

Simple and Highly Sensitive Spectrophotometric Flow Injection Method for the Determination of Iodate in Iodized Salt

Kanchana Uraisin¹, Toshio Takayanagi¹, Mitsuko Oshima¹, Duangjai Nacapricha² and Shoji Motomizu^{1*}

¹Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushimanaka, Okayama, 700-8530, Japan

²Department of Chemistry, Faculty of Science, Mahidol University, Rama VI Road, Bangkok 10400, Thailand

Abstract

A simple and rapid flow injection (FI) spectrophotometric method is newly proposed for the determination of iodate in iodized salt. The method is based on the oxidation of 2-Chloro-10-[3-(4-methyl-1-piperazinyl) propyl] phenothiazine maleate (prochlorperazine / PCP) by iodate in acidic medium to form a red product: the increase in absorbance of the oxidation product is detected at 525 nm. Various chemical and physical experimental variables of the FI method were optimized, and the effect of interfering ions was also examined. Under the optimal conditions, iodate can be determined in the range of 1×10^{-6} to 3×10^{-5} mol l⁻¹ with high precision (RSD=0.1% at 8×10^{-6} mol l⁻¹ of iodate, n=15). The detection limit (S/N=3) of the method was down to 8.5×10^{-8} mol l⁻¹. The proposed method was validated against the FI with I₃⁻-starch reaction and the conventional titration method: the results obtained for three methods were statistically analyzed by the analysis of variance (ANOVA). It was found that there is no significant difference among these methods at 95% confidence. The method was applied to the determination of iodate in iodized salt.

Keywords spectrophotometry, flow injection, prochlorperazine, iodate, iodized salt

1. Introduction

Iodine is one of the natural elements required for a human body for proper physical and mental development. It is necessary for the biosynthesis of the thyroid hormones, thyroxine (T₄) and triiodothyronine (T₃), through the precursor protein, thyroglobulin, and the action of enzyme thyroid peroxidase in the thyroid gland [1]. More than one billion people worldwide are at the risk of iodine deficiency disorder (IDD) because they lack in access to foods which contain iodine. IDD can be easily avoided by taking sufficient amounts of salt supplement containing iodine added during the salt refining process. Salt fortification is a highly cost-effective method of distributing the necessary of iodine. Iodine in the form of both potassium iodide and potassium iodate are added into salt. However, the latter is preferred in some countries, particularly in tropical regions because it is more stable than potassium iodide under a hot and humid condition.

The most common techniques for iodate determination are ion chromatography [2-4] and capillary electrophoresis [5]. However, their instrumentation is expensive, needs high operation skills; therefore it is not suitable for analysis of large number of samples. Flow injection (FI) method is also presented for the determination of iodate. Such methods are based on amperometric detection [6] and spectrophotometric detection [7-12]. The latter is widely used as detection techniques in FI analysis because of the low cost of the instrument, the simplicity of procedures, as well as their rapidity, precision and accuracy. Several authors reported the use of chromogenic reagents for iodate determination by spectrophotometric methods [7, 8]. Yaqoob et al. developed the sensitive color reaction of iodate and *p*-aminophenol with the detection limit of 5×10^{-5} mol l⁻¹ [7].

Catalytic spectrophotometric method for the determination of iodate also reported. The iodide catalytic reaction between Ce(IV) and As(III) was reported for this purpose [9], which As(III) was also used as the reducing agent for converting iodate to iodide: the stopped-FI system was utilized with the sample throughput of 26 h⁻¹. The method based on the reaction of iodate with an excess amount of iodide to form triiodide was used for the spectrophotometric determination of iodate at 350 nm [10, 11]. Choengchan et al. proposed the spectrophotometric method for iodate determination by using the intense blue colored complex of triiodide starch (I₃⁻-starch), where the detection was shifted to the visible region (590 nm) [12]. However, cleaning the complex deposited on the wall tubing and flow-through cell was necessary after each injection, which caused the system to be complicated.

In this work, we propose an FI system based on the spectrophotometric method for the determination of iodate, in which the oxidation of 2-Chloro-10-[3-(4-methyl-1-piperazinyl) propyl] phenothiazine maleate (prochlorperazine / PCP) to a red intermediate by iodate occurred and the reaction product was measured at 525 nm. The method is highly sensitive with good accuracy, reproducibility and high sampling frequency. Application of the proposed method to the determination of iodate in iodized salt samples can be achieved.

