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Isotope ratio analysis of individual sub-micrometer plutonium particles with inductively coupled plasma mass spectrometry

Fumitaka Esaka*, Masaaki Magara, Daisuke Suzuki, Yutaka Miyamoto, Chi-Gyu Lee, Takaumi Kimura

Research Group for Radiochemistry, Japan Atomic Energy Agency, 2-4 Shirakata-Shirane, Tokai, Naka, Ibaraki 319-1195, Japan

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ABSTRACT

Information on plutonium isotope ratios in individual particles is of great importance for nuclear safeguards, nuclear forensics and so on. Although secondary ion mass spectrometry (SIMS) is successfully utilized for the analysis of individual uranium particles, the isobaric interference of americium-241 to plutonium-241 makes difficult to obtain accurate isotope ratios in individual plutonium particles. In the present work, an analytical technique by a combination of chemical separation and inductively coupled plasma mass spectrometry (ICP-MS) is developed and applied to isotope ratio analysis of individual sub-micrometer plutonium particles. The ICP-MS results for individual plutonium particles prepared from a standard reference material (NBL SRM-947) indicate that the use of a desolvation system for sample introduction improves the precision of isotope ratios. In addition, the accuracy of the $^{241}Pu/^{239}Pu$ isotope ratio is much improved, owing to the chemical separation of plutonium and americium. In conclusion, the performance of the proposed ICP-MS technique is sufficient for the analysis of individual plutonium particles.

1. Introduction

Isotope ratio analysis is widely used in environmental sciences, which gives important information on origins of samples such as aerosols and soils. The method has recently been utilized to analyze individual uranium particles in environmental samples taken at nuclear facilities [1,2]. Since uranium isotope ratios vary significantly with nuclear activities such as production of nuclear weapons, enrichment and reprocessing, we can find out the traces of undeclared nuclear activities by measuring the isotope ratios in individual particles. For this purpose, secondary ion mass spectrometry (SIMS) is successfully applied to the analysis of individual uranium particles [3–6]. A well-known drawback in SIMS analysis is interferences by molecular ions emitted from other particles, giving inaccurate analytical results. In particular, the signals of uranium minor isotopes (^{234}U and ^{236}U) are easily affected by molecular ions, due to their smaller count rates. In order to overcome this problem, the authors developed a method by a combination of particle manipulation under scanning electron microscope (SEM) and isotope ratio analysis with SIMS [6]. The particle manipulation allows to transfer only uranium particles for subsequent SIMS analysis. Another approach to eliminate molecular ion interferences was proposed by Ranebo et al. [7]. They used a state-of-the-art SIMS instrument to separate peaks of uranium and molecular ions, obtaining accurate isotope ratio results.

As well as uranium, plutonium has an important role in nuclear power generation. The use of plutonium will become more dominant in near future. Although undeclared nuclear activities using plutonium should also be revealed, only a few studies were conducted to analyze isotope ratios of individual plutonium particles due to the difficulty in measurement [5,8]. One of the reasons is the isobaric interference of ^{241}Am to ^{241}Pu. Americium-241 is formed by the decay of ^{241}Pu with the half life of 14.325 years [9], meaning that ^{241}Am and ^{241}Pu usually coexist in a single plutonium particle. The particle manipulation would not be able to remove this kind of interference. In addition, there is no chance to separate the peaks of ^{241}Am and ^{241}Pu, even if SIMS analysis is carried out with considerably high mass resolution mode. Therefore, in order to obtain accurate $^{241}Pu/^{239}Pu$ isotope ratios, other kinds of approaches are necessary.

In previous studies [10–12], we developed an experimental technique for isotope ratio analysis of individual uranium and plutonium particles with inductively coupled plasma mass spectrometry (ICP-MS). Consequently, we enabled to analyze isotope ratios for individual micrometer particles. This technique includes particle manipulation and chemical dissolution of individual particles for subsequent isotope ratio analysis with ICP-MS. This approach was also utilized to the age determination of individual plutonium particles by a combination of chemical separation and thermal ionization mass spectrometry (TIMS) [13].

