Microfluidic Analysis with Front-Face Fluorometric Detection for the Determination of Total Inorganic Iodine in Drinking Water

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A microfluidic method with front-face fluorometric detection was developed for the determination of total inorganic iodine in drinking water. A polydimethylsiloxane (PDMS) microfluidic device was employed in conjunction with the Sandell–Kolthoff reaction, in which iodide catalyzed the redox reaction between Ce(IV) and As(III). Direct alignment of an optical fiber attached to a spectrofluorometer was used as a convenient detector for remote front-face fluorometric detection. Trace inorganic iodine (IO_3^- and I^-) present naturally in drinking water was measured by on-line conversion of iodate to iodide for determination of total inorganic iodine. On-line conversion efficiency of iodate to iodide using the microfluidic device was investigated. Excellent conversion efficiency of 93 – 103% (%RSD = 1.6 – 11%) was obtained. Inorganic iodine concentrations in drinking water samples were measured, and the results obtained were in good agreement with those obtained by an ICP-MS method. Spiked sample recoveries were in the range of 86%(±5) – 128%(±8) (n = 12). Interference of various anions and cations were investigated with tolerance limit concentrations ranging from 10^{-6} to 2.5 M depending on the type of ions. The developed method is simple and convenient, and it is a green method for iodine analysis, as it greatly reduces the amount of toxic reagent consumed with reagent volumes in the microfluidic scale.

Keywords Microfluidic analysis, front-face fluorescence detection, total inorganic iodine, drinking water

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Introduction

Iodine is one of the important nutrients required for the synthesis of the thyroid hormones, thyroxine and triiodothyronine. These hormones contain iodinated molecules of the amino acid tyrosine and they regulate a variety of important physiological processes.[1] An iodine-deficient diet causes various disorders such as endemic cretinism, congenital anomalies, hypothyroidism, as well as goiter and mental retardation.[2] Iodine deficiency remains a severe public health problem especially in children who suffer severe developmental disorders.[1-3] Low levels of iodine are a significant cause of delayed physical development and lower IQ levels in school-aged children.[2,4] Adolescents and adults need iodine intake of 150 g iodine per day according to WHO.[2] There are various dietary sources of iodine, including water, beverages and foods. Drinking water is the most common source for iodine administration.[5,6] Accurate and sensitive methods for measurement of iodine content in drinking water have been of great interest for better evaluation of the impact of drinking water with iodine supplementation on public health, such as the effects on the intelligence of youth and the link between the regional distribution of iodine in drinking water and goiter.[4-6] Therefore, a simple and convenient method with a greener approach for iodine analysis is needed. There are a variety of methods reported in the literature for measurement of trace iodine.[7] These methods are based on principles such as electrochemistry,[8-10] separation techniques,[11] chemiluminescence,[12,13] spectrophotometry[14-21] and spectrofluorometry.[22] Although conventional ICP techniques[23] have been employed for iodine measurement, it requires high-cost instrumentation, high maintenance costs, with low sample analysis throughput. Several methods have been developed employing flow-based techniques, which were previously reported to achieve sensitive detection of iodine in an automated manner. Measurement of

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Table 1 Comparison of flow-based method for kinetic determination of total inorganic iodine with mol and volume of Ce(IV) and As(III) consumption, characteristics of the method (linearity and LOD) and heating requirement

Ref.	Total Ce(IV) and As(III) consumed/run (μmol [μL])	Inorganic iodine species (I^-, IO_3^-) (conversion study)	Linearity, LOD (μg L^{-1}, μg L^{-1})	Temperature applied to the reaction zone (°C), flow procedure	Application	Advantage of method of iodine analysis
Visible absorption detection						
Flow injection analysis (FIA)						
18	73.9 [1360]	(I^- + IO_3^-)	50 - 200, 2.3	T = 43°C, continuous flow	Urine	High-throughput
	30.7 [560]	NA[a]		No heating, stopped-flow		
21	58.8 [2600]	(I^- + IO_3^-)	50 - 1000, 9.3	No heating, stopped-flow	Drinking water	Wide linear range
Sequential injection analysis (SIA)						
14	4.0 [500]	I^-	10 - 200, 1.5	T = 40°C, sequential flow	Pharmaceuticals and drinking water	Full automation
		NA[a]				
Multi-syringe flow system (MSFIA)						
15	0.5 [600]	I^-	4.3 - 70, 0.5	T = 45°C, continuous flow	Pharmaceuticals and seawater	Low detection limit
		NA[a]				
Fluorescence emission detection						
Multi-syringe flow system (MSFIA)						
22	18.6 [600]	I^-	1 - 100, 0.3	No heating, continuous flow	Seawater	Portable Low detection limit
		NA[a]				
Microfluidic system						
This work	1.1 [23]	(I^- + IO_3^-)	50 - 400, 7.7	No heating, stopped-flow	Drinking water	Very low reagent consumption, simple and green method