2. Experimental

2.1. Flow injection (FI) manifold

Figure 1 depicts the proposed FI system for the determination of iodate in iodized salt. A double plunger pump (PUMP 201, F.I.A. Instrument, Japan) was used for propelling a carrier and a reagent solution. A six-port injection valve (SNK, Japan) with a sample loop (300 μl) was used for introducing standard iodate solutions, as well as sample solutions, into the carrier stream. The absorbance at 525 nm was measured using

* Corresponding author.

E-mail: motomizu@cc.okayama-u.ac.jp

a spectrophotometer (Soma Visible Detector S-3250, Japan) equipped with a 10 mm flow-through cell. The signal was recorded using FIA monitor/data processing apparatus (F.I.A. Instrument, Japan). The manifold was constructed from PTFE tubing of 0.5 mm i.d.

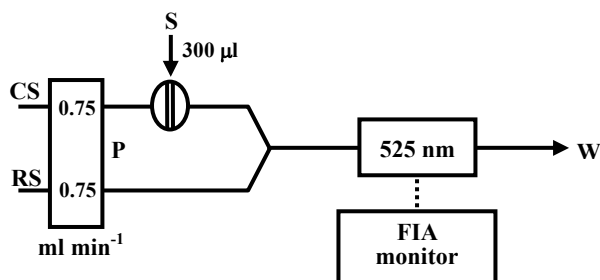


Fig. 1 The proposed FI system for the determination of iodate in iodized salt. S: Standard/sample injection valve; P: Double plunger pump; CS: Carrier stream of 2% (w/v) NaCl; RS: Reagent stream of $2 \times 10^{-3} \text{ mol l}^{-1}$ prochlorperazine (PCP) in 0.75 mol l^{-1} HCl; W: Waste.

2.2. Chemicals and reagents

All chemicals were of analytical reagent grade. Deionized and distilled water was used for the preparation of solutions. A stock solution ($1 \times 10^{-2} \text{ mol l}^{-1}$) of standard iodate was prepared by dissolving 0.2140 g of potassium iodate (crystal: Wako Pure Chemicals, Japan) in 100.0 ml of water. Working standard solutions of iodate were subsequently prepared by appropriate dilution of the stock solution with 2% (w/v) sodium chloride.

The carrier stream of 2% (w/v) sodium chloride was made by dissolving approximately 20 g of sodium chloride (Wako Pure Chemicals) in 1000 ml of water. This solution was also used for the preparation of working standard solutions of iodate.

The reagent stream was a solution of $2 \times 10^{-3} \text{ mol l}^{-1}$ prochlorperazine in 0.75 mol l^{-1} hydrochloric acid. This solution was prepared by dissolving 0.7576 g of prochlorperazine dimaleate (Sigma, USA) in hot solution of 250 ml of 0.04 mol l^{-1} sulfuric acid (Wako Pure Chemicals) to give a $5 \times 10^{-3} \text{ mol l}^{-1}$ prochlorperazine: the solution was stable for 1 month when stored in a refrigerator. An aliquot of 40 ml of $5 \times 10^{-3} \text{ mol l}^{-1}$ prochlorperazine was then mixed with 15 ml of 5 mol l^{-1} hydrochloric acid (Wako Pure Chemicals). The solution was then transferred to 100 ml volumetric flask and diluted to the mark with water. The reagent stream solution was prepared daily.

2.3. Sample preparation for method validation for the determination of iodate in iodized salt

All samples were purchased in Thailand. Sample solutions were prepared by dissolving an accurate amount of 25 g of iodized salt in water. Filtration with a filter paper (No. 5B: Advantec, Japan) may be required for some sample solutions which may contain undissolved particulate matters. The solutions were then transferred to 250 ml volumetric flask and diluted to the mark with water. These sample solutions resulted in 10% (w/v) of iodized salt sample solutions, and were analyzed by the standard titration method (iodometric method) [13]. For the FI system with I_3^- -starch detection (Figure 2) [12] and the proposed FI system, the samples of iodized salt solutions were diluted to 6% (w/v) and 2% (w/v) before the measurement, respectively.

