

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 $^{129}\text{I}/^{127}\text{I}$, and its limit of detection reaches as low as $^{129}\text{I}/^{127}\text{I} < 2 \times 10^{-14}$. Recently triple quadrupole ICP-MS (ICP-MS/MS) is becoming an alternative analytical method for the rather high isotopic ratio range, $^{129}\text{I}/^{127}\text{I} > 10^{-8}$. Absolute ICP-MS/MS measurements require reliable standard materials for calibration. In this study, ^{129}I standard solutions “tRIC-1” and “tRIC-2” were prepared from a laboratory-stored ^{129}I solution and the ^{129}I radioactivity standard of NIST SRM 4949d, respectively. The isotopic ratios of $^{129}\text{I}/^{127}\text{I}$ were determined to be $(6.54 \pm 0.23) \times 10^{-5}$ for tRIC-1 and $(3.41 \pm 0.12) \times 10^{-6}$ for tRIC-2 from the measurement results of AMS ($^{129}\text{I}/^{127}\text{I}$ ratio) and ICP-MS/MS (^{127}I concentration). From the ^{129}I and ^{127}I concentrations each calibration line in ICP-MS/MS was used to calculate the $^{129}\text{I}/^{127}\text{I}$ isotopic ratios which were $(6.51 \pm 0.26) \times 10^{-5}$ for tRIC-1 and $(3.34 \pm 0.13) \times 10^{-6}$ for tRIC-2. These isotopic ratios of $^{129}\text{I}/^{127}\text{I}$ 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 $^{129}\text{I}/^{127}\text{I}$ were obtained.

1. Introduction

A large amount of ^{129}I ($t_{1/2} = 1.57 \times 10^7$ 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 $^{129}\text{I}/^{127}\text{I}$ from 10^{-14} to 10^{-1} in the terrestrial environment.¹⁻⁴ The ^{129}I 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 ^{129}I (n, γ) ^{130}I , which is determined by measurement of γ rays at 536 keV. The limit of detection (LOD) of RNAA is $10^{-10} - 10^{-9}$ for $^{129}\text{I}/^{127}\text{I}$ isotopic ratios.^{5,6} Thus, AMS has been the only method for the determination of wide range of $^{129}\text{I}/^{127}\text{I}$ isotopic ratios. The LOD of $^{129}\text{I}/^{127}\text{I}$ ratio achieved by AMS $< 2 \times 10^{-14}$.⁷ 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 the $^{129}\text{I}/^{127}\text{I}$ isotopic ratios. The $^{129}\text{I}/^{127}\text{I}$ ratios have been normalized by standard reference materials provided by PRIME Lab at Purdue University.⁸

Recent developments in analytical techniques using the triple quadrupole inductively coupled plasma mass spectrometry (ICP-MS/MS) have allowed observation of high ^{129}I contents (LOD of ICP-MS/MS for the $^{129}\text{I}/^{127}\text{I}$ isotopic ratio $> 10^{-8}$ is more than six orders of magnitude higher than the LOD of AMS for the ratio).⁹⁻¹¹ 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 pro-

vides 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 ^{129}I content samples. In ICP-MS/MS, the dominant interferences are $^{129}\text{Xe}^+$ from argon plasma gas and polyatomic species, $^{127}\text{IH}_2^+$ ($^{127}\text{ID}^+$), $^{97}\text{MoO}_2^+$ and $^{113}\text{CdO}^+$, from ^{129}I -containing sample. The $^{129}\text{Xe}^+$ signal can be efficiently lowered by reaction with O_2 to a negligible level (ca. 1 count per second).¹²⁻¹⁴ But the severe polyatomic interference of $^{127}\text{IH}_2^+$ ($^{127}\text{ID}^+$) cannot be entirely removed, meaning that the LOD of ^{129}I is restricted to $0.5 \mu\text{Bq mL}^{-1}$ (corresponding to $^{129}\text{I}/^{127}\text{I} = 10^{-8}$).⁹⁻¹¹ This dominant interference can be partially decreased by taking an integration time for $m/z = 128$ prior to $m/z = 129$. The standard reference material with certified isotopic ratio is essential to the accurate ^{129}I 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 ^{129}I environmental studies.