a. NA: Not available.

iodine content in various sample matrices including pharmaceuticals,[13-15] urine,[10,16-19] seawater specimens,[15,22] iodized salts,[10,20] plant,[9] and drinking water.[14,21] Most of these methods utilized the Sandell-Kolthoff reaction[24] in which iodide catalyzed the redox reaction between Ce(IV) and As(III) due to its sensitivity for detection of very low levels of iodide (parts per billion) (see Table 1). Iodate ion is also present in water samples. Hence an "on-line" conversion of iodate to iodide, prior to performing the catalytic reaction of As(III) and Ce(IV), is required for the analysis of total inorganic iodine. As(III) has been used as the reducing agent as it is already a component of the Sandell-Kolthoff reaction.[18,21,25,26]

In this work, a simple microfluidic method employing the Sandell-Kolthoff reaction, with front-face fluorometric detection of Ce(III) in the stopped-flow mode, was developed for the determination of inorganic iodine in natural drinking water. The developed microfluidic platform is convenient for attachment of fiber-optics for fluorometric detection and reduction of toxic reagents consumption. Cerium and arsenic are toxic and therefore minimizing the volumes of these chemicals would be beneficial for an environmentally friendly analytical method.

Experimental

Chemicals and preparation

All solutions were prepared using ultra-purified water (18.0 MΩ cm^{-1}) from an Ultra Clear™ TWF system (Siemens, Munich, Germany). Standard iodide solution of 1000 mg L^{-1} was prepared as a stock solution of potassium iodide (99.5% assay, Merck, Germany). The As(III) solution (0.1 M) was prepared by dissolving 2.0 g of As_2O_3 (95.5% assay, Ajax, New Zealand) and 4.7 g of NaCl (Merck, Germany) in 50.0 mL water with heating on a hot plate. After cooling to room temperature, 2.8 mL of concentrated H_2SO_4 (Merck, Germany) was gradually added. The solution was then diluted with water to 100.0 mL. Ce(IV) solution (0.8 mM) was prepared by dissolving 0.5 g of $Ce(NH_4)_4(SO_4)_4{\cdot}2H_2O$ (98% assay, Merck, Germany) in 100.0 mL of 1.75 M H_2SO_4 solution.

Front-face fluorescence with microfluidic analysis system

Figure 1(a) shows the set-up of the microfluidic flow system. The PDMS microfluidic device has three inlets for Ce(IV), As(III) and sample solution lines. The microchannel was 300 μm deep and 500 μm wide. The detection window was circular in shape (4.5 mm diameter). Fabrication details of the PDMS device can be found in Supporting Information A. PTFE tubing (0.5 mm i.d.) was used for all the flow lines. A black acrylic box (36.5 cm width, 38.5 cm length, 36.5 cm height) was used for light protection during detection of the fluorescence emission. The syringe pump (SP1) (Model 11 plus, Harvard, USA) was employed for delivery of the reagent solutions (As(III) and Ce(IV) solutions, see Fig. 1(a)). The pump SP2, a metering syringe pump, Model KSD 200 (KD Scientific, USA) was used for injection of a fixed volume of a sample/standard solution into the microfluidic manifold. The volume of the two syringes of pump SP1 was 10.0 mL and the volume of syringe of the SP2 was 1.0 mL. Fluorescence detection was carried out at λ_{ex} = 254 nm, λ_{em} = 365 nm of the Ce(III) product (see Supporting Information B for the emission spectrum). Front-face fluorometric detection was carried out at the circular area of the PDMS microchip using a fiber optic accessory cable (L225-0144, Perkin Elmer, UK) connected to the LS-50B spectrofluorometer (Perkin Elmer, UK). The illumination end of the fiber optic was held in place by an in-house constructed acrylic holder mounted over the detection zone (see Fig. 1(b)).

