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Determination of the chemical forms of iodine with IC-ICP-MS and its application to environmental samples

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An online analytical system using ion chromatography (IC) followed by inductively coupled plasma mass spectrometry (ICP-MS) was developed for the separate determination of I^- and IO_3^- in aqueous solutions with a detection limit 0.1–1 μg I/l. The total iodine concentration was also directly determined by ICP-MS. Iodine in several environmental samples (i.e., rain, river water, brine, and soil solution) was successfully determined with information on its chemical form. The release of I^- into soil solution with decreasing Eh was observed in an incubation experiment with flooded soil. An iodine form other than I^- and IO_3^- was observed in several environmental samples.

Introduction

Iodine-129 is one of the important radionuclides released into the environment from nuclear weapons testing and from nuclear facilities such as nuclear fuel reprocessing plants. Knowing its long-term behavior in the environment is a major concern because of its long half-life ($1.57 \cdot 10^7$ y). As ^{129}I is expected to act together with stable iodine (^{127}I) in the environment after a long time, the biogeochemical cycling of stable iodine in the environment can be used for the reliable safety assessment of ^{129}I.

Chemical form is one of the important factors controlling iodine behavior in the environment. Iodide (I^-) and iodate (IO_3^-) are known to be the major chemical forms in aqueous solutions. However, information on chemical forms of iodine in environmental samples is limited because reliable analytical techniques are lacking for trace levels of environmental iodine. Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most sensitive analytical techniques for iodine, and it has been applied to environmental iodine samples.[1–3] Chromatography combined with ICP-MS presents a powerful tool for the determination of chemical forms of trace elements, and it has also been used for iodine determination.[4,5] However, the data obtained were limited, since the systems used were not simple enough for the combined technique to become a common method.

In this study, an analytical system using ion chromatography (IC) with a standard anion-exchange column followed by ICP-MS was developed for the separate determination of I^- and IO_3^- in aqueous solutions. The system was applied to different types of environmental samples such as rain, river water, brine, and soil solution.

Experimental

Analytical system

The IC-ICP-MS system used for the analyses is summarized in Table 1. The anion exchange column used here is commonly used for IC analyses of Cl^-, NO_3^-, and SO_4^{2-}, etc., with a mixture of Na_2CO_3 and $NaHCO_3$ as eluant. Since introducing a high concentration of Na causes matrix interference and a heavy load for the ICP-MS system, $(NH_4)_2CO_3$ was used as eluant instead. The outlet of the column was directly connected to the ICP-MS nebulizer for online determination of iodine. Standard solutions used for making calibration curves were prepared from KI or KIO_3. The I^- and IO_3^- were successfully separated and determined for their concentrations as shown in Fig. 1 with the detection limit 0.1–1 μg I/l.

Table 1. Operating conditions of the IC-ICP-MS system used for the analyses of I^- and IO_3^-

IC	
Model	Yokogawa IC7000S
Column	EXCELPAK ICS-A23
Guard column	ICS-A2H
Eluant	30 mM $(NH_4)_2CO_3$
Flow rate	0.8–1.0 ml/min
Sample loop	50–200 μl
Oven temperature	40 °C
ICP-MS	
Model	Yokogawa PMS-2000, HP-4500 or Agilent 7500
m/z	127
Mode	Time analysis

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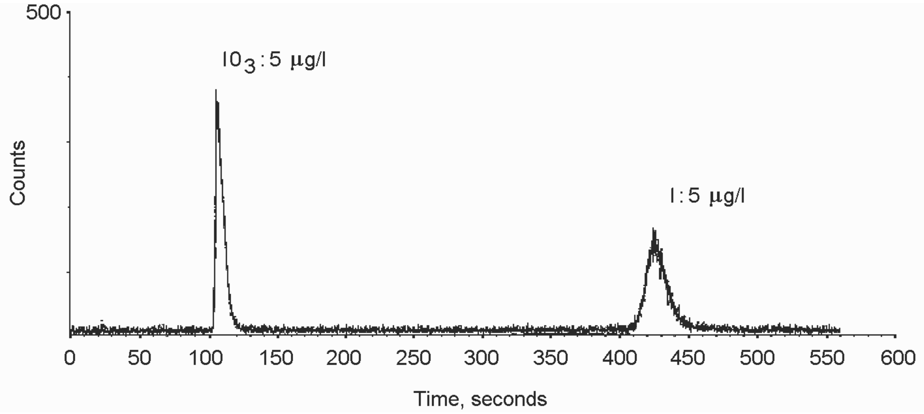

Fig. 1. IC-ICP-MS chromatogram for standard solution containing 5 μg/l of I^- and IO_3^-