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* Corresponding author. Tel.: +81 29 282 6165; fax: +81 29 282 6950.
E-mail address: esaka.fumitaka@jaea.go.jp (F. Esaka).

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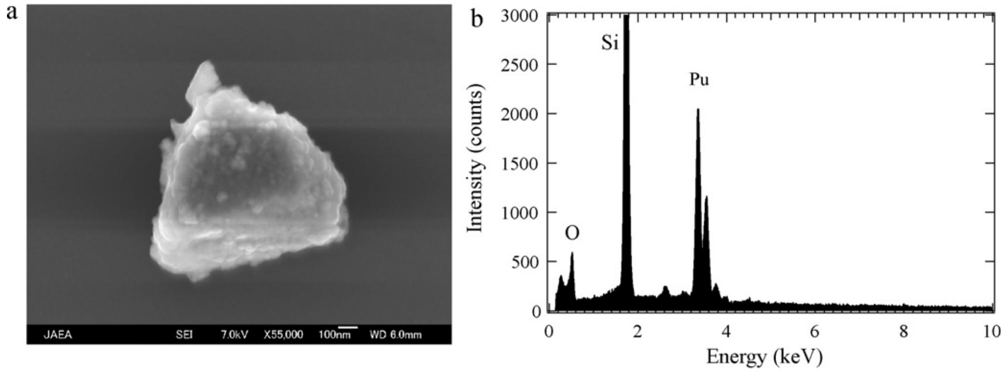

Fig. 1. The scanning electron image (a) and the EDX spectrum (b) of a plutonium particle prepared from SRM-947 solution.

In the present work, in order to perform isotope ratio analysis of individual sub-micrometer plutonium particles, a desolvation sample introduction system is used for ICP-MS. In addition, a purification process of Pu from Am by an anion-exchange method is added to analyze the ^{241}Pu/^{239}Pu isotope ratios accurately. Finally, the ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu isotope ratios are determined for individual plutonium particles with ICP-MS, and compared with those obtained by a conventional technique, i.e. SIMS.

2. Experimental procedure

2.1. Samples

Plutonium particles prepared from a standard reference material (SRM-947, plutonium sulfate tetrahydrate, New Brunswick Laboratory (NBL), USA) were used in this study. Since plutonium particles taken at nuclear facilities are usually oxides, we converted the chemical state from sulfate tetrahydrate to oxide by using the following procedure. Purification for the plutonium solution was conducted to remove americium by using an anion exchange method on July 14, 2008. The 30 μL of the purified plutonium solution with the concentration of 330 μg/mL were pipetted into a quartz glass and heated at 800 °C to produce plutonium oxide particles. Then, the obtained particles were suspended in n-decanol and pipetted onto a Si planchet with a diameter of 25 mm (Nihon Exceed Co. Ltd., Japan). Fig. 1 shows the scanning electron image and the energy dispersive X-ray (EDX) spectrum of a plutonium particle prepared. The EDX spectrum has the peaks assigned to plutonium and oxygen and no peak attributed to sulfur, implying that the particle is in the form of plutonium oxide.

2.2. Sample preparation for SIMS

The Si planchet containing plutonium particles and a glassy carbon planchet (25 mm Ø, Hitachi Chemical Co. Ltd., Japan) were introduced into the main chamber of a scanning electron microscope (SEM, JSM-6700F, Jeol Co. Ltd., Japan). Each plutonium particle to be analyzed was manipulated with a glass needle attached to a manipulator and transferred onto the glassy carbon planchet. The glass needles were fabricated from glass rods with a diameter of 1 mm using a micropipette puller (Narishige, PC-10) and thinly coated with gold [14].

