Kinetic Spectrophotometric Determination of Trace Amounts of Iodide in Food Samples

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A simple, selective and sensitive kinetic method has been developed for the determination of trace amounts of iodide. This method is based on a catalytic effect of iodide on the reaction between Janus Green and bromate in acidic media. Trace amounts of iodide increase the rate of a reaction that is monitored spectrophotometrically at 618 nm by a fixed-time method at 30 s. Effective parameters on the reaction rate, such as the concentration of reactants, temperature and reaction time, were investigated and the optimum conditions were obtained (6.0×10^{-2} mol L⁻¹ of sulfuric acid, 2.50×10^{-5} mol L⁻¹ of Janus Green, 1.75×10^{-2} mol L⁻¹ of bromate, 30°C and 180 s). The calibration curve was linear between 0.5 – 190.0 µg L⁻¹ of iodide, and the relative standard deviations ($n = 5$) for 10.0 and 100.0 µg L⁻¹ of iodide were 1.2 and 1.8%, respectively. The limit of detection was 0.12 µg L⁻¹ of iodide concentration. The effects of various substances upon the reaction rate were determined for assigning the selectivity of the method. The proposed method was successfully applied to the determination of iodide in food samples. The new developed method was found to have fairly good selectivity, sensitivity, simplicity and rapidity.

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Introduction

Iodine is a highly volatile element, and is emitted into troposphere by natural anthropogenic sources, such as burning coal, smelting ores and evaporation of soil iodine. This element is an essential nutrient in the human diet, which is naturally found in or added as a supplement to many food samples.¹ The daily requirement of iodide is 0.14 mg for adult men and 0.10 mg for adult women,² which is normally met by well-balanced diets and drinking water.^{3,4} The absence of this element in the diet may result in serious biochemical disturbances, *i.e.* myxedema and cretinism. Iodide deficiency causes goiter disease, and its excessive intake may contribute to thyrotoxicosis.⁵ Therefore, the determination of iodide in food samples is important with respect to environmental and biochemical aspects.

Several sensitive methods used for determination of trace amounts of iodide in various samples include inductively coupled plasma-atomic emission spectrometry (ICP-AES),^{6,7} inductively coupled plasma-mass spectrometry (ICP-MS),^{8,9} neutron activation analysis (NAA),^{10,11} ion chromatography (IC),¹²⁻¹⁴ molecular absorption spectrometry¹⁵ and an optical redox sensor.¹⁶ These methods are expensive and require preconcentration⁶⁻¹⁴ and/or separation¹⁰⁻¹⁴ of the samples or special instruments.^{6-11,15,16} However, we need a simple, sensitive and selective method that does not require any excess process of foods in order to analyze a large number of samples.

Various reports on iodide determination by spectrophotometric methods are available.¹⁷⁻³⁸ The NO_2^- -[Fe(SCN)]²⁺ reaction has been adopted as a standard method for iodide determination in

natural and waste water samples as well as in food and biological samples.³⁹

In this paper, a kinetic spectrophotometric method is proposed based on a catalytic effect of iodide on the reaction between Janus Green and bromate in acidic media. The reaction was followed spectrophotometrically by monitoring the decrease in the absorbance of Janus Green at 618 nm with a fixed-time method. The proposed method is suitable for the determination of iodide in food samples.

Experimental

Reagents and chemicals

Analytical-grade chemicals and redistilled water were used. First, 100 mL of an iodide stock solution of 100.0 mg L⁻¹ (as iodide stock solution) was prepared by dissolving 0.0131 g of potassium iodide (Merck) in water and diluting to 100 mL in a volumetric flask. Working solutions were prepared by appropriate dilution with water. A solution of Janus Green (1.0×10^{-3} mol L⁻¹) was prepared by dissolving 0.0511 g of it in water, and then diluting to 100 mL in a volumetric flask. A sulfuric acid solution (2.0 mol L⁻¹) was prepared by diluting 54.35 mL of conc. sulfuric acid ($a = 98\%$, $d = 1.84$ kg L⁻¹) to 500 mL; a 0.25 mol L⁻¹ of potassium bromate stock solution was subsequently prepared by dissolving 10.4380 g of KBrO₃ (Merck) in water and diluting to 250 mL in a volumetric flask.

