Preparation of Iodine-129 Standard Solutions for Triple Quadrupole ICP-MS

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Accelerator mass spectrometry (AMS) has been recognized as the most sensitive analytical method for the isotopic ratio of 129I/127I, but its limit of detection reaches as low as 129I/127I > 2×10⁻¹⁴. Recently triple quadrupole ICP-MS (ICP-MS/MS) is becoming an alternative analytical method for the rather high isotopic ratio range of 129I/127I > 10⁻⁸. Absolute ICP-MS/MS measurements require reliable standard materials for calibration. In this study, 129I standard solutions “tRIC-1” and “tRIC-2” were prepared from a laboratory-stored 129I solution and the 129I radioactivity standard of NIST SRM 4949d, respectively. The isotopic ratios of 129I/127I were determined to be (6.54 ± 0.23) × 10⁻⁵ for tRIC-1 and (3.41 ± 0.12) × 10⁻⁶ for tRIC-2 from the measurement results of AMS (129I/127I) ratio and ICP-MS/MS (127I concentration). From the 129I and 127I concentrations each calibration line in ICP-MS/MS was used to calculate the 129I/127I isotopic ratios which were (6.51 ± 0.26) × 10⁻⁵ for tRIC-1 and (3.34 ± 0.13) × 10⁻⁶ for tRIC-2. These isotopic ratios of 129I/127I agree with the value from AMS. It was proved that the two home-made standard solutions could be measured using the latest ICP-MS/MS and reliable isotopic ratios of 129I/127I were obtained.

1. Introduction

A large amount of 129I (t½ = 1.57 × 10⁻⁷ y) has been introduced into the terrestrial environment through nuclear weapon testing, spent nuclear fuel reprocessing operations, and nuclear accidents, and this has led to a wide range of isotopic ratios of 129I/127I from 10⁻¹⁴ to 10⁻⁷ in the terrestrial environment. The 129I determination in natural samples is commonly carried out at big facilities with radiochemical neutron activation analysis (RNAA) and accelerator mass spectrometry (AMS) capabilities. RNAA is based on neutron activation by 129I (n, γ) 130I, which is determined by measurement of γ rays at 536 keV. The limit of detection (LOD) of RNAA is 10⁻¹⁰ - 10⁻⁹ for 129I/127I isotopic ratios. Hence, AMS has been the only method for the determination of wide range of 129I/127I isotopic ratios. The LOD of 129I/127I ratio achieved by AMS < 2 × 10⁻¹⁴, AMS is applied as a certification method for the isotopic standard materials provided from the National Institute of Standards and Technology (NIST, USA) because AMS is the most reliable method for determination of 129I/127I isotopic ratios. The 129I/127I ratios have been normalized by standard reference materials provided by PRIME Lab at Purdue University.

Recent developments in analytical techniques using the triple quadrupole inductively coupled plasma mass spectrometry (ICP-MS/MS) have allowed observation of high 129I contents (LOD of ICP-MS/MS for 129I/127I isotopic ratio > 10⁻⁸) is more than six orders of magnitude higher than the LOD of AMS for the ratio). The ICP-MS/MS has a compact bench-top design and is a simple system resulting that is easier to maintain than RNAA or AMS systems. The ICP-MS/MS provides versatile applications by combining it with other devices such as gas or ion chromatographs and lasers and it offers high sample throughput for routine measurements. It may also be useful for screening of high 129I content samples. In ICP-MS/MS, the dominant interferences are 129Xe⁺ from argon plasma gas and polyatomic species, 129I₂⁺ (127I₂⁺), 129I²⁻, 129I²⁻, 129I²⁻, and 129I²⁻, which can be completely removed by taking an integration time for 129I/127I = 10⁻⁷. This dominant interference can be partially decreased by taking an integration time for m/z = 129 plus prior to m/z = 129. The standard reference material with certified isotopic ratio is essential to the accurate 129I analysis by ICP-MS/MS. However, there is no commercial isotopic standard reference material, and that has prevented widespread use of ICP-MS/MS for 129I environmental studies.

In this study, two types of home-made 129I standard solutions for ICP-MS/MS, designated “tRIC-1” and “tRIC-2”, were prepared from a laboratory-stored 129I solution and the 129I radioactivity standard of NIST SRM 4949d, respectively, and reliable isotopic ratios of 129I/127I were obtained.