Microfluidic flow procedure

The manifold of the microfluidic flow system is shown in Fig. 1(a). The flow rate for the two reagent solutions was 10.0 μL min^{-1}. Sample injection of 10.0 μL was carried out at a flow rate of 20.0 μL min^{-1}. The three flow lines meet at a single point (CP in Fig. 1(c)) just before the spiral mixing line. The following stepwise flow procedure was performed.

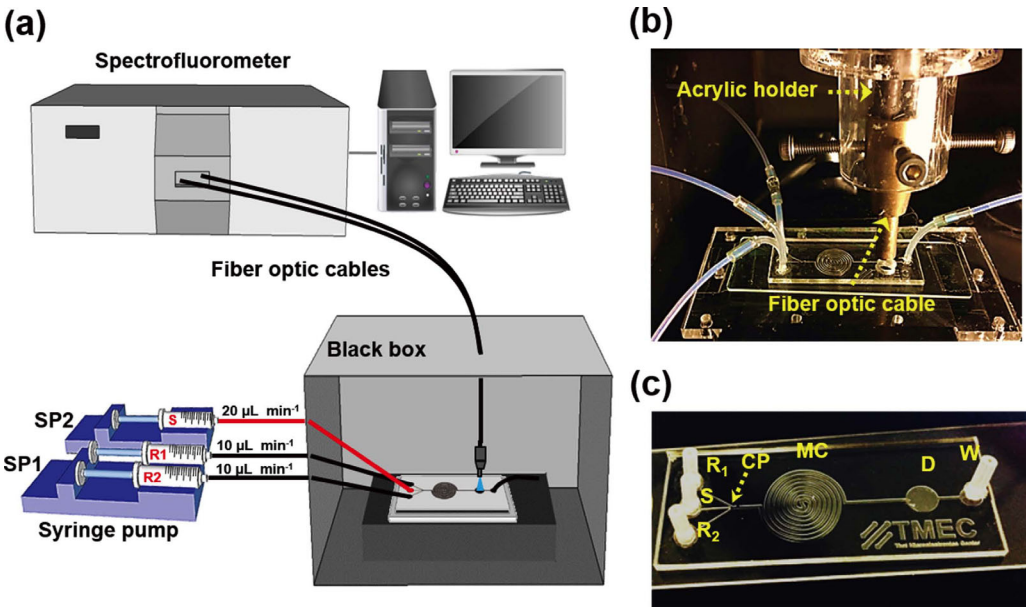

Fig. 1 (a) Schematic diagram of the microfluidic system for kinetic determination of trace inorganic iodine by front-face fluorometric detection. It consists of SP1: syringe pump for reagents, SP2: syringe pump for introduction of sample. The channel in the PDMS microchip is 300 µm deep and 500 µm wide. A fiber optic cable from the spectrofluorometer is installed above the detection window for excitation (λ_{ex} = 254 nm) and emission (λ_{em} = 365 nm). (b) Experimental setup for front-face fluorescence at the detection zone. (c) Design of the microfluidic platform. S, Sample inlet; R1, As(III) reagent solution; R2, Ce(IV) solution; CP, confluence point; MC, mixing channel (spiral); D, detection window; W, waste.

Step 1: The reagent solutions; R1 and R2 (As(III) and Ce(IV) solutions) were simultaneously pumped into the manifold by SP1. Step 2: Standard/sample solution at a flow rate of 50.0 µL min^{-1} was pumped by SP2 for 40 s (*i.e.* 34.0 µL) to flush out the old solution in the S line (Fig. 1(a)). Step 3: A 10.0-µL plug of standard/sample solution at a flow rate of 20.0 µL min^{-1} was injected to mix with the reagents using pump SP2. Step 4: The syringe pump SP1 was paused for 2.0 min (stopped-flow mode) for measurement of fluorescence emission. Step 5: The solution in the detection zone was propelled to the outlet by re-starting pump SP1. For the replicate analysis, Steps 3 to 5 was performed. For a new sample/standard solution, the pumps were stopped and the sample solution of the SP2 syringe replaced. Then, Steps 1 to 5 was carried out.