The total iodine concentration was also directly determined by ICP-MS. Sample solutions were prepared with 3% tetra-methyl ammonium hydroxide (TMAH) and 0.005% Na_2SO_3. The detection limit of the measurement was 0.05 μg/l. Details for the analyses of total iodine have been described previously.[1,3] The iodine fraction for forms other than I^- and IO_3^- was calculated as "the others" by:

$$\text{The others} = \text{total iodine} - (I^- + IO_3^- - I).$$

Environmental samples

Rain samples were collected in polyethylene bottles in Tokai-mura (at a village site about 5 km from the Pacific Ocean), Ibaraki, Japan. River water was collected from the Kuji River. These specimens were filtered through 0.45 μm membrane filters and stored at 5 °C in a refrigerator. Brine samples were collected from wells in Mobara area, Chiba, Japan, where iodine has been commercially produced from brine since 1934. These samples were filtered through 0.20 μm membrane filters and diluted with de-ionized water for the determination of iodine. Detailed information about brine in the Mobara area has been given by MURAMATSU et al.[3]

In order to observe the release of iodine from soil to soil solution under the reducing condition, a soil incubation experiment was done in the laboratory. Air dried andosol (1 l), containing 32.6 mg/kg of natural iodine, was put in two plastic pots and the pots were flooded with de-ionized water and were placed in the dark at 30 °C for 24 days. The soil solutions were collected from three positions, surface water, 1 cm deep from the soil surface, and 10 cm deep from the soil surface as shown in Fig. 2 at 0, 2, 4, 8, 16, and 24 days. The solutions at 1 and 10 cm depths were collected with a soil water sampler (Daiki DIK-301A-A1), which was set horizontally at the appropriate depth. The soil Eh was measured at the center of the soil in one of the pots. The solutions collected were filtered through 0.20 μm membrane filters for iodine determinations.

Results and discussion

Rain, river water and brine samples

A typical chromatogram obtained by the IC-ICP-MS for a rain sample is shown in Fig. 3. This figure also demonstrates the possible determination of Cl^- and Br^- together with iodine species. The analytical results for rain, river water and brine samples are summarized in Table 2. The sums of I^- and IO_3^- for 3 rain samples were around 1 μg I/l, and were in the range of iodine concentrations in rainfall previously observed over land (0–5 μg I/l).[6] The percentage of I^- ranged from 73 to 83%. The average total-iodine of 2.2 μg I/l in rainfall at 4 sites in the United Kingdom was reported to be composed of 55% I^- and 45% IO_3^-.[6] The percentage of IO_3^- in rainfall was also reported to decrease with the distance from the coast.[7]

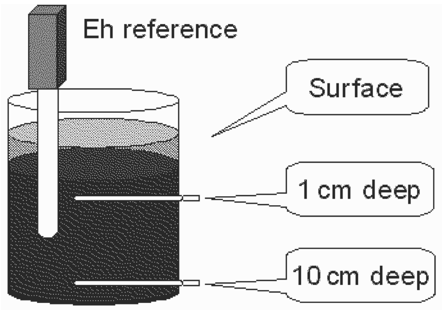

Fig. 2. Soil incubation experiment to observe the release of iodine from soil to soil solution under reducing condition

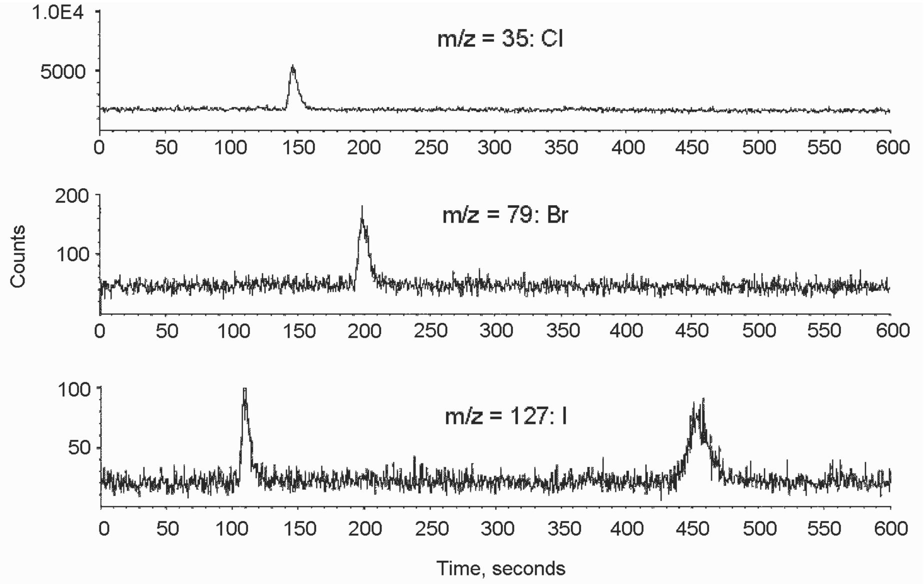

Fig. 3. Typical IC-ICP-MS chromatogram for a rain sample (R605)

Table 2. Analytical results of rain, river water and brine samples for I^- and IO_3^-

Sample type	Code	Location	I^-, μg/l	IO_3^-, μg/l	μg I/l	$I^- + IO_3^-$, μg I/l	I^-, %
Rain-1	R509	Tokai-mura	0.61	0.31	0.22	0.83	73
Rain-2	R605	Tokai-mura	0.89	0.46	0.33	1.22	73
Rain-3	R606	Tokai-mura	0.94	0.29	0.21	1.15	82
River-1	RW0129	Kuji River	1.60	3.21	2.33	3.93	41
River-2	RW0229	Kuji River	0.91	1.52	1.10	2.01	45
			mg/l	mg/l	mg I/l	mg I/l	
Brine-1	RN209	Mobara	107.8	<0.002	<0.001	107.8	100
Brine-2	RN115	Mobara	100.3	<0.002	<0.001	100.3	100
Brine-3	RN402	Mobara	115.5	<0.002	<0.001	115.5	100

The sums of I^- and IO_3^- for river water samples were 3.9 μg I/l for River-1 and 2.0 μg I/l for River-2. The percentages of I^- were 41% for River-1 and 45% for River-2, and were lower than those for rain samples.

