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Kinetic Determination of Traces of Iodide by Its Inhibitory Effect on the Oxidation of Gallocyanin by Bromate in Micellar Medium

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A new, simple and selective kinetic spectrophotometric method was developed for the determination of ultra trace amounts of iodide over the range of 0.1-100 ng/mL.The method is based on the inhibitory effect of iodide on the oxidation of gallocyanin by bromate in acidic and micellar medium. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of gallocyanin at 542 nm with a fixed-time 0.5-2.0 min from initiation of the reaction. The relative standard deviation of 1 and 40 ng/mL iodide was 2.3 and 1.9 %, respectively. The method was applied to the determination of iodide in water.

Key Words: Iodide, Inhibitory, Gallocyanin, 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 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)[6,7], inductively coupled plasma-atomic emission spectrometry (ICP-AES)[8,9] and inductively coupled plasma-mass spectrometry (ICP-MS)[10,11]. The high instrumental costs and need for preconcentration and/or separation are common disadvantages. 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 very 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]. Some method based on inhibitory effect of iodide has an

unsufficient determination limit[31]. In order to overcome these problems, a rapid, sensitive and selective kinetic spectrophotometric method is developed for the determination of I^-, which is based on its inhibitory effect on the oxidation of gallocyanin by $KBrO_3$ in micellar media.

EXPERIMENTAL

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 542 nm. A thermostat water batch was used to keep the reaction temperature at 25 ºC.

Doubly distilled water and analytical reagent grade chemicals were used throughout the experimental studies.

Gallocyanin solution 1.5×10^{-3} M was prepared by dissolving 0.0253 g of the compound (Aldrich) in 50 mL of 10^{-5} M NaOH 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 bromate (M = 167) 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.

Triton-X-100 (Merck) stock solution 0.066 M was prepared by dissolving 2.0 mL Triton-X-100 in water and diluted to the mark with in a 100 mL volumetric flask. The other surfactants tested, namely, sodium dodecyl sulfate (SDS), Triton-X-100 and cetyl pyridinium chloride (CPC) were prepared in a similar way.

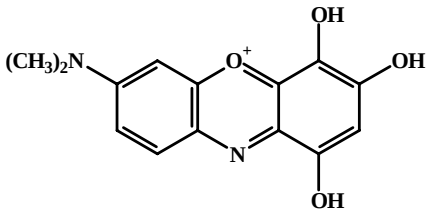
Solution (1000 µg/mL) of interfering ions were prepared by dissolving suitable salts in water, hydrochloric acid or sodium hydroxide solution.

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.

Recommended procedure: All the solutions and distilled water were kept in a thermostated water batch at 25 ºC for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 1-1000 ng/mL iodide was transferred into a 10 mL volumetric flask and then 0.40 mL of H_2SO_4 (6.0 M), 1.6 mL of Triton-X-100 (0.066 M) and 0.5 mL of gallocyanin (1.5×10^{-3} M) were added to the flask.The solution was diluted to *ca.* 8 mL with water. Then 1 mL of bromate (0.10 M) 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 542 nm for 0.5-2.0 min from initiation of the reaction. This signal (sample signal) was labelled as ΔA_s. The same procedure was repeated without addition of iodide solution and the signal (blank signal) was labelled as ΔA_b. Time was measured just after the addition of last drop of bromate. Analytical signal was deference between blank signal and sample signal (ΔA_b-ΔA_s).

RESULTS AND DISCUSSION

Gallocyanin (**I**) 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 gallocyanin for a fixed time of 0.5-2.0 min initiation of the reaction, the iodide contents in the sample can be measured.



Structure of gallocyanin (**I**)

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

The accelerating effect of micelles arises essentially from electrostatic and hydrophobic interactions between the reactants and micellar surface[32]. Cationic (CPC, CTAB), anionic (SDS) and non-ionic (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 Triton-X-100 and sodium dodecyl sulfate, iodide have an inhibitory effect on the oxidation of gallocyanine by bromate. Triton-X-100 has a more positive effect on the analytical signal than sodium dodecyl sulfate. Thus, Triton-X-100 was chosen for further study.

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

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

The effect of sulfuric acid concentration on the rate of reaction was studied in the range of 0.12-0.36 M (Fig. 1). The results show that the analytical signal increases with increasing sulfuric acid concentration up to 0.24 M and decreases at higher concentrations. Therefore, a sulfuric acid concentration of 0.24 M was selected for further study.

The influence of gallocyanin concentration on the analytical signal was studied in the concentration range of 3×10^{-5}–1.2×10^{-4} M (Fig. 2). The results show that analytical signal increases with increasing gallocyanin concentration up to 7.5×10^{-5} M and decreases at higher concentrations. Therefore, a gallocyanin concentration of 7.5×10^{-5} M was selected for further study.

