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Spectrophotometric Determination of Iodine by Oxidation of Dibromo-*p*-chloro-arsenazo

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A new method for the determination of iodine by kinetic spectrophotometry was established with the oxidation of dibromo-*p*-chloro-arsenazo (DBC-ASA) by IO_3^- in presence of KBr. In the medium of 0.30 mol L^{-1} nitric acid, the maximum absorption peak of IO_3^--(DBC-ASA)-KBr system locates at 510 nm. The absorbance difference (ΔA) is linearly related with the concentration of IO_3^- over the range of 0.10-0.55 μg mL^{-1}. The detection limit of the method was 7.2 ng mL^{-1}. The method was used to determine iodine in kelp, seaweed and dried small shrimps. The relative standard deviation was 1.76-2.09 % for 11 replicate determinations. The recovery of the standard addition was 98.50-102.0 %.

Key Words: Iodine, Dibromo-*p*-chloro-arsenazo, Potassium bromide, Catalytic kinetic spectrophotometry.

INTRODUCTION

Iodine is a trace element of vital importance to human beings, which is closely related to the human growth and development, metabolism and especially plays an important role in brain development. Iodine can be absorbed in different parts of the digestive tract and the rate of iodine absorption is particularly high in the form of iodides. Absorption of organic iodine is very high, but slow. Iodine when absorbed into the bloodstream becomes the form of I^-, easily absorbed by thyroid, in which it is oxidized to I. It is then combined with tyrosine residues in thyroid ball protein, finally releases the iodine with hormone activity when in water, can get into other tissues through blood circulation. 80 % of thyroxine in organs is decomposed by deiodinase, then releases iodine from the circulation into the thyroid for synthesis. Inorganic iodine has a fast metabolism and organic iodine has a slow metabolism. Because the kidneys can not preserve iodide ion, the excess iodine is excreted in urine, the minority is discharged from the feces and sweat[1]. The iodine in human body mainly comes from food.

The methods for the determination of iodine are volumetric method, catalytic colorimetry, ion-selective electrode, X-ray fluorescence spectroscopy, cathodic stripping voltammetry, ion chromatography, neutron activation analysis, inductively

coupled plasma atomic emission spectroscopy, *etc.*, but they have the shortcomings of expensive apparatus and complicated operation, *etc*. Spectrophotometry has many advantages such as simplicity of operation and low price, which has been applied to the determination of iodine[2-6]. Similarly, due to the benefits of high sensitivity and low detection limit, kinetic spectrophotometry has attracted widespread interest.

Dibromo-*p*-chloro-arsenazo (DBC-ASA)[7] is a reagent, whose molecular formula is $C_{22}H_{14}N_4O_{11}S_2Br_2ClAs$ and its structural formula is given in Fig. 1.

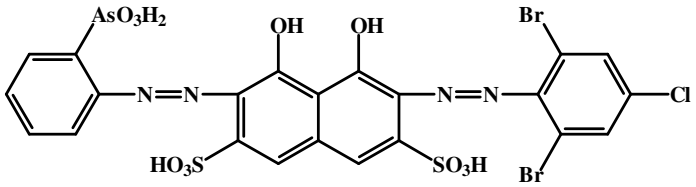


Fig. 1. Molecular structure of dibromo-*p*-chloro-arsenazo (DBC-ASA)

In the aryl derivative of DBC-ASA, there are a number of functional groups, such as -OH, $-SO_3H$, $-AsO_3H_2$ and -N=N- containing N and O. The reagent has the strong ability of chelate and can chelate with metallic ion to form various aqueous complexes. The -N=N- group itself can produce colour and the colour of solution may be weak or even colourless when -N=N- group is oxidized or reduced. In this paper, a method for the determination of trace amounts of iodine was established based on study on properties of IO_3^--(DBC-ASA)-KBr. This method displays high sensitivity, easy operation and low cost and has been successfully used in the determination of iodine in biological samples, such as kelp, seaweed and dried small shrimps.

EXPERIMENTAL

A 722S spectrophotometer (Shanghai Lingguang Technique Co., Ltd, China), with 1 cm optical glass cells, was used for absorbance measurements. A HH-2 thermostat water bath kettle (Jiangsu Jintan Ronghua Apparatus Manufacture Co., Ltd., China) was used for heating.