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

2. Experimental

2.1. Standard solution preparation. The first standard solution, tRIC-1, was prepared from a laboratory-stored ^{129}I solution that included approximately 0.1 M KOH, 0.1 M K_2SO_3 , 1 mg mL^{-1} ^{127}I and 0.5 Bq mL^{-1} ^{129}I , and the calculated atomic $^{129}\text{I}/^{127}\text{I}$ ratio was 7×10^{-5} . A 10.1-g amount of the ^{129}I solution was added to a PFA bottle (1000 mL) and diluted with 2% tetramethyl ammonium hydroxide (TMAH) solution

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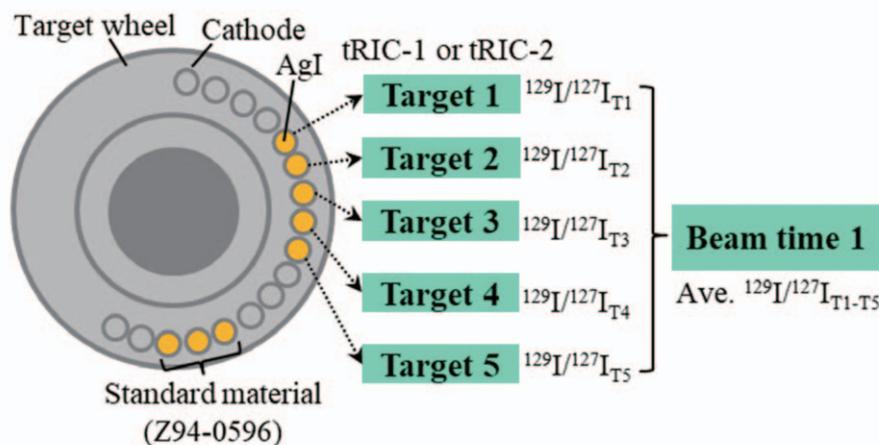


Figure 1. Schematic drawing explaining the AMS measurement of targets prepared from tRIC-1 and tRIC-2. Five or four solid AgI targets and standard materials were pressed into aluminum cathodes. These aluminum cathodes were then mounted on a target wheel so they could be analyzed at five times sequentially. The $^{129}\text{I}/^{127}\text{I}$ measurement results of each target were averaged to get a beam time.

(TAMAPURE-AA, Tama Chemicals) to 1015 g. Therefore, the ^{129}I of tRIC-1 was calculated to be about 5 mBq g^{-1} .

The second standard solution, tRIC-2, was prepared from the ^{129}I radioactivity standard of NIST SRM 4949d that included 0.007 M Na_2SO_3 and 2.747 ± 0.03 kBq g^{-1} ^{129}I . 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 Na_2SO_3 (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 $^{129}\text{I}/^{127}\text{I}$ ratio was $(3.33 \pm 0.04) \times 10^{-6}$. The ^{129}I 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 M Ω cm) obtained from a PURELAB Ultra (ELGA) purifier.

2.2. Preparation of AMS targets and determination of the $^{129}\text{I}/^{127}\text{I}$ 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% Na_2SO_3 and 698 mg of iodine (55 mL of Orion Ionplus, Application Solution Iodine Standard 0.1 M) to dilute the $^{129}\text{I}/^{127}\text{I}$ ratio for AMS. The iodine in mixed solution was precipitated as an AgI with 3 mL of 50% AgNO_3 (analytical grade, Wako Pure Chemical) and 0.2 mL of conc. HNO_3 (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 $^{129}\text{I}/^{127}\text{I}$ 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 ^{129}I -AMS system at MALT is typically $^{129}\text{I}/^{127}\text{I} < 2 \times 10^{-14}$.⁷ The $^{129}\text{I}/^{127}\text{I}$ ratios were all normalized by the standard material of Z94-0596 provided by the PRIME Lab at Purdue University. The nominal value $^{129}\text{I}/^{127}\text{I} = 6.54 \times 10^{-11}$ is

