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Trace level determination of iodide, iodine and iodate by gas chromatography–mass spectrometry

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Abstract

A technique is proposed for the determination of iodine, iodide and iodate in aqueous solution. The sample preparation consists of the derivatization of iodine in the presence of 2,6-dimethylphenol and a single-step extraction of the derivative with diethyl ether. Iodine can be quantitatively converted into 4-iodo-2,6-dimethylphenol, which is then measured by gas chromatography–mass spectrometry with selected-ion monitoring. Iodide is oxidized by 2-iodosobenzoate to iodine, and iodate is reduced with ascorbic acid to iodide. Limits of detection and the sensitivity of the procedure are discussed. The procedure is applicable to the quantification of the compounds in drinking water.

Keywords: Derivatization, GC; Iodine; Iodide; Iodate

1. Introduction

Iodine is an essential trace element that is necessary for normal thyroid function. It is used in the synthesis of thyroxine (T_4) and triiodothyronine (T_3) within the thyroid gland [1,2]. Daily adult requirements are about 100–300 μg. When iodine requirements are not adequately met, a range of deficiency disorders can develop. Iodine intakes consistently lower than 0.050 mg/day usually result in thyroid hypertrophy (endemic goitre) and severe and prolonged iodine deficiency may result in hypothyroidism. Otherwise, an excess of iodine and iodides can produce goitre and hypothyroidism as well as hyperthyroidism [1,2]. Therefore, the ingestion of iodine in foods, drugs and water can have profound effects on the thyroid status of individuals.

Iodine is also employed as a disinfectant. The use of iodine as a drinking water disinfectant is well established. Strongly basic quaternary ammonium anion-exchange resin triiodide (resin-I_3) and pentaiodide (resin-I_5) behave as demand-type disinfectants against a wide variety of bacteria and viruses [3,4]. For long-term use of these halogenated resins, adequate post-treatment measures must be taken to remove or reduce the halogens to an acceptable level.

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The trace level determination method of iodine compounds is indispensable for the regulation of the minimum content in natural water and the maximum allowed amounts in halogenated resin-treated water. It is also necessary to analyse mixtures of iodide, iodine and iodate individually, because the various forms of iodine may be not equivalent toxicologically.

Many methods based on different principles have been proposed for the determination of iodine and iodide. For the determination of microgram and nanogram amounts of iodide in natural waters and biological fluids, the most frequently used method is ion chromatography [5–7]. The determination of iodide using ion-interaction chromatography with semi-permeable surface packings has been described [8]. However, these methods are not sensitive enough to determine the trace levels of iodine compounds present in drinking waters. Iodide can be determined by spectrophotometric methods based on catalytic reactions [9–11]. These methods, however, are time consuming and subject to interference from certain divalent cations. Trace levels of iodide have been determined by their catalytic effect on the cerium(IV)–arsenic(III) reaction [12,13]. Precolumn derivatization of halides to organohalogen compounds allows their improved separation and detection utilizing conventional HPLC [14,15]. Sensitive determinations of iodide were obtained by gas chromatography (GC) and electron-capture detection (ECD) of iodoketone [16,17] and pentafluorobenzyl derivatives (18).

Many oxidizing agents such as permanganate [19], peroxomonosulfate [20] and chloramine-T [21,22] have been tried for single halides. The selectivity of 2-iodosobenzoic acid as an oxidizing agent has also been demonstrated [15,23,24]. It could produce selectively halogens from halides under properly controlled reaction conditions.

For the selective and highly sensitivity determination of iodine, iodide and iodate we propose a GC separation with mass-selective detection after a suitable derivatization followed by an extraction with diethyl ether.

2. Experimental

2.1. Chemicals and reagents

Iodine, potassium iodide and potassium iodate were obtained from Sigma (St. Louis, MO, USA). 2,4,6-Trichlorophenol (TCP), 2-iodosobenzoate, 2,6-dimethylphenol (DMP) and ascorbic acid were obtained from Aldrich (Milwaukee, WI, USA). Diethyl ether, pentane, potassium hydroxide, sodium sulfate were used as reagents and solvents.