IO_3^- standard solution: An amount of 0.0122 g of KIO_3 was dissolved in water, which was placed into a 100 mL calibrated flask and diluted up to the mark with water. 100 mg L^{-1} IO_3^- stock solution was obtained and kept in cold storage at 2 ºC. 10 mg L^{-1} IO_3^- working solution was prepared by diluting the stock solution with water. DBC-ASA(Shanghai Jinsheng Chemical Co., Ltd., China) solution: 0.0500 g of DBC-ASA was dissolved in 100 mL water and 0.5 g L^{-1} DBC-ASA was obtained. 0.10 mol L^{-1} KBr solution: 0.5950 g of KBr was dissolved in 50 mL water and kept in cold storage at 2 ºC. 1.5 mol L^{-1} HNO_3 solution. Deionized water was used and all the reagents were of analytical grade.

Experimental procedures: Take two 10 mL calibrated flasks. 0.50 mL of 10 mg L^{-1} IO_3^- solution was placed into one calibrated flask, while the solution was

not placed into the other. Then 0.80 mL of 0.5 g L^{-1} DBC-ASA solution, 2 mL of 1.5 mol L^{-1} HNO_3 solution and 2 mL of 0.10 mol L^{-1} KBr solution were subsequently placed into each 10 mL calibrated flask, which were diluted up to the mark with water. Shake the mixed solutions well and heat them at 100 ºC for 8 min. Once they were taken out rapidly, cooled by running water for 10 min. Using 1 cm cells against water, the absorbance A of reaction system with IO_3^- solution added and the absorbance A_0 of reaction system without IO_3^- solution were measured and $\Delta A = A_0 - A$ was calculated.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectra were drawn based on the measurement of absorbance values of colour solution by experimental method. The results (Fig. 2) showed that under the test conditions, the maximum absorption wavelengths of the one reaction system with IO_3^- solution added and the other without IO_3^- solution were 420 and 500 nm. The maximum value of ΔA appeared at 510 nm, thus 510 nm was selected as the measurement wavelength.

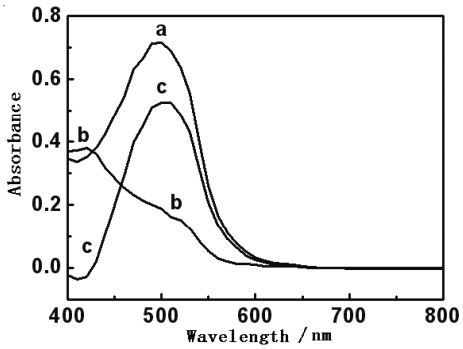


Fig. 2. Absorption spectra: (a) DBC-ASA + KBr - A_0; (b) DBC-ASA + KBr + IO_3^- - A; (c) ΔA; [DBC-ASA] = 4×10^{-2} g L^{-1}; [KBr] = 2×10^{-2} mol L^{-1}; [HNO_3] = 0.30 mol L^{-1}; [IO_3^-] = 0.50 mg L^{-1}; reaction temperature T = 100 ºC; heating time t = 8 min

Effect of the amount of nitric acid: The experimental results (Fig. 3) showed that with the increase of amount of the nitric acid solution over the range of 0-2 mL, the value of ΔA gradually increased and reached a maximum and the sensitivity of the reaction was the highest at 2 mL. When the amount of nitric acid solution was more than 2 mL, ΔA began to decrease, thus 2 mL of 1.5 mol L^{-1} nitric acid solution was selected. The concentration of the nitric acid solution was 0.30 mol L^{-1} in the reactive system.

Effect of the amount of DBC-ASA and KBr: The experimental results (Fig. 4) showed that with the increase of amount of DBC-ASA solution over the range of 0-0.80 mL, the value of ΔA increased and reached a maximum at 0.80 mL. When the amount of DBC-ASA solution was more than 0.80 mL, ΔA began to decrease, thus 0.80 mL of 0.5 g L^{-1} DBC-ASA solution was selected.

