

Rapid Analysis of ^{129}I in Natural Water Samples Using Accelerator Mass Spectrometry

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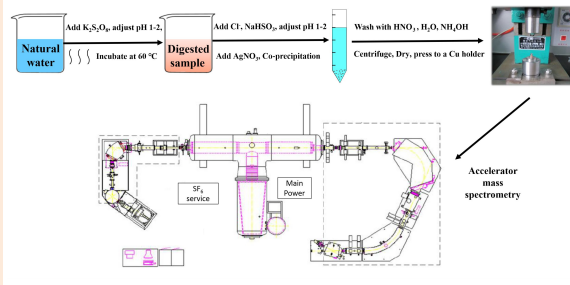
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ABSTRACT: A rapid and simple co-precipitation method for iodine separation from natural samples was developed for determination of ^{129}I using accelerator mass spectrometry (AMS). The method includes three steps, i.e. decomposition of organic iodine, iodine separation and target preparation using co-precipitation, and sensitive measurement of $^{129}\text{I}/^{127}\text{I}$ ratio using AMS. The recovery of iodine was higher than 90% for most natural water samples in the decomposition step using $\text{K}_2\text{S}_2\text{O}_8$. Iodine in the digested sample was then co-precipitated as $\text{AgI-AgCl-Ag}_2\text{SO}_3\text{-Ag}_2\text{SO}_4$ with a typical recovery of 95-98%. It was observed that addition of 0.2 mg ^{127}I carrier can significantly improve the measurement uncertainty of low-level ^{129}I samples by enhancing iodine ion current. The overall recovery of iodine in the entire procedure was higher than 80%, and a detection limit of 1.0×10^5 atoms (or 2.2×10^{-17} g) for ^{129}I was achieved. The developed method was validated by certified reference material (IAEA-418) and five types of natural water samples in comparison with results using the conventional solvent extraction method. Analytical results showed good agreement with the reference values for all samples, confirming the reliability of the developed method. The simple operation, with no need for organic solvent and small amount of iodine carrier addition make the developed method suitable for rapid and reliable determination of low level ^{129}I in natural water samples.



INTRODUCTION

As a long-lived (15.7 Ma) radioisotope of iodine, ^{129}I is naturally produced mainly through spallation reaction of atmospheric Xe with cosmic rays, the spontaneous fission of ^{238}U , and thermal neutron-induced fission of ^{235}U in the earth's crust.^{1,2} The natural abundance of ^{129}I in the hydrosphere was reported to be about 1.5×10^{-12} ($^{129}\text{I}/^{127}\text{I}$) based on the measurement of marine sediment samples.³⁻⁵ However, the $^{129}\text{I}/^{127}\text{I}$ atomic ratios have been significantly increased to more than 10^{-10} due to anthropogenic input including nuclear weapons tests, spent fuel reprocessing

plants and nuclear accidents,^{5,6} even up to 10^{-4} in the heavily contaminated area.⁷⁻¹¹ Iodine is a water-soluble and biophilic element, it mainly occurs as iodide, iodate and various organic associated forms in the nature. Due to its unique sources, chemical properties and long half-life, the ^{129}I has attracted high interests of geologists, chemists and environmental scientists for its application in dating of geological events,¹² environmental tracing,¹³ geochemical cycle of iodine,^{14,15} and safety assessment of nuclear facilities.¹⁶ These works require a reliable, sensitive and rapid analytical method for determination of ^{129}I in different types

of samples including water samples. Solvent extraction is the most commonly used method for separation of iodine from water samples.^{3,17} This method was used to directly separate ¹²⁹I from samples with high iodine concentration, or from samples spiked with 0.5–2 mg of stable iodine carrier before extraction. The major limitation of this method is that iodine concentration in the samples has to be sufficiently high (> 0.5 mg/L) to obtain a high chemical yield of ¹²⁹I (>50%).¹⁸ In addition, the water volume is limited to a few liters in this method due to difficulty in practical operation. For analysis of a large volume of water samples, anion exchange chromatography was used to pre-concentrate iodine, which is time-consuming since the flow rate needs to be controlled within 1 mL/min. Meanwhile, this method is not well suitable for determine ultra-low level ¹²⁹I in water sample, because ¹²⁷I carrier (0.5–2 mg) which contains some amount of ¹²⁹I has to be added to the sample in the solvent extraction operation after the chromatographic separation. The often-used iodine reagent of low ¹²⁹I content was prepared from old brine, such as that supplied by Woodward Iodine Corporation, the measured ¹²⁹I/¹²⁷I ratios normally range from 0.5 to 2.0×10^{-13} ,^{19–21} although the lowest value of 0.2×10^{-13} has been reported.^{22–24} This small amount of ¹²⁹I in iodine carrier might be negligible for the analysis of samples with ¹²⁹I/¹²⁷I > 10^{-10} . However, the contribution of ¹²⁹I in the carrier makes it difficult to determine ultralow level ¹²⁹I, which is often required in geological, environmental and geochemical studies. In addition, the method of solvent extraction with CCl₄ or CHCl₃ generates toxic organic waste, which is not environment friendly.