Sodium 2-iodosobenzoate reagent was prepared by stirring 1 g of 2-iodosobenzoic acid with a slight molar excess of NaOH (20 ml of 0.2 *M* NaOH) and diluting to 250 ml with distilled water.

2.2. Procedure

Derivatization was performed according to the method of Verma et al. [23].

2.2.1. Derivatization and extraction of iodine

In a 20-ml glass-stoppered test-tube were placed 10 ml of drinking water containing 0.05–20 μg of iodine. A 2-ml volume of phosphate buffer (containing 20 g each of KH_2PO_4 and K_2HPO_4 in 500 ml of water and adjusted to pH 6.4) and 20 μl of 2,6-DMP solution (2500 μg/ml in MeOH) were added and the solution was mixed by mechanical shaking for 20 min at room temperature. A 20-μl volume of 2,4,6-TCP solution (8.25 μg/ml in MeOH) as an internal standard was added to the solution, and the sample was extracted with 2 ml of diethyl ether by mechanical shaking for 15 min. The two phases were separated by centrifugation (5 min at 1500 *g*) and the organic phase was transferred into a 20-ml glass-stoppered test-tube and a 2-μl portion of the organic phase was injected directly onto the GC system.

2.2.2. Derivatization and extraction of iodide

A 10-ml volume of drinking water containing 0.05–20 μg of iodide was placed into a 20-ml glass-stoppered test-tube. A 2-ml volume of

phosphate buffer, 20 μl of 2,6-DMP solution (2500 μg/ml in MeOH) and 1 ml of sodium 2-iodosobenzoate reagent were added and the solution was shaken mechanically for 20 min at room temperature. A 20-μl volume of 2,4,6-TCP (8.25 μg/ml in MeOH) as an internal standard was added to the solution. The sample was extracted with diethyl ether as described above. A 2-μl volume of the organic phase was injected directly onto the GC system.

2.2.3. Derivatization and extraction of iodate

To 10 ml of drinking water containing 0.05–20 μg of iodate was added 1 ml of ascorbic acid solution (100 mg of ascorbic acid/100 ml of distilled water) and the solution was stirred by vortex mixing for 2 min. Then, 2 ml of phosphate buffer, 20 μl of 2,6-DMP (2500 μg/ml in MeOH) and 1 ml of sodium 2-iodosobenzoate reagent were added and extracted as described previously. A 2-μl volume of the separated organic phase was injected onto the GC system.

2.3. Calibration and quantification

Calibration graphs for iodine, iodide and iodate were established by adding 10, 50, 250, 1000 and 2000 ng of standards and 165 ng of internal standard (2,4,6-TCP) to 10 ml of distilled water. The ratio of the peak area of the standard to that of internal standard was used in the quantification of the compounds.

The ions selected in this study by quantitative selected-ion monitoring were m/z 121 and 248 for 4-iodo-2,6-DMP and m/z 196 and 197 for 2,4,6-TCP.

2.4. Gas chromatography–mass spectrometry

All mass spectra were obtained with a Hewlett-Packard (HP) Model 5890/5971 instrument. The ion source was operated in the electron impact (EI) ionization mode (70 eV, 150°C). Full-scan mass spectra (m/z 40–450) were recorded for analyte identification. An HP cross-linked 5% phenylmethylsilicone capillary column (HP-5MS, 30 m × 0.25 mm I.D.; film thickness 0.25 μm) was used. Samples were injected in the split mode with a splitting ratio of 1:10. The flow-rate of helium as carrier gas was 1.23 ml/min. The injector temperature was 280°C, the transfer line temperature was 280°C and the oven temperature was programmed from 100°C (held for 2 min) at 15°C/min to 220°C.

2.5. Resin preparation and water treatment

Resin-I_3 was prepared by the method of Fina et al. [4]. Resin-I_5 under the trade name Pentacide was purchased from Water Technologies (Ann Arbor, MI, USA). Columns (16 cm × 1.8 cm I.D.) of the four preparations were assembled: (1) pure triiodide 3 g; (2) triiodide 3 g + active carbon 1 g; (3) triiodide 3 g + active carbon 1 g + Dowex 1 (Dow Chemical) 1 g; and (4) pentaiodide 3 g + active carbon 1 g. Distilled water was pumped through each at 250 ml/min at room temperature (25°C) and the iodine compounds present in the eluent were determined using the proposed experimental procedure.