Apparatus

A Shimadzu spectrophotometer (160-A, Japan) with 1-cm glass cell was used to measure the absorbance. A thermostated water bath (Heidolph, Germany) was used to keep the temperature of all solutions at the working temperature ($25 \pm 0.1^\circ\text{C}$). A stop-watch was used to record the reaction time.

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Fig. 1 Effect of the sulfuric acid concentration on the reaction rate: Janus Green, 0.25 mL of 2.5×10^{-5} mol L⁻¹; iodide, 10.0 μ g L⁻¹; bromate, 0.4 mL of 0.25 mol L⁻¹; temperature, 25°C; time, 5.0 min.

Fig. 2 Effect of the Janus Green concentration on the reaction rate: sulfuric acid, 0.3 mL of 2.0 mol L⁻¹; iodide, 10.0 μ g L⁻¹; bromate, 0.4 mL of 0.25 mol L⁻¹; temperature, 25°C; time, 5.0 min.

Recommended procedure

After initial spectrophotometric kinetic studies of the reaction, the reagent concentrations (except the catalyst) were judiciously chosen for the analytical procedure. To a series of 10 mL calibrated flasks, 0.25 mL of 2.0 mol L⁻¹ sulfuric acid, 0.25 mL of a 1.0×10^{-3} mol L⁻¹ Janus Green solution and 1.0 mL of 0.1 mg L⁻¹ of iodide were added. Then, 0.4 mL of 0.25 mol L⁻¹ bromate solution was added and the solution diluted to the mark with redistilled water. A time measurement started just after adding the last drop of the oxidant solution. After thorough mixing, a portion of this solution was transferred to a glass cell, and the absorbance was measured against water at 618 nm and 25°C for fixed times of 0.5 and 5.0 min. The measurements were repeated in the absence of iodide to obtain the value for the uncatalyzed reaction as the absorbance of the blank. The absorbance changes of the catalyzed and uncatalyzed reactions were labeled ΔA_c and ΔA_u , respectively. The difference in the absorbance (ΔA) was considered as the response.

Procedure for food sample preparation

Food samples were subjected to an alkaline ashing process to decompose any organic matter and to convert iodine organically bound to the catalytically active inorganic form. During an ashing process, ultrasonication was performed so as to minimize the adsorption of iodide.³³ For treating food samples, several tubes were simultaneously run along with a blank, as follows. We accurately transferred 0.70 – 1.00 g of a homogenized (finely blended) sample to a 25 × 150 mm Pyrex tube. To decompose nitrite, 2 mL of 3% sulfamic acid was added and placed in an ultrasonic bath for 10 min. Then, 1 mL of a 2 mol L⁻¹ KOH solution was added, followed by 1 mL of a 10% ZnSO₄ solution. These were mixed well and heated at 150°C for 30 min, after which the temperature rose to 500°C and was maintained for 2 h. We then cooled the tube, dissolved the formed iodide in about 10 mL of water, and centrifuged at 3000 rpm for 3 min to separate the extract from carbonaceous matter. The formed extract was decanted into a 25-mL calibrated flask, added further 10 mL of water, and repeated the dissolution, centrifugation, and decantation steps. The combined extracts were diluted to the mark in a calibrated flask.^{33,40}

Results and Discussion

Janus Green is a basic dye of a mono-azo group that can be

Fig. 3 Effect of the bromate concentration on the reaction rate: sulfuric acid, 0.3 mL of 2.0 mol L⁻¹; Janus Green, 0.25 mL of 1.0×10^{-3} mol L⁻¹; iodide, 10.0 μ g L⁻¹; temperature, 25°C; time, 5.0 min.

oxidized by strong oxidizing agents, such as bromate in an acidic media at a slow reaction to produce a colorless oxidized form.^{41,42} It was used as an indicator for the catalytic determination of formaldehyde⁴² and silver,⁴³ and also for the catalytic determination of iodide.

The effect of such parameters as the reagent concentration, temperature and time on the reaction rate was studied based on a fixed-time method to obtain the best sensitivity, and to find the optimum conditions. Under these conditions, a calibration curve was constructed by plotting $\Delta A = \Delta A_c - \Delta A_u$ versus the iodide concentration.