A co-precipitation method has been proposed to separate iodine from seawaters for measurement of ¹²⁹I using accelerator mass spectrometry,^{25–27} which can avoid the utilization of organic solvent and large amount of ¹²⁷I carrier. This work aims to further extend this method, with focus on rapid separation and sensitive determination of ¹²⁹I in natural waters (lake, river, rain, and ground water).

EXPERIMENTAL

Samples and chemicals. Four fresh water samples from Xi'an, China in 2019 and one seawater from the East China Sea were collected. The collected water was stored in PE containers. A rain water sample was collected on the roof of Xi'an Accelerator Mass Spectrometry Center (34° 13.42' N, 109° 0.01' E) on 19th May, 2019. The river water samples were first kept still for overnight to allow for the settlement of suspending materials (mud/sand), and the supernatants were collected. All water samples were filtered through 0.45 μm membrane within 2 days after collection.

NaI gamma detector (Model FJ-2021, Xi'an Nuclear Instrument factory, Xi'an, China) was used for measuring ¹²⁵I to monitor chemical recovery of iodide during separation. A pneumatic press

(Model J1303/GBWN, Jiangsu Audt riveting & pressure equipment Co., LTD, China) was used to target preparation. An inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 8800) was used to measure stable ¹²⁷I. A 3 MV Tandetron AMS (HEVV, The Netherlands) in the Xi'an AMS Center was used for measure ¹²⁹I/¹²⁷I atomic ratio in the prepared targets.

All chemical reagents used were of analytical grade reagent, including K₂S₂O₈, NaHSO₃, HNO₃, NaNO₂, and AgNO₃. All solutions were prepared using deionized water of 18.2 MΩ·cm, produced by Cascada™ Lab Water System (Pall Life Sciences, USA). Iodine crystal with a ¹²⁹I/¹²⁷I atomic ratio of 2×10^{-14} was provided by Woodward Inc. (USA), and dissolved in 0.40 mol/L NaOH-0.05 mol/L NaHSO₃ solution. ¹²⁹I standard solution (NIST-SRM-4949C) from the National Institute of Standard and Technology (Gaithersburg, MD, USA) was used to prepare ¹²⁹I standard by mixing with certain amount of ¹²⁷I (Woodward Inc. USA). Na¹²⁵I solution (Chengdu Gaotong isotope corporation, China) as the tracer solution was diluted in 0.001 mol/L NaOH. Niobium powders (325 mesh) was purchased from Alfa Aesar Company (Ward Hill, MA, USA).

Separation of iodine from environmental samples. Filtered fresh water or seawater (0.6 L) was weighed to a beaker. 0.2 mg of ¹²⁷I carrier and 5.0 kBq of ¹²⁵I tracer solution were spiked. 18 g of K₂S₂O₈ was added to sample to a final concentration of 30 g/L, and 3.0 mol/L HNO₃ was added to adjust pH 1–2. The prepared water sample was heated on a hotplate and incubated at 60 °C for 20 h, in order to decompose organic substances and convert organic iodine into inorganic forms.²⁸ After cooled to room temperature, 0.5 mL of 2.0 mol/L NaHSO₃ and 3.0 mol/L HNO₃ were added to adjust pH 1–2 to reduce all inorganic iodine to iodide. After addition of 0.5 mg chloride (as NaCl, to fresh water samples), 30 mL of 0.03 mol/L AgNO₃ was dropwised to the solution (fresh water and seawater) under stirring to form AgI-AgCl-Ag₂SO₃-Ag₂SO₄ coprecipitate. ¹²⁵I in the supernatant (1 mL) was measured using a gamma detector, and the recovery of iodine in this step was measured by comparing the ¹²⁵I activity in the supernatant with ¹²⁵I standard spiked to the sample. The supernatant was decanted, and the precipitate was separated by centrifuge. The separated precipitate was sequentially rinsed with HNO₃, H₂O, and diluted NH₄OH (5–10%) (only for seawater) to remove Ag₂SO₃ and most of AgCl respectively, until 1–3 mg of precipitate was obtained. The separated AgI-AgCl coprecipitate was dried in an oven at 60–70 °C, ground to a fine power, and mixed with five times by mass of niobium powder, which was finally pressed into a copper holder using a pneumatic press. Procedure blank was prepared using the same procedure but without sample. A schematic diagram of the separation procedure is shown in Fig. 1.