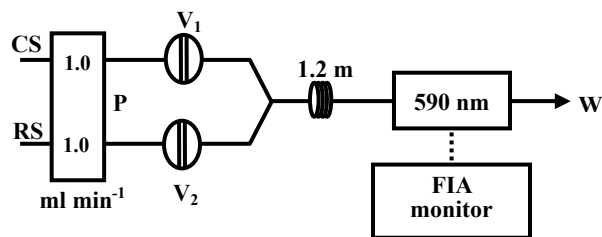


Fig. 2 The FI system with I_3^- -starch detection for the determination of iodate in iodized salt. P: Double plunger pump; CS: Carrier stream of $2.5 \times 10^{-2} \text{ mol l}^{-1}$ KI in 6% (w/v) NaCl; RS: Reagent stream of 0.1% starch in $1.0 \times 10^{-2} \text{ mol l}^{-1}$ H_2SO_4 ; V_1 : 250 μl injection of sample solution or standard; V_2 : 100 μl injection of $1.0 \times 10^{-3} \text{ mol l}^{-1}$ $\text{Na}_2\text{S}_2\text{O}_3$; W: Waste.

2.4. Procedure

In the proposed FI system, each flow rate of the double plunger pump (Figure 1) was set at 0.75 ml min^{-1} . The standard iodate solutions containing 2% (w/v) sodium chloride or 2% (w/v) iodized salt sample solutions were injected into the carrier stream containing 2% (w/v) of sodium chloride, and then it was merged with the reagent stream. The red color product was produced and directly passed through the flow cell, where the absorbance of the product was measured spectrophotometrically at 525 nm.

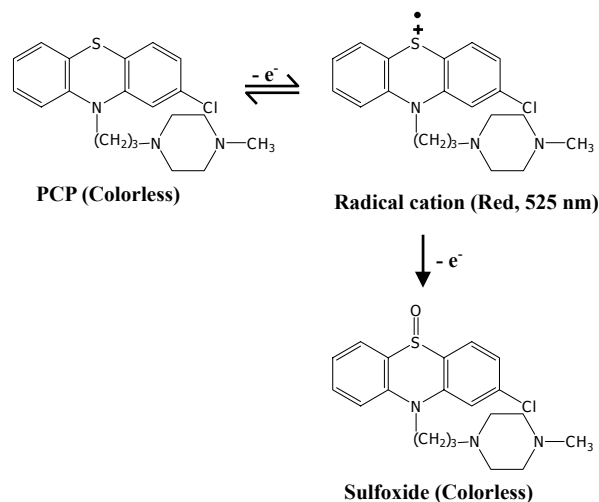
In the FI system with I_3^- -starch detection, the experimental conditions used were similar to those reported by Choengchan et al. [12], which were shown in Figure 2.

3. Results and discussion

3.1. Optimization of the FI system

3.1.1. Experimental variables for chemical parameters

In the present FI system, the determination of iodate is based on the oxidation reaction of prochlorperazine (PCP) with iodate in acidic medium to form the red intermediate, which is considered to be a radical cation of PCP [14, 15]. The product is further slowly oxidized to a colorless compound (Scheme 1).



Scheme 1 Oxidation reaction of prochlorperazine (PCP) through an intermediate to the final product.

In Figure 3, absorption spectra of products were shown. PCP in acidic medium has a strong maximum absorbance at 305 nm (curve 1). The curve (2) and (3) the spectra obtained after the reagents and iodate were mixed. The absorbance at 525 nm is attributed to the intermediated (radical cation). The product of sulfoxide compound gave the maximum absorbance at 300 nm (curve 3).

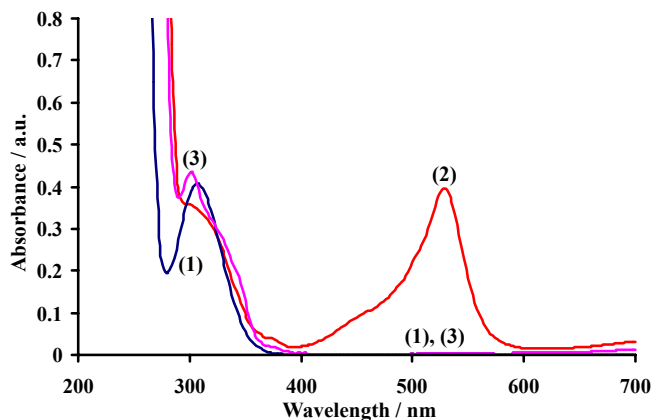


Fig. 3 Absorption spectra of (1) prochlorperazine, (2) intermediate (20 s after the reagents were mixed) and (3) product in the oxidation reaction (2 h after the reagents were mixed). Condition: 1×10^{-4} mol l^{-1} PCP, 8×10^{-6} mol l^{-1} IO_3^- and 1 mol l^{-1} HCl.