2. Experimental

2.1. Standard solution preparation. The first standard solution, tRIC-1, was prepared from a laboratory-stored 129I solution that included approximately 0.1 M KOH, 0.1 M K₂SO₃, 1 mg mL⁻¹ 127I and 0.5 Bq mL⁻¹ 129I, and the calculated atomic 129I/127I ratio was 7 × 10⁻². A 10.1-g amount of the 129I solution was added to a PFA bottle (1000 mL) and diluted with 2% tetramethyl ammonium hydroxide (TMAH) solution.
The second standard solution, tRIC-2, was prepared from the 129 I radioactivity standard of NIST SRM 4949d that included 0.007 M Na2SO3 and 2.747 ± 0.03 kBq g-1 129I. A 10.1-mg amount of NIST SRM 4949d was mixed with 54 g of iodine solution (Orion Ionplus Application Solution Iodine Standard 0.1 M, Thermo Scientific) and 1.3 g Na2SO3 (analytical grade, Wako Pure Chemical). This mixed solution was diluted with deionized purified water to 1510 g in a PFA bottle (2000 mL), and thus the calculated atomic 129I/127I ratio was (3.33 ± 0.04) × 10-6. The 129I value of tRIC-2 was calculated to be 18.4 ± 0.2 mBq g-1.

All solutions prepared in this study were diluted with deionized purified water (18.2 MΩ cm) obtained from a PURELAB Ultra (ELGA) purifier.

2.2. Preparation of AMS targets and determination of the 129I/127I ratio by AMS. A 0.1-mL amount of tRIC-1 was transferred to a glass beaker, and this solution was mixed with 0.1 mL of 1% Na2SO3 and 698 mg of iodine (55 mL of Orion Ionplus, Application Solution Iodide Standard 0.1 M) to dilute the 129I/127I ratio for AMS. The iodine in mixed solution was precipitated as an AgI with 3 mL of 50% AgNO3 (analytical grade, Wako Pure Chemical) and 0.2 mL of conc. HNO3 (TAMAPURE-AA, Tama Chemicals). A 0.1-mL amount of tRIC-2 was treated as the same manner of tRIC-1 and the iodine was precipitated as an AgI. The precipitate was washed with 10% ammonia water followed by washing with pure water three times. The precipitate was collected by centrifugation at 3000 rpm and decanting, and then dried at 60°C. The dried precipitate AgI was pressed into an aluminum cathodes as the ion source targets of the AMS measurements. The AMS measurements were conducted at the The University of Tokyo’s Micro Analysis Laboratory, Tandem accelerator (MALT). The samples (that is, the dried precipitate AgI in the aluminium cathode targets) prepared from the tRIC-1 standard solution were measured in five different beam times, while the analogous samples prepared from the tRIC-2 standard solution were measured in one beam time. In each beam time, 4 or 5 cathode targets were mounted on the target wheel and measured at five times. The measured 129I/127I ratios were averaged to get the result for the beam time (Figure 1). The typical measurement time for one cathode target was 5 minutes. The LOD of the 129I-AMS system at MALT is typically 129I/127I < 2 × 10-14. The 129I/127I ratios were all normalized by the standard material of Z94-0596 provided by the PRIME Lab at Purdue University. The nominal value 129I/127I = 6.54 × 10-11 is used in MALT. The nominal value has a potential uncertainty of 2.9% (2σ) that comes from the source material. The 129I/127I ratio and 129I concentration (mBq g-1) of the home-made 129I standard solutions were calculated by the 129I/127I ratio from AMS and the 127I amounts (atoms) from ICP-MS/MS. Total uncertainty for the 129I/127I ratio was 3.6% (2σ) that was evaluated from the statistical errors of AMS (2.0%, 2σ), ICP-MS/MS (<1%, 2σ), and the total uncertainty of standard material (2.9%, 2σ). Total uncertainty for the 129I concentration was also 3.6% (2σ) and was evaluated in the same manner.

2.3. 129I measurement with ICP-MS/MS. The experimental parameters and configuration of the ICP-MS/MS (Agilent Technologies, model 8800) are summarized in Table 1. The set of a micro-uptake type glass concentric nebulizer (MiroMist™) and a quartz torch with a 1.5 mm internal diam-
3. Results and Discussion

The AMS results were corrected to the original isotopic ratios of the home-made standard solutions considering the isotopic dilution effect by the added stable iodine carrier. A good reproducibility was obtained in the $^{129}$I-AMS at MALT, as shown in Figure 2. The averaged isotopic $^{129}$I/$^{127}$I ratio results for five beam times ranged from $(6.51 \pm 0.05) \times 10^{-5}$ to $(6.57 \pm 0.03) \times 10^{-5}$. The $^{129}$I/$^{127}$I ratio of tRIC-1 was the averaged value for the five beam times and $6.54 \times 10^{-5}$ with total uncertainty of $3.6\%$ (2$\sigma$). The $^{127}$I concentration of tRIC-1 was determined to be $9.51 \pm 0.04 \mu g g^{-1}$ (2$\sigma$). The concentration of $^{129}$I of tRIC-2 was determined to be $4.13 \text{ mBq g}^{-1}$ (corresponding to $0.622 \text{ ng g}^{-1}$) with total uncertainty of $3.6\%$. The isotopic $^{129}$I/$^{127}$I ratio of tRIC-2 was evaluated from the result of one beam time measurement to be $3.41 \times 10^{-6}$ with total uncertainty of $3.6\%$ (2$\sigma$) (Figure 3). The concentration of $^{127}$I of tRIC-2 was determined to be $831 \pm 7 \mu g g^{-1}$ (2$\sigma$).
The concentration of $^{129}$I was determined to be 18.8 mBq g$^{-1}$ (corresponding to 2.83 ng g$^{-1}$) with total uncertainty of 3.6%.