Measurement of ¹²⁹I and ¹²⁷I. Atomic ratios of ¹²⁹I/¹²⁷I in the prepared AgI-AgCl targets were measured by AMS using 3MV Tandem AMS system (HVEE) in the Xi'an AMS center. I⁻ ions sputtered from the ion source was accelerated, and then stripped

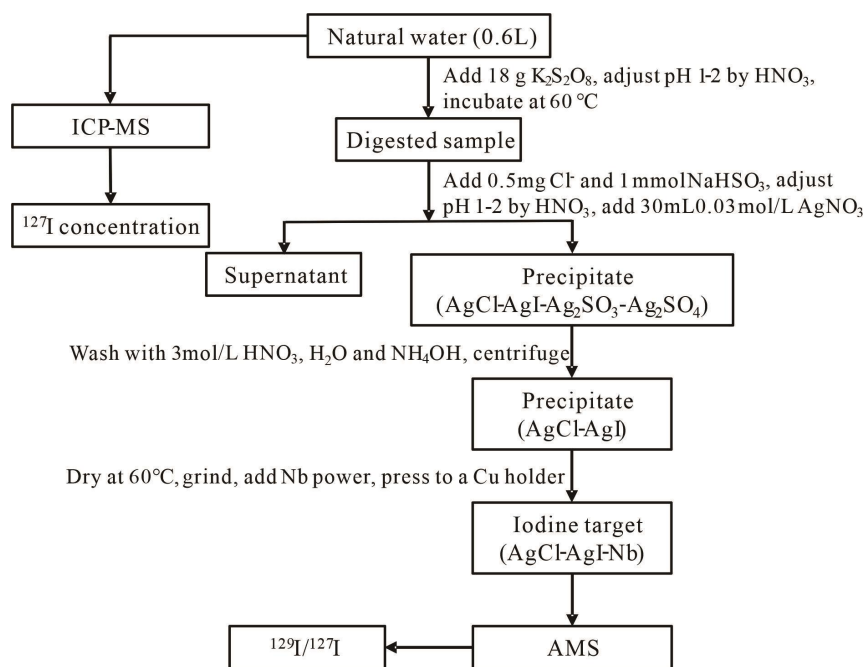


Fig. 1 Schematic diagram of procedure for separation of total iodine from natural water.

in the stripper with Ar gas, I^{5+} was chosen, and $^{127}I^{5+}$ 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.²⁹

Stable iodine (^{127}I) in fresh water samples and seawater were measured using ICP-MS (Agilent 8800) after dilution for 2 times for fresh water and 20 times for seawater using 1% NH_4OH . Cs^+ solution was spiked to a concentration of 2 ng/mL as internal standard. The detection limit of the method for ^{127}I was estimated as 3 times of blank to be 0.02 ng/mL.

RESULTS AND DISCUSSION

Decomposition of organic iodine in natural waters. For fresh water, such as lake, river and rain water, large fraction of iodine occurs in organic form,^{30,31} mainly as humic substances associated iodine. In these substances, iodine is covalently bound to aromatic or phenolic groups, and difficult to be separated from matrix without decomposition of organic substances. Iodine in fresh water is normally low ($<5 \mu g/L$), a large volume of sample (>500 mL) is therefore needed for determination of low level ^{129}I in these samples. Decomposition by oxidation using $K_2S_2O_8$ has been proposed to release iodine from organic substance in natural water samples at a temperature higher than $40^\circ C$ by formation of sulfate and/or hydroxyl radicals.^{28,32-34} Hydrogen ions might be involved in the reaction with organic matter,^{35,36} which makes pH of the