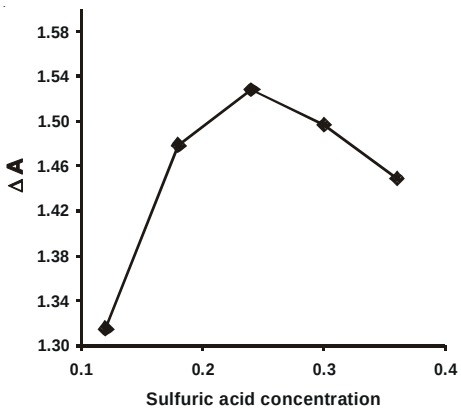


Fig. 1. Influence of H_2SO_4 concentration on the analytical signal, conditions: [Gallocyanin 9.0×10^{-5} M; BrO_3^- 6×10^{-3} M; Triton-X-100 7.92×10^{-3} M; iodide, 40.0 ng/mL; temperature 25 ºC

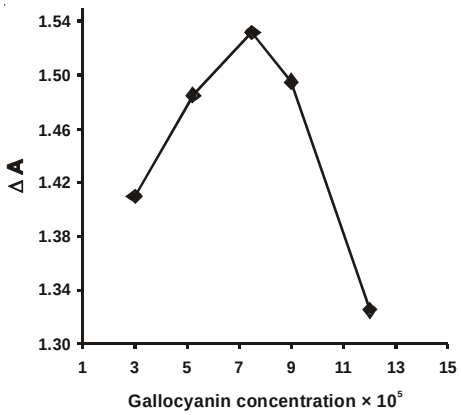


Fig. 2. Effect of gallocyanin concentration on the analytical signal, conditions: H_2SO_4 0.24 M, BrO_3^- 6×10^{-3} M; Triton-X-100 7.92×10^{-3} M; iodide, 40.0 ng/mL; temperature 25 °C

Fig. 3 shows the effect of the bromate concentration on the analytical signal for the range of 6.0×10^{-3}–1.4×10^{-2} M. This analytical signal increases with increasing bromate concentration up to 1.0×10^{-2} M and decreases at higher concentrations. Therefore, a final concentration of 1.0×10^{-2} M of bromate was selected as the optimum concentration.

Fig. 4 shows the effect of the Triton-X-100 concentration on the analytical signal for the range of 5.3×10^{-3}–1.3×10^{-2} M. Analytical signal increases with increasing Triton-X-100 concentration up to 1.05×10^{-2} M and decreases at higher concentrations. Therefore, a final concentration of 1.05×10^{-2} M of Triton-X-100 was selected as the optimum concentration.

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.

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 0.5-2.0 min from initiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration range 0.1-100 ng/mL of iodide.

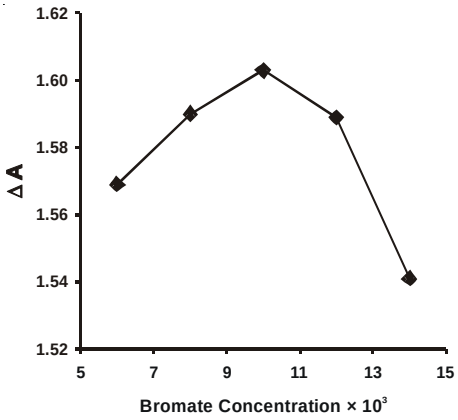


Fig. 3. Effect of boromate concentration on analytical signal. Conditions: H_2SO_4 0.24 M, gallocyanin concentration 7.5 × 10^{-5} M; Triton-X-100 7.92 × 10^{-3} M; iodide, 40.0 ng/mL; temperature 25 °C

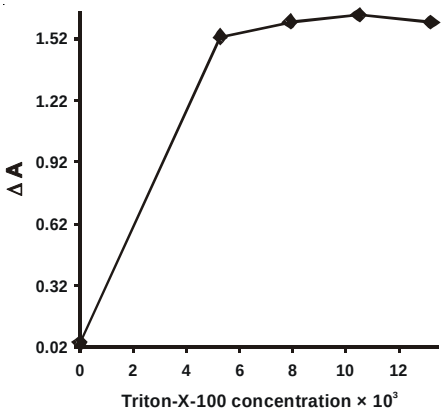


Fig. 4. Effect of Triton-X-100 concentration on the analytical signal. Conditions: H_2SO_4 0.24 M, gallocyanin concentration 7.5 × 10^{-5} M; BrO_3^- 1.0 × 10^{-2} M; iodide, 40.0 ng/mL; temperature 25 °C

