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Chemiluminescence determination of iodide and/or iodine using a luminol–hexadecyltrimethylammonium chloride reversed micelle system following on-line oxidation and extraction

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A rapid and sensitive flow method, based on the combination of on-line oxidation–solvent extraction with reversed micellar mediated luminol chemiluminescence detection, was found to be suitable for the determination of iodide in aqueous solution. The flow procedure involved the oxidation of iodide to iodine, extraction of iodine into cyclohexane followed by membrane phase separation, and its chemiluminescence detection using the reaction of iodine with luminol in a reversed micellar solution of hexadecyltrimethylammonium chloride in 6 + 5 (v/v) chloroform–cyclohexane/water (buffered with sodium carbonate). The optimum conditions for iodide oxidation were evaluated using 2-iodosobenzoate as an oxidizing agent and a detection limit of 0.02 ng mL^{-1} iodide was achieved. Using different oxidants, 2-iodosobenzoate and peroxodisulfate, linear calibration graphs were obtained with dynamic ranges from 5 to 200 and from 50 to 5000 ng mL^{-1}, respectively. The proposed method was also applied to a mixture of iodine and iodide, where iodine was determined directly without using an oxidizing agent, total iodine (iodine + iodide) was determined using an oxidizing agent, and iodide was calculated by difference. The method was applied to the differential determination of iodide and iodine in gargle samples with a precision of *ca*. 4% relative standard deviation.

Introduction

Iodine is an essential nutrient in the human diet and is found in many foods, both naturally or added as a supplement. Iodine compounds are also sometimes used in the dairy industry and can be found in milk mainly as iodide. In order to determine low concentrations of iodide, many methods based on different principles have been proposed.[1–5] However, most of the reported methods either lack selectivity or are less sensitive. The selective procedures require relatively extensive sample preparation and are time consuming. Complicated instruments are also used when high sensitivity is desired.

With respect to sensitivity and time/cost budget, chemiluminescence (CL) methods of analysis have been shown to have the advantages of experimental simplicity, sensitivity, and low unit cost of equipment compared with other methods. CL reactions have been reported for the determination of halogens, halides and hypohalites with much lower detection limits.[6] The use of the CL reaction of luminol oxidation is interesting because it permits the determination of iodine with a detection limit of 0.1 ng mL^{-1}.[7] Since halides do not cause luminol CL, it is necessary to convert them into a form that is active in the CL reaction (*e.g.*, conversion of iodide into iodine), with subsequent separation from the oxidant and acid which could interfere with the CL determination.[8,9] However, the determination of iodine in aqueous solution has some handicaps: *e.g.*, the pH-dependent and concentration-dependent equilibria of iodine with hypoiodous acid, iodide ion, triiodide ion, *etc*., and the irreversible loss by iodate formation in alkaline solution.[7,10] Moreover, by using the luminol CL reaction, several metal ions in aqueous solution may interfere with iodine determination and thus their removal is needed by incorporating separation science techniques into the procedure.[8,9] Also, some of the organic solvents used to dissolve luminol have a suppressing effect on the luminol CL reaction.[11] Before CL detection in aqueous solution, extraction into the aqueous phase or evaporation of the organic solvent was carried out.[9]

To achieve enhanced sensitivity and improved selectivity in addition to other advantages, a reversed micellar medium was successfully incorporated and several systems were studied with respect to their analytical utility.[12–14] By dispersing a small amount of water in the bulk apolar organic medium containing surfactant molecules, a macroscopically homogeneous solution of reverse micelles is produced. The structure of reverse micelles is such that a water droplet is surrounded by surfactant polar heads, while the surfactant hydrophobic chains are directed into the bulk organic phase; the reverse micelle functions as a microreactor.[15] With the additional advantage of sensitivity, the microreactor has the capability to transfer species of experimental interest quantitatively into the water pool and convert them into CL active species at the surfactant/water interface,[14,16,17] where the reversed micellar mediated CL (RMM-CL) reactions are believed to occur.[13,18] New CL methods for the trace level quantification of iodine,[14] gold(III),[19–22] rhodium(III),[23] iron(III),[16,24] iron(II),[24] vanadium(IV)[17,18] and atropine[25] were developed using flow systems and the aforementioned problems associated with aqueous phase CL detection were either eliminated or greatly reduced by