The concentration of iodate in iodized salt was ranging from 10 to 100 mg I kg^{-1} salt, which correspond to 1.6×10^{-6} to 1.6×10^{-5} mol l^{-1} of iodate in 2% (w/v) of iodized salt solutions. Such concentrations are in the calibration range of iodate determination by using the FI system in Figure 1. In order to eliminate the refractive index effect [16], a 2% (w/v) NaCl solution without iodate was used as the carrier solution. In order to examine the effect of NaCl in sample solutions, standard iodate solutions of 4×10^{-6} to 1.6×10^{-5} mol l^{-1} in 1, 2 and 3% (w/v) of NaCl were prepared. The linear equations obtained from these three conditions were $\text{Abs} = (3.09 \times 10^4)[\text{IO}_3^-] - 11.33$, $\text{Abs} = (3.12 \times 10^4)[\text{IO}_3^-] - 13.21$ and $\text{Abs} = (3.13 \times 10^4)[\text{IO}_3^-] - 15.30$, respectively, where Abs corresponds to the absorbance of the oxidizing product (the intermediate) of PCP at 525 nm in absorbance unit. The difference in slope and the intercept of each calibration graphs are very small. The relative error of the slope, when compared with standard iodate in 2% (w/v) NaCl, was approximately 1%, which indicates that the proposed FI system can be applied to the determination of iodate in various contents (1-3 %) of NaCl in iodized salt solutions. However, 2% (w/v) of NaCl was recommended for the preparation of the standard iodate solutions, as well as the iodized salt solutions.

The optimization of experimental variables was performed in order to achieve the highest sensitivity and the best reproducibility. The system was optimized by varying each variable while other conditions were kept identical. Standard iodate solutions of 2×10^{-6} to 1.6×10^{-5} mol l^{-1} were used for the optimization.

The influence of PCP concentrations in the range of 0.1×10^{-3} to 3×10^{-3} mol l^{-1} on sensitivity was investigated. The results are shown in Figure 4(A), which demonstrates that the signal intensity gradually increases with an increase in PCP concentrations up to 1.5×10^{-3} mol l^{-1} , above which the intensity is almost identical. The value of 2×10^{-3} mol l^{-1} of PCP was

selected.

The effect of HCl concentrations on the sensitivity was studied over the range of 0.1 to 1 mol l^{-1} . The results in Figure 4(B) show that the increase in HCl concentration from 0.1 to 0.25 mol l^{-1} can accelerate the reaction, and the signals intensity was almost identical at concentrations of HCl between 0.5 and 1 mol l^{-1} . In this work, 0.75 mol l^{-1} of HCl was chosen.

3.1.2. Experimental variables for physical parameters

The experimental parameters of the FI assembly that can affect the dispersion of sample zones was optimized. The variables selected for the optimization were the mixing coil length, the sample injection volume and the flow rate. The optimization was carried out by injecting the standard iodate solutions of 2×10^{-6} to 1.6×10^{-5} mol l^{-1} . Sensitivity, in terms of the slope of the calibration graph, is considered as one of the most important parameters of FI variables, and also "analysis time", which is defined as the time taken from the injection of sample until the top of a peak, is very important.

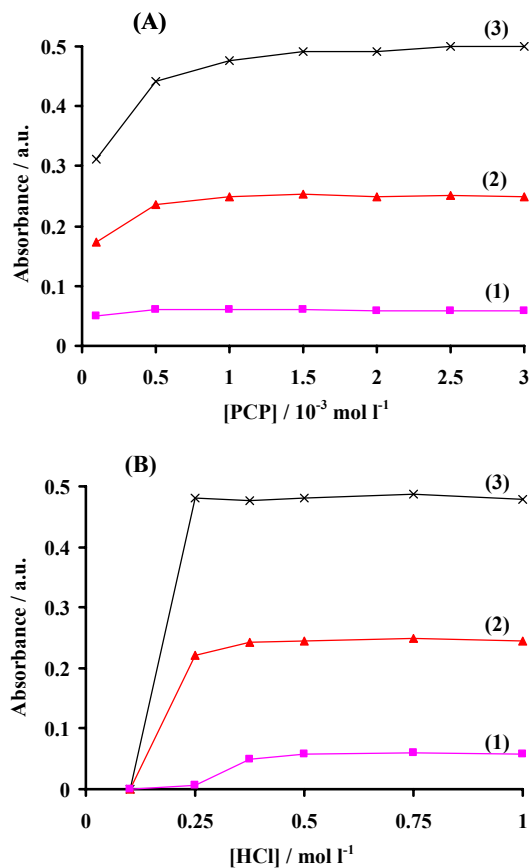


Fig. 4 Effect of reagent concentrations on analytical signal. (1-3): standard iodate solution of 2×10^{-6} , 8×10^{-6} and 1.6×10^{-5} mol l^{-1} , respectively. (A) Effect of PCP concentration and (B) effect of HCl concentration.

