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Speciation analysis of ^{129}I in seawater using coprecipitation and accelerator mass spectrometry and its applications

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Abstract Speciation analysis of long-lived ^{129}I in seawater can provide useful information on the source of water masses. This paper presents an improved method for speciation analysis of ^{129}I based on coprecipitation of iodide as AgI with Ag_2SO_3 and AgCl. By adding a small amount of ^{127}I carrier, the separation efficiency of iodine species and the accuracy and precision of ^{129}I measurement are remarkably improved. ^{129}I species in depth profiles of seawater from the Antarctic were analyzed for investigation of water circulation in the Antarctic.

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Introduction

Iodine is a conservative element in the ocean and mainly exists as iodide and iodate with a minor organic iodine [1]. Iodine is also a biophilic element and is highly concentrated in algae [2, 3]. Meanwhile, iodine is a redox sensitive element, and in the marine environment biological activities significantly influence the species of iodine present. ^{129}I (15.7 Ma) is the only long-lived radioisotope of iodine. In the nuclear age, ^{129}I is dominantly originated from human nuclear activities, mainly nuclear reprocessing plants, nuclear weapons testing in 1940s–1980s and nuclear accidents [3]. Anthropogenic ^{129}I therefore provides us an excellent oceanographic tracer for water circulation and marine environment [2, 4].

Solvent extraction is the most commonly used method for separation of iodine from solution [5, 6]. Due to low concentration of iodine and high salinity in seawater, iodine (^{127}I) has to be added as carrier to enhance the extraction efficiency and provide a physical sample for AMS target preparation. This is not suitable for the determination of low level ^{129}I in seawater, such as those collected in the southern hemisphere including the Antarctic and deep seas because of the interference of minor ^{129}I in the iodine carrier. In addition, solvent extract cannot be used to separate single species of iodine from water. A coprecipitation method based on selective precipitation of iodide as AgI has been proposed for separation of iodide from iodate in seawater for speciation analysis of ^{129}I in seawater using accelerator mass spectrometry (AMS) measurement [7]. AMS is the most suitable method for determination of ultralow level ^{129}I/^{127}I in natural samples with a ^{129}I/^{127}I atomic ratio <10^{-10} [2, 7–11], such as those collected from the southern hemisphere, the deep seas and the Antarctica water. However, due to the

low concentration of iodine in samples, the ^{127}I signal in the AMS measurement of a target prepared using the carrier-free coprecipitation method is very weak, causing a high uncertainty in the AMS measurements of the $^{129}I/^{127}I$ ratio. This work aims to improve the method for speciation analysis of ^{129}I by increasing the ^{127}I signal in AMS measurement thereby reducing the uncertainty in the $^{129}I/^{127}I$ ratio. Meanwhile, depth profiles of seawater collected from the Amundsen Sea in the Antarctic were analyzed for species of ^{129}I, in order to use it as an oceanographic tracer of water circulation and marine environment in this region.

Materials and methods

Samples and chemicals

Three depth profiles of seawater were collected using a CTD rosette consisting of Niskins bottles and CTD sensors in the research vessel N.B. Palmer during cruise in the Amundsen Sea, Antarctica (73°–74°S, 111°–114°E) in Dec., 2010. Figure 1 shows the sampling locations. Salinity, seawater temperature and concentrations of chlorophyll, phosphate and nitrite were measured by on-line detecting system of the research vessel (Table 1). One seawater sample was collected in open sea of the Yellow Sea (43°29.5′N, 121°59.1′E) in Jan., 2013 and South China Sea in 2013 (not shown in Fig. 1). All seawater samples were filtered through a 0.45 membrane to remove suspended particles immediately after collection. All seawater samples were collected in a pre-cleaned polyethylene bottle (using deionized water in the lab and original seawater on

site) and stored in the dark at room temperature until analysis. A certified seawater reference material for ^{129}I (IAEA-418), which was collected at the DY-FAMED station (43°25.117′N, 7°50.040′E) in the Mediterranean Sea on 18 Feb., 2001, was provided by International Atomic Energy Agency.

^{129}I standard solution (NIST-SRM-4949c) was purchased from the National Institute Standard and Technology (Gaithersburg, MD). ^{127}I carrier solution with a low ^{129}I level ($^{129}I/^{127}I$ atomic ratio $<2 \times 10^{-14}$) was prepared by dissolving iodine crystals (Woodward iodine, Woodward Iodine Corporation, Oklahoma, U.S.A.) in 0.40 mol/L NaOH–0.05 mol/L $NaHSO_3$ solution. $^{127}I^-$ carrier (KI, $^{129}I/^{127}I$ atomic ratio of $(2.0 \pm 0.3) \times 10^{-13}$) was purchased from Shantou Xilong Chemical Factory in Shantou, China. All chemical reagents used were of analytical grade, and all solutions were prepared using deionized water (18.2 MΩ·cm).