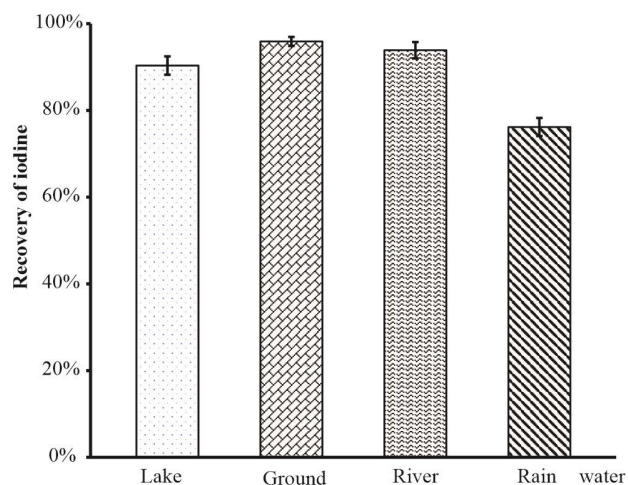
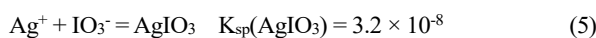
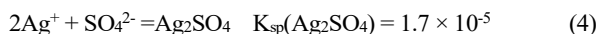
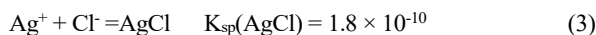
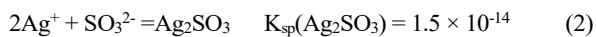
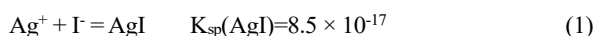


Fig. 2 Recovery of iodine in oxidizing decomposition using $K_2S_2O_8$ (at $60^\circ C$ for 20 h), error bars are standard deviation of the recovery results in four parallel experiments.

solution critical for the decomposition of organic substances. It was reported that the $pH < 2$ is helpful for reduce the loss of iodine during decomposition of organic matter.²⁸ Our results (Fig. 2) show that the recovery of iodine monitored by measurement of the spiked ^{125}I is higher than 90% for most natural samples, and can reach $95.9 \pm 1.0\%$ for ground water. This confirms that nearly all iodine is kept stable during decomposition and $K_2S_2O_8$ can successfully decompose organic iodine in all water samples.

Separation of ^{129}I from natural waters. In the $AgI-AgCl$ co-

precipitation process, many precipitation reactions might be involved, the most important reactions and their solubility products (K_{sp}) of the corresponding precipitation products are listed below:



It was reported that low concentration of iodine in natural fresh water samples *e.g.* 0.4–15 $\mu\text{g/L}$ in rain water and 0.1–18 $\mu\text{g/L}$ in river water was measured.^{9,37} The chloride concentration in precipitation in mid-continental regions (far from oceans and other salt sources) which is less than 1 mg/L, and often less than 0.1 mg/L,³⁸ more than thousands times lower chlorine compared to that in seawater, 19.0 g/L.³⁹ Therefore, a small amount of precipitate will be formed when an excess amount of AgNO_3 was added. For 1 L of rain water with low chloride (<0.1 mg/L), less than 0.4 mg of co-precipitate will be formed, which makes it impossible to be effectively separated from the supernatant of the large volume of sample. Meanwhile, this cannot cope with the requirement for iodine target preparation, as nearly 1–3 mg precipitate need to be pressed into holder for AMS measurement. The amount of sulfite and chloride added as co-precipitation agents—and amount of Ag^+ added to form precipitation are key parameters for separation of iodine in large volume fresh water by co-precipitation.