Results and Discussion

A simple front-face fluorescence detection for microfluidic system

Front-face fluorescence detection was carried out by focusing the excitation light near the surface of the microfluidic detection area and the fluorescence emission measured at the same front surface of the device. Front-face fluorometric detection has the advantage of simple optical alignment and is especially suitable for a device with very short optical path length. It also has been successfully used for measuring fluorescing compounds in samples with very large absorbances.[27,28] The LS-50B spectrofluorometer (Perkin Elmer, UK) has a fiber optic accessory cable for front-face fluorescence detection. Figure 1(b) shows the positioning of the optical fiber on top of the microfluidic platform. The PDMS microfluidic device has a 500 µm channel depth, which constitutes the optical path length for the fluorescence detection. Iodide ion catalyzed the redox reaction between As(III) and Ce(IV), producing the fluorescing Ce(III) product ion. Front-face detection avoids direct contact between the highly acidic reagent solutions and the fiber optics.[21]

Optimization of flow conditions

The flow conditions were investigated to optimize the detection sensitivity for trace iodine detection. Concentrations of reagent solutions (0.1 M As(III) in 0.5 M H_2SO_4 containing 0.8 M NaCl and 8 mM Ce(IV), in 1.75 M H_2SO_4) were adopted from previous work.[18] The micro-flow system is shown in Fig. 1(a). Effect of flow rates of reagent and sample streams, and volume of sample injected were studied. Other parameters of this investigation are listed in Table S1 (Supporting Information C). Standard iodide solutions at concentrations of 0 – 100 µg L^{-1} were used to construct the linear calibration lines.

Flow rate of reagents and sample streams. Figure S3(a) (Supporting Information C) shows the effect of flow rates of 5.0 to 20.0 µL min^{-1} of the reagents on the slope of the calibration curves (sensitivity). The sensitivity of detection decreased 60% upon increasing the flow rate of the reagents. This reduction of sensitivity at high flow rate of reagent is due to the shorter reaction time before the commencement of the stopped-flow mode. The flow rate of the metering pump SP2 for sample injection was varied but set to deliver 10.0 µL of sample. The flow rate of sample line was varied to check the effect of flow rate on the sensitivity of iodide detection (slope of calibration line). Figure S3(b) shows that there was no change in the sensitivity with the use of the sample line flow rates between 5.0 – 20.0 µL min^{-1}, and the 20.0 µL min^{-1} flow rate was selected for faster analysis. In summary, flow rates of 10.0 µL min^{-1} were thus chosen for delivery of the reagents whereas 20.0 µL min^{-1} was used for the introduction of a sample solution, giving suitable sensitivity and sample throughput.

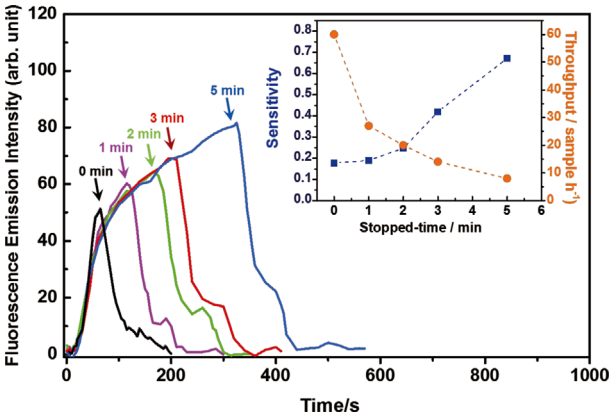

Fig. 2 Fluorometric signal profiles for stop time intervals of 0, 1.0, 2.0, 3.0, and 5.0 min. Inset shows the plot of the effect of stop time interval *vs.* sensitivity (slope of calibration line) and number of analysis per hour (sample throughput).