Separation of iodine and its chemical species in seawater

0.60 L of seawater was transferred to a beaker, 0.5 kBq of $^{125}IO_3^-$ tracer was spiked, 0–1.0 mg of ^{127}I carrier and 0.50 mL of 2.0 mol/L $NaHSO_3$ solution were added into the beaker, and then 3.0 mol/L HNO_3 was added to adjust pH 1–2 to convert all iodine species to iodide. 30 mg Ag^+ (28 mL of 0.01 mol/L $AgNO_3$ solution) was dropwise added to the sample solution under stirring to form AgI–AgCl–Ag_2SO_3–AgBr coprecipitate. The precipitate was separated by centrifuge and sequentially washed with 3.0 mol/L HNO_3, H_2O, 30 % and 20 % NH_4OH to remove
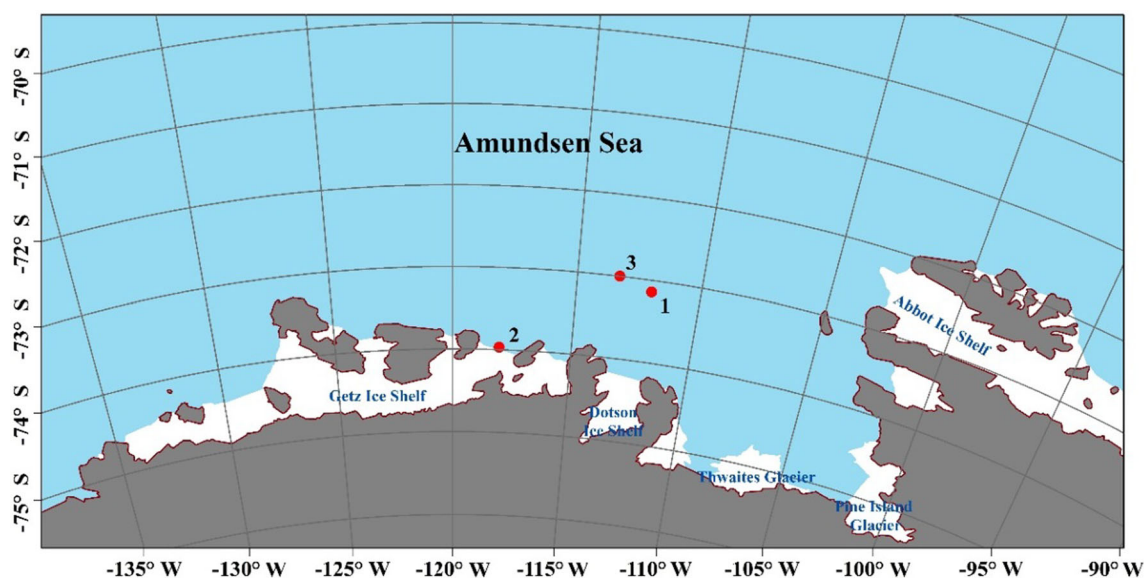

Fig. 1 Sampling locations (indicated as *red dots*) of seawater profiles in the Amundsen Sea, the Antarctic. (Color figure online)

Table 1 Information of seawater samples collected in the Amundsen Sea, Antarctica

Sampling station	Depth (m)	Salinity (psu)	Seawater temperature (°C)	Chlorophyll (μg/L)	Phosphate (μM)	Nitrite (μM)
1	2	33.8	−0.81	20.5	0.97	0.0284
	100	34.1	−1.63	–	1.93	0.0461
	200	34.1	−1.72	–	1.97	–
	350	34.3	−1.11	–	2.16	–
	394	34.4	0.19	–	2.18	–
2	2	33.9	−1.45	1.41	1.85	0.0284
	100	34.0	−1.70	–	1.89	0.0235
	260	34.1	−1.79	–	1.91	0.0306
	640	34.5	0.44	–	2.16	–
	750	34.5	0.62	–	2.13	–
	1227	34.6	−0.79	–	2.12	–
3	2	33.8	0.12	26.2	1.07	0.0268
	100	34.1	−1.63	–	1.89	0.0496
	240	34.2	1.24	–	2.02	–
	350	34.3	−0.19	–	2.12	–
	422	34.6	0.56	–	2.15	–

Ag_2SO_3 and most of the AgCl and AgBr until 1–3 mg of coprecipitate was obtained.

1.20 L seawater was transferred to a beaker for separation of iodide. 0.5 kBq of $^{125}I^-$ tracer and 0–1.0 mg of $^{127}I^-$ carrier (KI, $^{129}I/^{127}I$ atomic ratio of $<2.0 \times 10^{-13}$ carrier) were spiked, $NaHSO_3$ was added into the sample to a final concentration of 0.30 mmol/L, and then 0.5 mol/L HNO_3 was slowly added under stirring to adjust pH 4.2–5.5 (measured using a pH meter). 150 mg Ag^+ (45 mL of 0.03 mol/L $AgNO_3$) was dropwise added to the solution to form AgI–AgCl–Ag_2SO_3–AgBr coprecipitate. The precipitate was separated by centrifuge and the supernatant was used for separation of iodate. The separated precipitate was sequentially washed with 3.0 mol/L HNO_3, H_2O, 30 % and 20 % NH_4OH until 1–3 mg of precipitate were obtained. To the supernatant, 0.5 kBq $^{125}IO_3^-$ tracer was spiked, 0.1–0.2 mg of ^{127}I carrier, 0.5 mL of 2.0 mol/L $NaHSO_3$ solution were added, and then 3.0 mol/L HNO_3 was added to adjust pH 1–2 to convert all iodine species to iodide. The following procedure was the same as that for total iodine. The diagram of the analytical procedure is schematically shown in Fig. 2.

