Determination of Iodide, Iodate and Total Iodine in Natural Water Samples by HPLC with Amperometric and Spectrophotometric Detection, and Off-line UV Irradiation

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We developed a rapid, simple method for the iodine speciation analysis of water and applied it to natural water samples. Simultaneous determinations of I^- and IO_3^- were achieved with an HPLC system with amperometric detection for I^- and spectrophotometric detection after a postcolumn reaction for IO_3^-. We determined the I^- and IO_3^- concentrations in 20-μL water samples within 10 min. Total I concentrations in water samples were determined after the decomposition of organics by off-line UV irradiation for 30 min, followed by reduction to I^-. The analytical conditions were optimized by using test solutions rich in organic matter extracted from soils. We tested the new method with samples of groundwater, spring water, precipitation, soil percolate, stream water, and seawater as well as solutions extracted from soil. The method worked well, although the concentrations of some I species were below detection. This method is suitable for routine speciation analysis, which is important for studies of I behavior in the environment.

Introduction

Iodine (I) is an essential micronutrient for the synthesis of thyroid hormones in humans; its deficiency causes goiter. Two billion individuals worldwide are estimated to have insufficient I in their diet.[1] In contrast, the behavior of radioiodine released from nuclear facilities is of special concern because of its transferability in the environment and its ability to accumulate in the human thyroid. Radioiodine, especially [129]I (half-life 1.6×10^7 y) and [131]I (half-life 8.02 d), is released into the atmosphere and ocean from nuclear facilities (*e.g.*, nuclear fuel reprocessing plants). Understanding the behavior of radioiodine in the short and long terms is required to assess the radiation dose from these radionuclides. Stable iodine ([127]I) can be used as a natural analogue to predict the long-term behavior of [129]I in the environment. Iodine is found mainly as I^-, IO_3^-, and organic-I in the environment, and is easily transformed between these forms in response to changes of the environmental conditions. In the environment, chemical forms of I often change rapidly,[2-8] and each species has a different mobility in environmental media.[9-14] In the context of the movement of iodine *via* the liquid phase in terrestrial and aquatic environments,

the speciation of I in liquids is a key to understanding its mobility.

  Several methods have been developed to determine the forms of I in natural water samples.[15] High-performance liquid chromatography (HPLC) can be used to separate I^-, IO_3^-, and other I species in liquid samples. An inductively coupled plasma mass spectrometer (ICP-MS) coupled with an HPLC or an ion chromatograph may be used to simultaneously determine I^- and IO_3^- without the need for any pretreatment to convert the I species.[16-21] In spite of the relatively low ionization efficiency of I, the sensitivity of an ICP-MS to I is satisfactory for the analysis of various types of natural-water samples. Although an HPLC-ICP-MS is widely recognized as a powerful tool for determining I speciation in water samples, it is not suitable for routine analysis in many laboratories because of the high cost of the instrument and of sample analysis. Machine time on an ICP-MS also generally tends to be inadequate because of competing demands for multi-element analyses for various purposes. In addition, coupling an HPLC and ICP-MS requires time-consuming and tedious work.

  In an HPLC system, I^- concentrations can be determined with several different detectors: UV spectrometers,[22-25] fluorescence detectors,[23] and electrochemical detectors.[10,26,27] To determine the concentration of IO_3^- with an HPLC system, IO_3^- is converted to I^- prior to analysis with a reducing agent, such as ascorbic acid.[22,23,28-30] However, the process of reduction can result in an overestimation of the IO_3^- concentration in the solution, because other species of iodine, such as organic iodine, may be converted

