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Kinetic Catalytic-Spectrophotometric Determination of Trace Amount of Iodide

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A new, simple, sensitive and selective catalytic spectrophotometric method was developed for the determination of ultra trace amounts of iodide. The method is based on the catalytic effect of iodide on the oxidation of Indigo carmin by iodate. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of Indigo carmin at 612 nm with a fixed-time method. The decrease in the absorbance of Indigo carmin is proportional to the concentration of iodide in concentration range 40.0-200.0 ng/mL, with a fixed time of 0.5-2.5 min from initiation of the reaction. The limit of detection is 34 ng/mL iodide.The relative standard deviation of 0.060 and 0.10 µg/mL iodide was 1.8 and 2.2 %, respectively. The method was applied to the determination of iodide in water.

Key Words: Kinetic, Spectrophotometric, Iodide.

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 I^- 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.

Several methods have been reported for the determination of iodide. Sensitive techniques for determination of trace amounts of iodide include neutron actiovation analysis (NAA)[4,5], ion chromatography (IC)[6,7], inductively coupled plasma-atomic emission spectrometry (ICP-MS)[8-11]. 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 I^- with poor reproducibility. Various catalytic kinetic methods for I^- 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[27-30]. In order to overcome these problems, a new method has been developed and validated a rapid, sensitive and selective kinetic spectrophotometric method for the determination of I^-. Herein, a kinetic method for trace determination of I^-, based on its catalytic effect on the oxidation of Indigocarmin by KIO_3 in micellar media has been reported.

EXPERIMENTAL

Absorption spectra were recorded with a Cary model 100 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 612 nm. A thermostate water batch was used to keep the reaction temperature at 30°C.

All glassware were cleaned with detergent solution, rinsed with tap water, soaked in dilute HNO_3 solution (2 %) (v/v), rinsed with water and dried. Doubly distilled water and analytical reagent grade chemicals were used during all of the experimental studies. Indigo carmin solution 6.43×10^{-4} M was prepared by dissolving 0.030 g of the compound (Merck) in water and solution was diluted to the mark in a 100 mL volumetric flask.

Iodate stock solution 0.10 M, was prepared by dissolving 2.14 g of potassium iodate (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 0.10M 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.

Recommended procedure

All the solutions and distilled water were kept in a thermostated water batch at 30°C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 0.40-2.0 µg/mL iodide was transferred into a 10 mL volumetric flask and then 0.20 mL 5.0 M HCl, 1.0 mL 0.10 M SDS and 1.6 mL 6.43×10^{-4} M Indigo carmin were added to the flask.The solution was diluted to *ca.* 8 mL with water. Then, 0.8 mL of 0.10 M iodate was added and the solution was diluted to the mark with water. The solution was gently mixed and a portion of the solution was

transferred to the spectrophotometer cell. The reaction was followed by measuring the decrease in absorbance of the solution against water at 612 nm for 0.5-2.5 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 iodate.

RESULTS AND DISCUSSION

Indigo carmin undergoes a oxidation reaction with iodate in acidic medium to from a colourless product at very slow rate. It is found that this reaction rate is sharply increased by addition of trace amount of iodide.

There are many methods, such as fixed-time, initial rate, rate constant and variable time methods for measuring the catalytic species. Among these, the fixed-time method is the most conventional and simplest, involving the measurement of ΔA at 612 nm. Fig. 1 shows the relationship between absorbance (A) and reaction time. It was found that the rate of reaction is proportional to the iodide concentration. This process was monitored spectrophotometrically by measuring the decrease in absorbance of the characteristic band of Indigo carmin (612 nm) (Fig. 1). Therefore, by measuring the decrease in absorbance of Indigo carmin for a fixed time of 0.5-2.5 min initiation of the reaction, the iodide contents in the sample can be measured.

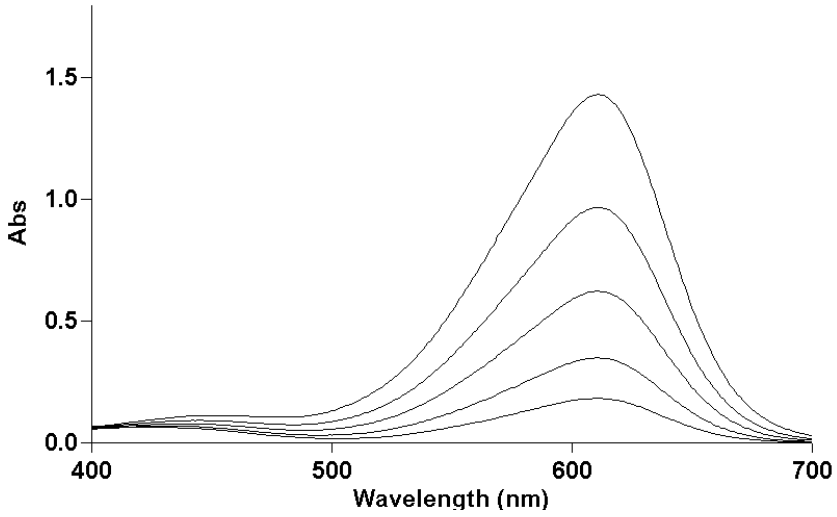

Fig. 1. Variation of the Inigo carmin-IO_3^--iodide with time HCl 0.10 M, Inigo carmin 1.03×10^{-4} M; IO_3^- 8×10^{-3} M; SDS 0.010 M, iodide 50.0 ng/mL; temperature 30°C