Effect of mixing coil length was examined in the range of 0 to 6 m. The results in Figure 5(A) demonstrate that the sensitivity decreases with an increase in coil length. This is due to the higher dispersion of sample zone at longer mixing coil length and the large conversion efficiency of the colored intermediate product to the colorless product. Therefore, only straight tube of 20 cm from the merging point to the detector was recommended for further studies.

The influence of a sample injection volume was examined by varying the volumes from 100 to 500 μl . The slope of the calibration graph increased with an increase in sample volumes, and the identical peak heights were obtained at the volumes greater than 300 μl , as shown in Figure 5(B). The injection volume of 300 μl was chosen for further studies, as a compromise between sensitivity and sampling frequency.

In order to simplify the FI system in Fig. 1, the flow rate of the carrier and the reagent stream were set to the equal rate. The effect of total the flow rate was examined from 0.5 to 3 ml min^{-1} . According to Figure 5(C), the flow rate of 0.5 ml min^{-1} gave the lowest sensitivity, and the slope of the calibration graph was almost identical between 1 and 3 ml min^{-1} . This is due to the fact that the dispersion of the sample can decrease with an increase in the flow rate. As a compromise between the sensitivity, the analysis time and the reagent consumption, 1.5 ml min^{-1} was adopted.

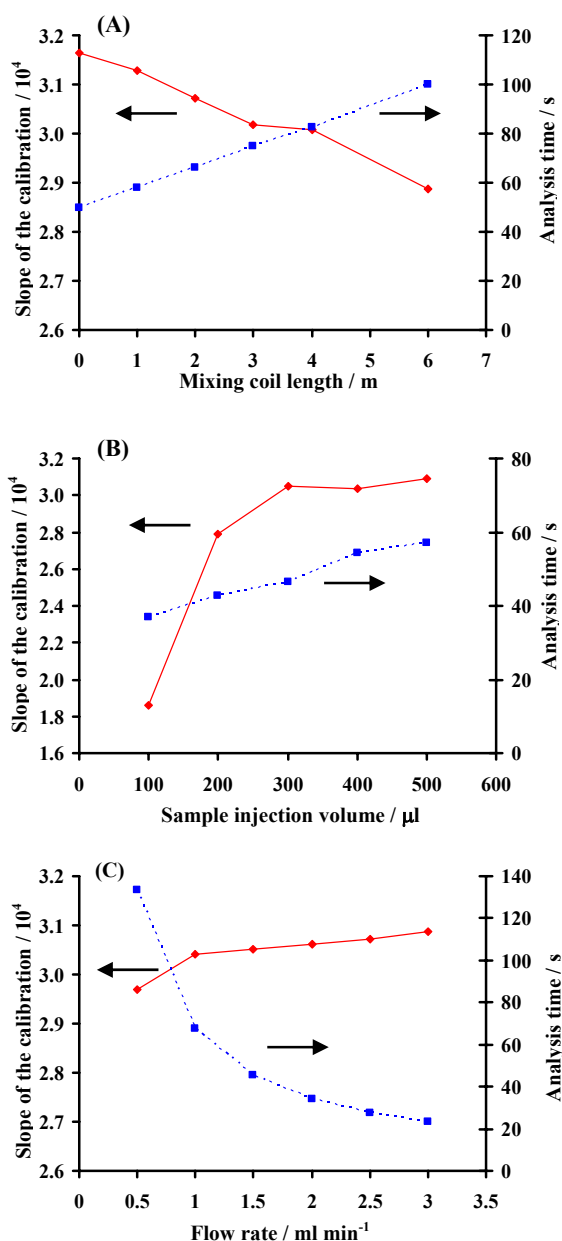


Fig. 5 Effect of FI variables on the slope of the calibration curve (\diamond) and analysis time (\blacksquare). (A) Effect of mixing coil length, (B) effect of sample injection volume and (C) effect of flow rate.