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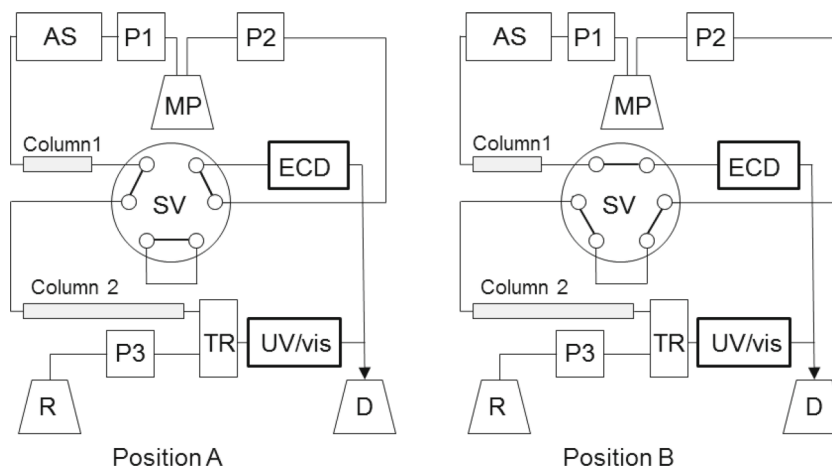
Fig. 1   Schematic diagram of the HPLC system for simultaneous determination of I^- and IO_3^-. P1 and P2, pumps (0.2 mL min^{-1}); P3, pump (0.09 mL min^{-1}); AS, autosampler (injection, 20 μL); column 1, C8 column (2×35 mm); column 2, C18 column (2×250 mm); SV, six-port switching valve (valves were switched from position A to B at a retention time of 2 – 8 min); TR, thermoreactor (90°C); ECD, electrochemical detector (Ag/AgCl, +50 mV); UV/vis, UV/visible light spectrometer (450 nm); MP, mobile phase (20% CH$_3$CN, 50 mM NaH$_2$PO$_4$, 10 mM tetrabutylammonium phosphate); R, reagent for postcolumn reaction (10% ethanol, 1 M HNO$_3$, 100 mM KBr, 2 mM o-dianisidine); D, drain.

to I^- in the process.   In contrast, an HPLC postcolumn derivatization method with o-dianisidine has been widely used for the determination of BrO_3^- in drinking water[31–33] and in bread.[34]   Because IO_3^- can also be sensitively detected by this method without the need to reduce IO_3^-,[35] we adopted this method for I speciation analysis of natural waters.

Dissolved organic-I (DOI) is considered to be one of the major forms of I in natural waters, and is often estimated to be the difference between the total I and inorganic I (I^- and IO_3^-).[22,30,36,37]   ICP-MS systems have been widely used for direct determination of total I in natural water samples.[38–41]   Total I concentrations have also been determined after the decomposition of dissolved organic matter with HPLC systems designed to detect inorganic I.[22,30]   A UV-photooxidation technique is a powerful tool for decomposition of organic matter in natural water samples,[42,43] and has been used for I analysis.[44,45]

In this study, we developed and applied a new method for the simultaneous determinations of I^- and IO_3^- concentrations that is suitable for routine analysis of natural water samples without pretreatment.   The method employs the combination of an HPLC coupled with amperometric detection for I^- and spectrophotometric detection after postcolumn derivatization for IO_3^-.   Organically bound I is also determined by subtracting the inorganic I concentration from the total I concentration.   The latter was equated to the inorganic I concentration after pretreatment with a UV photo-oxidation step.

Experimental

Reagents and chemicals

Guaranteed reagent (GR)-grade sodium iodide (NaI), sodium iodate (NaIO$_3$), and potassium bromide (KBr) were obtained from Merck (Darmstadt, Germany).   Acetonitrile (HPLC grade), sodium dihydrogenphosphate (NaH$_2$PO$_4$, GR grade), nitric acid (for toxic metal analysis) and L(+)-ascorbic acid (GR grade) were obtained from Kanto Chemical (Tokyo, Japan).   HPLC-grade ethanol and tetrabutylammonium dihydrogen phosphate (TBA) solution were obtained from Wako Pure Chemical Industries (Osaka, Japan).   *Ortho* dianisidine (ODA) was

obtained from Sigma-Aldrich (St. Louis, MO, USA).   A tetramethylammonium hydroxide solution (TMAH, TAMAPURE-AA-100) was obtained from Tama Chemicals (Kawasaki, Japan).

Standard solutions (1000 mg-I L^{-1}) of I^- and IO_3^- were prepared by the dissolution of NaI and NaIO$_3$, respectively, in deionized water.   Mixtures of standard solutions of I^- and IO_3^- were prepared from stock solutions before the analysis.   The mobile phase of the HPLC system described below consisted of a solution of 20% (v/v) acetonitrile and 80% (v/v) deionized water with 50 mM NaH$_2$PO$_4$ and 10 mM TBA.   The solution for the postcolumn reaction consisted of 10% (v/v) ethanol, 1 M HNO$_3$, 100 mM KBr, and 2 mM ODA.   A solution of 0.2 M ascorbic acid solution in deionized water was prepared before use.

Apparatus

An HPLC system (Nanospace SI-2, Shiseido, Tokyo, Japan) equipped with a UV/visible light absorption spectrometer (UV/vis) (Model 3002, Shiseido) with a tungsten lamp (measurement wavelength for oxidized ODA, 450 nm) and an electrochemical detector (ECD) (Model 3005, Shiseido) with an Ag/AgCl electrode (+50 mV) was used in this study.   Two reverse-phase columns [Capcel Pak C8 DD 2.0×50 mm (C8 column) and Capcel Pak C18 MGII 2.0×250 mm (C18 column), Shiseido] were used as separation columns in the HPLC system.   A UV irradiation system (Model 705 UV Digester, Metrohm AG, Herisau, Switzerland) was used for UV photolysis of dissolved organic matter in liquid samples.