^{125}I in the precipitate was measured using a NaI gamma detector (Model FJ-2021, Xi'an Nuclear Instrument factory, Xi'an, China) for monitoring the chemical yield of iodine in the procedure. The recoveries of iodine species in the entire procedure for total iodine and species of iodine are higher than 80 %.

Two ^{129}I standard solutions with a total iodine concentration of 1.00 mg/mL and $^{129}I/^{127}I$ atomic ratios of 9.954×10^{-12} and 1.138×10^{-10}, respectively, were first prepared by dilution of ^{129}I standard solution (NIST-SRM-4949c) with ^{127}I carrier solution [12]. Two ^{129}I working solutions were prepared by mixing the above prepared ^{129}I standard solutions with NaCl solution in Cl/I mass ratio of 2:1. From each standard, 1.0 mL of working solution was taken to a 15 mL centrifuge tube, 0.5 kBq of $^{125}I^-$ tracer, 0.10 mL of 2.0 mol/L $NaHSO_3$, 0.20 mL of 3.0 mol/L HNO_3 were added and the solution is mixed. 0.20 mL of 1.0 mol/L $AgNO_3$ was then added to coprecipitate iodine as AgI–AgCl. After centrifuging, the precipitate was sequentially washed with 3.0 mol/L HNO_3 and deionized water. For ^{129}I standards in AgI form, the $^{129}I/^{127}I$ standard solution with a total iodine concentration of 1.0 mg/mL was first converted to iodide by $NaHSO_3$ in acidic medium, and then $AgNO_3$ was added to directly precipitate iodide as AgI.

The procedure blank samples were prepared using the same procedure as for separation of total iodine, iodide and iodate in seawater.

Iodine in the commercial ^{125}I tracer exists as iodide (NaI). To synthesize $^{125}IO_3^-$ tracer, $^{125}I^-$ solution was taken to a beaker, NaClO was added, then HCl is added to adjust pH 1–2 to oxidize iodide to iodate. The remained NaClO in the solution was decomposed by heating at 80 °C. The residue is dissolved in water, and the solution passed through a small anion exchange column (AG1- × 4 resin, NO_3^- form, 1.0 cm in diameter and 5 cm in height). The effluent containing iodate was collected and used as $^{125}IO_3^-$ tracer.

50 mL of seawater was taken to a beaker and $^{125}I^-$ was spiked. The sample was loaded to an anion exchange
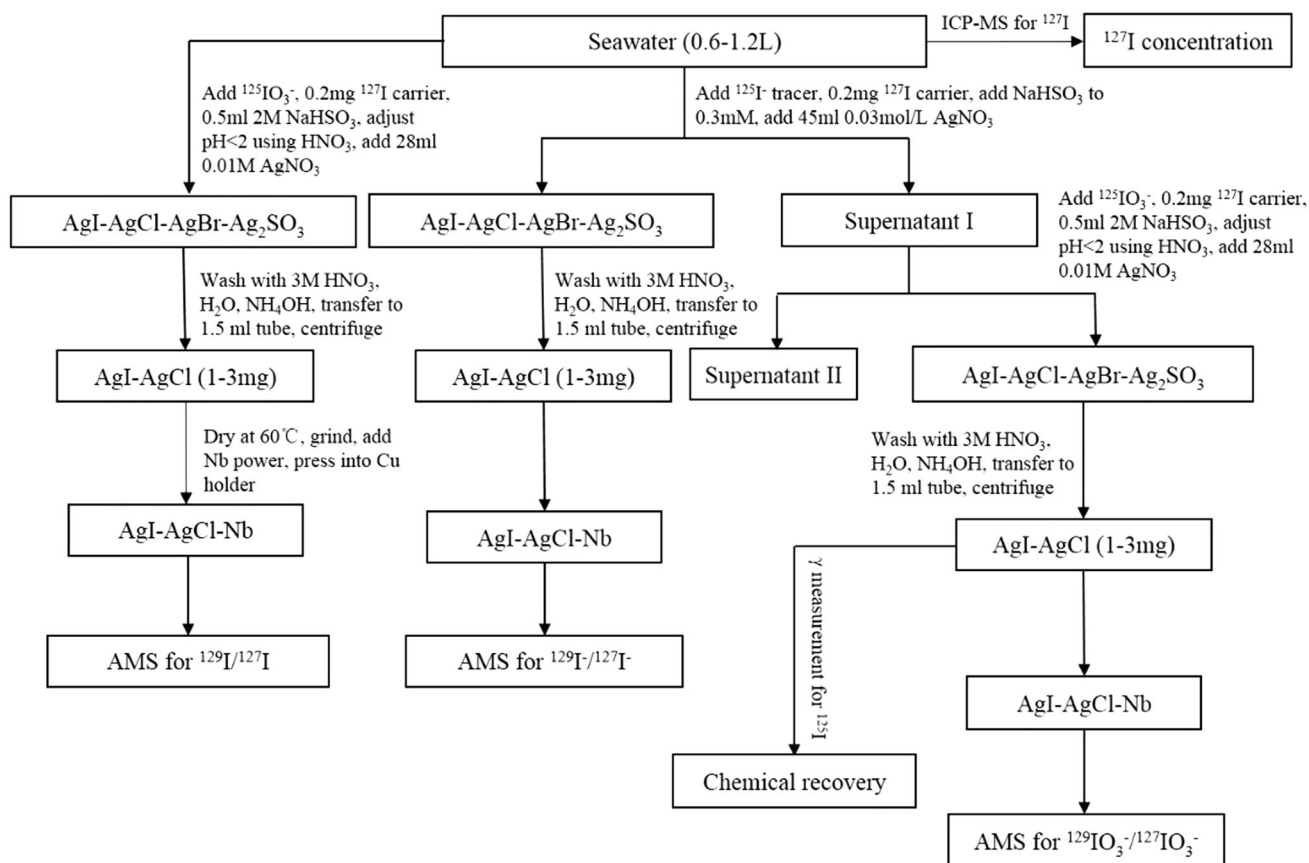
Fig. 2 Schematic diagram of the analytical procedure for speciation analysis of ^{129}I in seawater