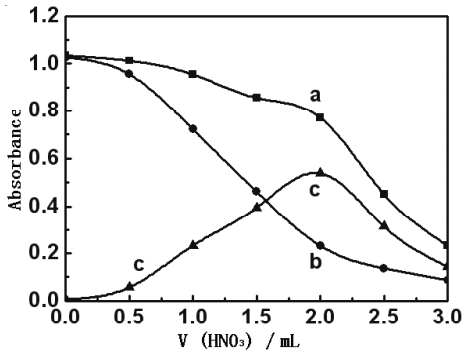


Fig. 3. Effect of acidity: (a) DBC-ASA + KBr - A_0; (b) DBC-ASA + KBr + IO_3^- - A; (c) ΔA; [DBC-ASA] = 4×10^{-2} g L^{-1}; [KBr] = 2×10^{-2} mol L^{-1}; [IO_3^-] = 0.50 mg L^{-1}; reaction temperature T = 100 ºC; Heating time t = 8 min; λ = 510 nm

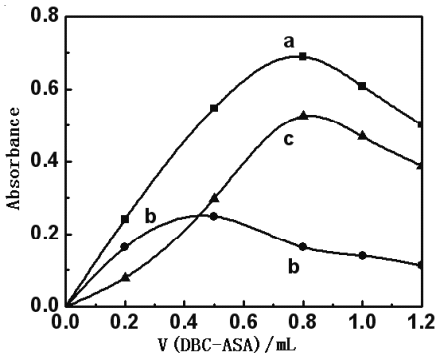


Fig. 4. Effect of amount of DBC-ASA: (a) DBC-ASA + KBr - A_0; (b) DBC-ASA + KBr + IO_3^- - A; (c) ΔA; [HNO_3] = 0.30 mol L^{-1}; [KBr] = 2×10^{-2} mol L^{-1}; [IO_3^-] = 0.50 mg L^{-1}; reaction temperature T = 100 ºC; heating time t = 8 min; λ = 510 nm

The results on the effect of the amount of KBr (Fig. 5) showed that with the increase of amount of KBr solution over the range of 0-1.5 mL, ΔA increased. When the amount of KBr solution was 1.5-2.0 mL, ΔA obtained a maximum value and the highest sensitivity of the reaction. When the amount of KBr solution was more than 2 mL, the sensitivity of the reaction decreased. Thus 2 mL of 0.10 mol L^{-1} KBr solution was selected to be appropriate.

Effect of the adding order of the reagents: The different adding order of the reagents had no effect on experimental results. In this paper, the adding order was IO_3^- + DBC-ASA + HNO_3 + KBr.

Stability of reactive system: For the determination of 0.50 mg L^{-1} IO_3^- the change of ΔA was less than 5 % within 1.5 h and the system kept stable.

Determination of kinetic parameters: The results (Fig. 6) showed that catalytic reaction almost did not happen when the temperature was lower than 70 ºC. With the increase of temperature, ΔA increased gradually and got a maximum when

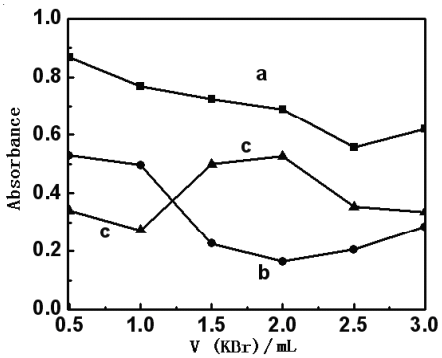


Fig. 5. Effect of amount of KBr: (a) DBC-ASA + KBr - A_0; (b) DBC-ASA + KBr + IO_3^- - A; (c) ΔA; [DBC-ASA] = 4×10^{-2} g L^{-1}; [HNO_3] = 0.30 mol L^{-1}; [IO_3^-] = 0.50 mg L^{-1}; reaction temperature T = 100 ºC; heating time t = 8 min; λ = 510 nm

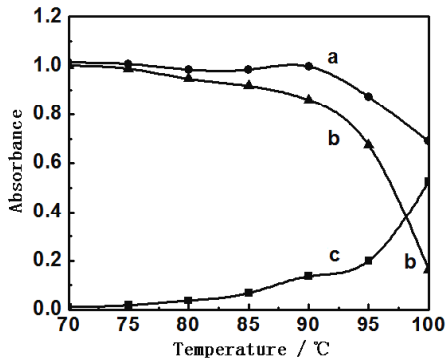


Fig. 6. Effect of heating temperature: (a) DBC-ASA + KBr - A_0; (b) DBC-ASA + KBr + IO_3^- - A; (c) ΔA; [DBC-ASA] = 4×10^{-2} g L^{-1}; [HNO_3] = 0.30 mol L^{-1}; [KBr] = 2×10^{-2} mol L^{-1}; [IO_3^-] = 0.50 mg L^{-1}; heating time t = 8 min; λ = 510 nm

the temperature reached 100 ºC. Therefore, 100 ºC was selected as optimum experimental temperature. The data measured over the range 70-95 ºC was processed by regression and the linear regression equation obtained is as follows: log ΔA = -6643.9/T + 16.83, γ = 0.9974. The apparent activation energy calculated was E_a = 127.2 KJ mol^{-1}.