The HPLC system was coupled with the UV/vis and ECD through a six-port switching valve (Model 3011, Shiseido) (Fig. 1).   The flow rate of the mobile phase was adjusted to 0.2 mL min^{-1} with pumps.   Two reverse-phase columns were serially connected *via* a six-port switching valve (Columns 1 and 2 in Fig. 1).   A 20-μL aliquot of the sample solution was injected through an autosampler.   The I^- and IO_3^- in the sample solution were separated in the first C8 column; IO_3^- eluted first, while I^- was retained.   Up to 2 min after the sample was introduced through the switching valve (position A in Fig. 1), the IO_3^- eluted into the second C18 column for further separation

from other halogen oxoacids (*e.g.*, BrO_3^- and ClO_2^-). The purified IO_3^- was reacted with KBr and ODA in a thermoreactor at 90°C for measuring the 450-nm absorbance of oxidized ODA with the UV/vis. The I^- eluted from the first column with a retention time of 2 – 8 min was introduced through the six-port switching valve (position B in Fig. 1) into the ECD for direct measurements of its concentration.

To validate this analytical methodology, we assayed for I^- and IO_3^- independently with the HPLC-ICP-MS system. The HPLC-ICP-MS system consisted of an HPLC system (LC1100; Agilent Technologies, Santa Clara, CA, USA) with an anion-exchange column (IC-1, 4.6×100 mm; GL Sciences, Tokyo, Japan) coupled with an ICP-MS (VG PQ Excel; Thermo Elemental, Winsford, UK). An aliquot of 100 μL of sample water was injected into the column with a mobile phase of 50 mM Na_2CO_3 solution at a flow rate of 1.0 mL min^{-1}.

Determination of total iodine

For determining total I in the sample solution, we used UV irradiation to photodissociate the DOI. An aliquot of 1 – 10 mL of the sample solution was pipetted into a quartz tube. The tube was sealed with a silicon stopper and irradiated with UV light (500 W) at 60°C. After irradiation for up to 60 min, ascorbic acid was added to the sample solution to convert all I species to I^-. The final concentration of ascorbic acid was 10 mM. The concentration of I^- was determined with the HPLC-ECD system previously described in *Apparatus*. The concentration of total I in the sample solution was independently determined by ICP-MS after diluting the solution with 0.25% (v/v) TMAH and adding Cs as an internal standard.

Test solution for validation of the analytical system

Solutions extracted with water from soils were used as test samples to validate the analytical system. Six soil samples collected from four different sites in Rokkasho, Aomori, Japan (Table S1) were used. Soils A and B were surface soils from different grasslands; soil C was collected from a broadleaf forest and contained a high concentration of I. Soils D1, D2, and D3 were collected from different depths of a coniferous forest soil profile and contained variable total carbon and I concentrations. The soil samples were dried in a drying oven at 50°C for 1 week and passed through 2-mm sieve. Total carbon concentrations in the soil samples were determined to be ranged from 13 to 97 g kg^{-1} by means of dry combustion method. The I concentrations in the soils were determined to be 8.7 – 90 mg kg^{-1} by means of polarizing, energy-dispersive, X-ray fluorescence spectrometry.[46] The I was extracted from the dried soils with water, and these aqueous solutions were used as test solutions for optimizing the analytical conditions. After an aliquot of the dried soil sample was shaken with deionized water (1:10 ratio of soil weight to water volume) for 1 h, the supernatant was separated by centrifugation, and was filtered through 0.22-μm pore size membrane filters. To assay test solutions rich in organic substances, a solution containing 0.01 M NaOH was also used to extract the I from soil A (Table S1), following the same protocol as that used for the deionized water extractions.