2.3. Sample preparation for ICP-MS

Si chips with the dimension of 5 mm × 5 mm (Semitec Co. Ltd., Japan) were cleaned, in sequence, with 40% HNO_3, 2% HNO_3 (TAMA-pure, Tama Chemicals Co. Ltd.) and deionized Milli-Q water (resistivity: 18 MΩ cm). The Si chips and the Si disk containing plutonium particles were introduced into a chamber of the SEM instrument simultaneously. Individual plutonium particles on the Si disk were manipulated with the glass needle attached to the manipulator and transferred onto the center of each Si chip. Teflon bottles with a volume of 8 mL were cleaned with 4% HNO_3 and deionized Milli-Q water. Each Si chip containing a single plutonium particle was put into the bottle and 2 mL of deionized Milli-Q water was added. After ultrasoneration for 5 min, the Si chip was removed and the water was evaporated. Mixed solution of 1 mL HF and 1 mL HNO_3 was added to the bottle and evaporated to dryness to dissolve the particle. This dissolution process was repeated twice. The plutonium in the evaporation residue was purified by using anion exchange columns (MCL GEL, CA08P, pore size: 75–150 μm Ø, column size: 3.6 mm Ø × 25 mm). The evaporation residue was dissolved with 2 mL of 8 M-HNO_3. The solution was loaded on the column, and americium was eluted with 3 mL of 8 M-HNO_3. Plutonium fraction was eluted with 3 mL of mixed solution of 0.5 M-HCl and 0.01 M-HF. The obtained plutonium solution was finally adjusted to 3 mL with 5% HNO_3.

2.4. Instrumentation

Plutonium isotope ratios were measured using a high resolution ICP-MS model ELEMENT 1 (Thermo Fisher Scientific, USA), which has an ICP ion source with guard electrode and a double-focusing mass spectrometer. The instrument was operated in electric scanning (E-scan) modes with a mass resolution ($M/\Delta M$) of 300. A PFA micro-flow nebulizer (self-aspirating mode) was used in combination with a Scott-type double pass spray chamber cooled at 4 °C. An Apex-Q desolvation system (Elemental Scientific Inc., USA) was also used for sample introduction to ICP-MS. This system consists of a heated cyclonic spray chamber, a Peltier cooled condenser and an ACM Naflon fluoropolymer membrane desolvation module, allowing high efficient sample introduction. Four mono-atomic ions ($^{239}Pu^+$, $^{240}Pu^+$, $^{241}Pu^+$ and $^{242}Pu^+$) were measured in a peak-jumping mode. The operating condition for the ICP-MS is listed in Table 1. The mass bias factor assuming the following equation was determined using 5.14 pg/mL NBL SRM-947 standard solution:

$$R_t = R_m(1 + C)^{\Delta M} \qquad (1)$$

where R_t is the certified isotope ratio, R_m is the measured isotope ratio, ΔM is a difference in mass and C is a mass discrimination factor.

A secondary ion mass spectrometer (IMS-6f, Cameca, France) was used for measuring plutonium isotope ratios in individual particles. In SIMS analysis, an $O_2{}^+$ focused beam of 15 keV with a current of 4–20 nA was rastered over a 50 μm × 50 μm area. Positive secondary ions emitted from a particle were accelerated

Table 1
Analytical condition in ICP-MS.

Parameter	Setting
ICP-MS	
RF power	1148 W
Cooling gas flow rate	16.0 L/min
Auxiliary gas flow rate	0.85 L/min
Sample gas flow rate	0.79–0.86 L/min
Solution uptake rate	0.18 mL/min
Sampling time per isotope	50 ms
Scan per replicate	400
Number of replicates	5
Resolution ($\Delta M/M$)	300
Apex-Q desolvation system	
Spray chamber temperature	100 °C
Condenser temperature	2 °C
Nitrogen flow	1.5 mL/min
Additional gas (Ar)	0.08–0.15 L/min