column (1.0 × 5.0 cm, AG1- × 4 resin, NO$_3^-$ form), the column is rinsed with 10 mL of 0.2 mol/L NaNO$_3$. The influent and rinse solution were collected and combined for ^{127}IO$_3^-$ determination. Iodide on the column was eluted with 5 % NaClO, and the eluate was used for determination of ^{127}I$^-$. ^{125}I in the iodide fraction was measured by gamma spectrometer to monitor chemical recovery of iodide during column separation.

AMS measurement of ^{129}I

The separated AgI–AgCl coprecipitate was dried in an oven at 60–70 °C for 3–6 h, the dried precipitate was ground to fine powder and mixed with five times by mass of niobium powder (325-mesh, Alfa Aesar, Ward Hill, MA), which was finally pressed into a copper holder using a pneumatic press (Zhenjiang Aode Presser Instruments Ltd.). ^{129}I/^{127}I atomic ratios in the prepared targets were measured by AMS using 3MV Tandem AMS system (HVEE) in the Xi'an AMS center. I^{5+} ions were chosen for the measurement, where ^{127}I^{5+} was measured as charges (current) using a Faraday cup and ^{129}I^{5+} was measured using a gas ionization detector. All samples were measured for 6 cycles and 5 min per sample in each cycle. A detailed

description of AMS system and measurement of ^{129}I has been reported elsewhere [13].

Measurement of ^{127}I concentration by ICP-MS

1.0 mL sample solution of the iodide fraction and the iodate fraction separated using anion exchange column and the original seawater were taken to a vial, Cs solution (CsNO$_3$) was spiked to a concentration of 2 ng/mL and used as internal standard of ICP-MS measurement, and the samples were diluted for 10 times using 1 % NH$_4$OH solution. ^{127}I in the prepared samples was measured using ICP-MS (X-series II, Thermo Scientific, USA). A detection limit of 0.02 ng/mL for ^{127}I was obtained. Iodide concentration in the samples was corrected for chemical yield during column separation.

Results and discussion

Influence of the amount of ^{127}I carrier on ^{129}I measurement

Figure 3 shows the variation of measured concentration of ^{129}I with the amounts of added ^{127}I carrier in samples.
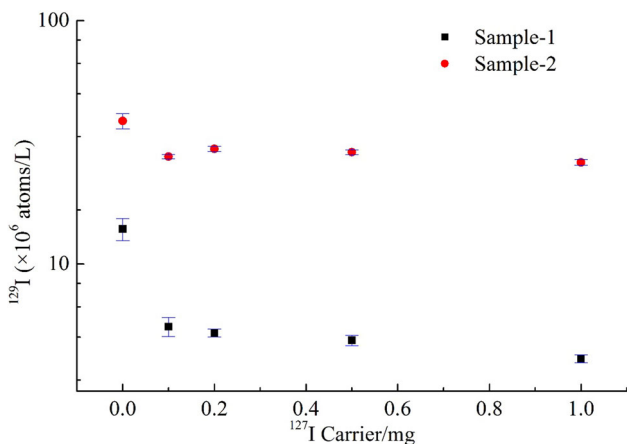
Fig. 3 Variation of the measured concentration of ^{129}I with the amount of ^{127}I carrier

Fig. 4 Variation of the measured ^{127}I current with the amount of ^{127}I carrier added

Sample-1 and Sample-2 were collected in open sea of the South China Sea and the Yellow Sea, respectively. They were analyzed after addition of different amount of ^{127}I carrier, as well as using carrier free method as described in the literature. The measured concentration of ^{129}I (13.9×10^6 atoms/L for sample-1 and 38.7×10^6 atoms/L for sample-2) by the carrier free AgI–AgCl coprecipitation method is 1.5–3.5 times higher than that in the target prepared by the carrier addition (0.1–1.0 mg) and AgI–AgCl coprecipitation method, in which concentrations of ^{129}I measured range from 4.08×10^6 atoms/L to 5.53×10^6 atoms/L for sample-1 and 26.1×10^6 atoms/L to 29.7×10^6 atoms/L for sample-2. The difference between the measured ^{129}I concentrations by two methods in the sample-1 is much bigger than that in sample-2, indicating that unreliable measurement results might be obtained when the target was prepared by carrier free method, especially for the low ^{129}I samples.