Natural water samples

The method developed for iodine analysis was used to analyze several natural-water samples collected in the eastern region of Aomori Prefecture, Japan (Table 1). Surface seawater samples were collected from coastal waters of the Pacific Ocean (40°55′N, 141°23′E) and Mutsu Bay (40°56′N, 140°51′E) in October 2013. A water sample from a spring was collected in

Table 1   Concentrations of I species in spring water, groundwater, and seawater

Sample	Date	I^- [a]/ μg-I L^{-1}	IO_3^- [a]/ μg-I L^{-1}	Total I[b]/ μg-I L^{-1}
Spring water	Jun. 24, 2014	< 0.5	11.4	16.7
Goundwater	Aug. 5, 2014	231	< 1.0	234
Seawater				
Pacific Ocean	Oct. 7, 2013	13.7	36.9	51.5
	Oct. 21, 2013	12.6	30.4	49.0
Mutsu Bay	Oct. 8, 2013	13.5	31.8	51.3
	Oct. 22, 2013	13.3	30.9	51.4

a. Concentrations of I^- and IO_3^- were determined simultaneously by HPLC.
b. Concentrations of total I were determined as I^- after 30-min UV irradiation and reduction by addition of ascorbic acid.

the town of Takko (40°17′N, 141°06′E) in June 2014, and a groundwater sample was collected from a shallow well in the village of Rokkasho (40°58′N, 141°21′E) in August 2014 with the use of a bailer sampler (Daiki Rika Kogyo, Saitama, Japan). The depth of the well was 25.8 m, and the sampler collected water through a strainer from depths of 22.8 – 25.8 m.[47] Terrestrial water samples were also collected in the town of Shichinohe (40°41′N, 141°06′E) from a Japanese cedar (*Cryptomeria japonica*) stand described by Baba *et al.*[48,49] Open bulk precipitation and canopy throughfall samples were collected using polypropylene funnels (17 cm in diameter) that were set up 1 m above the ground and connected to polypropylene bottles. Samples of water that had percolated through soil were collected at various depths in the soil. Stainless, tension-free lysimeters (13×30 cm) connected to polypropylene bottles were used for collection of soil percolate from just under the O horizon and from a depth of 10 cm. A porous cup (Daiki Rika Kogyo) and a porous plate (27-cm in diameter, Soilmoisture Equipment Corp., Goleta, CA, USA) connected to a vacuum Erlenmeyer flask were used for collecting soil percolate at depths of 50 and 90 cm, respectively. Soil percolate was collected from June to August 2013. Stream water samples were also collected from the Japanese cedar stand. All water samples were passed through 0.22-μm pore size membrane filters and stored at 4°C prior to analysis.

Results and Discussion

Simultaneous determination of I^- and IO_3^-

Typical HPLC chromatograms for standard solutions, which contained I^-, IO_3^-, or both, are shown in Fig. 2 together with chromatograms of blank solutions. Figure 2 depicts signals from both the ECD (upper subfigure) and UV/vis (lower subfigure). The chromatograms contained many ghost peaks caused by changes of the flow path with the switching valve as well as some unknown peaks. The peaks of I^- and IO_3^-, however, were clearly separated from the other peaks. The injected I^- was detected by the ECD at a retention time of about 5.7 min, and IO_3^- was detected at about 6.3 min by the UV/vis. The I^- and IO_3^- were successfully separated by the column system, and there was no interference between the two peaks (Figs. 2B, 2C). Analysis of each sample was completed within 10 min. Calibration curves for I^- and IO_3^- were linear over the ranges 0.5 – 25 and 1.0 – 50 μg-I L^{-1}, respectively. The limit of detection of I^- and IO_3^-, evaluated from the calibration curves,
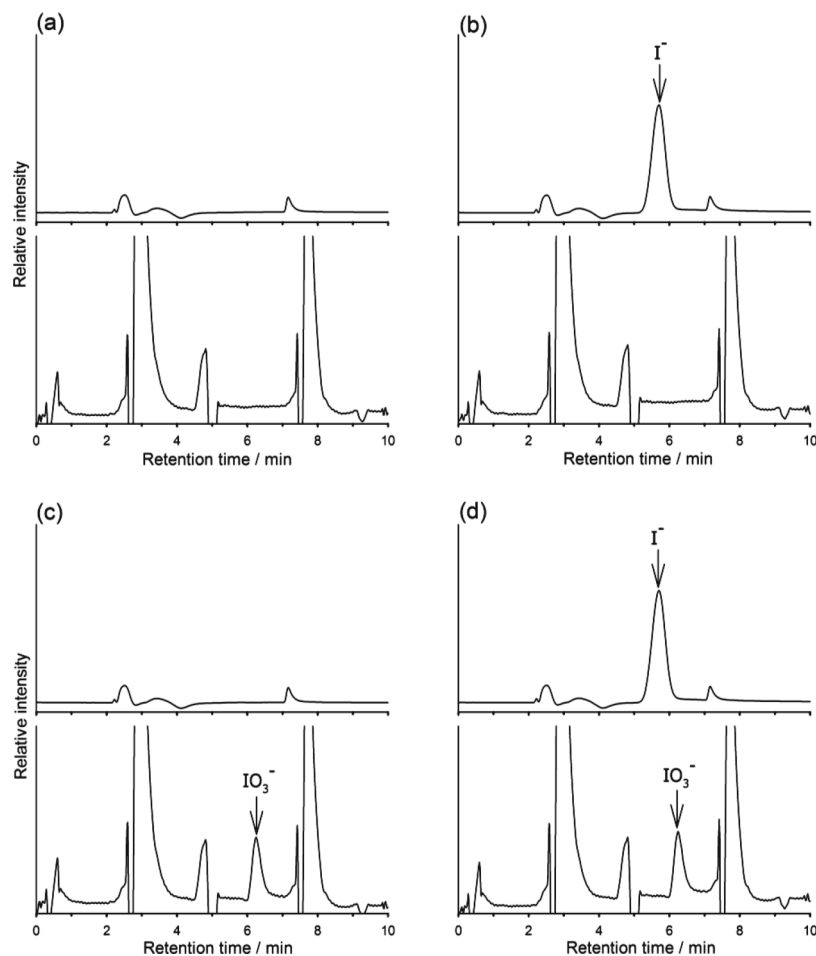
Fig. 2   HPLC chromatograms of standard solutions. (a) Blank solution; (b) standard solution of I⁻ (25 μg-I L⁻¹); (c) standard solution of IO₃⁻ (50 μg-I L⁻¹); (d) mixed standard solution of I⁻ and IO₃⁻ (I⁻, 25 μg-I L⁻¹; IO₃⁻, 50 μg-I L⁻¹). Upper subfigures, ECD for I⁻ detection; lower subfigures, UV/vis for IO₃⁻ detection.