Sample injection volume. The volume of a standard iodide solution was varied at the fixed flow rate of 20.0 µL min^{-1}. The metering pump SP2 was set to deliver 2.0, 3.0, 4.0, 5.0, 8.0, and 10.0 µL, respectively. As shown in Fig. S3(c) the highest injection volume employed (10.0 µL) gave the largest sensitivity and was therefore selected for the final routine procedure (see Fig. 1(a)).

Stopped-flow procedure for improvement of sensitivity of iodide detection

The reduction of Ce(IV) to Ce(III) by As(III) as catalyzed by iodide (Sandell–Kolthoff reaction) is specific and sensitive for trace iodide detection. However, the reaction is kinetically slow. Thus, the longer the reaction time is allowed for Ce(III) production the greater the fluorescence emission obtained. Flow-based methods, such as flow-injection analysis or sequential injection analysis, commonly employ a stopped-flow procedure for this purpose (see Table 1).[16,18,21] Therefore the stopped-flow procedure for the microfluidic device (Fig. 1(a)) with a reaction zone volume of only ~20 µL was carried out. The flow conditions are as given in Fig. 1(a). The stopped-flow procedure was performed by pausing the syringe pumps, which results in stopping the reaction zone during detection of the fluorescence emission. Stop time intervals of 1.0, 2.0, 3.0 and 5.0 min were studied. Figure 2 shows the profiles of fluorescence emission signal for various stopped-time of the reaction zone. As shown in Fig. 2 (inset) the stopped-flow procedure enhanced the detection sensitivity by 50% when using a stop time interval of 2.0 min as compared to detection using continuous flow (*i.e.* FIA mode). However longer stopping time led to less sample throughput (Fig. 2 (inset)). Consequently a 2.0-min stop interval was selected as an optimal period. A high precision of stopped-flow control was obtained (1.4 – 2.7% RSD). A sufficient LOD (7.7 µg iodide L^{-1}) was attained without the requirement of heating of the reaction mixture (see Table 1). Figure 3(a) illustrates the stopped-flow profiles and Fig. 3(b) shows the calibration line. The method demonstrated a wide linearity range of 50 – 400 µg iodide L^{-1} (r^2 >0.99). The precision of the method was 2.3% RSD (n = 7, 50 µg iodide L^{-1}), and the sample throughput was 20 samples h^{-1}, which is suitable for analysis of natural drinking water.

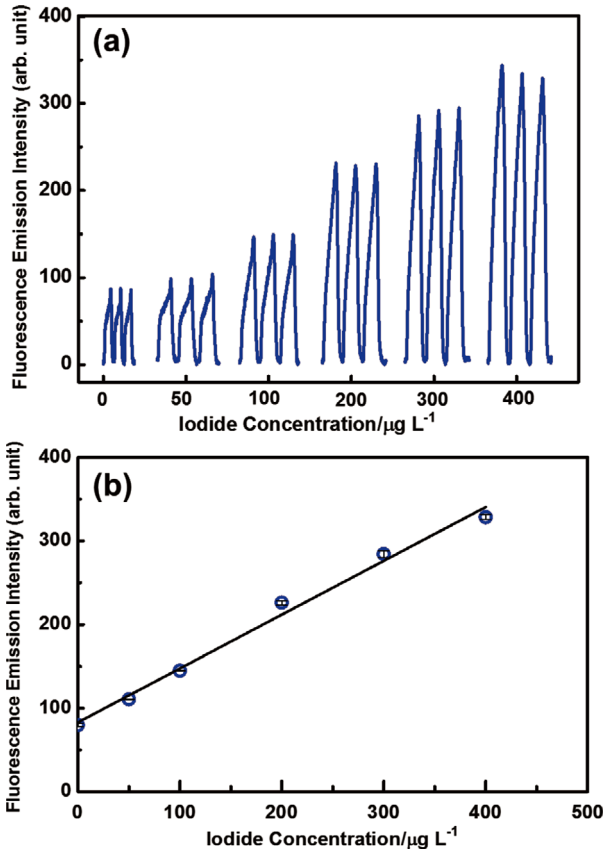

Fig. 3 (a) Fluorescence profile obtained from injection of standard iodide solutions (0, 50, 100, 200, 400 µg L^{-1}). (b) Calibration curve for standard iodide, $y = (0.6439 \pm 0.031)x + (82.99 \pm 6.932)$, r^2 = 0.9910. Flow conditions: flow rate of reagents 10.0 µL min^{-1}; injection volume 10.0 µL at 20.0 µL min^{-1}; fluorometric detection, λ_{ex} = 254 nm, λ_{em} = 365 nm.