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coupling solvent extraction directly to the RMM-CL detection. Previously, we have indicated the possible analytical usefulness of the RMM-CL reaction of luminol with iodine.[14] The present method was found to be potentially useful for the on-line differential and selective CL determination of iodine and iodide, where quantitative oxidation of iodide to iodine and membrane-based solvent extraction of iodine were simultaneously carried out prior to CL analysis. It was reported that 2-iodosobenzoic acid has the ability to oxidize iodide into iodine selectively under neutral or mildly acidic conditions.[1] In this work, the use of 2-iodosobenzoic acid as an oxidant was tested. Furthermore, a comparative study of the oxidant was carried out using sulfuric acid solutions of 2-iodosobenzoic acid, peroxodisulfate, and dichromate. The extraction procedure was effective in selectively separating iodine from the reactants, oxidant, acid, and metallic species that could otherwise interfere with the aqueous phase CL determination of iodine.

Experimental

Chemicals

Luminol was purchased from Aldrich (Milwaukee, WI, USA). The surfactant, hexadecyltrimethylammonium chloride or cetyltrimethylammonium chloride (CTAC), and 2-iodosobenzoic acid were obtained from Tokyo Kasei Kogyo (Tokyo, Japan). Ammonium peroxodisulfate and sulfuric acid (97%, trace analysis grade) were obtained from Kanto Chemical (Tokyo, Japan). Cyclohexane and iodine were purchased from Katayama Chemical Industries (Osaka, Japan). Chloroform (containing 0.5–0.9% v/v ethanol as stabilizer) and potassium iodide were purchased from Wako Pure Chemical Industries (Osaka, Japan). Anhydrous sodium carbonate (99.98%, analytical grade) was obtained from Asahi Glass (Tokyo, Japan). All other reagents were of analytical-reagent grade. All chemicals were used as received. De-ionized water was freshly collected from an Advantec Toyo (Tokyo, Japan) Model GSU-901 water-purification apparatus and utilized in the preparation of all aqueous solutions and related cleaning purposes. To prepare the oxidant solution (0.38 mM), 2-iodosobenzoic acid was dissolved in a small amount (10 mL) of 0.2 M sodium hydroxide and diluted to final volume with 2.5 M sulfuric acid. Also, a 0.10 M solution of ammonium peroxodisulfate was prepared in 2.5 M sulfuric acid and used as an oxidant. A 500 μg mL^{-1} stock solution of iodide was prepared by dissolving potassium iodide in water. Working solutions of iodide and iodine were prepared daily when required and kept in dark brown glass containers to protect the solutions from exposure to light or to avoid any photochemical reactions. All glassware was soaked in 20% nitric acid and thoroughly cleaned before use. Gargle samples were commercially available and purchased locally.

Apparatus

The multi-component instrument (Fig. 1), used for the reverse FI system of on-line continuous extraction, membrane phase separation and CL detection, was the same as that reported in our previous paper,[24] except that a home-made glass extraction coil (1.5 mm id, 1.5 m length) was used to avoid iodine loss due to adsorption by plastic tubing. The phase separator with a 0.22 μm microporous Teflon membrane (a thickness of 60 μm) was also the same as reported earlier.[22,24] At the aqueous waste end, a restrictor coil (0.5 mm id, 45 cm length) was used to facilitate phase separation *via* the Teflon membrane. PTFE tubing of 0.5 mm id was used throughout the flow system. An ordinary strip-chart recorder was used to record the CL signals.