During the decomposition of organic iodine, the iodine is converted to the iodate by oxidizing reagent $\text{K}_2\text{S}_2\text{O}_8$. Because of the relatively high solubility of AgIO_3 ($K_{sp} = 3.2 \times 10^{-8}$) compared to AgI ($K_{sp} = 8.5 \times 10^{-17}$) and a low concentration of iodine in the solution, iodate was reduced to iodide using sulfite at $\text{pH} < 2$ to obtain a better recovery of iodine in the co-precipitation process. Excessive amount of sulfite was added in this step to form Ag_2SO_3 precipitate. Our investigation showed that Ag_2SO_3 - AgI co-precipitation significantly improved the recovery of iodine, which is attributed to the similar particle sizes of AgI (mainly 0.5–2.0 μm) and Ag_2SO_3 (mainly 0.5–1.5 μm) crystals.²⁷ In this step, NaHSO_3 not only converts the iodine to iodide, but also as a co-precipitation agent forms sufficient amount of co-precipitate with iodide. It is worth noting that sulfite compete with iodide to form precipitate with Ag^+ , large amount of sulfite might reduce the recovery of iodine if the amount of Ag added is not sufficient. In this work, 1.0 mmol sulfite (*i.e.* 0.5 mL of 2 mol/L NaHSO_3) was added after digestion of the sample. The excess of Ag_2SO_3 and Ag_2SO_4 precipitate needs to be removed to reduce the total precipitate to 1–3 mg for pressing to the target holder with niobium metal powder for AMS measurement. Meanwhile, it increases the iodine

concentration in the precipitate and improve the sensitivity of AMS measurement of ^{129}I . Based on the high solubility of Ag_2SO_3 and Ag_2SO_4 in acidic solution, Ag_2SO_3 and Ag_2SO_4 in the co-precipitates are easily removed by rinsing with 3 mol/L HNO_3 . In this case, almost all of Ag_2SO_3 and Ag_2SO_4 precipitates are dissolved, meanwhile, AgI particles are dispersed in the solution. Since the amount of AgI is too small (< 50 μg), it is suspended in the solution and could not be precipitated and handled in the following centrifugation step. Meanwhile, it is hard to get sufficient amount of co-precipitate (< 1 mg) to be handled in the target preparation due to the low concentration of iodine and chloride in the samples. Therefore, 0.5 mg of Cl^- was added to the digested sample to ensure sufficient amount of precipitate for the AMS measurement of ^{129}I .

In AMS measurement, ^{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 be adjusted to take $^{129}\text{I}^{5+}$ through 115° magnet as much as possible before reach to the detector. Therefore, the ^{129}I was adjusted according to the measured ^{127}I ion current, and the low iodine content in the target causes a high uncertainty of ^{127}I current, which consequently influence the stability of ^{129}I signal intensity measured in AMS. It has been observed that the measurement stability and reliability of ^{129}I can be significantly improved when the ^{127}I carrier increased from 0 to 0.2 mg.⁴⁰ Since the addition of large amount of stable iodine carrier (^{127}I) containing small amount of ^{129}I is not suitable for the determination of low-level ^{129}I in nature water, 0.2 mg of ^{127}I carrier was added to nature water samples in this work. The ^{129}I level in the analyzed environmental samples might vary within a few orders of magnitude, for example, the $^{129}\text{I}/^{127}\text{I}$ atomic ratios range from 10^{-12} in the deep-sea water or ground water samples to 10^{-8} in the surface water or rainwater. It is crucial that small amount of ^{127}I carrier should be used in the analysis of ground or deep-sea water to reduce the contribution of ^{129}I in the iodine carrier to the sample.

In this work, AgI - AgCl - Ag_2SO_3 - Ag_2SO_4 co-precipitation was used to separate iodine from the digested solution, and iodine recoveries of 95–98% were obtained when adding 0.5 mg of Cl^- in the solution containing 1.0 mmol NaHSO_3 . Considering the loss of iodine in the decomposition of organic iodine, an overall recovery of iodine in the entire procedure is higher than 80% for the natural water samples.

In comparison with the conventional solvent extraction method, the reported co-precipitation method for ^{129}I determination in natural water has following advantages. (1) addition of less carrier ^{127}I , which reduces the contribution of external ^{129}I and thus improves the reliability of analytical results for low-level ^{129}I samples; (2) single-step separation, which makes the separation

Table 1 Results of ^{127}I and ^{129}I Signals in Procedure Blanks Using Co-Precipitation Separation and AMS Measurement

No	Average ^{127}I current (nA)	Average ^{129}I count rate (Counts/min)	Measured $^{129}\text{I}/^{127}\text{I}$ ratio ^a
1	184.2	2.9 ± 0.5	(2.28 ± 0.32) × 10 ⁻¹³
2	88.1	1.4 ± 0.3	(2.11 ± 0.46) × 10 ⁻¹³
3	149.3	2.2 ± 0.4	(2.01 ± 0.34) × 10 ⁻¹³
4	78.3	0.9 ± 0.2	(1.85 ± 0.47) × 10 ⁻¹³
5	164.1	2.3 ± 0.4	(1.81 ± 0.25) × 10 ⁻¹³
6	110.7	1.2 ± 0.3	(1.46 ± 0.31) × 10 ⁻¹³
Average			(1.92 ± 0.36) × 10 ⁻¹³

^a All data is presented as average of six measurements.

easy to operate and less time-consuming; (3) less chemicals, especially exclusion of toxic organic solvent; (4) rapid analysis, the co-precipitation does not only single step separation, but also operated for a batch of sample, such as 16 or even 24 samples, so easy to handle and analyze large number of samples.

