Asian Journal of Chemistry Vol. 21, No. 4 (2009), 2715-2720

Kinetic-Photometric Determination of Iodide Based on Its Inhibitory Effect on The Bromate Oxidation of Indigo Carmine in Micellar Medium

MOHSEN KEYVANFARD
Faculty of Science, Islamic Azad University-Majlesi Branch, Isfahan, Iran
E-mail: keyvan45638@yahoo.com

A new, simple, sensitive and selective kinetic spectrophotometric method was developed for the determination of ultra trace amounts of iodide over the range of 0.060-0.20 µg/mL.The method is based on the inhibitory effect of iodide on the oxidation of indigo carmine by bromate in acidic and micellar medium. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of indigo carmine at 612 nm with a fixed-time 0.5-2.0 min from initiation of the reaction. The relative standard deviation of 0.08 and 0.1 µg/mL iodide was 1.7 and 2.3 %, respectively. The method was applied to the determination of iodide in water.

Key Words: Iodide, Inhibitory, Indigo carmine, Bromate.

INTRODUCTION

Determination of iodide in natural and mineral waters, soil and food samples is very important for environmental reasons. Iodide 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 exessive 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)[6,7], inductively coupled plasma-atomic emission spectrometry (ICP-MS)[8,9]. 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)[10-12] and NO_2^--$[Fe(SCN)]^{2+}$ reactions[13-15] have been frequently used. The reaction system bromopyrogallol red chloramin T[16] was applied for determination of I^- with very poor reproducibility. Various catalytic kinetic methods for I^- determination of trace levels have also been published using various types of indicator reaction[17]. Some of these methods have poor selectivity towards some ions[17-20]. Besides, the reactions

are carried out at elevated temperatures to improve sensitivity[21-23]. In order to overcome these problems, the author 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^- is reported, based on its inhibitory effect on the oxidation of indigo carmine by $KBrO_3$ in micellar media.

EXPERIMENTAL

Doubly distilled water and analytical reagent grade chemicals were used during all of the experimental studies.

Indigo carmine 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. Bromate stock solution 0.10 M, was prepared by dissolving 1.67 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 0.10 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.

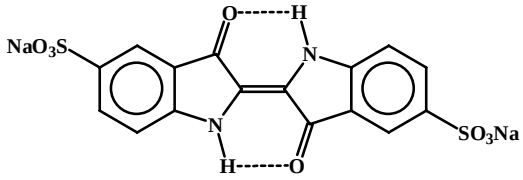
All glassware were cleaned with detergent solution, rinsed with tap water, soaked in dilute HNO_3 solution (2 %, v/v), rinsed with water and dried.

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 25 °C.

Recommended procedure: All the solutions and distilled water were kept in a thermostated water batch at 25 °C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 0.6-2.0 µg/mL iodide was transferred into a 10 mL volumetric flask and then 0.60 mL 6.0 M H_2SO_4, 1.0 mL 0.10 M SDS and 1.6 mL 6.43×10^{-4} M indigo carmine were added to the flask. The solution was diluted to *ca.* 8 mL with water. Then, 0.8 mL 0.10 M bromate 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 spectrophotometer cell. The reaction was followed by measuring the decrease in absorbance of the solution against water at 612 nm for 0.5-2.0 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 iodate. Analytical signal was deference between blank signal and sample signal (ΔA_b-ΔA_s).

RESULTS AND DISCUSSION

Indigo carmine undergoes a oxidation reaction with bromate in acidic and micellar medium to from a colourless product at very fast rate. It is found that trace amount of iodide have a inhibitory effect on the this reaction.Therefore, by measuring the decrease in absorbance of indigo carmine for a fixed time of 0.5-2.0 min initiation of the reaction, the iodide contents in the sample can be measured.



Influence of variables: In order to take full advantage of the procedure, the reagent concentrations must be optimized. The effect of acid concentration, indigo carmine and bromate concentration, type of surfactants and temperature on analytical signal was studied.

The accelerating effect of micelles arises essentially from electrostatic and hydrophobic interactions between the reactants and micellar surface[24]. Cationic (CPC, CTAB), anionic (SDS) and nonionic (Triton-X-100) micelles were tested at a concentration greater than that critical micelle concentration (CMC). The results are shown in Table-1. The results show that in the presence of SDS, iodide have an inhibitory effect on the oxidation of indigo carmine by bromate. Thus SDS was chosen for the study.

TABLE-1
SURFACTANT TESTED AS A POTENTIAL MICELLAR CATALYST FOR THE ENHANCED ANALYTICAL SIGNAL OF INDIGO CARMINE–BrO_3^-–IODIDE SYSTEM

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

The effect of sulfuric acid concentration on the analytical signal was studied in the range of 0.12-0.60 M (Fig. 1). The results show that the analytical signal increases with increasing sulfuric acid concentration up to 0.36 M and decreases at higher concentrations. Therefore, a sulfuric acid concentration of 0.36 M was selected for further study.