were 0.25 and 0.61 μg-I L⁻¹, respectively. The coefficients of variation for repeated measurements (n = 20) of I⁻ and IO₃⁻ in a mixed solution of I⁻ (10 μg-I L⁻¹) and IO₃⁻ (20 μg-I L⁻¹) were 2 and 4%, respectively. To check for interference by other halogen oxoacids, a mixed solution of ClO₂⁻, BrO₃⁻, and IO₃⁻ was analyzed. The IO₃⁻ peak was cleanly separated from the other peaks (Fig. S1).

Solution extracted with water from the soils

The solutions extracted with water from the six soils were used as test solutions to check the applicability of the present methods to DOC-rich water samples (Table S1).   The concentrations of the total I in the extracted solutions determined by the ICP-MS were 3 – 30 μg L⁻¹, the indication being that 0.1 – 1.1% of the I in the soils was water-soluble.

We used the speciation results of I determined with the HPLC-ICP-MS as a reference for checking the HPLC-ECD system. Figure 3 shows typical HPLC-ICP-MS chromatograms of the standard I⁻ and IO₃⁻ mixed solution and the solution extracted with water. With this analytical system, I⁻ and IO₃⁻ in the standard solution were clearly separated and detected with satisfactory sensitivity. In the water extract from soil A, no peak was detected other than I⁻. Because the difference between the total I and I⁻ concentrations in the sample was large (13 μg-I L⁻¹ in Table S1), the DOI probably adsorbed irreversibly to the anion-exchange column. In contrast, I⁻ and

an unknown broad peak were detected in the water extract from soil B. The concentration of I⁻ was 9.1 μg-I L⁻¹, and the area under the unknown peak was equivalent to 8.3 μg-I L⁻¹. The sum of the concentrations associated with these two peaks accounted for 92% of the total I concentration in the solution. In the case of the water extract from soil C, small, unknown peaks were detected at retention times of 6 – 9 min, though their peak areas were much smaller than that of I⁻. In other soils (soils D1, D2, and D3), the shapes of the chromatograms (not shown in Fig. 3) were similar to those of soils A and C. These observations reflect the complexity of the dissolved I species in the soils.   Reifenhäuser and Heumann[44] have reported the presence of two types of DOI in natural water samples: anionic DOI elutable from the anion-exchange column and non-elutable DOI. The variation of the two kinds of DOI in our study is consistent with their results.

The contribution of I⁻ to the total I of the extracted solutions was 27 – 63%; IO₃⁻ was not detected in any of the solutions extracted with water from soils. These results suggest that DOI, which we estimated from the difference between the total I and the sum of I⁻ and IO₃⁻, and I⁻ were the predominant forms of I in the extracted solution.