Detection limit of analytical method for ^{129}I . Procedure blanks were prepared using the same procedure as the sample, and the measurement results including the measured intensities of ^{127}I and ^{129}I in these blanks are presented in Table 1. The detection limit was calculated to be 1.0 × 10⁵ atoms (or 2.2 × 10⁻¹⁷ g) using three times the standard deviation of the $^{129}\text{I}/^{127}\text{I}$ ratios, sampling volume of 600 mL and 0.2 mg ^{127}I carrier. For fresh water including groundwater with iodine concentration of 1.0 μg/L, a $^{129}\text{I}/^{127}\text{I}$ ratio higher than 3.5 × 10⁻¹¹ can be determined in 600 mL water sample using the developed method. For samples with $^{129}\text{I}/^{127}\text{I}$ lower than 3.5 × 10⁻¹¹, a large size sample has to be analyzed. As for seawater, the iodine concentration is normally 45–60 μg/L,⁴¹ which is about two orders of magnitude higher than that in fresh water. Therefore, the developed method can be used to determine a $^{129}\text{I}/^{127}\text{I}$ ratio higher than 5.9 × 10⁻¹³ in seawater. It is critical to control the amount of the final precipitate (AgI–AgCl) by partially removal of AgCl with NH₄OH rinsing. The variation of ^{127}I ion currents (78–184 nA) is mainly affected by the final amount of the co-

precipitation in addition to the AMS instrument stability in ionization and ion transfer and measurement efficiencies.

Method validation. A certified reference material (IAEA-418) for ^{129}I value was analyzed using the developed method. The measured ^{129}I concentration of (24.8 ± 3.2) × 10⁷ atoms/L is in good agreement with the certified value ((24.4 ± 2.7) × 10⁷ atoms/L), indicating that the developed method is reliable and accurate for determination of ^{129}I in natural water samples (Table 2).

In addition, the developed method was validated by analysis of five natural water samples collected from China by both the developed co-precipitation method and the conventional solvent extraction method.^{41,42} The concentrations of total ^{129}I obtained by two methods are presented in Table 2, which shows a good agreement of ^{129}I concentration (p < 0.05) between two methods. This confirms that the presented co-precipitation method is reliable and suitable for determination of total ^{129}I in natural water. For lake, river and sea water samples, two aliquots of each sample (e.g. Lake water-1 and Lake water-2) were analyzed, analytical results of ^{129}I in two aliquots samples for these three types of sample agree very well, indicating a very good repeatability of the analytical method.

Determination of ^{129}I in natural water samples. Table 2 shows the analytical results of some natural water samples using the developed method. The ^{129}I concentrations and $^{129}\text{I}/^{127}\text{I}$ ratios in the surface waters (lake water and river water) are (1.6–1.8) × 10⁷ atoms/L and (4.1–4.5) × 10⁻⁹, respectively (Table 2), this is similar to the reported value in a river water from the west of Xi'an ((1.4 ± 0.3) × 10⁷ atoms/L for ^{129}I concentration and (3.7 ± 0.6) × 10⁻⁹ for $^{129}\text{I}/^{127}\text{I}$ ratio).⁹ Meanwhile, the ^{129}I concentration in surface water includes surface sea water is 1–2 orders of magnitudes lower than that contaminated region by human nuclear activities, such as adjacent areas of nuclear fuel reprocessing plants in Europe.^{8,43} The measured ^{129}I concentration of rain water collected in 2019 in Xi'an (23.0 × 10⁷ atoms/L) falls into the range of the reported ^{129}I

Table 2. Analytical Results of Total ^{129}I and ^{127}I in Natural Water Samples Using Co-precipitation and Solvent Extraction for Separation and AMS Measurement^a