through 5 keV. Transfer optics of 150 μm and a field aperture of 1800 μm were used. An energy slit was adjusted for a band pass of 50 eV. The mass resolution was set at 300. Secondary ions at masses 239, 240, 241 and 242 were counted in an automatic peak-jumping mode. An electron multiplier was operated in an ion counting mode with a dead time of 27 ns. Here, the effective dead time was considered to be larger than 27 ns, since a focused ion beam was rastered over a small particle. Mass calibration was performed each time before starting measurements of particles. Mass bias corrections were conducted by comparing the measured isotope ratios for other particles from the same batch with the reference values.

3. Results and discussion

3.1. SIMS analysis

Fig. 2(a) displays the mass spectrum of a plutonium particle measured with SIMS. The peaks assigned to plutonium isotopes on the masses ranging from 238 to 242 are clearly observed. The peak on the mass 241 also has the contribution of ^{241}Am produced by β-decay of ^{241}Pu. Since the ^{241}Pu and ^{241}Am have almost the same mass, it is impossible to resolve these peaks in SIMS analysis. A peak on the mass 237 is slightly observed, which is presumably due to the contribution of ^{237}Np remaining in the plutonium solution used for particle preparation. In SIMS analysis, the interferences by hydride ions are a problem to perform accurate isotope ratio analysis. For uranium particles, hydride formation rates can be estimated by measuring ^{238}U^{1}H/^{238}U ratios. Here, the count rate of ^{238}U is intense enough to measure the count rate of ^{238}U^{1}H. Therefore, we can correct the contribution of hydride ions. On the other hand, the estimation of the hydride formation rates by measuring ^{242}Pu^{1}H/^{242}Pu ratios is difficult due to the smaller count rates of ^{242}Pu and ^{242}Pu^{1}H. In the present work, we prepared ^{242}Pu particles and measured as shown in Fig. 2(b). Consequently, the hydride formation rate of 5.4×10^{-4} is obtained. This value is lower than that reported by Ranebo et al. (6.5×10^{-3}) [8] and higher than that reported by Simons (2×10^{-4}) [15]. In the analysis of real samples, it is considered that the hydride formation rate varies for each particle. Therefore, the correction of the contribution by hydrides would be difficult in the SIMS analysis for individual plutonium particles in real samples.

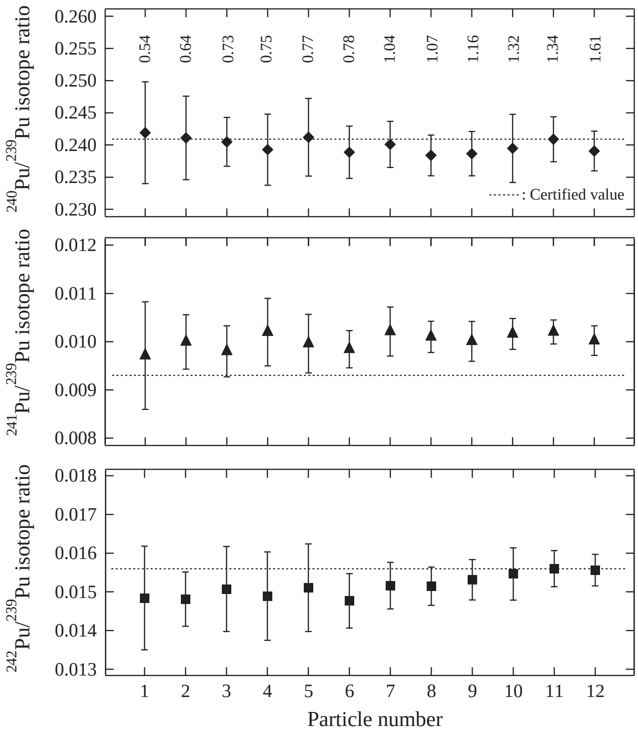

Fig. 3. Plutonium isotope ratios in individual particles measured with SIMS. The error bar represents the uncertainty, which corresponds to one standard deviation. The dotted line represents the certified value. The diameters (μm) of individual particles are noted. The measurement date was July 12, 2010.