The equation of the calibration graph is $\Delta A = 1.605 + 9 \times 10^{-4}$ C (n = 6, r = 0.9997). 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 of 1 and 40 ng/mL iodide was 2.3 and 1.9 %, 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 50 ng/mL iodide was studied. The tolerance limit was defined as the concentration of a added ions causing a relative error less than 3 % the results are summarized in 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 0.050 μg/mL IODIDE

Species	Tolerance limit (w_{ion}/w_{I^-})
Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Rb^+, Zn^{2+}, Ba^{2+}, Co^{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+}, Mn^{2+}	100
$S_2O_8^{2-}$, ClO_3^-, Cd^{2+}, Ni^{2+}, Hg^{2+}	50
Pb^{2+}, Ag^+	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	-	38	-	-
Well water	30	65	95.6	2.7
Well water + Ru^{3+} (5.0 µg/mL) + Rh^{3+} (5.0 µg/mL) + Mn^{2+} (5.0 µg/mL)	50	92	104.5	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 iodide without the need for any pre-concentration step.

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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 Analytical Chemist, AOAC, Arlington,VA, edn. 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. A.K. Anderson and P. Markowski, *J. Assoc. Off. Anal. Chem.*, **83**, 225 (2000).
9. K. Krengel-Rothensee, U. Richter and P. Heitland, *J. Anal. At. Spectrom.*, **14**, 699 (1999).
10. F.L. Sanchez and J. Szpunar, *J. Anal. At. Spectrom.*, **14**, 1697(1999).
11. H.E. Larsen, P. Knuthsen and M. Hansen, *J. Anal. At. Spectrom.*, **14**, 41 (1999).
12. E. Greenberg, S.L. Clesceri and D.A. Eaton, Standard Methods for Examination of Water and Wastewater, American Public Health Association, Washington, DC, 19th (1995).
13. B.E. Sandell and M.I. Kolthoff, *J. Am. Chem. Soc.*, **56**, 1426 (1934).
14. R. Pedriali, E. Giuliani, A. Margutti and E. Degli-Uberti, *Ann. Chim. (Rom)*, **87**, 449 (1997).
15. K.A. Ayianniddis and N.A. Voulgaropoulos, *Analyst*, **113**, 153 (1998).
16. L.J. Garwin, S.N. Rosenholtz and A. Abdollahi, *J. Food Sci.*, **59**, 1135 (1994).
17. D.E. Moxon and J.E. Dixon, *Analyst*, **105**, 344 (1980).
18. T.J. Pastor, G.A. Milovanovic and G.M. Petkovie, *Microchem. J.*, **60**, 8 (1998).
19. K. Sriramam, P. Ravindranath, S.V. Sastry and P.R. Rao, *Analysis*, **15**, 248 (1987).
20. E.I. Yasinskene and O.P. Umbrazhyunaite, *Zh. Anal. Khim.*, **30**, 962 (1975).

21. S.U. Krejngold, L.I. Sosenkova, A.A. Panteleimonova and L.V. Lavrelashvili, *Zh. Anal. Khim.*, **33**, 2168 (1978).
22. M.S. Garcia, C. Sanchez-Pedreno, I. Albero and C. Sanchez, *Analyst*, **116**, 653 (1991).
23. E.I. Yasinskene and O.P. Umbrazhyunaite, *Zh. Anal. Khim.*, **28**, 2025 (1973).
24. R.P. Igov, M.D. Jaredic and T.G. Pecev, *Mikrochim. Acta*, **33**, 171 (1979).
25. T. Tomiyasu, H. Sakamoto and N. Yonehara, *Anal. Sci*., **8**, 293 (1992).
26. S.S. Mitic, G.Z. Miletic and D.A. Kostic, *Anal. Sci.*, **19**, 913 (2003).
27. Z.X. Guo, Y. Xiao and S.Y. Zhang, *Fenxi Shiyanshi*, **15**, 32 (1996).
28. Z.X. Guo and S.Y. Zhang, *Fenxi Shiyanshi*, **14**, 31 (1995).
29. A.M. Zhang and S.H. Wang, *Fenxi Huaxue*, **26**, 967 (1998).
30. C.J. Liu and H. Zhang, *Fenxi Huaxue*, **26**, 222 (1998).
31. V.D. Mitic, S.D. Nikolic and V.P. Stankov-Jovanovic, *Anal. Sci.*, **20**, 931 (2004).
32. S. Rubio and D. Perez-Bendito, *Anal. Chim. Acta*, **224**, 85 (1989).

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