The concentrations of I⁻ and IO₃⁻ in the solution extracted from the soils were determined simultaneously with the HPLC system (Fig. 1) developed in this study. The IO₃⁻ concentrations of all the samples were found to be below the limit of detection.
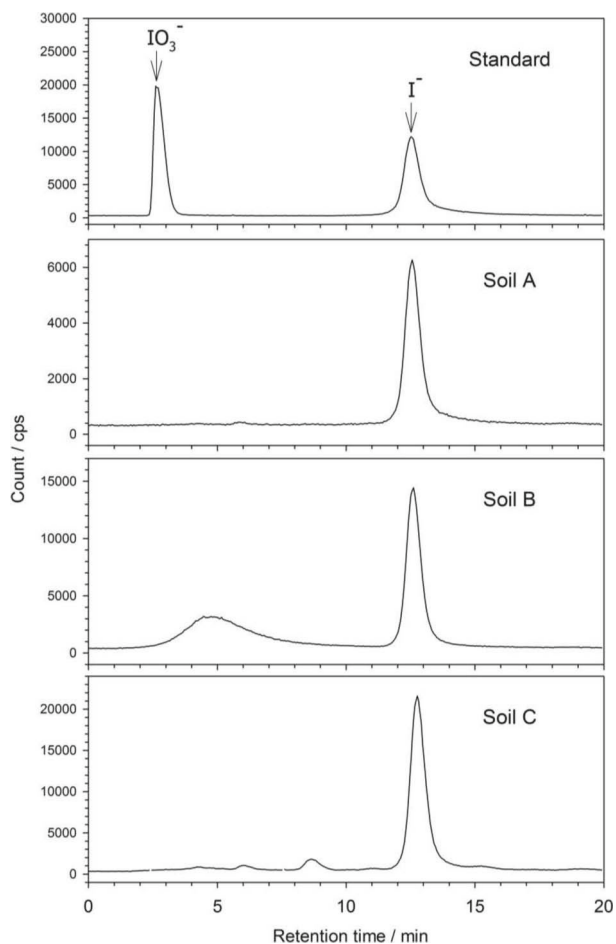
Fig. 3   HPLC-ICP-MS chromatograms of a mixed standard solution (I^-, 10 μg-I L^{-1}; IO_3^-, 10 μg-I L^{-1}) and water extract from soils.

Fig. 4   Comparison of the method developed in this study (HPLC-ECD) and the ICP-MS method for I^- and total I concentrations in water extracts from soils.

Fig. 5   Changes of I^- and dissolved organic carbon (DOC) concentrations in standard solution (10 μg-I L^{-1} of I^- or IO_3^-) and aqueous extract from soil A after different UV-irradiation times. Concentrations of I^- were determined after addition of ascorbic acid. Each plot indicates mean values of duplicate treatments.

Figure 4 compares the concentrations of I^- in the extracted solutions determined with the HPLC-ECD and HPLC-ICP-MS methods.   The concentrations of I^- determined by the two methods were in good agreement.   The HPLC-ECD system can therefore be used to assay for I^- in soil extracts that contain relatively high DOC concentrations.