Efficiency of the on-line reduction iodate to iodide

As iodate ion is also present in drinking water samples[29-31] reduction of iodate to iodide is required prior to its determination by the Sandell–Kolthoff reaction. A solution of As(III) can be employed as the reducing agent.[18,21,25,26] We also employed chloride at a concentration of 0.8 M, which is contained in the As(III) solution (R1, Fig. 1(a)). Chloride ions have been found to catalyze the reduction of iodate to iodide by As(III).[16] Thus As(III) takes part in two chemical reactions. It acts as a reducing agent for conversion of iodate to iodide (catalyzed by chloride ion) and is then employed in the reduction reaction of Ce(IV) to Ce(III) (catalyzed by iodide ion).[26]

The on-line procedure for the conversion of iodate to iodide of the microfluidic device was investigated. Figure 4 shows the bar graphs of the measured concentrations of iodide. The flow conditions used in this study are as given in Fig. 1(a). Standard solutions of pure iodate, pure iodide and a mixture of iodate and iodide (mole ratio 1:1) were employed with various concentrations of measured iodide (50, 100, 200 and 400 µg iodide L^{-1}). As shown in Fig. 4 the reduction of pure iodate or a mixture of iodate and iodide is complete using the on-line flow procedure. The percentage of conversion was 96 – 103% for iodate concentration of 50, 100 and 200 µg iodide L^{-1}. The mixtures of iodate and iodide gave similar conversion efficiencies of 93 – 102%. Thus the microfluidic system achieved effective and rapid conversion of iodate to iodide.

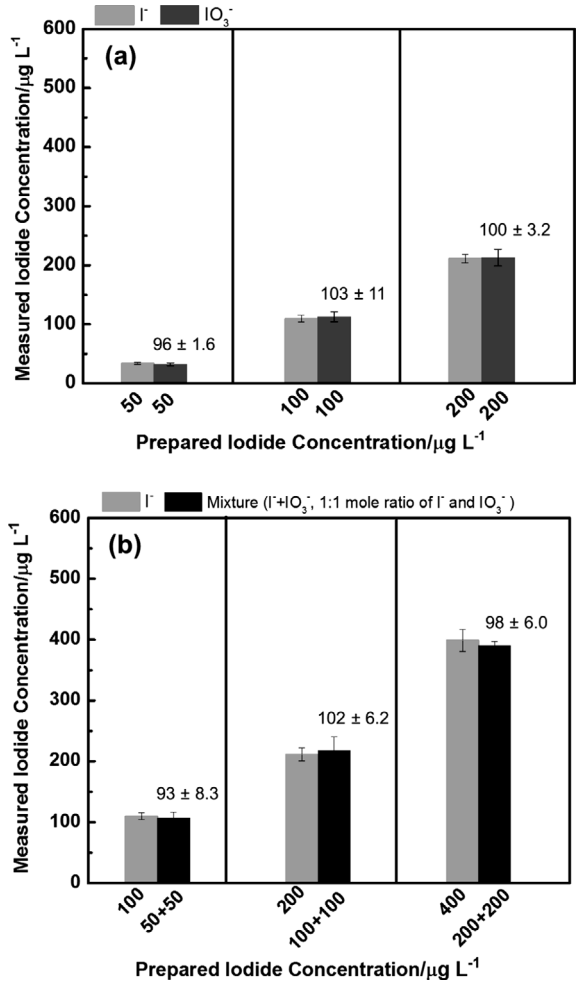

Fig. 4 (a) Percentage conversion of iodate (IO_3^-) to iodide (I^-) at various concentrations of iodate. (a) Iodate concentrations equivalent to 50, 100 and 200 μg iodide L^{-1} compared to pure iodide solution of 50, 100 and 200 μg L^{-1}. (b) Mixtures of iodate and iodide (mole ratio 1:1) with total iodide of 100, 200 and 400 μg L^{-1} compared to pure iodide solution of 100, 200 and 400 μg L^{-1}.