Analytical procedure

Using peristaltic pumps (Fig. 1), the aqueous sample solution (100 mL) of only iodide (0.5–200 and 0.02–0.5 ng mL^{-1} when the oxidant solutions in 2.5 M H_2SO_4 and in 5 mM H_2SO_4 were used, respectively) or iodide containing iodine (0.05–5000 ng mL^{-1})[14] was pumped with a flow rate of 8 mL min^{-1} and mixed with the oxidant solution of 2-iodosobenzoic acid (0.38 mM) at a flow rate of 3 mL min^{-1}. For the determination of iodine alone, distilled, de-ionized water was pumped into the line instead of oxidant solution. Using a plunger pump with a flow rate of 2 mL min^{-1}, the organic solvent stream of cyclohexane was mixed with the combined aqueous stream of sample and oxidant; the resulting ratio of the flow rates dictated an aqueous-to-organic volume ratio of 11 : 2. The mixture was passed through the glass extraction coil where iodine was transferred from the aqueous into the organic phase. The two phases were separated using a Teflon membrane. Nearly 85% of the organic phase was membrane-transferred and passed onward in the line. The reversed micellar solution of luminol was prepared daily as described previously[24] by dispersing a certain volume of the carbonate-buffered stock solution (0.2 M Na_2CO_3, pH 11.5) of luminol in a reversed micellar bulk solvent of chloroform–cyclohexane (6 + 5, v/v) containing 0.130 M CTAC; a water-to-surfactant molar concentration ratio ($[H_2O]$: [CTAC]) of 10 : 1 was used in making the reversed micellar solution which was 2.0×10^{-4} M with respect to the final luminol concentration. After suction into a loop of 20 μL, the reversed micellar luminol solution was inserted into the carrier stream of chloroform by using a rotary injection valve. The carrier was driven at a flow rate of 3 mL min^{-1}. In a 70 μL spiral flow cell mounted in front of the phototube of the photometer, the luminescent reagent was mixed with the organic phase containing iodine and the CL signal produced was recorded. An aqueous solution of 100 ng mL^{-1} iodide was used in optimizing experimental and chemical parameters.

Results and discussion

Oxidation of iodide into iodine

The oxidation of iodide into iodine is a delicate step and needs an appropriate oxidant. Several oxidants have been tried in the past for the selective oxidation of iodide into iodine.[1,8] For the oxidation of iodide, a moderate oxidant is needed to convert iodide into iodine selectively in weakly acidic solution. In this work, potassium dichromate, ammonium peroxodisulfate and 2-iodosobenzoic acid were checked in a comparative study for oxidants. Potassium dichromate was used for the batch extraction system in our previous work,[14] but in view of the

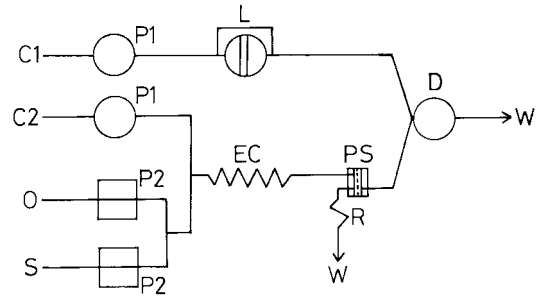

Fig. 1 Schematic diagram of the on-line oxidation–solvent extraction–RMM-CL flow system for the determination of iodide. C1: Chloroform (3 mL min^{-1}); C2: cyclohexane (2 mL min^{-1}); O: oxidizing agent (3 mL min^{-1}); S: sample (8 mL min^{-1}); L: luminescent reagent; EC: extraction coil; PS: phase separator; D: detector; R: restrictor; W: waste; P1: plunger pump; P2: peristaltic pump. The injection loop of the reversed micellar luminol reagent was 20 μL.

possible environmental hazards associated with its usage, it was not the oxidant of choice. Compared with potassium dichromate, CL signals for ammonium peroxodisulfate were more intense at the same normality of the oxidants. On the other hand, ammonium peroxodisulfate was suitable for iodide concentration at higher levels while 2-iodosobenzoate worked better at levels lower than 50 ng mL^{-1} as described below.

Iodine chemistry in the reversed micellar medium

In our previous work,[14] it was observed that the violet color of iodine solution in cyclohexane immediately changed into brownish yellow, indicative of the formation of triiodide ion as shown below in reaction (4), when it was mixed with a reversed micellar solution of the carbonate buffer (pH 11.5) even though iodine was insoluble in the aqueous solution at pH 11.5. In this work, moreover, such a color change was never observed by simply shaking the cyclohexane solution of iodine with the aqueous alkaline medium. These results demonstrated that, on mixing of the cyclohexane solution of iodine with the buffered reverse micellar solution of CTAC, iodine could be instantly transferred from the organic phase into the water pool of the reverse micelles. In the CTAC reverse micelles, the following reactions are presumed to be possible for the iodine as reported in aqueous alkaline solution:[7,26]