Effect of the reagents concentration

The effects of the sulfuric acid concentration on the catalyzed and uncatalyzed reactions were studied over the range of 0.02 to 0.08 mol L⁻¹. As shown in Fig. 1, the reaction rate increased with increasing sulfuric acid concentration up to 0.06 mol L⁻¹, whereas at higher concentrations the rate of the reaction decreased. Therefore, a 0.06 mol L⁻¹ sulfuric acid solution was used for a further study.

The effect of the Janus Green concentration on the reaction rate was studied in the range of 1.0×10^{-5} to 3.5×10^{-5} mol L⁻¹. As shown in Fig. 2, by increasing the Janus Green concentration up to 2.5×10^{-5} mol L⁻¹, the rate of the catalyzed reaction increased. Therefore, 2.5×10^{-5} mol L⁻¹ Janus Green was

chosen as the optimum value.

The effect of the bromate concentration on the rate of the catalyzed oxidation of Janus Green was studied in the range of 5.0×10^{-3} to 2.25×10^{-2} mol L⁻¹ of bromate. As shown in Fig. 3, under the optimum concentrations of H₂SO₄ and Janus Green, the rate of the reaction was increased up to 1.75×10^{-2} mol L⁻¹ of bromate, which was selected as being the optimum concentration of the oxidant.

Effect of the ionic strength, temperature and reaction time

The effect of the ionic strength was studied by using a potassium nitrate solution (3.0 mol L⁻¹) under the optimum reagent concentration. The results showed that the sensitivity dose not depend on the ionic strength up to 0.5 M of the potassium nitrate concentration, whereas greater amounts of it

decreased the sensitivity. This may be attributed to the absorption behavior of Janus Green under this condition. At higher concentrations of potassium nitrate, the close proximity of ions to Janus Green alters the molar absorptivity of dye due to electrostatic interactions.

The effect of the temperature on the reaction rate was studied in the range of 15 to 40°C in the optimum concentrations of the reagents. Increasing the temperature up to 30°C caused an increase in the sensitivity, whereas at higher temperatures it decreased. Thus, 30°C was selected as being the optimum temperature.

The optimum time was found by measuring the change in the absorbance during 0.5 – 5.0 min. The reaction rate increased for up to 180 s, and for longer times the rate was almost constant. Therefore, 180 s was selected for further study.

Analytical parameters

After optimizing the reaction conditions, a calibration curve was obtained over the range of 0.5 – 190.0 µg L⁻¹ of iodide. An analysis of the data gave the following regression equation: $\Delta A = 0.0072[I^-] + 0.2529$ ($R^2 = 0.9995$), where ΔA is the difference in the absorbance between the blank and the sample, $[I^-]$ is the iodide concentration in µg L⁻¹ and R^2 is the correlation coefficient. Moreover, data analyses of the calibration curve in the range of 0.5 – 10.0 µg L⁻¹ gave the regression equation: $\Delta A = 0.004[I^-] + 0.2703$ ($R^2 = 0.9959$) for iodide. This correlation coefficient shows results at low concentrations that are in good agreement. The detection limit ($3S_b/m$) was 0.12 µg L⁻¹ iodide. The relative standard deviations ($n = 5$) were 1.21 and 1.80% for 10.0 and 100.0 µg L⁻¹ iodide, respectively.

Interference studies

The effect of various substances on the determination of 100.0 µg L⁻¹ of iodide was studied; the results are given in Table 1. The tolerance was defined as the concentration of added substance causing a change of less than 5.4% in the rate

Table 1 Tolerance limit for foreign species on the determination of 100.0 µg L⁻¹ of iodide

Foreign species	Tolerance limit
Glucose, saccharose, fructose, EDTA, methanol, ethanol, sulfamic acid, citric acid	1000
Ascorbic acid, oxalic acid	950
Benzaldehyde, acetaldehyde	400
Formaldehyde	50
Li ⁺ , Na ⁺ , K ⁺ , Mg ²⁺ , Al ³⁺ , NH ₄ ⁺ , Co ²⁺ , Cd ²⁺	1000
Ca ²⁺ ^a	850
Fe ³⁺ ^a , As ³⁺ ^a , Cr ³⁺ ^a	600
NO ₃ ⁻ , SO ₄ ²⁻ , CO ₃ ²⁻ , CH ₃ COO ⁻ , PO ₄ ³⁻ , HPO ₄ ²⁻ , H ₂ PO ₄ ⁻ , F ⁻ , NO ₂ ^{-b}	1000
Cl ⁻	15
VO ₃ ⁻	2
Br ⁻	1

a. After masking with 2 mL of 2% EDTA solution.

b. After addition 2 mL of 3% sulfamic acid solution.