Figure 4 shows the variation of the measured ^{127}I current with the amounts of ^{127}I carrier added in samples. The intensity of ^{127}I current (4.4 nA) in the sample-2 prepared by carrier free coprecipitation method is only about 5 times higher than that in the blank (0.77 nA). In the AMS facilities using in Xi'an AMS center, the ^{127}I intensity is measured by Faraday cup while ^{129}I is counted by ionization detector. According to the deflection of ^{127}I measuring position by Faraday cup, terminal voltage of AMS can automatically adjust to take ^{129}I^{5+} through 115° magnet as much as possible before reach to the detector. Therefore, the ^{129}I was adjusted according to the measured ^{127}I intensity, the low iodine concentration in sample causes a higher measurement uncertainty of ^{127}I current, which consequently influence the stability of ^{129}I counts measured in AMS.

For sample-2, addition of ^{127}I carrier significantly enhanced the ^{127}I current intensity by factors of 30–140 to 137–620 nA compared to the carrier free target (4.4 nA).
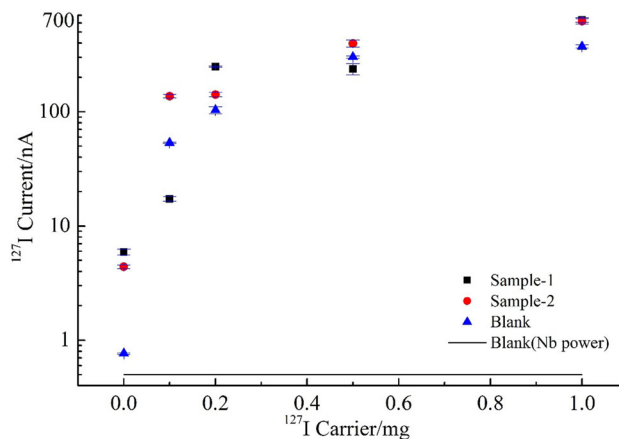
Meanwhile the measurement stability and reliability of ^{129}I can be significantly improved.

The amount of ^{127}I carrier is therefore a key parameter for the measurement accuracy and precision of ^{129}I by AMS. Figure 5 shows variation of the measured ^{129}I/^{127}I ratios with the amount of added ^{127}I carrier in samples. The difference between the ^{129}I/^{127}I ratio in the samples and procedure blank decreases as the amount of ^{127}I carrier added increases. When 1.0 mg ^{127}I carrier was added, the measured ^{129}I/^{127}I value in sample-1 [$(0.65 \pm 0.02) \times 10^{-12}$] is close to the procedure blank [$(0.26 \pm 0.02) \times 10^{-12}$], causing an increased analytical uncertainty of ^{129}I in the sample after a correction for the blank. Therefore, addition of higher amount of ^{127}I carrier is not suitable for the determination of low level ^{129}I in seawater because of contribution of ^{129}I in the iodine carrier to the sample. When the amount of ^{127}I carrier was reduced to 0.1–0.2 mg, the measured ^{129}I/^{127}I value in the sample-1 is more than one order of magnitude higher than that in the procedure blank,
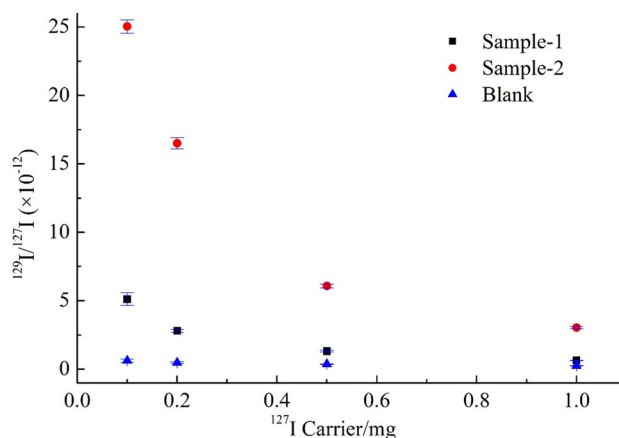

Fig. 5 Variation of the measured ^{129}I/^{127}I ratios with amount of ^{127}I carrier

making the measurement results of ^{129}I more reliable. These results reveal that addition of a small amount of carrier (0.1–0.2 mg) can significantly improve the measurement uncertainty in AMS measurement, especially in low level samples.