TABLE 1: The experimental parameters and configuration of ICP-MS/MS

Sample introduction system	Parameters
Plasma	
RF power	1550 W
Plasma gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	0.90 mL min^{-1}
Nebulizer gas flow rate	1.01 mL min^{-1}
Solution uptake rate	0.1 mL min^{-1}
Spray chamber temperature	2°C
Sampling depth	8 mm
Lens	
Extraction lens 1, 2	0 V, -200 V
Cell focus	2.0 V
Cell entrance	-50 V
Cell exit	-60 V
Deflection	2.0 V
Plate bias	-60 V
Cell	
O_2 gas flow rate	0.8 mL min^{-1}
Octopole bias	-5.0 V
Octopole RF	200 V
Energy discrimination	-7.0 V
Other	
Integration time for $m/z = 127, 128, 129$	0.5, 1.0, 10 s
Repetition, sweep	10, 100 times

used in MALT. The nominal value has a potential uncertainty of 2.9% (2 σ) that comes from the source material.⁸ The $^{129}\text{I}/^{127}\text{I}$ ratio and ^{129}I concentration (mBq g^{-1}) of the home-made ^{129}I standard solutions were calculated by the $^{129}\text{I}/^{127}\text{I}$ ratio from AMS and the ^{127}I amounts (atoms) from ICP-MS/MS. Total uncertainty for the $^{129}\text{I}/^{127}\text{I}$ ratio was 3.6% (2 σ) that was evaluated from the statistical errors of AMS (2.0%, 2 σ), ICP-MS/MS (<1%, 2 σ), and the total uncertainty of standard material (2.9%, 2 σ). Total uncertainty for the ^{129}I concentration was also 3.6% (2 σ) and was evaluated in the same manner.

2.3. ^{129}I 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 (MiroMistTM) and a quartz torch with a 1.5 mm internal diam-