Table 2 Determination of iodide in food samples

Sample ^a		Iodide ^b		RSD, %	Recovery, %	AOAC ³⁹	Recovery, %
Type	Weight/g	Added	Found $\pm$ SD ($n = 5$)			Found $\pm$ SD ($n = 5$)	
Milk	0.617	—	34.35 $\pm$ 0.50	1.5	—	34.96 $\pm$ 0.37	100.7
		100	134.98 $\pm$ 1.39	1.0	100.6	135.62 $\pm$ 1.49	
Butter	0.598	—	56.45 $\pm$ 0.49	0.9	—	55.78 $\pm$ 0.32	99.9
		100	156.18 $\pm$ 1.44	0.9	99.0	155.71 $\pm$ 1.51	
Egg (hen)	0.724	—	78.32 $\pm$ 0.91	1.2	—	77.69 $\pm$ 0.82	100.1
		100	177.09 $\pm$ 1.54	0.87	98.8	177.84 $\pm$ 1.51	
Beef	0.968	—	222.75 $\pm$ 4.19	1.9	—	220.89 $\pm$ 3.71	99.9
		100	323.65 $\pm$ 3.75	1.2	100.9	320.79 $\pm$ 3.59	
Carrot ^c	0.761	—	38.47 $\pm$ 0.56	1.5	—	39.21 $\pm$ 0.56	99.8
		100	139.31 $\pm$ 1.69	1.2	100.8	139.02 $\pm$ 1.28	
Potato ^c	0.689	—	44.63 $\pm$ 0.58	1.3	—	43.68 $\pm$ 0.57	101.5
		100	142.91 $\pm$ 1.71	1.2	98.3	145.21 $\pm$ 1.45	
Tomato ^c	0.926	—	14.83 $\pm$ 0.25	1.7	—	14.75 $\pm$ 0.22	100.6
		100	116.31 $\pm$ 1.72	1.5	101.5	115.38 $\pm$ 1.16	
Cabbage ^c	0.895	—	31.43 $\pm$ 0.66	2.1	—	33.02 $\pm$ 0.62	99.1
		100	130.79 $\pm$ 1.85	1.4	99.4	132.08 $\pm$ 1.89	
Apple ^c	0.967	—	22.54 $\pm$ 0.19	0.8	—	23.12 $\pm$ 0.20	101.7
		100	125.09 $\pm$ 1.08	0.9	102.5	124.79 $\pm$ 1.11	

a. Food samples were collected from the local market; the determined weight of a given food sample was subjected to the alkaline ashing step of the recommended procedure; the ash was treated, dissolved, and diluted in a 50-mL calibrated flask and then the suitable volume was used for analysis. b. Total iodide concentration expressed in µg L⁻¹ (or µg kg⁻¹); data are averages of five replicate determinations.

c. Samples were dried in a thermostatted oven at 50°C to constant weight.

Table 3 Comparison of the figures of merit for the proposed method with other methods

Reaction system	Determination range/ $\mu\text{g L}^{-1}$	Detection limit/ $\mu\text{g L}^{-1}$	Application	Ref.
Variamine blue leucu base- H_2O_2	NA	21	—	17
Chlorpromazine- BrO_3^-	5 – 70	5	Table salts, rate thyroid glands	18
Pyrochatechol violet- H_2O_2	0 – 50	NA	Hot spring water	19
[Co-EDTA]- H_2PO_2 -Pd(II)	2 – 28	2	Table salt, milk, pharmaceuticals	20
Chlorpromazine- H_2O_2	0.2 – 10	0.2	River water	21
Ce(IV)-As(III)	0 – 80	1	Waters, foods, biological samples	22
Methyl violet- IO_4^-	300 – 1400	220	Table salt	23
Crystal violet- IO_4^-	8 – 200	3.8	Table salt	24
Bromopyrogallol red- BrO_3^-	4.5 – 90	4.5	—	25
Metanil yellow- BrO_3^-	20 – 400	15	Laver, kelp, shrimp, table salt	26
NO_2^- -[Fe(SCN)] $^{2+}$	0 – 100	0.99	Waters, foods, biological samples	27
Mn(III)-As(III)	0.76 – 1.27	0.76	—	28
Amaranath- IO_4^-	0 – 20	0.66	Laver, shrimp, table salt	29
Toulidine blue- CINH_3OH	0 – 8	0.4	Laver, kelp, table salt, soybean	30
O-Dianisidine-chloramine B	0 – 0.004	0.0004	Natural waters	31
Malachite green-chloramine T	0 – 80	1.6	Laver, kelp	32
Triupromazine- H_2O_2	0 – 4.5	0.04	Natural waters, food samples	33
Fe^{3+} -SCN $^-$ -CP $^{+}$ -nBPY	5 – 120	0.1	Water samples	34
MBDA-chloramine T	0.1 – 6.0	0.05	Pharmaceutical products	35
I $^-$ -Br $_2$	20 – 3000	8	Synthetic samples of iodized salts	36
Ce(IV)-As(III)	0.3 – 20.0	NA	Seaweed samples	37
Rhodamine B- BrO_3^-	2.0 – 6.0, 1.0 – 6.0	0.06, 0.07	Kelp	38
Janus Green- BrO_3^-	0.5 – 190.0	0.12	Food samples	This work