Reliability of the measurement of ^{129}I and its species in seawater

Many parameters affect the reliability of the measurement of ^{129}I and its species. Besides the addition of ^{127}I carrier presented above, the chemical yield of ^{129}I during separation, procedure blank and instrument background are also important factors for the reliable measurement of low level ^{129}I. The chemical yield of ^{129}I in the overall separation procedure was monitored using ^{125}I which was spiked into the sample at the beginning of the separation; a chemical yield for ^{125}I of more than 80 % was obtained for total ^{129}I and its species, which is sufficient to ensure accurate measurement of ^{129}I in low level samples, such as those collected from the Antarctic.

The procedure blanks were prepared using the same procedure as the sample, and the instrumental background was assessed by directly pressed Nb powder into a target holder. The measurement results including the measured intensity of ^{127}I and ^{129}I signal in these blanks, as well as the standards and IAEA-418 reference materials are presented in Table 2. The measured ^{129}I/^{127}I atomic ratios in the procedure blanks are lower than 4×10^{-13}, which are 2–3 orders of magnitude lower than those in the standards and IAEA-418 reference material. Meanwhile it is also more than one order of magnitude lower than the ^{129}I/^{127}I ratios in the seawater samples from the Antarctic (Fig. 6). This low procedure blank level and the high sensitivity of

AMS for ^{129}I measurement ensure the reliability of the analytical results of ^{129}I in these low-level samples. However, it can be observed that the intensity of the ^{129}I signals (4.6–5.4 counts/min) in the procedure blanks of seawater is higher than that in the instrumental background [(0.2 ± 0.1) counts/min] by a factor of more than 10. This might be contributed to the existence of tiny amount of ^{129}I in the ^{127}I carrier, which also confirms that it is critical to add suitable amount of ^{127}I carrier in the analysis of low level seawater samples.

The measured ^{129}I/^{127}I ratios in two types of standards prepared by AgI precipitation and AgI–AgCl coprecipitation are $(11.3 \pm 0.2) \times 10^{-11}$ and $(1.02 \pm 0.03) \times 10^{-11}$, respectively (Table 2), which are in a good agreement ($p > 0.05$) with the known value of $(11.38 \pm 0.15) \times 10^{-11}$ and $(0.9954 \pm 0.0150) \times 10^{-11}$, respectively. All these features indicate that the analytical results of low level ^{129}I in the Antarctic seawater samples by the improved method are reliable.

A certified reference material, IAEA-418 (Mediterranean Sea water) was analyzed using the improved method as well as the traditional solvent extraction method, i.e., after addition of iodine carrier and NaHSO$_3$, the pH of solution was adjusted to 1–2 using HNO$_3$ and then after the procedures of solvent extraction and back-extraction iodine was precipitated as AgI and finally measured by AMS. The measured concentrations of ^{129}I and ^{129}I/^{127}I atomic ratios in IAEA-418 (Table 2) by the two methods are in agreement ($p > 0.05$). The measured ^{129}I concentration in IAEA-418 seawater [$(2.71 \pm 0.01) \times 10^8$ atoms/L for coprecipitation method] also agrees well with the certified value [$(2.16$–$2.73) \times 10^8$ atoms/L] [14]. This confirms the reliability of the presented method for ^{129}I in seawater.

Table 2 Results of ^{129}I and ^{127}I signals in background, blanks and standards, as well as in IAEA-418 treated using solvent extraction and coprecipitation and measured by AMS in the AgI−AgCl targets

Sample	Intensity of signals[a]		Measured ^{129}I concentration ($\times 10^8$ atoms/L)	Measured ^{129}I/^{127}I ratio ($\times 10^{-11}$)
	^{127}I^{5+}, nA in 5 min	^{129}I^{5+}, counts/min		
Background (Nb power)	0.27 ± 0.12	0.21 ± 0.10		
Procedure blank1	209.5 ± 17.4	5.41 ± 0.42		0.031 ± 0.003
Procedure blank2	164.1 ± 17.9	4.63 ± 0.73		0.040 ± 0.004
Standard-1 (AgI)	590.7 ± 1.9	5030 ± 300		11.35 ± 0.17
Standard-1 (AgI–AgCl)	198.4 ± 1.04	1697 ± 198		11.41 ± 0.18
Standard-2 (AgI–AgCl)	264.6 ± 6.0	202.4 ± 23.0		1.02 ± 0.03
IAEA-418 (solvent extraction)[c]	432.7 ± 21.3	662.6 ± 32.6	2.68 ± 0.08[b]	
IAEA-418 (coprecipitation)[c]	342.2 ± 15.3	1229 ± 58.0	2.71 ± 0.08[b]	