3.2. Analytical characteristics

A calibration graph was constructed under the optimum conditions. A linear relationship between the absorbance and the concentration of iodate (mol l^{-1}) in the range of 1×10^{-6} to $3 \times 10^{-5} \text{ mol l}^{-1}$ was found with a linear equation: $\text{Abs} = (2.92 \pm 0.10) \times 10^4 [\text{IO}_3^-] + (1.26 \pm 0.9)$; $R^2 = 0.999$. Each point in the calibration graph corresponds to the average of three replicate injections of standard iodate solutions. The peak profile of iodate is shown in Figure 6. The repeatability of the method in term of relative standard deviation (RSD) was 0.1 % for $8 \times 10^{-6} \text{ mol l}^{-1}$ of iodate ($n=15$). The detection limit ($S/N=3$) of the method was down to $8.5 \times 10^{-8} \text{ mol l}^{-1}$, which corresponds to 0.5 mg I kg^{-1} of iodized salt, and the sample throughput of 80 injection h^{-1} was achieved.

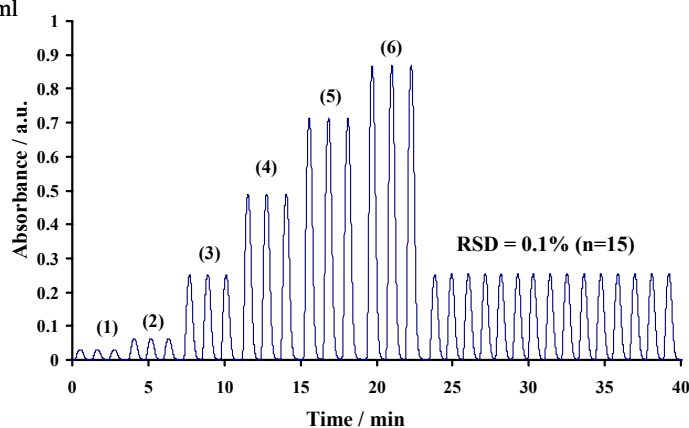


Fig. 6 Flow injection signals for iodate determination. (1-6) standard iodate solution: (1) 1×10^{-6} , (2) 2×10^{-6} , (3) 8×10^{-6} , (4) 1.6×10^{-5} , (5) 2.4×10^{-5} and (6) $3 \times 10^{-5} \text{ mol l}^{-1}$, respectively.

3.3. Interference study

Table 1 Effect of foreign ions ($1 \times 10^{-2} \text{ mol l}^{-1}$) on iodate ($8 \times 10^{-6} \text{ mol l}^{-1}$) determination by the proposed method.

Foreign species ^a	Add as	Relative absorbance / %
None	-	100.0
K^+	KCl	102.0
Ca^+	CaCl_2	102.2
Mg^{2+}	MgCl_2	102.1
SO_4^{2-}	Na_2SO_4	102.4
NO_3^-	NaNO_3	100.3
F^-	NaF	102.4
Br^-	KBr	102.7
I^- ^b	KI	97.2

^a $1 \times 10^{-2} \text{ mol l}^{-1}$

^b $8 \times 10^{-6} \text{ mol l}^{-1}$

The selectivity of the method was assessed by examining the effect of various potential interferences concurrently present in iodized salt on the determination of iodate. Foreign ions may present in sea salt listed in Table 1 were studied for possible effect on the analysis of iodate in iodized salt. Standard iodate of $8 \times 10^{-6} \text{ mol l}^{-1}$ containing a fixed concentration of foreign species of $1 \times 10^{-2} \text{ mol l}^{-1}$ was injected into the FI system in Fig. 1. The results of this study are shown in Table 1. Most of all species gave the deviation in the peak height of iodate within 3% compared to the one obtained for the standard iodate solution. Table 2 shows the percentage of major contents of minerals and elements present in sea salt. It was found that most of metal species present in sea salt at very low concentration. Therefore,

the effect of these ions can be negligible in this work. The result in Table 1 also demonstrates that the tolerance concentration of iodide was at the same amount of iodate tested. However, iodine supplement in iodized salt in tropical countries is iodate form. Moreover, iodide contents in natural sea salt are very low. Therefore, the all major interfering ions possibly present in sea salt do not interfere with the determination of iodate.

Table 2 Major contents of minerals and elements in sea salt.