MBDA, 4,4-methylene bis(*N,N*-dimethylaniline). NA, Not available.

of the catalyzed reaction (three-times the standard deviation in $100.0 \mu\text{g L}^{-1}$ of iodide). Many foreign species did not interfere, even in a 1000-fold iodide. Sulfamic acid is an effective reagent for nitrite decomposition, which was used for this purpose. The addition of 2 mL of 3% sulfamic acid solution improved the interfering effect of nitrite to 1000-fold. The interfering effect of some of cations was removed in the presence of 2 mL of a 2% EDTA solution. Chloride, bromide and vanadate ions had a seriously interfering effect.

Application

To evaluate the analytical applicability of the method, it was used for the determination of iodide in various food samples. Food samples were prepared according to the mentioned procedure. The results of the analysis of food samples by the proposed procedure and the standard method³⁹ are given in Table 2. The recoveries were close to 100%, which indicate there was no serious interference in such food samples. The *t*-test did not show any significant difference between the data obtained from the two methods (the 95% confidence level and eight degrees of freedom). As given in Table 3, the method surpasses most kinetic methods^{17–38} for iodide determination in both the dynamic range and the detection limit. Therefore, the developed method is suitable for the analysis of food samples with satisfactory results.

Conclusions

The behavior of a selected system allowed the development of a kinetic method for the determination of trace amounts of iodide without any separation or preconcentration step. Hence, the use of organic solvents, which are generally toxic pollutants, is avoided. The proposed method is simple, sensitive and relatively selective compared with other methods. The procedure is

suitable for the analysis of various food samples with satisfactory results.

References

1. E. J. Underwood, "Trace Elements in Human and Animal Nutrition", **1977**, Academic Press, New York.
2. WHO, "Handbook of Nutritional Requirement", **1974**, WHO, Geneva.
3. A. C. Pandey, *Everymans Sci.*, **1986**, 21, 1.
4. W. Clements, "Nutrition in Preventive", **1976**, WHO, Geneva.
5. C. Guyton, "Text Book of Medical Physiology", **1986**, W. B. Sanders, London.
6. K. A. Anderson and P. Markowski, *J. Assoc. Off. Anal. Chem.*, **2000**, 83, 225.
7. Y. Kregel-Rothensee, U. Richter, and P. Heitland, *J. Anal. At. Spectrom.*, **1999**, 14, 699.
8. L. F. Sanchez and J. Szpunar, *J. Anal. At. Spectrom.*, **1999**, 14, 1697.
9. E. H. Larsen, P. Knuthsen, and M. Hansen, *J. Anal. At. Spectrom.*, **1999**, 14, 41.
10. E. A. Arafa, F. H. Beshewa, A. I. Saleh, and H. A. Das, *J. Trace. Microprobe Tech.*, **2000**, 18, 137.
11. X. L. Hou, H. Dahlgaard, B. Rietz, U. Jacobsen, S. P. Nielsen, and A. Aarkrog, *Anal. Chem.*, **1999**, 71, 2745.
12. R. A. Niemann and D. L. Anderson, *J. Chromatogr. A*, **2008**, 1200, 193.
13. T. Kimbeni Malongo, S. Patris, P. Macoursc, F. Cottona, J. Nsangub, and J. M. Kauffmanna, *Talanta*, **2008**, 76, 540.
14. H. Jing, L. Li-Na, M. Shi-Fen, C. Ya-Qi, and L. Yi-Qiang, *Chin. J. Anal. Chem.*, **2008**, 36, 187.
15. M. D. Huang, H. Becker-Ross, S. Florek, M. Okruss, B. Welz, and S. Morés, *Spectrochim. Acta, Part B*, **2009**,