Influence of variables on the sensitivity

In order to take full advantage of the procedure, the reagent concentrations must be optimized. The effect of acid concentration, Indigo carmin and iodate concentration, type and concentration of surfactants and temperature on the rate of catalyzed and uncatalyzed reaction was studied.

The accelerating effect of micelles arises essentially from electrostatic and hydrophobic interactions between the reactants and micellar surface[31]. Cationic (CPC, CTAB), anionic (SDS) and nonionic (Triton-X-100) micelles were tested at a concentration greater than that critical micelle concentration (c.m.c). The results are shown in Table-1. The results show that the SDS enhance the rate of Indigo carmin-iodide-iodate reaction. Thus SDS was chosen for the study.

TABLE-1
SURFACTANT TESTED AS A POTENTIAL MICELLAR CATALYST FOR THE ENHANCED RATE OF INDIGO CARMIN - IO_3^- - IODIDE REACTION

Surfactant	Type	c.m.c. (M)	Micellar catalysis
Trition-X-100	Non-ionic	3.0×10^{-4}	Negative
SDS	Anionic	8.1×10^{-4}	Positive
CTAB	Cationic	1.3×10^{-4}	Negative
CPC	Cationic	1.2×10^{-4}	Negative

The effect of hydrochloric acid concentration on the rate of reaction was studied in the range of 0.020-0.20 M. (Fig. 2). The results show that the net reaction rate increases with increasing hydrochloric acid concentration up to 0.10 M and decreases at higher concentrations.This mean that the rate of uncatalyzed reaction increases with hydrochloric acid concentration (> 0.10 M) to a greater extent than the catalyzed reaction. The difference between the rates of catalyzed and uncatalyzed reactions (ΔA_s-ΔA_b) diminishes at higher hydrochloric acid concentrations. Therefore, a hydrochloric acid concentration of 0.10 M was selected for further study.

The influence of iodate concentrations on the reaction rate was studied in the concentration range of 0.004-0.012 M (Fig. 3). The results show that the net reaction rate increases with increasing iodate concentration up to 0.008 M and decreases at higher concentrations. This mean that the rate of uncatalyzed reaction increases with iodate concentration (> 0.008 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 iodate concentrations.Therefore, a iodate concentration of 0.008 M was selected for further study.

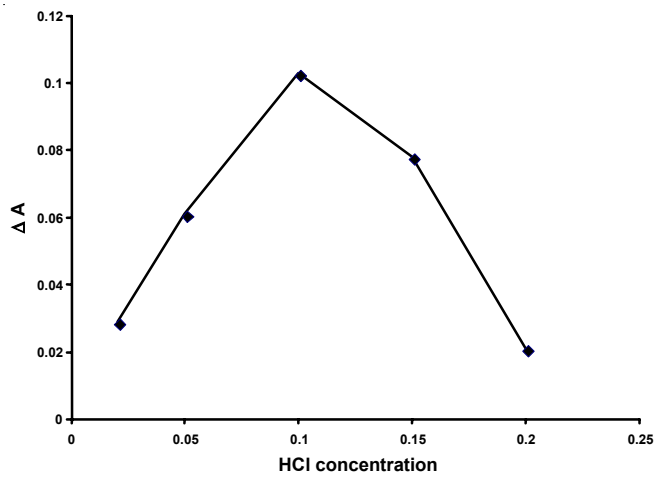

Fig. 2. Influence of HCl concentration on the sensitivity, conditions: HCl 0.10 M, Inigo carmin 9.0×10^{-5} M; IO_3^- 8×10^{-3} M; SDS 0.010 M; iodide, 100.0 ng/mL; temperature 35°C

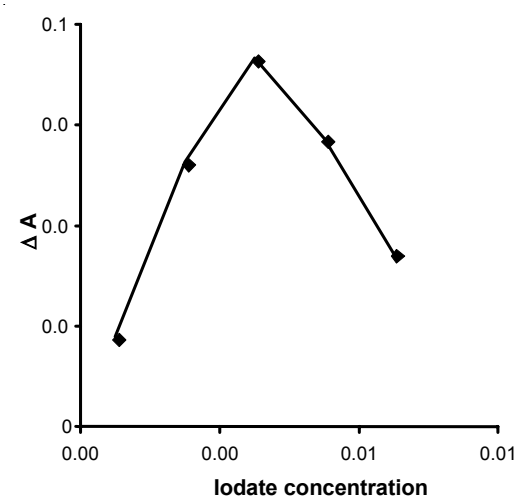

Fig. 3. Effect of iodate concentration on the sensitivity, conditions: HCl 0.10 M, Inigo carmin 9.0×10^{-5} M; SDS 0.010 M; iodide, 100.0 ng/mL; temperature 35°C