[a] The results are given as average and 1 standard division of 6 measurements

[b] Value in sample, corrected for blank

[c] 0.315 and 0.817 mg ^{127}I carrier are added in the coprecipitation and solvent extraction method respectively, and the chemical recoveries of ^{125}I tracer are 95.8 and 70.3 %, respectively
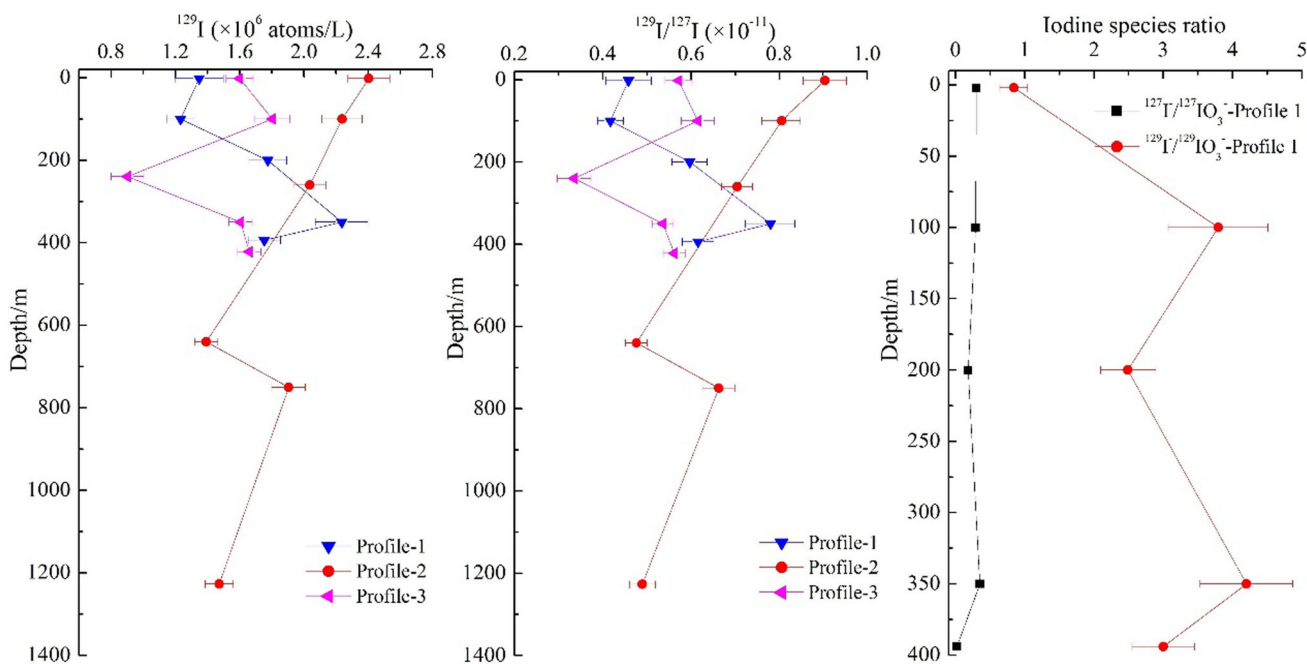
Fig. 6 Depth distribution of ^{129}I concentration (**a**), $^{129}I/^{127}I$ (**b**) in three seawater depth profiles and iodide/iodate molar ratios (**c**) in one depth profile of seawater, error bars indicate the analytical uncertainty

Due to lack of certified reference materials of seawater for ^{129}I species, a seawater sample collected from Yellow Sea was analyzed for iodide and iodate using the improved coprecipitation method presented in this work and the conventional anion-exchange chromatography method [2, 15] for control of the analytical quality. The analytical results of ^{129}I concentrations and $^{129}I/^{127}I$ atomic ratios for total ^{129}I, $^{129}I^-$, $^{129}IO_3^-$ obtained by the two methods are presented in Table 3. The results show a good agreement between the analytical results for ^{129}I and its species obtained by two methods ($p > 0.05$). This confirmed that the improved coprecipitation method for speciation analysis of ^{129}I presented here is reliable and suitable for analysis of ^{129}I in seawater. In addition, the sample was

analyzed twice (Table 3), and the results show good reproducibility for both ^{129}I concentrations and $^{129}I/^{127}I$ ratios for both iodide and iodate species (RSD < 5 %). Meanwhile, the cross contamination was also investigated, iodide precipitated in the iodate fraction is less than 3 %, and less than 1 % of iodate is precipitated in the iodide fraction, therefore the cross contamination of iodine species is therefore negligible.

In addition, the improved method presented in this work is less chemicals consuming, and very easy to operate in field compared to the conventional anion-exchange chromatography method for separation of iodine species in seawater [15]. These features make this method suitable for in situ separation of iodine species on board sampling

Table 3 Comparison of improved coprecipitation with conventional ion exchange chromatography methods for speciation analysis of ^{129}I in seawater (Yellow Sea water, China)

Species	Method	$^{129}I \times 10^7$ atoms/L	$^{129}I/^{127}I \times 10^{-10}$
Total iodine	Improved coprecipitation	5.43 ± 0.10	3.29 ± 0.06
		5.47 ± 0.11	3.31 ± 0.07
	Ion exchange chromatography	5.69 ± 0.14	3.44 ± 0.09
		5.64 ± 0.14	3.41 ± 0.09
I^-	Improved coprecipitation	3.93 ± 0.07	12.99 ± 0.22
		3.73 ± 0.07	12.34 ± 0.22
	Ion exchange chromatography	3.92 ± 0.12	12.96 ± 0.41
		3.99 ± 0.11	13.2 ± 0.38
IO_3^-	Improved coprecipitation	2.14 ± 0.07	1.59 ± 0.05
		2.13 ± 0.06	1.60 ± 0.04
	Ion exchange chromatography	1.79 ± 0.08	1.32 ± 0.06
		1.92 ± 0.08	1.42 ± 0.06

vessels during expedition. In particular, the method is apprciate for the separation of low level ^{129}I from seawater collected in the area far away from nuclear activity such as the Antarctic.