Element	%	Element	%
Chloride	50.90%	Zinc	.00275%
Sodium	33.00%	Copper	.00195%
Sulfur	.820%	Erbium	.00195%
Magnesium	.441%	Tin	.00192%
Potassium	.227%	Manganese	.0018%
Calcium	.128%	Cerium	.00172%
Silicon	.052%	Fluoride	.00109%
Carbon	.049%	Rubidium	.00084%
Iron	.012%	Gallium	.00083%
Aluminum	.0095%	Boron	.00082%
Praseodymium	.0029%	Titanium	.00079%
Strontium	.00275%	Bromine	.00071%

3.4. Application of the proposed method to the analysis of iodized salt samples and method validation

In order to investigate the analytical applicability of the proposed method, the method was applied to the determination of iodate in iodized salts. The recovery of iodate in the samples was checked by the addition of 4×10^{-6} mol l⁻¹ standard iodate to 2% (w/v) iodized salt solutions. The results are shown in Table 3. The recovery ranged from 99.3 to 106.8 % (n=9), which indicates that the proposed method was successfully applied to the determination of iodate in iodized salt without interfering effect from the components in samples.

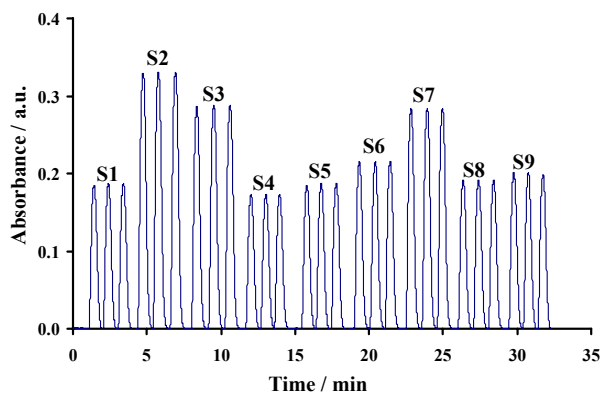


Fig. 7 Flow injection signals for salt sample solution obtained by the proposed FI method (Fig. 1).

Determination of iodate contents in nine samples was carried out. In Figure 7 and 8, flow injection signals for real salt samples were shown: they were obtained by the proposed method and I₃⁻-starch detection method, respectively. The validity of the proposed method was verified by FI system with I₃⁻-starch detection [12] and the standard titration method [13]. Table 4 shows the results obtained by the three methods for the determination of iodate in the iodized salts. The iodate contents obtained by the proposed method, FI with I₃⁻-starch detection and the titration method were statistically comparable by the analysis of variance (ANOVA) test [17], and there was no

significant difference among three method at the P = 0.05 ($F_{\text{observed}} = 0.003$, $F_{\text{critical}} = 3.403$). However, the proposed FI system is simpler and more practical than the other two validating methods. When compared to the FI with I₃⁻-starch detection, cleaning the system after the injection of standards/samples is unnecessary.

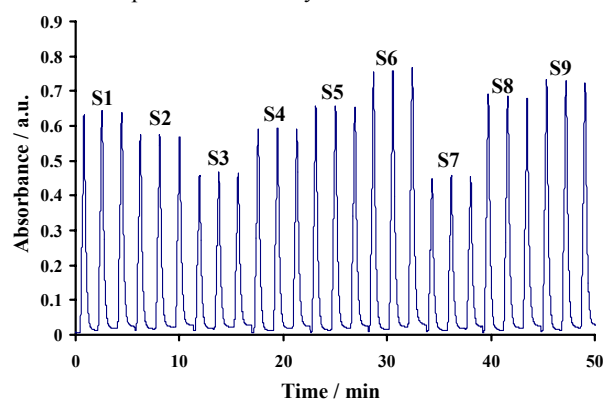


Fig. 8 Flow injection signals for salt sample solution obtained by the FI with I₃⁻-starch detection (Fig. 2). S2, S3, S7: With the dilution of two times prior to the injection into the system.

Table 3 Recovery study of iodate added to the solution of iodized salt samples

Samples	Iodate ^a	Iodate	Found ^a	Recovery
	/ 10 ⁻⁶ mol l ⁻¹	added	/ 10 ⁻⁶ mol l ⁻¹	
		/ 10 ⁻⁶ mol l ⁻¹		
S1	9.68 ± 0.05	4.00	13.9 ± 0.01	105.7
S2	17.9 ± 0.05	4.00	22.0 ± 0.03	103.2
S3	15.6 ± 0.01	4.00	19.6 ± 0.01	100.6
S4	9.35 ± 0.00	4.00	13.6 ± 0.04	106.8
S5	10.2 ± 0.06	4.00	14.4 ± 0.01	106.8
S6	11.7 ± 0.02	4.00	15.9 ± 0.01	105.0
S7	15.4 ± 0.03	4.00	19.4 ± 0.01	101.3
S8	10.4 ± 0.00	4.00	14.5 ± 0.02	104.5
S9	10.9 ± 0.04	4.00	14.9 ± 0.01	99.3

^aMeans (m) of three determinations; m ± σ.