3. Results and discussion

3.1. Derivatization and extraction

We found, as stated by Verma et al. [23], that the derivatization technique is an attractive method to avoid the difficulties found with many other oxidizing agents. The derivatization of iodine compounds was accomplished as follows (Fig. 1).

In the absence of 2-iodosobenzoate, only 1 mol of 4-iodo-2,6-DMP is formed for every mole of iodine by substitution reaction I. The quantitative oxidation of iodide to iodine can be performed by 2-iodosobenzoate (reaction II) without the interference of other reducing substances. The iodide liberated in reaction I is again oxidized by 2-iodosobenzoate until all iodide has been converted into 4-iodo-2,6-DMP.

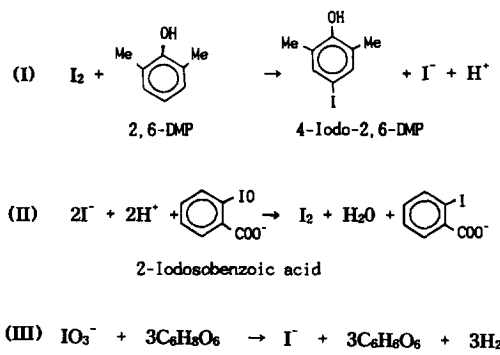

Fig. 1. Derivatization procedures for iodine compounds.

Iodate is reduced to iodide with ascorbic acid before subjecting it to reaction I and II.

The reaction rates of iodine, iodide and iodate with derivatizing reagents were studied. The sample was analysed at reaction times of 20, 40, 60 and 120 min (Fig. 2). Complete reaction takes place in about 20–30 min at room temperature, provided that a sufficiently high concentration of 2,6-DMP is present in the reaction mixture. No significant variation in reaction yield was noted over this time period.

Diethyl ether was found to be efficient for the extraction of 4-iodo-2,6-DMP from aqueous solution. The extract was injected directly onto the GC system without any concentration procedure. Because of its simplicity, rapidity and specificity, this procedure offers general advantages over existing methods.

3.2. Stability

Freshly prepared standard solutions of iodine, iodide and iodate were compared with standard solutions stored at 4°C for 2 weeks. The variations in peak-area ratio at each compound level between 1 and 500 ng/ml were significant. These compounds were found to decompose slowly in standard solution even when stored at −10°C. Therefore, the standards should be prepared freshly on the same day. The derivative was stable during extraction and in the chromatographic system and it was stable for a minimum of 7 days at 4°C.

3.3. Mass spectrometry

The mass spectrum of 4-iodo-2,6-DMP is shown in Fig. 3. The molecular ion at m/z 248 and the diagnostic ions at m/z 77, 91, 103 and 121 indicated that iodine was converted into 4-iodo-2,6-DMP by substitution at the p-position of 2,6-DMP.

