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Catalytic Kinetic Determination of Trace Amounts of Iodide by The Spectrophotometric Method with Spadns in Micellar Medium

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A new, simple, sensitive and selective catalytic spectrophotometric method was developed for the determination of trace amounts of iodide. The method is based on the catalytic effect of iodide on the oxidation of Spadns by bromate in micellar medium. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of Spadns at 507 nm with a fixed-time method. The decrease in the absorbance of Spadns is proportional to the concentration of iodide in concentration range 60.0-300.0 ng/mL, with a fixed time of 0.5-3.0 min from initiation of the reaction.The limit of detection is 20 ng/mL iodide.The relative standard deviation of 0.08 and 0.10 μg/mL iodide was 1.7 and 2.4 %, respectively. The method was applied to the determination of iodide in water.

Key Words: Iodide, Catalytic, Spadns, Bromate, Micellar.

INTRODUCTION

Iodine is an essential nutrient in human diet that is naturally found in many food samples or added as a supplement to them[1-3]. A recommended daily allowance of 150-200 μg per iodide was adopted in the USA as well as in European and many other countries. Deficiency of iodide leads to goiter disease and excessive intake may contribute to thyrotoxicosis.

Many methods have been reported for the determination of iodide. Sensitive techniques for determination of trace amounts of iodide include neutron activation analysis (NAA)[4,5] ion chromatography (IC)[6-9] inductively coupled plasma-atomic emission spectrometry (ICP-MS)[10,11]. The high instrumental costs and need for preconcentration and/or separation are common disadvatages. On the other hand, kinetic methods of analysis are very simple and low-cost alternatives for iodide determination. Among them, the very sensitive Ce(IV)-As(III)[12-16] and NO_2^--$[Fe(SCN)]^{2+}$ reactions[17-19] have been frequently used. The reaction system Bromopyrogallol Red chloramin T[20] was applied for determination of iodide with very poor reproducibility. Various catalytic kinetic methods for iodide determination of trace levels have also been published using various types of indicator reaction[21-30]. Some of these methods have poor selectivity towards some ions[22-26]. Besides, the reactions are carried out at elevated temperatures to improve sensitivity[27-29]. In order to overcome these problems, a rapid, sensitive and selective kinetic spectrophotometric method is developed for the determination of iodide. Herein, a kinetic method for trace determination of iodide, based on its catalytic effect on the oxidation of Spadns by $KBrO_3$ in micellar media is reported.

EXPERIMENTAL

Doubly distilled water and analytical reagent grade chemicals were used during all of the experimental studies. All glassware were cleaned with detergent solution, rinsed with tap water, soaked in dil. HNO_3 solution (2 % v/v), rinsed with water and dried.

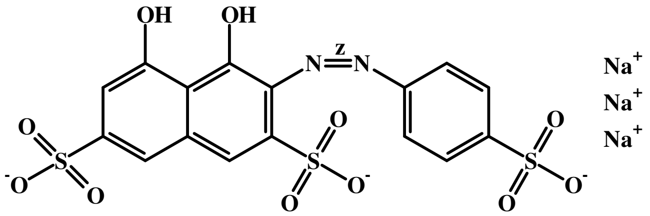
Spadns solution 7.36×10^{-4} M was prepared by dissolving 0.0419 g of the compound (Merck) in water and solution was diluted to the mark in a 100 mL volumetric flask. Potassium bromate stock solution 0.10 M, was prepared by dissolving 1.67 g of potassium bromate (M = 214) in water and diluting to 100 mL in a 100 mL volumetric flask. Standard stock iodide solution (1000 µg/mL) was prepared by dissolving 0.1308 g of KI (Merck) in water and diluted to 100 mL in a 100 mL volumetric flask. Sodium dodecyl sulfate (SDS) solution (0.10 M) was prepared by dissolving 8.011 g SDS (Merck) in water and diluting to 250 mL volumetric flask. The other surfactants tested, namely cetyltrimethylammonium bromide (CTAB), Triton-X-100 and cetylpyridinium chloride (CPC) were prepared in a similar way. Stock solution (1000 µg/mL) of interfering ions were prepared by dissolving suitable salts in water, hydrochloric acid or sodium hydroxide solution.