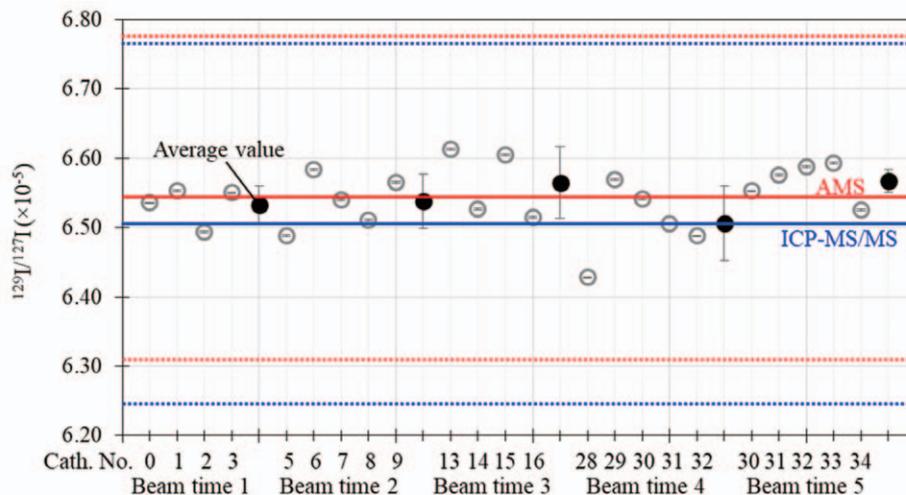


Figure 2. Measured isotopic ratios of $^{129}\text{I}/^{127}\text{I}$ of tRIC-1 standard solution obtained by AMS. Shown data were corrected values considering the isotopic dilution effect by the carrier. Open gray circles shows the $^{129}\text{I}/^{127}\text{I}$ ratios obtained from the measurement for each cathode and closed black circles show the averaged $^{129}\text{I}/^{127}\text{I}$ values calculated from each beam time. The $^{129}\text{I}/^{127}\text{I}$ isotopic ratio obtained by AMS is denoted as a solid red line that was evaluated as the averaged value for five beam times. Broken red lines show the total uncertainty of 3.6% (2σ) for the $^{129}\text{I}/^{127}\text{I}$ isotopic ratio. The solid blue line shows the $^{129}\text{I}/^{127}\text{I}$ ratio obtained by ICP-MS/MS. The broken blue line shows the total uncertainty of 4.0% (2σ) for the $^{129}\text{I}/^{127}\text{I}$ ratio.

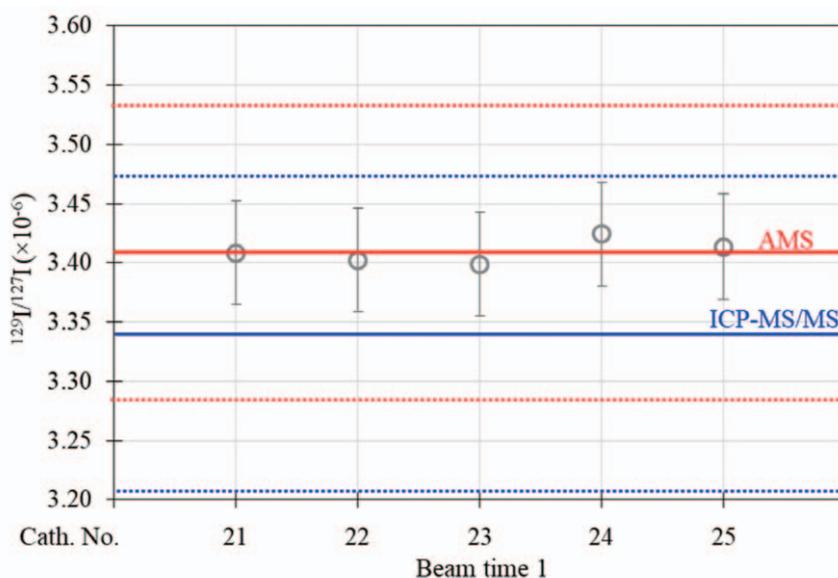


Figure 3. Measured isotopic ratios of $^{129}\text{I}/^{127}\text{I}$ of tRIC-2 standard solution obtained by AMS. Shown data here were corrected values considering the isotopic dilution effect by the carrier. Open gray circles show the $^{129}\text{I}/^{127}\text{I}$ ratios obtained from the measurement for each cathode. The $^{129}\text{I}/^{127}\text{I}$ ratio obtained by AMS is denoted as a solid red line that was evaluated as an averaged value for five cathodes. Broken red lines show the total uncertainty of 3.6% (2σ) for the $^{129}\text{I}/^{127}\text{I}$ isotopic ratio. The solid blue line shows the total uncertainty of 4.0% (2σ) for the $^{129}\text{I}/^{127}\text{I}$ ratio.

eter injector was applied for sample introduction.⁹ Plasma and carrier gases were 99.99% Ar, and reaction gas was 99.999% O_2 . The isotopic ratios of $^{129}\text{I}/^{127}\text{I}$ of the two home-made ^{129}I standard solutions were determined by the ^{127}I and ^{129}I concentrations using the calibration lines for ^{127}I and ^{129}I . These calibration lines were obtained from multiple dilutions of the iodine standard solution (Orion Ionplus, Application Solution Iodine Standard 0.1 M) and the ^{129}I radioactivity standard solution from NIST SRM 4949d. ^{127}I was measured under the same conditions as for ^{129}I . The total measurement time was about 5 minutes for one sample. Total uncertainty of the $^{129}\text{I}/^{127}\text{I}$ ratio was 4.0% (2σ) and that was evaluated from the statistical errors of the ^{127}I measurement ($<1\%$, 2σ), the ^{129}I measurement (3.8%, 2σ) and the total uncertainty of NIST SRM 4949d (1.1%, 2σ). The uncertainty of the ^{129}I concentration was 4.0% (2σ) and that evaluated from the statistical error of the ^{129}I measurement and the total uncertainty of NIST SRM 4949d.