The influence of indigo carmine concentration on the analytical signal was studied in the concentration range of 6.43×10^{-5}–1.29×10^{-4} M (Fig. 2). The results show that analytical signal increases with increasing indigo carmine concentration up to 1.03×10^{-4} M and decreases at higher concentrations. Therefore, a indigo carmine concentration of 1.03×10^{-4} M was selected for further study.

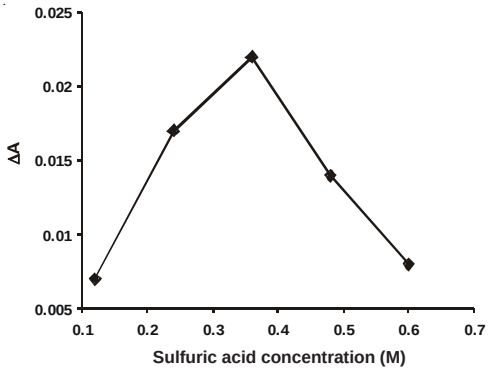


Fig. 1. Influence of H_2SO_4 concentration on the analytical signal, conditions: Indigo carmine 9.0×10^{-5} M; BrO_3^- 4×10^{-3} M; SDS 0.010 M; iodide, 0.2 µg/mL; temperature 25 ºC

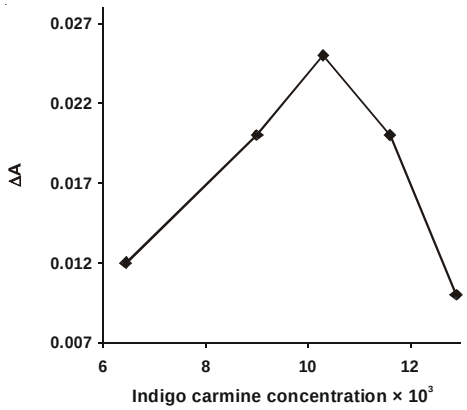


Fig. 2. Effect of indigo carmine concentration on the analytical signal. Conditions: H_2SO_4 0.36 M; BrO_3^- 4×10^{-3} M; SDS 0.010 M; iodide 0.2 µg/mL; temperature 25 ºC

Fig. 3 shows the effect of the bromate concentration on the analytical signal for the range of 4×10^{-2}–1.2×10^{-2} M. This analytical signal increases with increasing bromate concentration up to 8.0×10^{-3} M and decreases at higher concentrations. Therefore, a final concentration of 8.0×10^{-3} M of bromate was selected as the optimum concentration.

Fig. 4 shows the effect of the SDS concentration on the analytical signal for the range of 0-1.4×10^{-2} M. Analytical signal 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.

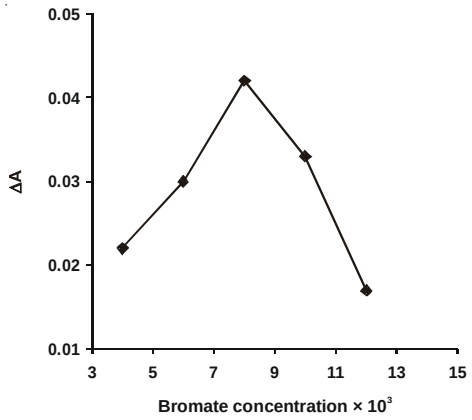


Fig. 3. Effect of bromate concentration on the analytical signal, conditions: H_2SO_4 0.36 M, Indigo carmine 1.03×10^{-4} M; SDS 0.010 M; iodide 0.2 µg/mL; temperature 25 ºC

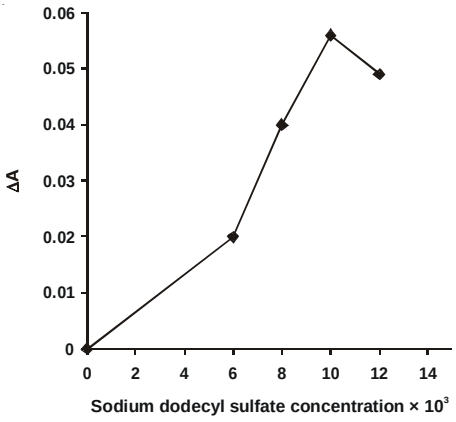


Fig. 4. Effect of SDS concentration on the analytical signal. Conditions: H_2SO_4 0.36 M, indigo carmine 1.03×10^{-4} M; BrO_3^- 8×10^{-3} M; iodide 0.2 µg/mL; temperature 25 ºC

The effect of the temperature on the analytical signal was studied in the range 20-45 °C with the optimum of the reagents concentrations. The results showed that, as the temperature increases up to 25 °C, the analytical signal increases, whereas higher temperature values decrease the analytical signal ($\Delta A = \Delta A_b - \Delta A_s$). Therefore, 25 °C was selected for further study.

Calibreation graph, precision and limit of detection: Calibration graph were obtained using the fixed-time method. This method was applied to the change in absorbance over an interval of 0.5-2.0 min from intiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration range 0.060-0.20 µg/mL of iodide.

The equation of the calibration graph is $\Delta A = 0.2814C - 0.0037$ ($n = 7$, $r = 0.9998$). The calibration graph was constructed by plotted of $\Delta A = \Delta A_b - \Delta A_s$ at a fixed-time method *versus* iodide concentration.