Performance comparison of the flow-based analysis method: Green method of analysis

There are reports on flow-based analysis methods, such as flow injection analysis (FIA) and sequential injection analysis (SIA), which are simple and, provide good linearity and LOD as listed in Table 1. Those flow methods employ visible absorption detection with high consumption of reagent volume (0.5 – 2.6 mL) (Table 1). A chip-based multi-syringe flow injection system (MSFIA) was reported for reducing the reagent consumption.[22] However, volumes consumed by the chip-based MSFIA method are higher than those required for microfluidic analysis, with volumes of reagent consumption of up to 600 μL. Sandell-Kolthoff reagents, *i.e.* As(III) and Ce(IV)), are highly toxic. Thus it is preferable to minimize their use in terms of both mass and volume. Our method provides a green alternative by allowing minimization of reagent consumption (only 23.0 μL, containing 1 μmol of As(III) and Ce(IV) per analysis), reducing the amounts of reagents required by up to 20-fold. In addition, it was observed that by reducing the scale to microfluidic analysis a sufficient LOD was attainable without the requirement of heating of the reaction mixture (see Table 1, column 4). Heating of solution generally makes the reaction more prone to production of air bubbles, which can interfere with detection process. There is also the further advantage of less electrical energy consumption (see Table 1, column 5).

Table 2 Tolerance limit study of various interfering ions by addition to standard iodide solutions (50 μg iodide L^{-1})

Interfering ion	Added as	Tolerance limit/M[a]
SCN^-	KSCN	1.0×10^{-6}
Br^-	KBr	4.0×10^{-2}
F^-, K^+	NaF, KCl	3.0×10^{-2}
HCO_3^-, PO_4^{3-}	$NaHCO_3$, K_3PO_4	2.0×10^{-2}
Ca^{2+}	$CaCl_2$	0.1
SO_4^{2-}	Na_2SO_4	0.2
Mg^{2+}	$MgCl_2$	0.5
Cl^-	NaCl	2.5

a. Tolerance limit is defined as the minimum concentration of the ion that caused a signal alteration of greater than ±5%.

Interference study

Interference studies of possible interfering ions on the iodine quantification were performed. Anions included F^-, Cl^-, HCO_3^- and SO_4^{2-}. Cations included K^+, Ca^{2+} and Mg^{2+}. These are species which can potentially be found in drinking water and could interfere with the Sandell-Kolthoff reaction. Limit of tolerance was defined as the concentration that led to signal change of a 50 μg L^{-1} standard iodide solution of more than 5%. As shown in Table 2, the order of potential interfering species is as follow: $SCN^- > Br^- > F^-$, $K^+ > HCO_3^-$, $PO_4^{3-} > Ca^{2+} > SO_4^{2-} > Mg^{2+} > Cl^-$, with the tolerance limits concentration ranging from 10^{-6} to 2.5 M depending on the type of ions. These ions are typically present in drinking water at concentrations in the range of 10^{-5} – 10^{-2} M. These values (*i.e.* 10^{-6} to 2.5 M) are not found in drinking water and thus they should not interfere with the iodine analysis.

Determination of total inorganic iodine in drinking water sample

Analysis of total inorganic iodine in four brands of drinking water samples, *i.e.* Sample A, B, C, and D, was performed by the developed microfluidics method with front-face fluorometric detection. The commercial drinking water samples were obtained from supermarkets located in Bangkok, Thailand. The drinking waters were labeled as natural water (ground water) from Pathumthani and Singburi provinces of central Thailand. For each sample three bottles were selected for analysis. The samples were directly injected into the microfluidic system. Table 3 lists the measured iodine content for the 12 samples as compared to values obtained from the ICP-MS analysis (see Supporting Information D). The two data sets were compared using paired *t*-test[32] (see Table 3, columns 1 and 2). It was found to be not significantly different at a 95% confidence level ($t_{obs} = -0.088$, $t_{cri} = 2.201$, $d_f = 11$). Iodine contents were in the range of 79.8 ± 3.8 – 133.6 ± 0.8 μg L^{-1}. These values were in the same range that has been previously reported.[6,21] As recommended, dietary iodine intake should be 150 μg per day for men and woman, while a slightly higher iodine intake of 250 μg per day is recommended for pregnant women.[2] Hence, approximately 1 to 2 liters of these drinking water containing iodine is enough to provide the daily intake of iodine.