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 507 nm. A thermostate water batch was used to keep the reaction temperature at 25 ± 0.1 °C.

Recommended procedure: All the solutions and distilled water were kept in a thermostated water batch at 25 ± 0.1 °C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 0.6-3.0 mg/mL iodide was transferred into a 10 mL Volumetric flask and then 1.8 mL 10 M sulfuric acid, 1.0 mL 0.10 M SDS and 1 mL 7.36×10^{-4} M Spadns solution were added to the flask. The solution was diluted to *ca.* 7 mL with water, then 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 spectrophotometic cell. The reaction was followed by measuring the decrease in absorbance of the solution against water at 507 nm for 0.5-3.0 min from initiation of the reaction. This signal (sample signal) was labeled as ΔA_s. The same procedure was repeated without addition of iodide solution and the signal(blank signal) was labeled as ΔA_b. Time was measured just after the addition of last drop of potassium bromate.

RESULTS AND DISCUSSION

Spadns undergoes a oxidation reaction with potassium bromate to form a colourless product at very slow rate. It is found that this reaction rate is sharply increased by addition of trace amount of Iodide in micellar medium. Spadns has the following structure:



Influence of variables: In order to optimize the reaction to get the best sensitivity the variables affect the sensitivity such as acid concentration, Spadns concentration, bromate concentration, the effect of different kinds of surfactantants, surfactant concentration and temperature on the rate of catalyzed reaction (with iodide) and uncatalyzed reaction (without iodide) was studied.

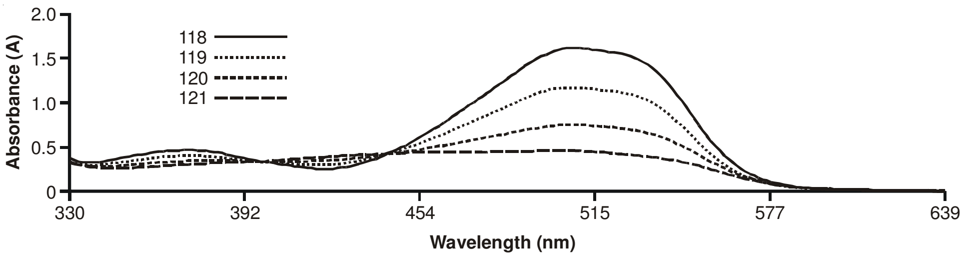


Fig. 1. Variation of the Spadns-BrO_3^--iodide with time; H_2SO_4 1.8 M, Spadns 7.36 × 10^{-5} M; BrO_3^- 1.4 × 10^{-2} M; SDS 0.010 M, iodide 100 ng/mL; temperature 25 ºC

The influence of sulfuric acid concentration on the sensitivity was studied in the range 1-2 M. Fig. 2 shows that the net reaction rate increases with sulfuric acid concentration up to 1.8 M and decreases at higher sulfuric acid concentration. This mean that the rate of uncatalyzed reaction increases with sulfuric acid concentration (> 1.8 M) to a greater extent than the catalyzed reaction and the difference between the rates of catalyzed and uncatalyzed reactions (ΔA_s-ΔA_b) diminishes at higher sulfuric acid concentrations. Therefore, a sulfuric acid concentration of 1.8 M was selected for further study.

Fig. 3 shows the effect of the Spadns concentration on the sensitivity for the range of 1.47 × 10^{-5}-1.03 × 10^{-4} M. This sensitivity (net reaction rate) increases with increasing Spadns concentration up to 7.36 × 10^{-5} M and decreases at higher concentration. This may be due to the aggregation of the dye at higher concentrations. Therefore, a final concentration of 7.36 × 10^{-5} M of Spadns was selected as the optimum concentration.

The effect of the potassium bromate concentration on the rate of reaction was studied in the range of 6 × 10^{-3}-2.4 × 10^{-2} M (Fig. 4). The results show that the net reaction rate increases with increasing bromate concentration up to 2.0 × 10^{-2} M and decreases at higher concentrations. Therefore, a bromate concentration of 2.0 × 10^{-4} M was selected for further study.