$$I_2 + OH^- = IOH + I^- \quad (1)$$

$$HOI + OH^- = OI^- + H_2O \quad (2)$$

$$3OI^- = 2I^- + IO_3^- \quad (3)$$

$$I_2 + I^- = I_3^- \quad (4)$$

$$I_3^- + OH^- = I_2OH^- + I^- \quad (5)$$

$$2IO^- = IO_2^- + I^- \quad (6)$$

In a comparative study, the carbonate-buffered aqueous solutions containing triiodide ion and iodate ion individually were dispersed in the CTAC reversed micellar solutions and then mixed with the CTAC reversed micellar luminol solution used. No CL emission was observed for the two ions while for the cyclohexane solution of iodine at the same concentration, an intense emission resulted. The fact that the triiodide ion is not a CL active species might be correlated with the formation of I_2OH^- in basic medium [reaction (5)].[7] In reversed micellar solutions of 1,4-bis(2-ethylhexyl)sulfosuccinate (AOT), the formation of a 1:1 complex between iodine and anionic AOT within the micelle was proposed.[27] We found no generation of CL emission on mixing the cyclohexane solution of iodine with the AOT reversed micellar solution of luminol using the same reagent conditions.

In the aqueous phase CL reaction of luminol with iodine, the hypoiodous acid [reaction (1)] and the iodite ion generated from another hypoiodite disproportionation [reaction (6)] have been proposed as oxidants.[7] On iodine uptake by the reverse micelle, these oxidizing agents may be produced initially from reactions (1) and (6) at the surfactant–water pool interface. However, the hypoiodite ion produced from reaction (2) undergoes disproportionation rapidly because the equilibrium constant for reaction (3) is very favorable.[26] Thus, the hypoiodite ion is presumed to be present transiently at the interface. In fact, when the cyclohexane solution of iodine was first mixed with the reversed micellar solution containing carbonate buffer (pH 11.5) only and the resulting mixture was then mixed with the luminescent reversed micellar solution, no CL signals were produced. In this case, it was just like the mixing of two water pools, one containing iodine and the other luminol; the iodine did not transfer through the interface of the reverse micelle in the first place. A possible explanation would be that at the reversed micellar interface the oxidant reacts with luminol anion to generate luminescence[14] and the CL oxidation would compete with the disproportionation reaction (3). Additionally, the charged surfactant–water interface of the micelles perhaps plays a significant role in the RMM-CL process.[17,18] The chloride ion, the counter ion of CTAC, might facilitate the quantitative uptake of iodine into the water pools of the micelles as the chloride ion is considered to be mainly located at the interface[28] and the following equilibrium[29] is likely:

$$I_2 + Cl^- = I_2Cl^- \quad (7)$$

Since a decrease in the hydration number for ions in reverse micelles has been reported,[30] the effect of the reverse micelles on the chemistry of iodine may be attributed to the dehydration process, which could lead to an increase in the activity of the hydroxide ion to initiate and/or propagate iodine reactions at the interface. In addition, an iodine concentration effect can be achieved by the iodine entering into a small volume of the water pool and thus association of luminol with iodine or the generated hypoiodous acid seems to be enhanced in reverse micelles. Further work will be needed to elucidate the reversed micellar effect on the iodine chemistry mentioned above.

Optimization studies

The luminescent reagent conditions optimized previously for the RMM-CL reaction of luminol with iodine[14] were used in this work, except that a luminol concentration of 2.0×10^{-4} M in the reversed micellar solution (twice as high as earlier) was chosen as optimum, probably due to the difference in the flow rate of the luminescent reagent stream. In the flow system coupled with the continuous extraction (Fig. 1), an extraction coil of large diameter provided the highest CL intensity because of more efficient mixing of the cyclohexane with the aqueous reaction mixture containing the analyte, iodide, oxidant, and acid. However, the precision of CL measurements was found to be poor when a coil of larger (*e.g.*, id > 1.8 mm) diameter was used. Therefore, an extraction coil of 1.5 mm diameter was selected as optimum. The flow rates (Fig. 1) were chosen so as to optimize the phase separation efficiency, leading to high CL intensity. Although chloroform was used for extraction in our previous studies,[20–22] the CL intensity obtained by using cyclohexane as a solvent was about 2-fold greater than that with chloroform. In this work, cyclohexane was thus selected as the extractant.