The results on the effect of heating time (Fig. 7) showed that the reactive system was heated for 4, 5, 6, 7, 8, 9 and 10 min, respectively, ΔA was nearly zero within 0-4 min; ΔA and t showed a good linear relationship within 4-8 min and ΔA got a maximum at 8 min; ΔA decreased over 8 min. Thus, 8 min was selected as optimum time in the experiment. The linear regression equation obtained is as follows: ΔA = 0.125 t (min) - 0.497, γ = 0.9949. The reactive rate constant calculated was K = 2.083×10^{-3} s^{-1} and the half-life period was $t_{1/2}$ = 4.2 min.

Calibration graph: Under the optimum experimental conditions, ΔA and IO_3^- showed a good linear relationship over the range of 0.10-0.55 μg mL^{-1} and the

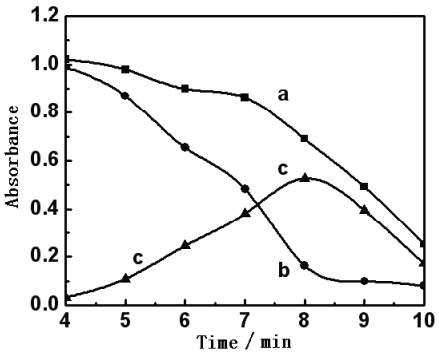


Fig. 7. Effect of heating time: Effect of heating time. (a) DBC-ASA + KBr - A_0; (b) DBC-ASA + KBr + IO_3^--A; (c) ΔA; [DBC-ASA] = 4×10^{-2} g L^{-1}; [HNO_3] = 0.30 mol L^{-1}; [KBr] = 2×10^{-2} mol L^{-1}; [IO_3^-] = 0.50 mg L^{-1}; heating temperature T = 100 ºC; λ = 510 nm

linear regression equation was ΔA = 0.6500C (C: μg mL^{-1}) + 0.1999 with a regression coefficient γ = 0.9923. 0.30 μg mL^{-1} of IO_3^- was determined 11 times and the relative standard deviation determined was 1.10 %. The reagent blank was determined 11 times and the detection limit determined was 7.2 ng mL^{-1} which was calculated by 3S/K (S is the standard deviation of the reagent blank for 11 times determination, K is the slope of the regression equation).

Effect of diverse ions: Under the optimum experimental conditions, the effect of diverse ions on the determination of 0.50 mg L^{-1} IO_3^- was studied. The tolerance limits (weight ratio) of the common ions tested (causing < ± 5 % relative error) are summarized as follows: Na^+, Cl^-, NO_3^- (2000); Ca^{2+} (200); SO_4^{2-} (100); Al^{3+}, Mg^{2+} (80); Bi^{3+}, Zn^{2+}, Pb^{2+}, Cu^{2+} (50); Mn^{2+}, Sr^{2+} (40); PO_4^{3-}, Ni^{2+} (20); W^{6+}, Mo^{6+}, Fe^{2+}, HOAc (10); Ti^{4+} (8); Cr^{3+}, $H_2C_2O_4$ (5); Ba^{2+}, $S_2O_7^{2-}$ (2); Fe^{3+} (1); VO_3^- (0.6); I^- (0.1); F^- (0.06); Si^{4+}; La^{3+}, Eu^{3+}, Li^+ (0.02); Th^{4+}, B^{3+}, Hg^{2+} (0.01); Ce^{4+} (0.005); MnO_4^-, Cr^{6+}, S^{2-} (0.002).