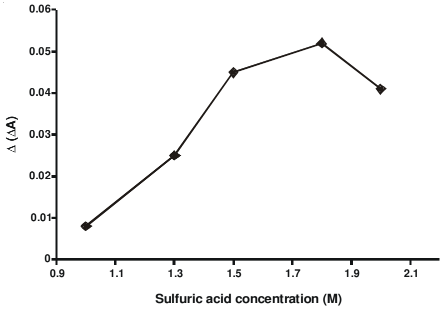


Fig. 2. Influence of H_2SO_4 concentration on the sensitivity, conditions: Spadns 7.36×10^{-5} M; BrO_3^- 1.4×10^{-2} M; SDS 0.010 M; iodide, 100 ng/mL; temperature 25 °C

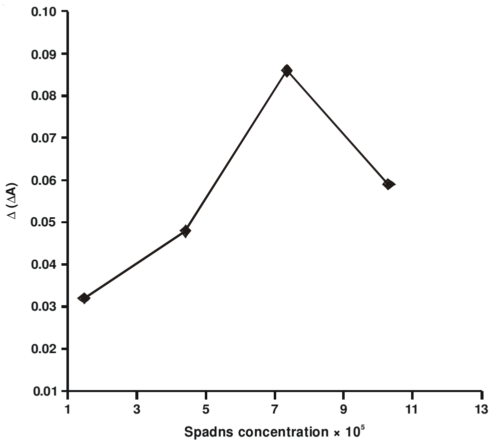


Fig. 3. Influence of Spadns concentration on the sensitivity, conditions: H_2SO_4 1.8 M; BrO_3^- 1.4×10^{-2} M; SDS 0.010 M; iodide, 100 ng/mL; temperature 25 °C

Suitable micelles can affect the rate of reactions[30-39]. 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 micelle system to enhance the sensitivity (rate of reaction rate), one must take into account the type of charge the reactants, because the accelerating effect of micells arises essentially from elecrotrostatic and hydrophobic interaction between the reactants and micellar surface[40].

Nonionic micelles (such as Triton-X-100), anionic micelle (sodium dodecyl sulfate, SDS) and cationic micelle (CTAB) and cetyl pyridinium chloride (CPC) were tested at concentration above their critical micelle concentration (CMC). The results are shown in Table-1. Therefore, from between these micelles, SDS was selected for practical purposes.

TABLE-1
SURFACTANTS TESTED AS POTENTIAL MICELLAR CATALYSTS TO ENHANCE THE RATE OF SPADNS-BrO_3^--IODIDE REACTION

Surfactant	Type	CMC (M)	Micellar catalysis
Triton-X-100	Nonionic	3.0×10^{-4}	Inert
SDS	Anionic	8.1×10^{-3}	Positive
CTAB	Cationic	1.3×10^{-3}	Inert
CPC	Cationic	1.2×10^{-4}	Inert

The effect of the SDS concentration on the rate of reaction was studied in the range of 0-1.4×10^{-3} M (Fig. 5). Fig. 5 shows the effect of the SDS concentration on the sensitivity for the range of 0-2.4×10^{-2} M. This sensitivity (net reaction rate) increases with increasing SDS concentration up to 0.010 M and decreases at higher concentrations. Therefore, a final concentration of 0.010 M of SDS was selected as the optimum concentration.

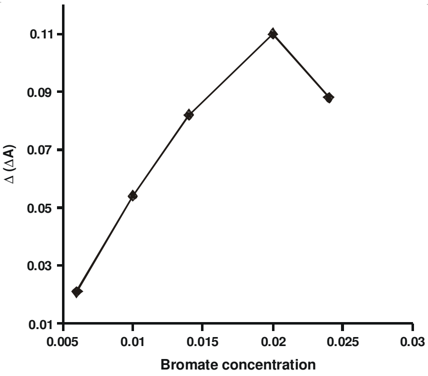


Fig. 4. Influence of bromate concentration on the sensitivity, conditions: H_2SO_4 1.8 M; Spadns 7.36 × 10^{-5} M; SDS 0.010 M; iodide, 100 ng/mL; temperature 25 ºC