The relative standard deviation for 6 replicate determination of 0.080 and 0.10 ng/mL iodide was 1.7 and 2.3 %, respectively.

Interference study: In order to assess the application of the proposed method to synthetic samples, the effect of various ions on the determination of 0.08 µg/mL iodide was studied. The tolerance limit was defined as the concentration of added ions causing a relative error less than ± 3 % and the results are summarized in Table-2. Many ions did not interfere, even when they were present in 400 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 0.080 µg/mL IODIDE

Species	Tolerance limit (w_{ion}/w_{I^-})
Na^+, K^+, Ca^{2+}, Mg^{2+}, Rb^+, Zn^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+} Cu^{2+}, Te^{4+}, Se^{4+}, $C_2O_4^{2-}$, HSO_4^-, CO_3^{2-}, NO_3^-, SO_3^{2-}, Tatarate	1000
Rh^{3+}, Ru^{3+}, Co^{2+}	800
$S_2O_8^{2-}$, ClO_3^-, Fe^{3+}, Ni^{2+}	400
V^{5+}, Ag^+, Hg^{2+}	100
SCN^-, Pb^{2+}	5

TABLE-3
DETERMINATION OF IODIDE IN WATER

Sample	Iodide added (ng/mL)	Iodide found (ng/mL)	Recovery (%)	RSD (n = 5)
Well water	-	55	-	-
Well water	20	71	94.6	2.5
Well water	50	109	103.8	2.9
Well water	80	130	96.2	2.3

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.

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 iodide without the need for any preconcentration step.

ACKNOWLEDGEMENT

Author is thankful to the Islamic Azad University-Majlesi Branch for the financial support of this work.

REFERENCES

1. E.J. Underwood, Trace Elements in Human and Animal Nutriton, Academic Press, New York, p. 271 (1977).
2. K. Helrich, Official Method of Analysis of the Association Official Analitical Chemist, AOAC, Arlington,VA, edn. 4,15, 4th Suppl., p. 192 (1990).
3. M.M. Heckman, *J. Assoc. Off. Anal. Chem.*, **62**, 1045 (1970).
4. A.E. Arafa, H.F. Beshewa, I.A. Saleh and A.H. Das, *J. Trace Microprob. Tech.*, **18**, 37 (2000).
5. L.X. Hou, H. Dahlgaard, B. Rietz, U. Jacobsen, P.S. Nielsen and A. Arkrog, *Anal. Chem.*, **71**, 2745 (1999).
6. W. Hu, R.P. Haddad, K. Hasebe, K. Tanaka, P. Tong and C. Khoo, *Anal. Chem.*, **71**, 1617 (1999).
7. Y. Bichsel and U. Von-Gunten, *Anal. Chem.*, **71**, 34 (1999).
8. F.L. Sanchez and J. Szpunar, *J. Anal. At. Spectrom.*, **14**, 1697 (1999).
9. H.E. Larsen, P. Knuthsen and M. Hansen, *J. Anal. At. Spectrom.*, **14**, 41 (1999).
10. E. Greenberg, S.L. Clesceri and D.A. Eaton, Standard Methods for Examination of Water and Waste-Water, American Public Health Association, Washington, D.C., edn. 19 (1995).
11. R. Pedriali, E. Giuliani, A. Margutti and E. Degli-Uberti, *Ann. Chim. (Rome)*, **87**, 449 (1997).
12. K.A. Ayianniddis and N.A. Voulgaropoulos, *Analyst*, **113**, 153 (1988).
13. D.E. Moxon and J.E. Dixon, *Analyst*, **105**, 344 (1980).
14. T.J. Pastor, G.A. Milovanovic and G.M. Petkovie, *Microchem. J.*, **60**, 8 (1998).
15. K. Sriramam, P. Ravindranath, S.V. Sastry and P.R. Rao, *Analysis*, **15**, 248 (1987).
16. E.I. Yasinskene and O.P. Umbrazhyunaite, *Zh. Anal. Khim.*, **30**, 962 (1975).
17. M.S. Garcia, C. Sanchez-Pedreno, I. Albero and C. Sanchez, *Analyst*, **116**, 653 (1991).
18. R.P. Igov, M.D. Jaredic and T.G. Pecev, *Mikrochim. Acta*, **33**, 171 (1979).
19. T. Tomiyasu, H. Sakamoto and N. Yonehara, *Anal. Sci.*, **8**, 293 (1992).
20. S.S. Mitic, G.Z. Miletic and D.A. Kostic, *Anal. Sci.*, **19**, 913 (2003).
21. Z.X. Guo, Y. Xiao and S.Y. Zhang, *Fenxi Shiyanshi*, **15**, 32 (1996).
22. A.M. Zhang and S.H. Wang, *Fenxi Huaxue*, **26**, 967 (1998).
23. C.J. Liu and H. Zhang, *Fenxi Huaxue*, **26**, 222 (1998).
24. S. Rubio and D. Perez-Bendito, *Anal. Chim. Acta*, **224**, 85 (1989).

(*Received*: 4 April 2008; *Accepted*: 10 January 2009) AJC-7111