The $^{129}$I concentrations for tRIC-1 and tRIC-2 were determined by the $^{129}$I calibration line obtained from ICP-MS/MS (Figure 4, bottom). The $^{129}$I concentration was 0.629 ng g$^{-1}$ (corresponding to 4.11 mBq g$^{-1}$) with total uncertainty of 4.0% for tRIC-1. For tRIC-2, the $^{129}$I concentration was 2.81 ng g$^{-1}$ (corresponding to 18.4 mBq g$^{-1}$) with total uncertainty of 4.0%. The $^{129}$I concentrations for tRIC-1 and tRIC-2 were determined by the $^{129}$I calibration line obtained from ICP-MS/MS (Figure 4, bottom). The $^{129}$I concentration was 0.629 ng g$^{-1}$ (corresponding to 4.11 mBq g$^{-1}$) with total uncertainty of 4.0% for tRIC-1. For tRIC-2, the $^{129}$I concentration was 2.81 ng g$^{-1}$ (corresponding to 18.4 mBq g$^{-1}$) with total uncertainty of 4.0%.

The isotopic ratios of $^{129}$I/$^{127}$I for tRIC-1 and tRIC-2 were calculated to be $(6.51 \pm 0.26) \times 10^{-5}$ and $(3.34 \pm 0.13) \times 10^{-6}$, respectively, from the determined each concentrations.

The LODs (3σ, $n = 10$) for $^{127}$I and $^{129}$I were 0.18 ng g$^{-1}$ and 0.10 pg g$^{-1}$, respectively, while the background equivalent concentrations for $^{127}$I and $^{129}$I were 1.0 ng g$^{-1}$ and 0.28 pg g$^{-1}$, respectively.

The $^{129}$I value of tRIC-1 from ICP-MS/MS (4.11 ± 0.16 mBq g$^{-1}$) agreed reasonably with that from AMS (4.13 ± 0.15 mBq g$^{-1}$). The $^{129}$I value of tRIC-2 from ICP-MS/MS (18.4 ± 0.7 mBq g$^{-1}$) agreed well with that calculated from the theoretical value (18.4 ± 0.2 mBq g$^{-1}$). The AMS result (18.8 ± 0.7 mBq g$^{-1}$) also showed good agreement with the theoretical value.

The isotopic ratio of $^{129}$I/$^{127}$I of the home-made $^{129}$I standard solutions measured by ICP-MS/MS agreed well with those by AMS. This result indicated that two suitable and reliable isotopic ratio $^{129}$I/$^{127}$I standard solutions for ICP-MS/MS, tRIC-1 and tRIC-2, were obtained from this study for the iodine isotope concentration and isotopic ratio determinations. The statistical uncertainty from ICP-MS/MS was around 2% for $^{129}$I concentration under the studied conditions. However, the statistical uncertainty by ICP-MS/MS can be improved by increasing the integration time.

4. Conclusions

Two types of the home-made $^{129}$I standard solutions “tRIC-1” and “tRIC-2” were prepared in this study and they gave reasonably reliable values for the isotopic ratio of $^{129}$I/$^{127}$I and each isotope concentration in ICP-MS/MS measurements. The home-made $^{129}$I standard solutions were prepared using the laboratory-stored $^{129}$I solution for tRIC-1 and the $^{129}$I radioactivity standard of NIST SRM 4949d for tRIC-2. The $^{127}$I concentrations were determined by ICP-MS/MS to be 9.51 ± 0.04 μg g$^{-1}$ for tRIC-1 and 831 ± 7 μg g$^{-1}$ for tRIC-2. From the AMS determinations for tRIC-1, the $^{129}$I concentrations and the isotopic ratios of $^{129}$I/$^{127}$I were 4.13 ± 0.15 mBq g$^{-1}$ and $(6.54 \pm 0.23) \times 10^{-5}$, respectively, and for tRIC-2, they were 18.8 ± 0.7 mBq g$^{-1}$ and $(3.41 \pm 0.12) \times 10^{-6}$, respectively. These home-made solutions were demonstrated to be applicable standards when using ICP-MS/MS.

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