Effect of oxidant. The effect of the 2-iodosobenzoic acid concentration on the CL intensity showed that CL signals increased with an increase in the concentration of 2-iodosobenzoic acid and reached a maximum at a concentration of 0.38 mM, which was hence chosen as the optimum concentration of the oxidant. The effect of the flow rate of the oxidant on the resulting CL signals was also examined. The results indicated a weak dependence of the CL signal intensity on the flow rate of the oxidant. However, by increasing the flow rate, the final concentration of iodide in the reaction mixture was decreased and *vice versa*. Therefore, an optimum flow rate of 3 mL min^{-1} was selected for subsequent studies.

Effect of acidity. A pH dependence of redox potential has been reported for 2-iodosobenzoic acid,[1] implying that the concentration of the acid needed to produce iodine from the oxidation of iodide is of particular importance. To establish the effect of H_2SO_4 concentration on the oxidation reaction in the present on-line system, the variation of the RMM-CL intensity with the concentration of the acid in the oxidant solution was investigated. With an increase in the concentration of H_2SO_4, an increase in the CL intensity was observed, reaching a maximum around 2.5 M, which was thus considered to be the optimum concentration of the acid. Beyond this concentration, the CL intensity remained unchanged. This was contrary to our

previous observations regarding the acid effect on the CL intensity, where a decline in the CL intensity was observed beyond the optimum value.[22,25] Therefore, no free H_2SO_4 seems to be accumulated in the cyclohexane during the extraction process. As a result, negligibly small CL signals due to the reversed micellar luminol reagent alone were observed for aqueous solutions in the absence of iodine and iodide which were used to determine blank signals. The analytical CL signal was taken as the difference in peak heights observed for the analyte and the blank.

Analytical performance

For aqueous samples of iodide, linear calibration graphs were obtained with dynamic ranges from 5 to 200 and from 50 to 5000 ng mL^{-1} by using the oxidants, 2-iodosobenzoate and peroxodisulfate in 2.5 M H_2SO_4, respectively, as given in Table 1. Also, the respective detection limits (DL) were 0.5 and 5 ng mL^{-1} for iodide in water, where the DL is given as the concentration for which the analytical signal is three times higher than the noise level of the baseline. These results indicated that 2-iodosobenzoate was more effective than peroxodisulfate at lower concentration levels of iodide, where iodine was presumed to be produced quantitatively by using 2-iodosobenzoate to avoid iodate formation. The peroxodisulfate worked better at concentration levels higher than 200 ng mL^{-1}. For 2-iodosobenzoic acid, however, it was reported that with an increase in the pH the redox potential was lowered and in neutral or weakly acidic solutions, only iodine was produced.[1] By use of a lower acid concentration of 5 mM H_2SO_4 with 2-iodosobenzoic acid (Table 1) in this work, lower amounts of iodide were detectable and a DL of 0.02 ng mL^{-1} iodide was achieved, indicative of less loss of the produced iodine. In the range from the DL to 0.5 ng mL^{-1}, however, linearity was not obtained and at higher concentration levels of iodide, this oxidant solution worked poorly. Relative standard deviations for ten replicate measurements at the 100 ng mL^{-1} iodide level were obtained with the respective oxidants and are also given in Table 1.

Interference effects

In our previous work,[14] it was confirmed that the extraction process was effective in separating iodine from the dichromate used as an oxidant. Also, no interference was observed from bromide when present in 800-fold excess over iodide, although it has been pointed out that the bromine produced *in situ* can convert iodide into iodate,[1] presumably due to inter-halogen reactions in the aqueous medium.[26] The aforementioned results on iodide oxidation indicated that the oxidants, peroxodisulfate and 2-iodosobenzoate, cause no interference as effective separation of the produced iodine from the oxidants was performed by the extraction. In this work, the specificity of the proposed method for iodide in the presence of some common metals and anions, which are capable of catalyzing the CL reaction of luminol[6,11] and/or are likely to be present with iodine, was studied further. The interference studies were conducted using the batch extraction system and 50 ng mL^{-1} iodide solutions containing the individual interfering species. The results showed that interference from the metals, chromium(III), manganese(II), iron(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), tin(II), calcium(II), barium(II), and lead(II), was significantly reduced or entirely eliminated when the interferent-to-iodide molar ratio was 1000. Also, 1000-fold molar excess of the anions, chloride, acetate, phosphate, nitrate, carbonate, and sulfate, did not interfere at all with iodide determination, but a 200-fold molar excess of nitrite ion and almost the same amount of sulfide ion decreased the analytical CL signal by more than 10%. Therefore, these interfering species needed to be removed before analysis, for example, by adding acid to the iodide samples containing the nitrite and sulfide ions and then heating at about 70 °C

