatalyzed reaction:



Sample analysis: 2 g of peanut was weighed, placed in porcelain crucible, heated on an electric stove until no longer no fume emitted. It was placed into a high temperature furnace, then firstly carbonized at low temperature and ashed at 650 °C, calcined for 10-12 h and taken out to be cooled down. To it were added 2 mL of concentrated hydrochloric acid, 1 mL of concentrated nitric acid and the contents were gently heated to near dryness. After it was cooled and dissolved with water, the contents were transferred into a 100 mL volumetric flask and diluted to the mark with water. 1 mL of the above test solution was pipetted and placed in a 100 mL volumetric flask and diluted to the constant volume with water as test solution. 2 mL of the test solution was pipetted and placed in a 10 mL colorimetric tube. Then, iron content was determined according to the standard procedure and the determined results are shown as Table-1. The standard addition recovery experiments were done and atomic absorption spectrometry were used to compare the experimental results. From the table it can be seen that the analytical results of samples obtained by the present method are satisfactory.

Conclusion

In the sulphuric acid medium whose systematic acidity is $5.0 \times 10^{-3} \text{ mol L}^{-1}$, trace Fe(III) catalyzes and accelerates the fading reaction between potassium bromate and DBM-arsenazo and a novel catalytic kinetic spectrophotometric method for the determination of trace Fe(III) was developed. At the wavelength of 530 nm, the amount of Fe(III) in the range of 0.5-7.0 $\mu\text{g/mL}$ and ΔA assume a good linear relationship. Its regression equation is: $\Delta A = 0.078C (\mu\text{g/mL}) + 0.0544$, with a correlation coefficient of $\gamma = 0.9913$. The activation energy of the catalytic reaction is: $E_a = 33.805 \text{ KJ/mol}$. This method has been satisfactorily applied to the determination of trace iron in peanut with satisfactory results.

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