Brine samples contained high amounts of I^- which ranged from 100 to 116 mg/l. On the other hand, the concentrations of IO_3^- were under the detection limit, indicating the reducing condition of the brine. The total concentrations of iodine determined by ICP-MS direct analyses were 119 mg/l for Brine-1, 107 mg/l for Brine-2, and 131 mg/l for Brine-3.[3] Slightly lower concentrations of I^- observed in the present work suggest the possible presence of iodine with a chemical form other than I^- and IO_3^-, although further studies are required.

Soil solution during incubation experiment

The change of iodine concentrations in soil solutions during the incubation experiment is summarized in Fig. 4 together with information on the chemical form. Change of soil Eh measured at the center of the soil is shown in Fig. 5. At the beginning (0 and 2 days), the concentrations of iodine in the soil solutions were low. This is consistent with the previous studies showing the strong sorption of iodine onto andosols under the oxidation condition.[8,9] The concentrations of iodine were increased with time with lowering of Eh. The increase was remarkable in the 10 cm deep sample, in which the lowest Eh among the three sampling positions was expected. Most of the increased iodine concentration was in the I^- form. The IO_3^- was under the detection limit in most samples. These findings indicated that iodine on the andosol surfaces was released into the solutions under the reducing condition mainly as I^-. Release of iodine from soil to soil solution with decreasing Eh has also been observed in radiotracer experiments.[10] Lower concentrations of iodine in paddy soils then those of upland and forest soils also suggested the release of iodine under the flooded condition.[11]

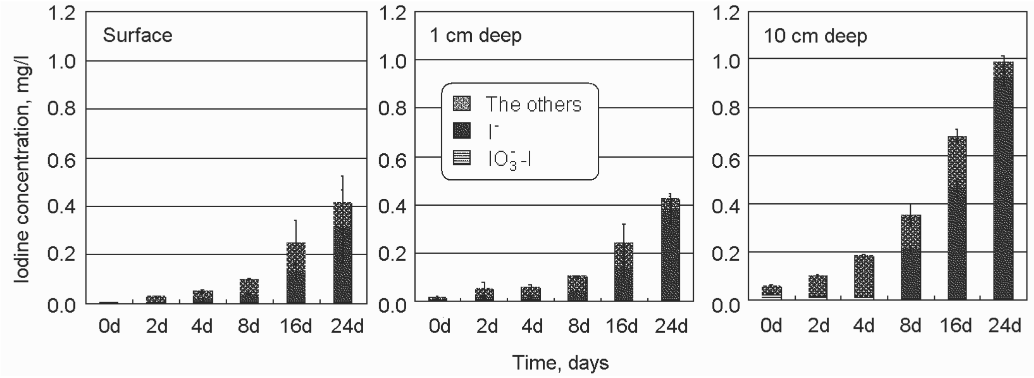

Fig. 4. Change of iodine concentrations in soil solutions during the incubation experiment

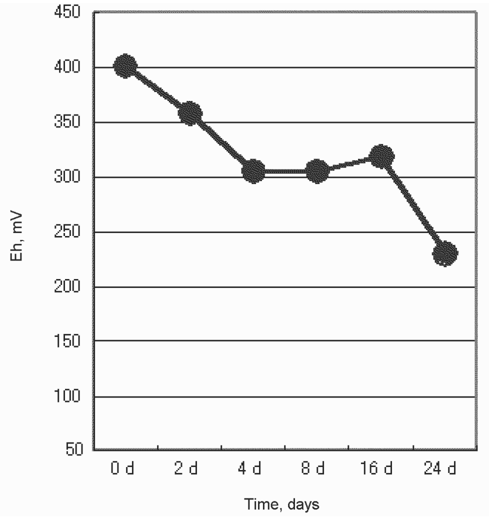

Fig. 5. Change of Eh during the incubation experiment

There is an iodine fraction with a form other than I^- and IO_3^- ("the others" in Fig. 4) in the soil solution. This might be an organic form or an organic bonding form, and needs further study.

Conclusions

Two different forms of iodine, I^- and IO_3^-, in aqueous solutions were successfully separated and determined by an analytical system using IC with a standard anion exchange column followed by ICP-MS with the detection limit 0.1–1 µg I/l. Rain, river water, and brine samples were analyzed for I^- and IO_3^-. The change of iodine concentrations in soil solutions during the incubation experiment is determined together with the information on the chemical form. The analytical method developed is expected to provide much information on iodine behavior in aqueous environment, which is important to understand the long-term behavior of ^{129}I released into the environment.

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