Sample recovery percentage

Sample recovery was determined by spiking pure iodide into the drinking water samples at added iodide concentrations of 50 μg L^{-1}.

Table 3 Determination of iodide content in four natural drinking water samples (A, B, C and D)

Sample	Total inorganic iodine (μg iodide L^{-1})				% Recovery (mean ± SD)
	ICP-MS (mean ± SD)	Microfluidic method with front-face fluorescence detection			
		Non-spiked sample (mean ± SD)	Standard spiked	Spiked-sample (mean ± SD)	
Sample A					
A1	90.1 ± 1.5	95.3 ± 4.8	50.0	143.5 ± 3.0	96 ± 6
A2	86.7 ± 1.5	90.2 ± 1.8	50.0	139.3 ± 3.6	98 ± 7
A3	88.3 ± 3.0	90.9 ± 4.6	50.0	141.2 ± 4.2	101 ± 10
Mean	88.4 ± 1.7	92.1 ± 2.8			
Sample B					
B1	86.7 ± 1.1	87.2 ± 3.2	50.0	133.5 ± 1.3	93 ± 4
B2	86.4 ± 0.9	81.6 ± 1.7	50.0	127.1 ± 2.2	91 ± 6
B3	88.0 ± 2.4	79.8 ± 3.8	50.0	124.2 ± 1.6	89 ± 6
Mean	87.0 ± 0.9	82.9 ± 3.9			
Sample C					
C1	90.2 ± 1.2	81.8 ± 3.1	50.0	145.7 ± 2.6	128 ± 8
C2	83.7 ± 3.4	88.3 ± 1.8	50.0	140.5 ± 1.2	104 ± 7
C3	91.2 ± 1.4	80.3 ± 2.5	50.0	103.1 ± 0.6	99 ± 8
Mean	88.4 ± 4.1	83.5 ± 4.3			
Sample D					
D1	93.9 ± 0.7	97.7 ± 5.0	50.0	143.2 ± 2.0	91 ± 3
D2	126.7 ± 1.0	131.7 ± 2.4	50.0	172.4 ± 2.5	86 ± 5
D3	128.5 ± 1.3	133.6 ± 0.8	50.0	182.0 ± 1.4	97 ± 8
Mean	116.4 ± 19.5	121.0 ± 20.2			

Content as determined by ICP methods are compared to those determined by the microfluidic method with front-face fluorescence detection. The percentage of spiked sample recovery for the microfluidic method is shown.

The recovery percentage was calculated as

$$\%\text{sample recovery} = \frac{S_1 - S_2}{S_0},$$

where S_0 is the peak height of the standard iodide solution, S_1 is the peak height of the spiked sample, and S_2 is the peak height of the non-spiked sample. The recovery percentages of spiked samples using our developed method were 86%(± 5) - 128%(± 8) (n = 12).

Conclusions

Our microfluidic analysis method was developed employing front-face fluorometric detection for trace inorganic iodine analysis in natural drinking water. The method employing a PDMS device greatly reduced the amounts of reagents consumed, as the volume of the microchip is approximately 28 μL. Our method provides a green alternative by minimizing toxic reagent consumption (reagent volume of only 23.0 μL with 1.1 μmol of As(III) and Ce(IV) per analysis), a 20-fold reduction compared with other flow-based systems (see Table 1). Previous reported methods employ volumes from 500 - 2600 μL per analysis.[14,15,18,20,21] This method also employs an on-line reduction process of the iodate ion using the same As(III) reagent employed in the iodide analysis. A stopped-flow procedure provided the sensitivity for analysis of total inorganic iodine (iodide and iodate ions) in natural drinking water without the need for heating the system. The developed system has the potential to be used as a cost-effective analysis method for monitoring the total inorganic iodine content in drinking water.

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Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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