Sample	^{127}I (μg/L)	^{129}I concentration (× 10 ⁷ atoms/L)		$^{129}\text{I}/^{127}\text{I}$ atomic ratio (× 10 ⁻⁹)	
		co-precipitation	solvent extraction	co-precipitation	solvent extraction
IAEA 418 ^b	56.6 ± 1.6	24.8 ± 3.2	23.3 ± 1.1	0.92 ± 0.12	0.87 ± 0.05
Lake water-1	0.83 ± 0.01	1.75 ± 0.05	1.74 ± 0.05	4.43 ± 0.13	4.40 ± 0.14
Lake water-2	0.83 ± 0.01	1.79 ± 0.07	1.86 ± 0.05	4.54 ± 0.19	4.70 ± 0.13
River water-1	0.84 ± 0.01	1.62 ± 0.06	1.55 ± 0.04	4.06 ± 0.16	3.90 ± 0.12
River water-2	0.84 ± 0.01	1.66 ± 0.05	1.63 ± 0.05	4.17 ± 0.12	4.09 ± 0.13
Rain water	4.73 ± 0.05	23.00 ± 0.32	21.43 ± 0.28	10.23 ± 0.18	9.55 ± 0.16
Ground water	2.06 ± 0.02	0.097 ± 0.026	0.096 ± 0.029	0.099 ± 0.026	0.098 ± 0.030
Sea water-1	11.0 ± 0.1	1.45 ± 0.07	1.59 ± 0.04	0.28 ± 0.01	0.31 ± 0.01
Sea water-2	11.0 ± 0.1	1.42 ± 0.14	1.41 ± 0.04	0.27 ± 0.03	0.27 ± 0.01

^a All data presented as average of six measurements; ^b The certified value of ^{129}I concentration is (24.4 ± 2.7) × 10⁷ atoms/L.

concentration collected in the same place from 2008 to 2016 ((0.33-152.9)×10⁷ atoms/L).⁴⁴ The lowest ¹²⁹I concentration of 9.7×10⁵ atoms/L and ¹²⁹I/¹²⁷I ratio of 9.9×10⁻¹¹ were measured in the ground water collected from Longxian, China, which is more than one order of magnitude lower than the surface water and two orders of magnitudes lower than the rain water, which indicates that only a small anthropogenic ¹²⁹I from atmospheric deposition entered to this ground water. However, the ¹²⁹I level in this ground water is significantly higher than the estimated pre-nuclear level of ¹²⁹I in surface water (approximate 5×10⁴ atoms/L),⁸ which might indicate that this shallow ground water has received small fraction of modern meteoric water containing anthropogenic ¹²⁹I, this also shed a light for the application of ¹²⁹I to trace the source of ground water. The ¹²⁹I concentration (1.4×10⁷ atoms/L) in the sea water samples collected in the coast of the East China Sea falls within the reported range of ¹²⁹I concentration in the East China Sea ((0.7-4.0) ×10⁷ atoms/L).¹⁰ The relatively low ¹²⁷I concentration in this seawater (11.0 μg/L) compared to the open seawater (60 μg/L) indicates that a large contribution of runoff water (Table 2).

CONCLUSIONS

A simple and rapid method for separation of iodine from natural water using oxidizing decomposition following AgI-AgCl coprecipitation was developed for determination of ultra-low level ¹²⁹I. Digestion with 30 g/L K₂S₂O₈ at pH 2 and 60 °C for 20 h can effectively release iodine from organic substance in natural waters. A recovery of higher than 90% for iodine was achieved in this process. Inorganic iodine was successfully separated by coprecipitation of AgI-AgCl-Ag₂SO₃-Ag₂SO₄ by addition of 0.5 mg of Cl⁻ and 1 mmol NaHSO₃ and excessive amount of AgNO₃, a recovery of higher than 95% was obtained for iodine in this step. The addition of small amount of carrier ¹²⁷I (0.2 mg) can improve the precision of AMS measurement by increasing the stability of the ¹²⁷I ion current, meanwhile, it limits the contribution of ¹²⁹I from the ¹²⁷I carrier and benefits for the determination of ¹²⁹I in ultra-low-level samples. The detection limit of this developed method for ¹²⁹I was estimated to be 1.0×10⁵ atoms (or 2.2×10⁻¹⁷ g) for 600 mL water sample. The method avoids the utilization of toxic organic solvent and suitable for analysis of large batch of samples.

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Notes

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