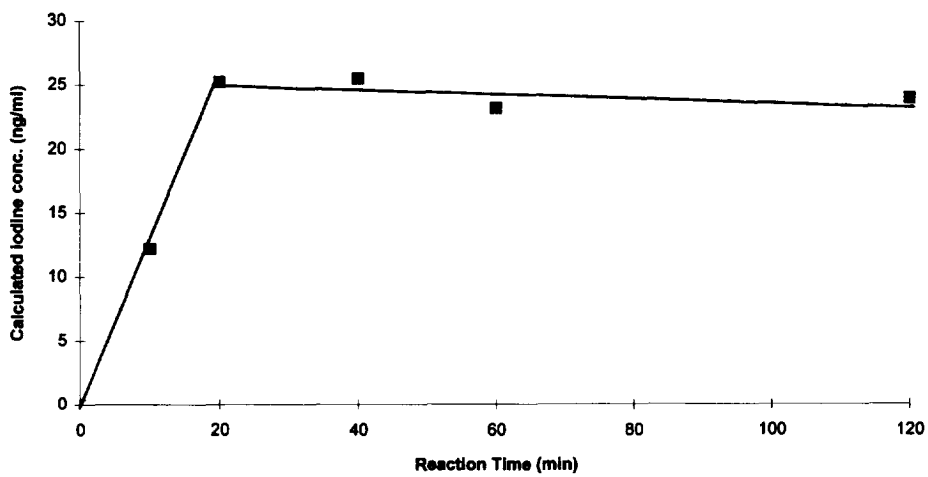

Fig. 2. Reaction rates of iodine, iodide and iodate with derivatizing reagents.

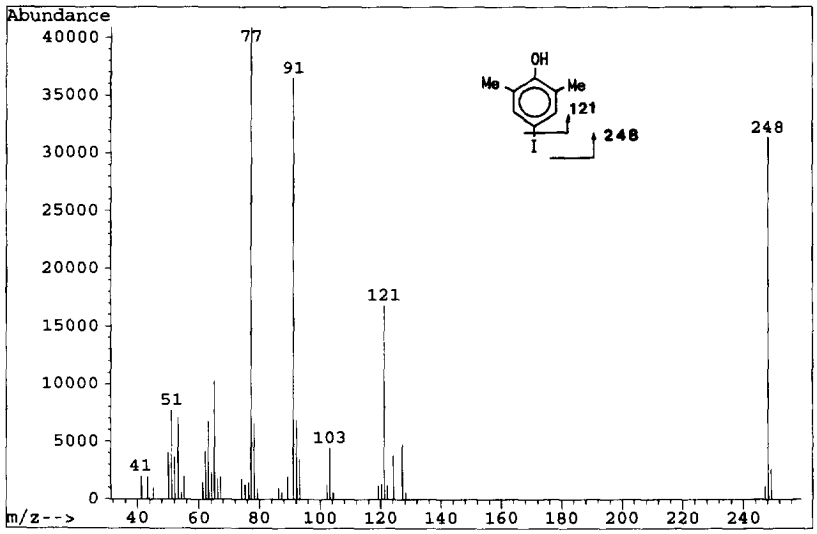

Fig. 3. Mass spectrum of 4-iodo-2,6-dimethylphenol.

3.4. Chromatography

For the GC separation of the derivative, the use of a non-polar stationary phase was found to be efficient. The column was stable over more than 1000 injections without a notable change in the separation characteristics. Chromatograms are shown in Fig. 4. Separation of the derivative and internal standard from the background compounds of water was very good. No extraneous peaks were observed in the chromatogram of blank water at retention times of 6.50 and 8.14 min.

3.5. Linearity

Examination of typical calibration graphs by calculating the regression line of the peak-area

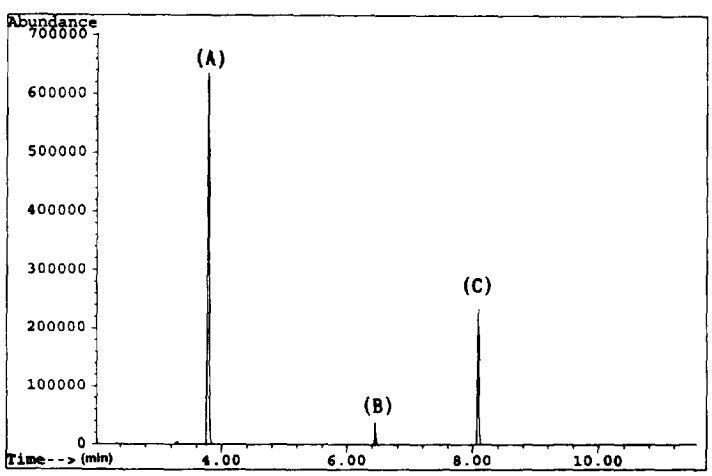

Fig. 4. Total ion chromatogram of the derivatives: (A) 2,6-dimethylphenol; (B) 2,4,6-trichlorophenol (internal standard); (C) 4-iodo-2,6-dimethylphenol.

ratios of 4-iodo-2,6-DMP to the internal standard on concentration using a least-squares fit demonstrated a linear relationship with correlation coefficients consistently higher than 0.999. The line of best fit is $y = 0.036x + 0.027$ for iodine, $y = 0.114x + 0.270$ for iodide and $y = 0.148x + 0.056$ for iodate, where x is the analyte concentration (ng/ml) and y is the peak-area ratio of the analyte to internal standard.