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 $^{129}\text{I}/^{127}\text{I}$ 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 $^{129}\text{I}/^{127}\text{I}$ ratio of tRIC-1 was the averaged value for the five beam times and 6.54×10^{-5} with total uncertainty of 3.6%. The ^{127}I concentration of tRIC-1 was determined to be $9.51 \pm 0.04 \mu\text{g g}^{-1}$ (2σ) from the calibration line in Figure 4 (top). The ^{129}I concentration of tRIC-1 was calculated by AMS and ICP-MS/MS results to be 4.13 mBq g^{-1} (corresponding to 0.622 ng g^{-1}) with total uncertainty of 3.6%. The isotopic $^{129}\text{I}/^{127}\text{I}$ ratio of tRIC-2 was evaluated from the result of one beam time measurement to be 3.41×10^{-6} with total uncertainty of 3.6% (Figure 3). The concentration of ^{127}I of tRIC-2 was determined to be $831 \pm 7 \mu\text{g g}^{-1}$ (2σ). The con-

centration 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 isotopic ratios of $^{129}\text{I}/^{127}\text{I}$ 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 ($4.11 \pm 0.16 \text{ mBq g}^{-1}$) agreed reasonably with that from AMS ($4.13 \pm 0.15 \text{ mBq g}^{-1}$). The ^{129}I value of tRIC-2 from ICP-MS/MS ($18.4 \pm 0.7 \text{ mBq g}^{-1}$) agreed well with that calculated from the theoretical value ($18.4 \pm 0.2 \text{ mBq g}^{-1}$). The AMS result ($18.8 \pm 0.7 \text{ mBq g}^{-1}$) also showed good agreement with the theoretical value.

The isotopic ratio of $^{129}\text{I}/^{127}\text{I}$ 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 $^{129}\text{I}/^{127}\text{I}$ 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 $^{129}\text{I}/^{127}\text{I}$ 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 $9.51 \pm 0.04 \mu\text{g g}^{-1}$ for tRIC-1 and $831 \pm 7 \mu\text{g g}^{-1}$ for tRIC-2. From the AMS determinations for tRIC-1, the ^{129}I concentrations and the isotopic ratios of $^{129}\text{I}/^{127}\text{I}$ were $4.13 \pm 0.15 \text{ mBq g}^{-1}$ and $(6.54 \pm 0.23) \times 10^{-5}$, respectively, and for tRIC-2, they were $18.8 \pm 0.7 \text{ mBq g}^{-1}$ 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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References

- (1) G. Snyder, A. Aldahan, G. Possnert, *Geochim. Geophys. Geosyst.* 11, 1 (2010).
- (2) R. Michel, J. Handl, T. Ernst, W. Botsch, S. Szidat, A. Schmidt, D. Jakob, D. Beltz, L.D. Romantschuk, H.-A. Synal, C. Schnabel, J.M. López-Gutiérrez, *Sci. Total Environ.* 340, 35 (2005).