Determination of total I in solution by UV irradiation

We irradiated the water-extracted solution from soil A to test the efficiency of DOI photolysis by UV.   To optimize the UV-irradiation time, the solutions were irradiated for 0 – 60 min, and their post-irradiation DOC and I^- concentrations were determined after addition of ascorbic acid as a reducing agent. Figure 5 shows the DOC and I^- concentrations as a function of the UV irradiation time.   The water extract from soil A contained 4.5 μg-I L^{-1} of I^- and <1.0 μg-I L^{-1} of IO_3^- (Table S1).   The concentration of I^- increased to 8.0 μg-I L^{-1} after the addition of ascorbic acid solution without UV irradiation (time of 0 in Fig. 5).   These results suggest that some species of I other than IO_3^- was converted to I^- by nothing more than the addition of ascorbic acid.   The concentration of I^- in the water extract increased after 10 min of irradiation, but remained constant after further irradiation.   In contrast, although the DOC concentrations in these soil extracts continued to decrease with irradiation time, ~1/3 of the DOC still remained after 60 min of irradiation.   These results suggest that the DOI in the solution was sensitive to UV irradiation, and the conversion of DOI to
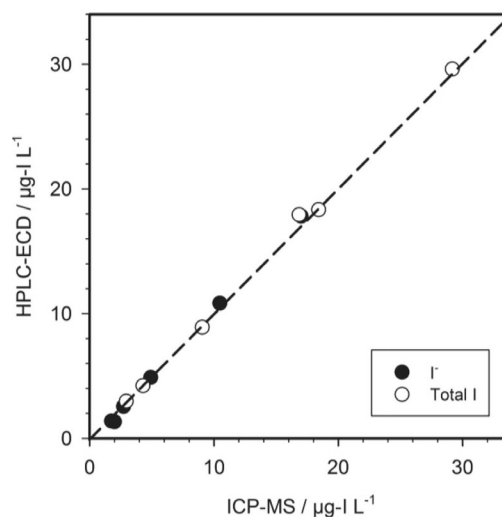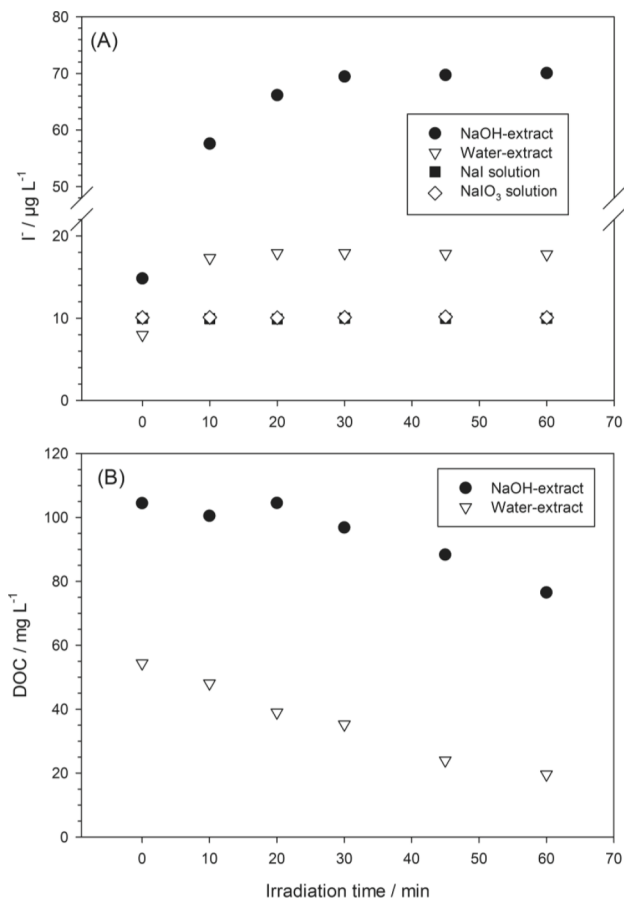
I^- by this methodology proceeded more rapidly than the photolysis of dissolved organic carbon.

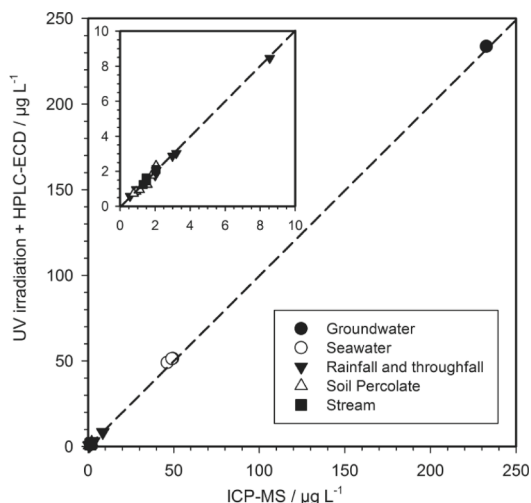To check the efficiency of total I detection by this method,

Fig. 6   Comparison of the method developed in this study (UV irradiation + HPLC-ECD) and the ICP-MS method for total I concentrations in various natural water samples.

the total I concentrations in the solutions extracted with water from the six soils were determined by using UV irradiation for 30 min, and compared with the concentrations determined by using ICP-MS (Fig. 4).   The results obtained with the UV-irradiation and ICP-MS methods agreed well with one another.   Total I in the water-extracted soil solution was therefore completely recovered with the UV-irradiation method.

To confirm the applicability of the present method to water samples with higher DOC concentrations, we assayed a solution extracted with 0.01 M NaOH from soil A for DOC and total I concentrations after UV irradiation for times up to 60 min (Fig. 5).   The I$^-$ concentration in the extract initially increased and reached a constant value after 30 min of irradiation.   Based on these results, 30 min was selected as the irradiation time, and was used in subsequent analyses of total I in water samples.

Finally, the stability of I$^-$ and IO$_3^-$ in the irradiated solution was tested by using a standard solution of both species.   The results (Fig. 5A) showed that the recovery of both species was complete and was unaffected by UV irradiation time.

Wong and Cheng[45] have recommended the addition of H$_2$O$_2$ and three hours of irradiation to convert DOI to IO$_3^-$ in seawater samples.   In the procedure described here, 30 min of irradiation without addition H$_2$O$_2$ was acceptable as a pretreatment for the determination of total I by a post-irradiation measurement of I$^-$.