Table 4 Iodate contents in iodized salts determined by the proposed method, FI with I₃⁻-starch detection and the titration method (n=3)

Samples	Iodate content (mg I kg ⁻¹ salt) ± SD		
	Proposed method	FI with I ₃ ⁻ -starch detection method	Titration
S1	61.41 ± 0.30	60.20 ± 0.53	62.50 ± 0.55
S2	113.7 ± 0.29	108.9 ± 1.39	113.9 ± 0.16
S3	98.90 ± 0.06	101.8 ± 0.62	98.08 ± 0.42
S4	59.33 ± 0.01	56.43 ± 0.45	59.62 ± 0.16
S5	64.48 ± 0.40	68.32 ± 0.55	65.69 ± 0.64
S6	73.93 ± 0.13	70.40 ± 0.20	73.46 ± 0.58
S7	97.41 ± 0.17	100.9 ± 0.73	95.27 ± 0.42
S8	65.72 ± 0.02	64.17 ± 1.04	66.05 ± 0.58
S9	69.43 ± 0.28	67.41 ± 0.55	68.64 ± 0.55

4. Conclusion

The FI system using a newly develop colorimetric detection reaction for the determination of iodate was accomplished. The proposed method was found to be a useful spectrophotometric

method for the determination of iodate in iodized salt with respect of simplicity, reliability, good accuracy and precision. Moreover, the method has a high sample throughput (80 h^{-1}), a wide dynamic range and a low limit of detection ($8.5 \times 10^{-8} \text{ mol l}^{-1}$). The proposed method can fulfill all the main demands for a routine analysis of iodized salts. The proposed FI system can be considered as an alternative method for quality control of iodized salts.

Acknowledgements

This work was supported partially by the Grant-in-Aid for Scientific Research (B) (No. 16350044) from Japan Society for the Promotion of Science (JSPS).

References

- [1] A.G. Gilman, L.S. Goodman, T.W. Rad, F. Murad, *The Pharmacological Basis of Therapeutics*, 7th Edition, Macmillan, New York, 1985.
- [2] S.D. Kumar, B. Maiti, P.K. Mathur, *Talanta*, **53**, 701 (2001).
- [3] K.A. Schwehr, P.H. Santschi, *Anal. Chim. Acta*, **482**, 59 (2003).
- [4] L. Rong, T. Takeuchi, *J. Chromatogr. A*, **1042**, 131 (2004).
- [5] K. Yokota, K. Fukushi, S. Takeda, S. Wakida, *J. Chromatogr. A*, **1035**, 145 (2004).
- [6] J. Jakmunee, K. Grudpan, *Anal. Chim. Acta*, **438**, 299 (2001).
- [7] M. Yaqoob, M. Masoom, *Anal. Chim. Acta*, **248**, 219 (1991).
- [8] A. Afkhami, F. Mosaed, *Anal. Sci.*, **18**, 667 (2002).
- [9] N. Choengchan, K. Lukkanakul, N. Ratanawimarnwong, W. Waiyawat, P. Wilairat, D. Nacapricha, *Anal. Chim. Acta*, **499**, 115 (2003).
- [10] A.A. Ensafi, M. A. Chamjangali, *Spectrochim. Acta Part A*, **59**, 2897 (2003).
- [11] Z. Xie, J. Zhao, *Talanta*, **63**, 339 (2004).
- [12] N. Choengchan, K. Uraisin, K. Choden, W. Veerasai, K. Grudpan, D. Nacapricha, *Talanta*, **58**, 1195 (2002).
- [13] J. Mendham, R.C. Denney, J.D. Barnes, M.J.K. Thomas, *Vogel's Textbook of Quantitative Chemical Analysis*, 6th Edition, Prentice Hall, London, 2000.
- [14] H. Sanke, S.A. Ahmed, *Talanta*, **26**, 233 (1979).
- [15] P. Vinas, M.H. Cordoba, C.S. Pedreno, *Talanta*, **34**, 351 (1987).
- [16] Z. Fang, *Flow Injection and Preconcentration*, VCH, New York, 1993.
- [17] J.N. Miller and J.C. Miller, *Statistics and Chemometrics for Analytical Chemistry*, 4th edn, Pearson Education, Essex, 1993.

(Received 16 March 2006)

(Accepted 26 April 2006)