3.6. Recovery

Several water samples with various compositions were prepared and the relative recovery was calculated from the percentage of derivative recovered. The mean recoveries were about 95% at a concentration of 25 ng/ml each of iodine, iodide and iodate, and it was found to be constant at several concentrations.

3.7. Precision and accuracy

The reproducibility of the assay was very good, as shown in Table 1. For six independent determinations at about 20 ng/ml, the relative standard deviation was less than 5%, and it was not more than 10% for the concentration range 1–10 ng/ml.

3.8. Sensitivity

The combination of low background, high extraction yield, high derivatization yield and high abundance of the molecular ion of the derivative permit their determination in water at concentrations well below those reported previously. Detection limits were 0.5 ng/ml for iodine, iodide and iodate based on an assayed water volume of 10 ml. The limits were defined by a minimum signal-to-noise ratio of 3 and relative standard deviations for replicate determinations ($n = 5$) of 15% or less. Because only a small portion of the sample was used for each determination, the sensitivity could be greatly improved by increasing the sample size (by using 50 ml instead of 10 ml of water) or by concentrating the sample extract.

Table 1
Within-run precision and accuracy ($n = 6$)

Compound	Concentration (ng/ml)	
	Added	Found [mean ± R.S.D. (%)]
Iodine	23.5	22.4 ± 0.22
Iodide	22.9	24.2 ± 4.16
Iodate	21.9	22.3 ± 2.47

3.9. Application

Partial application of the method to the determination of the three compounds in drinking water and halogenated resin-treated water was demonstrated. The results are given in Table 2.

In drinking water, we found <5 ng/ml of I^- but not IO_3^-. A relatively low I^- content was detected in drinking water and it may result in iodine deficiency with a high risk of endemic goitre. When considering iodine supplementation for endemic areas, some attempt should be made to determine the current iodine intake of the population. Therefore, the determination of iodine compounds in drinking water is necessary.

Experiments with four preparations, namely pure triiodide (resin A), triiodide with active carbon as a scavenger (resin B), triiodide with anion-exchange resin and active carbon as scavenger (resin C) and pentaiodide with active carbon as scavenger (resin D), were performed. The resins were eluted with distilled water. The

Table 2
Concentrations (ng/ml) of iodine compounds in the samples analysed ($n = 6$)

Sample[a]	I_2	I^-	IO_3^-
Drinking water	ND[b]	4	ND
Resin A-treated water	146	43	10
Resin B-treated water	34	57	7
Resin C-treated water	11	18	ND
Resin D-treated water	3	4193	ND

[a] Resin A = pure triiodide; resin B = triiodide + active carbon; resin C = triiodide + anion-exchange resin + active carbon; resin D = pentaiodide + active carbon.
[b] ND = not detected.

concentrations of the compounds present in the eluent are given in Table 2. As can be seen, the range of I^- eluted was from <20 ng/ml to a high of 4200 ng/ml. The triiodide column with two scavengers elutes little iodine compounds, but the pentaiodide column with one scavenger elutes iodide to a maximum concentration of 4000 ng/ml. The US Environmental Protection Agency (US EPA) states that halogenated resins could be used for long-term continuous application if a follow-up treatment (a scavenger system) is provided to remove halogens from the treated water. From our experiments, we can conclude that both an anion-exchange resin and active carbon are needed to remove iodine and iodide from the treated water. The response of the population to excess iodine is variable. Some people tolerate a large intake without side-effects, whereas others may respond adversely to levels close to recommended intakes. Any device that uses a halogenated resin to remove, kill or inactivate all types of disease-causing microorganisms from water, including bacteria, viruses and protozoan cysts, would therefore have to satisfy these rigorous test conditions.

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