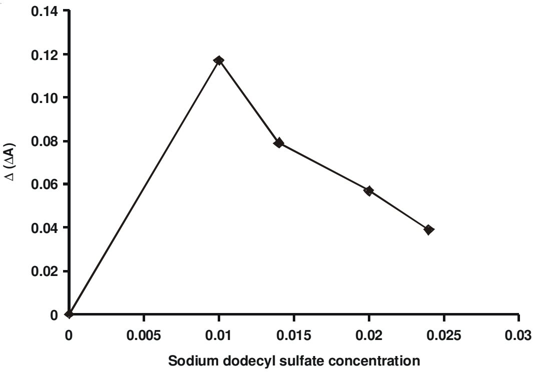


Fig. 5. Influence of SDS concentration on the sensitivity, conditions: H_2SO_4 1.8 M; Spadns 7.36×10^{-5} M; BrO_3^- 2.0×10^{-2} M; iodide, 100 ng/mL; temperature 25 ºC

The effect of the temperature on the sensitivity was studied in the range 15-35 ºC with the optimum sulfuric acid concentration and other reagent concentrations. The results showed that as the temerature increases up to 25 °C, the net reaction rate increases, whereas higher temperature values decrease the sensitivity ($\Delta A = \Delta A_s - \Delta A_b$). This means that the rate of uncatalyzed reaction increases with temperature to a greater extent and the uncatalyzed reaction occurred at a sutable rate. Therefore, 25 °C was selected for further study.

Calibration graph, precision and limit of detection: Calibration graphs were obtained using the fixed-time method. This method was applied to the change in absorbance over an interval of 0.5-3.0 min from intiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration range 0.06-0.3 µg/mL iodide.

The equation of the calibration graph is $\Delta A = 0.765 + 0.4781C_{I^-}$ (n = 6, r = 0.9997), where ΔA is change in absorbance for the sample reaction for 0.5-3.0 min from initiation of the reaction (catalytic reaction) and C is iodide concentration in µg/mL. The limit of detection from $Y_{LOD} = Y_b + 3S_b$ is 0.02 µg/mL, where, Y_{LOD} is signal for limit of detection, Y_b is average blank signal (n = 10) and S_b is standard deviation of blank signal (n = 10, uncatalyzed reaction). The relative standard deviation for six replicate determination of 0.070 and 0.1 µg/mL iodide was 1.7 and 2.4, respectively.

Interference study: In order to assess the application of the proposed method to synthetic samples, the efffect of various ions on the determination of 0.1 µg/mL iodide was studied. The tolerance limit was defined as the concentration of the added ions causing a relative error less than 3 % (Table-2). Many ions did not interfere, even when they were present in 100 fold excess over iodide. The results show that method is relatively selective for iodide determination.

TABLE-2
EFFECT OF FOREIGN IONS ON THE DETERMINATION OF 0.1 μg/mL IODIDE

Species	Tolerance limit (w_{ion}/w_{I^-})
Na^+, K^+, Ca^{2+}, Mg^{2+}, Rb^+, Pb^{2+}, Zn^{2+}, Ba^{2+},Co^{2+}, Ni^{2+}, Hg^{2+}, Mn^{2+}, Cu^{2+}, Te^{4+}, Se^{4+}, $C_2O_4^{2-}$, HSO_4^-,CO_3^{2-}, NO_3^-, SO_3^{2-}, BO_3^{3-}, Tatarate	1000
Rh^{3+}, Os^{8+}, Ru^{3+}, V^{5+}	500
ClO_3^{-} Fe^{2+}, Ag^+	200
SCN^-	20

Sample analysis: In order to evaluate the applicability of the proposed method, water samples and synthetic water, samples were analyzed to determine iodide contents. The results are presented in Table-2. Good recoveries with precise results show good reproducibility and accuracy of the method.

TABLE-3
DETERMINATION OF IODIDE IN SYNTHETIC SAMPLES

Sample	Iodide (ng/mL)		Recovery (%)	RSD (n = 5)
	Added	Found		
Well water	-	75	–	–
Well water	30	99	94	2.1
Well water	50	131	104.8	2.9

Conclusion

The kinetic-spectrophotometric method developed for the determination of iodide is inexpensive, uses readily available reagents, allows rapid determination at low operating costs and shows simplicity, adequate Selectivity, low limit of detection and good precision and accuracy compared to other kinetic procedures. With this method, it is possible to determine odide at levels as low as 0.02 μg/mL without the need for any preconcentration step.

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