- in press.
16. S. Rastegarzadeh, N. Pourreza, and I. Saeedi, *Talanta*, **2009**, 77, 1032.
 17. R. P. Igov, M. D. Jaredic, and T. G. Pecev, *Mikrochim. Acta*, **1979**, 117, 271.
 18. P. Vinas, M. Hernandez-Cordoba, and C. Sanchez-Pedreno, *Talanta*, **1987**, 34, 351.
 19. N. Yonehara, T. Yamane, T. Tomiyasu, and H. Sakamoto, *Anal. Sci.*, **1989**, 5, 175.
 20. M. S. Garcia, C. Sanchez-Pedreno, I. Albero, and C. Sanchez, *Analyst*, **1991**, 116, 653.
 21. T. Tomiyasu, H. Sakamoto, and N. Yonehara, *Anal. Sci.*, **1992**, 8, 293.
 22. J. L. Garwin, N. S. Rosenholtz, and A. Abdollahi, *J. Food Sci.*, **1994**, 59, 1135.
 23. Z. X. Guo and S. Y. Zhang, *Fenxi Shiyanshi*, **1995**, 14, 61.
 24. Z. X. Guo, Y. Xiao, and S. Y. Zhang, *Fenxi Shiyanshi*, **1996**, 15, 32.
 25. S. Q. Wu, *Fenxi Huaxue*, **1996**, 24, 24.
 26. A. M. Zhang, H. S. Wang, H. Cui, and C. G. Fu, *Fenxi Huaxue*, **1996**, 24, 689.
 27. A. R. de-Araujo-Nogueira, F. Mockiuti, G. B. de-Souza, and O. Primavesi, *Anal. Sci.*, **1998**, 14, 559.
 28. T. J. Pastor, G. A. Milovanovic, and G. M. Petkovic, *Microchem. J.*, **1998**, 60, 8.
 29. A. M. Zhang and S. H. Wang, *Fenxi Huaxue*, **1998**, 26, 967.
 30. C. J. Lui and H. Zhang, *Fenxi Huaxue*, **1998**, 26, 222.
 31. O. P. Shkadauskene and Y. Shadauskas, *Zh. Anal. Chem.*, **1999**, 54, 158.
 32. J. G. Li, Y. Qiao, and Y. Q. Wei, *Fenxi Huaxue*, **1999**, 27, 1072.
 33. A. A. Mohamed, *Monatsh. Chem.*, **2001**, 132, 919.
 34. A. Kamavisdar and R. M. Patel, *Microchim. Acta*, **2002**, 140, 119.
 35. Z. O. Tesfaldet, J. F. van Staden, and R. I. Stefan, *Talanta*, **2004**, 64, 1213.
 36. Z. Xie and J. Zhao, *Talanta*, **2004**, 63, 339.
 37. D. Gamallo-Lorenzo, M. C. Barciela-Alonso, A. Moreda Pineiro, A. Bermejo-Barrera, and P. Bermejo-Barrera, *Anal. Chim. Acta*, **2005**, 542, 287.
 38. X. Zhu and Y. Zhang, *Spectrochim. Acta, Part A*, **2008**, 70, 510.
 39. K. Helrich, "Official Methods of Analysis of the Association Official Analytical Chemists", 15th ed., **1990**, AOAC, Arlington, VA.
 40. R. E. D. Moxon and E. J. Dixon, *Analyst*, **1980**, 105, 344.
 41. S. Wang, L. Du, and A. Zhang, *Chin. J. Anal. Chem.*, **2000**, 28, 628.
 42. S. Abbasi, M. Esfandyarpour, M. A. Taher, and A. Daneshfar, *Spectrochim. Acta, Part A*, **2007**, 67, 578.
 43. A. Safavi and R. Mirzajani, *Anal. Sci.*, **2002**, 18, 329.
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