Application to various natural water samples

The method reported here for I speciation analysis with an HPLC system was applied to various natural water samples (Table 1 and Table S2).   The total I concentrations in the water samples determined by HPLC analysis after UV irradiation were in good agreement with those determined by ICP-MS over a wide range of concentrations (Fig. 6).

In the spring water sample, the concentration of total I was 16.7 μg-I L^{-1}, and I$^-$ was not detected (Table 1).   The predominant species of I in the sample was IO$_3^-$, which accounted for 69% of the total I; DOI accounted for at least 28%.

The total I concentration in the groundwater sample, which had a low dissolved oxygen concentration (6.4% of saturation) and oxidation-reduction potential (+78 mV), was 234 μg-I L^{-1}, the highest total I concentration measured in this study (Table 1).   That most of the dissolved I in the sample was present as I$^-$ is a

reflection of the anoxic condition of the aquifer.

Although seawater samples required a ten-fold dilution before analysis due to a high salt concentration, both I$^-$ and IO$_3^-$ were detected.   The total I concentration in the seawater samples ranged from 49.0 to 51.5 μg-I L^{-1}, with IO$_3^-$ being the dominant species (Table 1): the I$^-$ and IO$_3^-$ accounted for 26 – 27% and 60 – 75%, respectively, of the total I.   Total inorganic iodine accounted for 86 – 98% of the total I, the implication being that 2 – 14% of iodine existed as DOI.   Similar observations were reported in previous studies in coastal surface seawater samples.[21]

Concentrations of iodine species in various water samples, including precipitation, soil percolate, and stream water collected from the Japanese cedar stand, were determined by the HPLC-ECD method developed in this study.   The results are given in Table S2.   The samples of precipitation, soil percolate, and stream water had relatively low total I concentrations compared to the other water samples listed in Table 1; IO$_3^-$ was not detected in any of the samples.

In the bulk precipitation samples collected from an open field, the total I concentration ranged from 0.58 to 2.07 μg-I L^{-1}.   The total I concentrations in throughfall collected during the same sampling period were 3.0 – 4.1 times the concentrations in bulk precipitation.   Measurable total I concentrations were found in all precipitation samples.   That inorganic iodine species were not detected in most of the same samples indicates that inorganic species accounted for a small fraction of the total I.

The concentrations of total I in the soil percolate samples collected from just below the O horizon and at a depth of 10 cm ranged from 0.72 to 2.32 μg-I L^{-1}.   The soil percolates from just under the O horizon had relatively high total I concentrations compared to those from a depth of 10 cm.   Total I was not detected in any soil percolates from deeper soil.   Total I concentrations determined by ICP-MS were 0.27 – 0.30 μg-I L^{-1} and 0.09 – 0.14 μg-I L^{-1} at depths of 50 and 90 cm, respectively.   There was thus a tendency for the total I concentration to decrease with increasing soil depth.   The method developed in this study was not sensitive enough to detect the total I at such low concentrations.   In stream water, the concentrations of total I were 1.24 – 2.10 μg-I L^{-1}, and inorganic I was undetectable.

The concentrations of total I in precipitation (bulk and throughfall) samples were positively correlated with DOC concentrations ($r = 0.97$, $n = 8$).   Similarly, the concentrations of total I in the soil percolate collected just below the O horizon and at a depth of 10 cm were also positively correlated with the DOC concentrations ($r = 0.82$, $n = 6$) (Fig. S2).   Although I species could have changed during the sampling period in the precipitation and soil percolate samples, these observations suggest that the behavior of I is strongly influenced by that of dissolved organic matter in the surface soil environment in this area.   Knowledge of the characteristics of DOI would improve our understanding of the I behavior, especially in terrestrial environments.

Conclusions

A new method for the analysis of I speciation in various natural water samples was developed.   In this method; only 20-μL samples are required, and I$^-$ and IO$_3^-$ are successfully determined in the same sample within 10 min by using an HPLC system with two different detectors and a column-switching valve.   This simple and high-throughput analytical system is useful for routine analysis of I speciation, which requires rapid analysis after collecting samples of natural water.   Total I was also

determined after 30-min of UV irradiation and reduction to I$^-$. These methods are more cost-effective than an ICP-MS system, and are applicable to many types of natural-water samples without any complex pretreatment. Although the sensitivity of this system needs to be improved for some water samples with relatively low concentration of I species, it can be used as an alternative to HPLC-ICP-MS for I speciation analysis of a variety of water samples.

Acknowledgements

Supporting Information

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

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