Fig. 4 shows the effect of the Indigo carmin concentration on the sensitivity for the range of 7.72×10^{-5}–1.28×10^{-4} M. This sensitivity (net reaction rate) increases with increasing Indigo carmin concentration up to 1.03×10^{-4} M and decreases at higher concentrations. This may be due to the aggreagration of the dye at higher concentrations. Therefore, a final concentration of 1.03×10^{-5} M of Indigo carmin was selected as the optimum concentration.

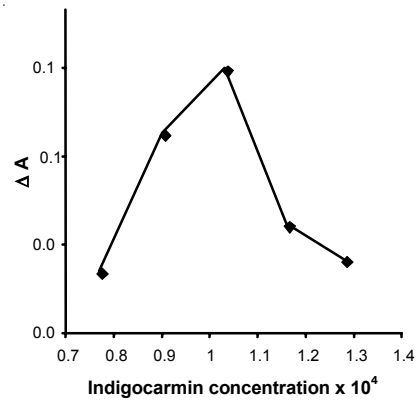

Fig. 4. Effect of Indigo carmin concentration on the reaction rate. Conditions: HCl 0.10 M; IO_3^- 8 × 10^{-3} M; SDS 0.010 M; iodide,100.0 ng/mL; temperature 35°C

Fig. 5 shows the effect of the SDS concentration on the sensitivity for the range of 6.0 × 10^{-3}–1.4 × 10^{-2} M. This sensitivity (net reaction rate) increases with increasing SDS concentration up to 0.10 M and decreases at higher concentrations. Therefore, a final concentration of 0.010 M of SDS was selected as the optimum concentration.

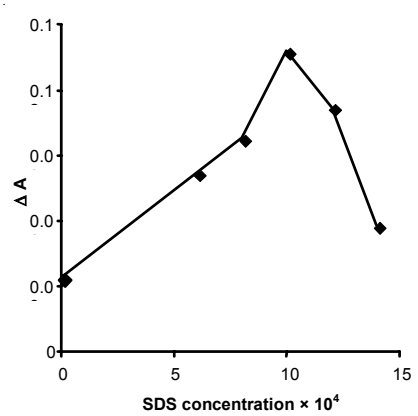

Fig.5. Effect of SDS concentration on the reaction rate. Conditions: HCl 0.10 M; indigo carmin 1.03 × 10^{-4}; IO_3^- 8 × 10^{-3} M; iodide 100.0 ng/mL; temperature 35°C

The effect of the temperature on the sensitivity was studied in the range 20-45°C with the optimum of the reagents concentrations. The results showed that, as the temerature increases up to 30°C, the net reaction rate increases, whereas higher temperature values decrease the sensitivity (ΔA

= ΔA_s-ΔA_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, 30°C was selected for further study.

Analytical parameters

Calibration graphs were obtained using the fixed-time method. This method was applied to the change in absorbance over an interval of 0.5-2.5 min from initiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration range 0.040-0.20 µg/mL of iodide has been obtained.

The equation of the calibration graph is $\Delta A = 0.3162 + 0.3796C$ (n = 7, r = 0.9999) where ΔA is change in absorbance for the sample reaction for 0.5-2.5 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 34 ng/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 0.060 and 0.10 µg/mL iodide was 1.8 and 2.2 % 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 0.06 µg/mL iodide was studied. The tolerance limit was defined as the concentration of added ions causing a relative error less than 3 %. The results are summarized in Table-2. Many ions did not interfere, even though, 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 0.060 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-}, Ag^+, Tatarate	1000
Rh^{3+}, Os^{8+}, Ru^{3+}, V^{5+}	800
$S_2O_8^{2-}$, ClO_3^-, Fe^{2+}	200
SCN^-	10

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-3. Good recoveries with precise results show good reproducibility and accuracy of the method.

TABLE-3
DETERMINATION OF IODIDE IN SYNTHETIC SAMPLES

Sample	Iodide added (ng/mL)	Iodide found (ng/mL)	Recovery (%)	RSD (n = 5)
Well water	–	75	–	–
Well water	30	99	94	2.1
Well water + Ni^{2+} (10.0 μg/mL) + Fe^{2+} (5.0 μg/mL)	50	131	105	2.6

Conclusion

The catalytic-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 catalytic procedures. With this method, it is possible to determine iodide at levels as low as 34 ng/mL without the need for any preconcentration step.

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