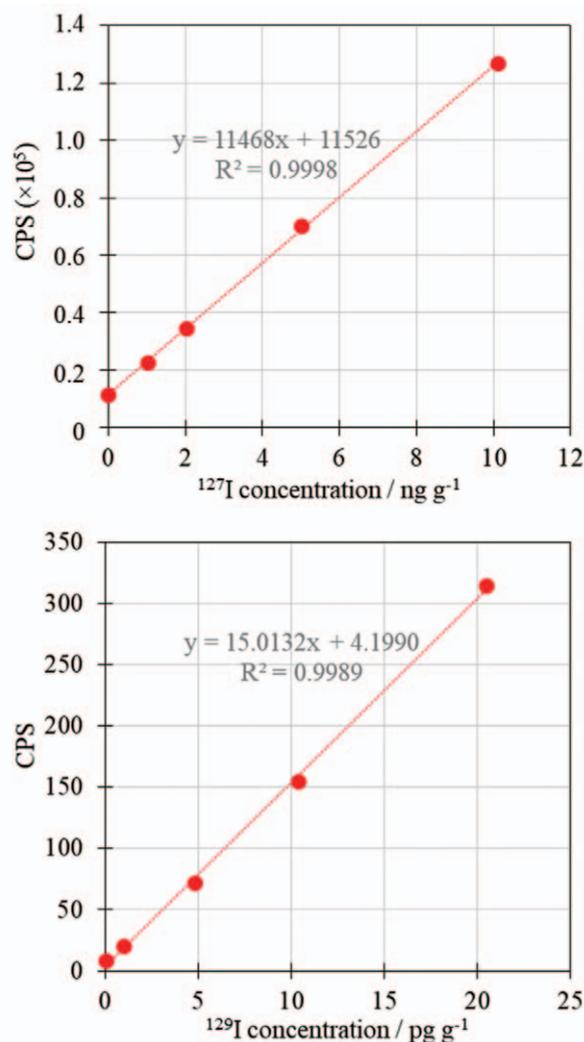


Figure 4. Calibration lines for ^{127}I (top) and ^{129}I (bottom). The ^{127}I and ^{129}I plots were obtained from the iodine standard solution (Orion Ionplus, Application Solution Iodine Standard 0.1 M) and the ^{129}I radioactivity standard solution (NIST SRM 4949d), respectively.

- (3) U. Rao and U. Fehn, *Geochim. Cosmochim. Acta.* 63, 1927 (1999).
- (4) P.J. Magno, T.C. Reavey, J.C. Apidianakis, ORP/SID 72-5, US Environmental Protection Agency, 1972.
- (5) Y. Muramatsu, Y. Ohmomo, D. Christoffers, *J. Radioanal. Nucl. Chem. Art.* 83, 353 (1984).
- (6) X. Hou, H. Dahlgaard, B. Rietz, U. Jacobsen, S. P. Nielsen, A. Aarkrog, *Analyst.* 124, 1109 (1999).
- (7) H. Matsuzaki, C. Nakano, Y.S. Tsuchiya, S. Ito, A. Morita, H. Kusuno, Y. Miyake, M. Honda, A.T. Bautista VII, M. Kawamoto, H. Tokuyama, *Nucl. Instrum. Methods Phys. Res.* 361, 63 (2015).
- (8) P. Sharma, D. Elmore, T. Miller, S. Vogt, *Nucl. Instrum. Methods Phys. Res.* 123, 347 (1997).
- (9) T. Ohno, Y. Muramatsu, C. Toyama, N. Kazumi S. Kakuta, H. Matsuzaki, *Anal. Sci.* 29, 271 (2013).
- (10) T. Ohno, Y. Muramatsu, Y. Shikamori, C. Toyama, N. Okabe, H. Matsuzaki, *J. Anal. At. Spectrom.* 28, 1283 (2013).
- (11) Y. Shikamori, K. Nakano, N. Sugimaya, S. Kakuta, Application note 5991-0321EN, Agilent, Japan. (2012).
- (12) G. C. Eiden, C. J. Barrinaga, and D. W. Koppenaal, *Rapid Commun. Mass Spectrom.* 11, 37 (1997).
- (13) D. R. Bandura, V. I. Baranov, and S. D. Tanner, *J. Am. Soc. Mass Spectrom.* 13, 1176 (2002).
- (14) A. V. Izmer, S. F. Boulyga, and J. S. Becker, *J. Anal. At. Spectrom.* 18, 1339 (2003).