Table 1 Sensitivity and precision of the on-line oxidation–solvent extraction–RMM-CL determination of iodide using different oxidizing agents

Oxidizing agent	Detection limit/ ng mL^{-1}	Range of linearity/ ng mL^{-1}	RSD[a] (%)
2-Iodosobenzoic acid[b]	0.5	5–200[c]	3.0
2-Iodosobenzoic acid[d]	0.02	(0.02–0.5)[e]	—
Ammonium peroxodisulfate[f]	5	50–5000[g]	5.0

[a] n = 10; an aqueous solution of 100 ng mL^{-1} iodide was used. [b] An oxidant concentration of 0.38 mM in 2.5 M H_2SO_4 was used. [c] A log–log calibration graph with a slope of 1.03 and a correlation coefficient of 0.999 was obtained. [d] An oxidant concentration of 0.38 mM in 5.0 mM H_2SO_4 was used. [e] No linear calibration graph was obtained. [f] An oxidant concentration of 0.1 M in 2.5 M H_2SO_4 was used. [g] A log–log calibration graph with a slope of 0.97 and a correlation coefficient of 0.991 was obtained.

Differential determination of iodide and iodine

The method described was applied to the determination of iodine and iodide in gargle samples available over the counter. For iodine determination, the method involved extraction without using the oxidant solution while total iodine was determined by the method involving oxidation of the iodide into iodine by 2-iodosobenzoic acid, followed by extraction into cyclohexane. Fig. 2 shows typical CL signals obtained for the gargle sample A. The data obtained by using directly a calibration graph are given in Table 2. Furthermore, iodide determination is easily possible from the difference. The satisfactory results confirmed the utility of the present procedure for the determination of iodide and/or iodine in samples of a diverse nature.

Conclusions

The application of on-line oxidation and solvent extraction coupled with RMM-CL detection was applied to the determina-

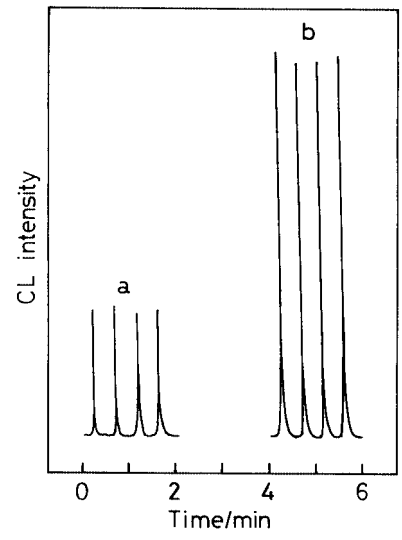

Fig. 2 Representative CL signals recorded after on-line solvent extraction without oxidation (a) and with oxidation using 2-iodosobenzoic acid (b) for the gargle sample A. The estimated amounts of iodine and total iodine, I_2 + I^-, are given in Table 2.

Table 2 Determination of iodine and iodide in gargle samples

Sample	Sample size/μL[a]	I_2/μg		$I_2 + I^-$/μg	
		Found[b]	Estimated[c]	Found[b]	Estimated[c]
A	10.0	5.1 ± 0.2	5.0	15.4 ± 0.4	15.0
B	4.0	4.7 ± 0.2	4.8	14.6 ± 0.6	14.4
C	7.5	5.3 ± 0.2	5.3	15.7 ± 0.6	—

[a] Each sample was diluted to 100 mL with de-ionized, distilled water before analysis. [b] $n = 6$. [c] Values were calculated from nominal values supplied with the product.

tion of iodine and iodide in commercial gargle products. With a simple experimental set-up using low-cost instrumentation, the proposed method allows the trace level quantification of iodine and iodide in aqueous samples. Also, the method has several advantages over the manual extraction procedure, *viz*., simplicity, less human exposure to toxic reagents/solvents, speed, sensitivity, precision, and minimum risk of contamination. Many common metals and anions do not interfere and no sample pre-treatment, preconcentration, screening, *etc*., is required prior to analysis. The proposed method can be confidently applied to the accurate determination of iodine and iodide in biological fluids, foodstuffs, supplements, and beverages.

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