Distribution of ^{129}I and ^{127}I species in seawater in the Antarctic

Seawater samples collected from three depth profiles in the Antarctic water were analyzed for species of ^{129}I using the presented method. Figure 6 shows depth distribution of ^{129}I concentrations and ^{129}I/^{127}I atomic ratios in these three seawater profiles and iodide/iodate molar ratios in one seawater profile. The concentrations of ^{129}I ranged from 0.90×10^6 to 2.40×10^6 atoms/L, with an average of 1.71×10^6 atoms/L, which is significantly lower than that in the Northern Hemisphere ($>1.0 \times 10^7$ atoms/L) [16]. The ^{129}I/^{127}I atomic ratios range from 3.4×10^{-12} to 9.0×10^{-12}, with an average of 6.0×10^{-12}. This ratio is 4 times higher than the pre-nuclear level (1.5×10^{-12}) in the marine system [17–20], and indicates that anthropogenic ^{129}I has not only reached into the Antarctic surface marine environment [21] but into deeper waters down to 1227 m. The main source of ^{129}I in the investigated area might be attributed to the global fallout of atmospheric nuclear weapons testing [21].

^{129}I concentrations and ^{129}I/^{127}I atomic ratios in profile 2 show a small but visible decreasing trend with increasing depth, which might reflect a downward migration of ^{129}I in the ice shelf zone. However, vertical variation of profile 1 and 3 in the Amundsen Sea Polynya fluctuates smoothly with increase of the depth in some ranges, indicating strong vertical exchange/mixture of the water masses between the surface and the deep water. The trend of profile 2 is similar to that in the Gulf of Mexico and the Makarov Basin, Arctic Ocean, which shows a decrease with the increase of depth and the highest ^{129}I concentration lies near the surface (<100 m) [22, 23]. The trend of ^{129}I level in the profile 1 and 3 is different from that in the profile 2 and most of reported seawater profiles in other locations, where ^{129}I level exponentially decreases with the increase of depth and the highest ^{129}I level lies in subsurface water (<200 m) [24–26]. This indicates that a strong mixing of the water masses between the surface and subsurface layer occurred in this region in the Antarctic.

The iodide/iodate molar ratios of ^{127}I and ^{129}I show an obviously different distribution for ^{129}I compared with ^{127}I in the profile 1 (Fig. 6). The ^{127}I$^-$/^{127}IO$_3$$^-$ values are normally below 0.35 and show a fairly small variation, while the ratios for ^{129}I$^-$/^{129}IO$_3$$^-$ lie at 0.84–4.20, indicating that ^{129}I exists predominantly as iodide. This difference of iodine species between ^{127}I and ^{129}I is likely attributed to the different sources of these two isotopes and the

comparatively long time it takes to reach equilibrium between iodide and iodate in the open sea. It is well known that iodine mainly exists as iodate in the open sea, and iodide is formed in the coastal water and surface water by reduction of iodate through biological activities and photochemical and chemical reactions [2, 24]. Profile 1 was collected from an open sea, and the ^{127}I$^-$/^{127}IO$_3$$^-$ ratios are typical values for the open sea. Meanwhile, there are higher concentrations of phosphate, nitrite and lower concentrations of chlorophyll in the whole profile (Table 1), indicating the relatively weak biological activity. Therefore, the ^{129}I species should be controlled by the source water. The higher ^{129}I$^-$/^{129}IO$_3$$^-$ values in the deep sea might reflect strong vertical mixture of water masses and originate from the upwelling of circumpolar deep water [27] that carried the higher ^{129}I$^-$/^{129}IO$_3$$^-$ values. These results imply that the chemical speciation analysis of ^{129}I can be used to investigate the mixing and circulation of the water masses.

Conclusions

Based on the results and discussion above, it can be concluded: (1) addition of a small amount of ^{127}I carrier (0.1–0.2 mg) remarkably improved the accuracy and precision of ^{129}I measurement; (2) Three seawater profiles collected from the Antarctic in 2011 were successfully analyzed utilizing the improved method; (3) The results show that anthropogenic ^{129}I has reached into the Antarctic deep water down to 1227 m and its main source might be the global fallout of atmospheric nuclear weapons testing; (4) Depth distribution of ^{129}I and its speciation indicate that a strong mixing of the water masses between the surface and subsurface layer occurred in the Antarctic. This is just a preliminary investigation for the dispersion and mixing of water in the Antarctic and a comprehensive investigation using ^{129}I will provide detailed information on the water circulation in this region.

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