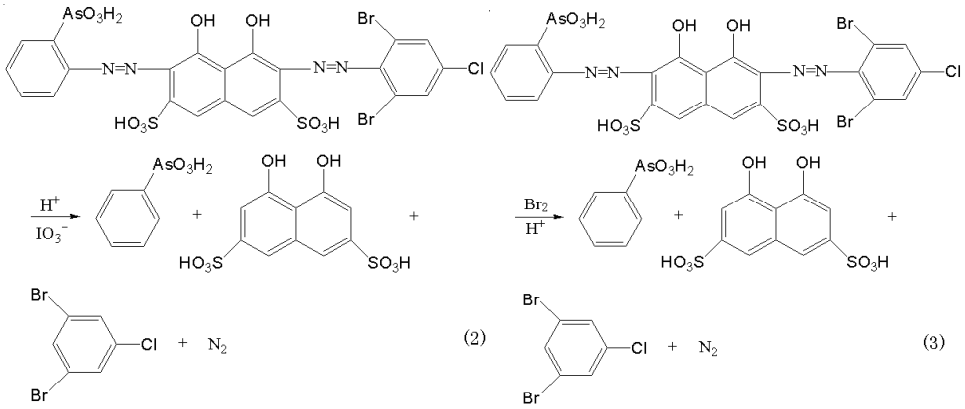
Mechanism of reaction: Br^- was oxidized to Br_2 in HNO_3 medium. Br_2 oxidized DBC-arsenazo to make it fade. This reaction was accelerated by adding IO_3^-.

The reaction mechanism was proposed as follows:

$$12H^+ + 2IO_3^- + 10Br^- \rightarrow I_2 + 5Br_2 + 6H_2O \quad (1)$$

Application

Analysis of kelp sample: 20 g of clean kelp was mashed. 10 mL of 100 g L^{-1} NaOH solution was added into the sample, which was soaked overnight, heated to dry and carbonized on an electric cooker, then was burned at 600 ºC for 6 h. The sample was cooled down and dissolved in water, in which 1 mol L^{-1} H_2SO_4 was added until neutral, filtered the solid residue and the filtrate was placed in a 100 mL of calibrated flasks, diluted to the mark with water. Then 1 mL of the solution was placed into a 10 mL calibrated flask, diluted to the mark, as the sample solution. 1 mL of this sample solution was placed into 10 mL calibrated flask and iodine was determined according to the experimental procedure.



Analysis of seaweed sample: 5 g of dried seaweed was cut into small pieces, heated to dry and carbonized on an electric cooker, then was burned at 600 ºC for 6 h. The sample was cooled down and dissolved in water, in which 1 mol L^{-1} H_2SO_4 was added until neutral, the solid residue was filtered. The filtrate was placed in a 50 mL of calibrated flask and diluted to the mark with water, as the sample solution. 1 mL of this sample solution was placed into 10 mL calibrated flask and iodine was determined according to the standard procedure.

Analysis of shrimp sample: 10 g of dried shrimp was mashed. 10 mL of 100 g L^{-1} NaOH solution was added into the sample, which was soaked overnight, heated to dry and carbonized on an electric cooker, then was burned at 600 ºC for 6 h. The sample was cooled down and dissolved in water, in which 1 mol L^{-1} H_2SO_4 was added until neutral, the solid residue was filtered. The filtrate was placed in a 50 mL of calibrated flask, diluted to the mark with water as the sample solution. 1 mL of this sample solution was placed into 10 mL calibrated flask and iodine was determined according to the standard procedure.

Meanwhile, the standard addition recovery experiments were made. The analytical results of the samples are shown in Table-1.

TABLE-1
ANALYTICAL RESULTS OF SAMPLES

Sample	Found (n = 11, μg g^{-1})	Average (μg g^{-1})	RSD (%)	Added (μg)	Recovered (μg)	Recovery (%)
Kelp	125.00,126.55, 128.82, 121.75, 122.98, 123.36, 124.45, 122.62, 127.32, 126.51, 125.64	125.00	1.76	2.00	1.97	98.50
Seaweed	66.73, 64.82, 64.81, 67.73, 66.11, 67.83, 64.25, 65.86, 64.65, 66.94, 67.69	66.13	2.04	2.00	2.04	102.00
Shrimp	8.26, 7.99, 8.55, 8.28, 8.16, 8.12, 8.18, 8.49, 8.42, 8.19, 8.22	8.26	2.09	2.00	2.03	101.50

Conclusion

The maximum absorption wavelength of IO_3^--(DBC-ASA)-KBr system was at 510 nm in the medium of 0.3 mol L^{-1} nitric acid. The amount of IO_3^- and the difference of absorbance (ΔA) showed a good linear relationship over the range of 0.10-0.55 μg mL^{-1} at this wavelength. This method was used in the determination of iodine in kelp, seaweed and shrimp samples with satisfactory results.

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