Fig. 3 shows the plutonium isotope ratios in individual particles measured with SIMS. The contribution of hydride ions was corrected by using a measured value (5.4×10^{-4}). The diameters (μm) of individual particles, which are averaged values between the lengths of the major and minor axes of each particle determined with SEM, are also presented in the Fig. 3. The ^{240}Pu/^{239}Pu isotope ratios are in good agreement with the certified value. As

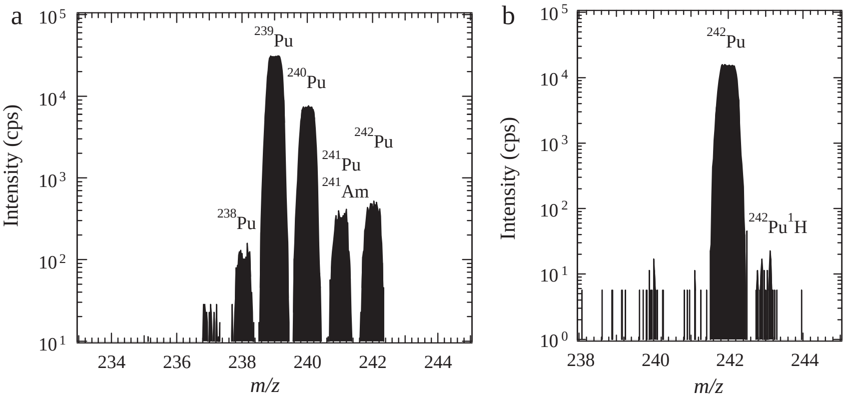

Fig. 2. The mass spectra of plutonium particles prepared from SRM-947 (a) and Pu-242 (b) measured with SIMS.

Table 2
The procedural blank values on masses 239, 240, 241 and 242 in ICP-MS without and with desolvation sample introduction.

m/z	Counts (s)	
	Without desolvation	With desolvation
239	0.3 ± 0.2[a]	0.7 ± 0.2
240	0.1 ± 0.1	0.3 ± 0.1
241	0.1 ± 0.1	0.1 ± 0.1
242	0.1 ± 0.1	0.3 ± 0.2

[a] Uncertainty, which corresponds to one standard deviation.

Table 3
The count rates for SRM-947 solution with the concentration of 5.14 ppt on masses 239, 240, 241 and 242 in ICP-MS without and with desolvation sample introduction.

m/z	Counts (s)	
	Without desolvation	With desolvation
239	8775 ± 557[a]	54393 ± 1078
240	2118 ± 129	13058 ± 279
241	388 ± 24	2376 ± 48
242	134 ± 10	835 ± 19

[a] Uncertainty, which corresponds to one standard deviation.

for the ^{241}Pu/^{239}Pu isotope ratios, higher values than the certified value are obtained, which is due to the contribution of ^{241}Am. Similar results in SIMS analysis giving higher ^{241}Pu/^{239}Pu isotope ratios were observed in a previous study [15]. Although most of the ^{242}Pu/^{239}Pu isotope ratios correspond to the certified value, the particles less than 1 μm give isotope ratios with inferior precision. These results imply that the use of SIMS analysis is limited to perform the analysis of ^{240}Pu/^{239}Pu and ^{242}Pu/^{239}Pu in individual particles with relatively larger size.

3.2. Procedural blank in ICP-MS analysis

Prior to the isotope ratio analysis of individual plutonium particles with ICP-MS, we checked the count rates of plutonium in procedural blank solution. Here, the Apex-Q desolvation system was also used to improve sensitivity for analysis of individual plutonium particles. The procedural blank solution was prepared by performing the same sample preparation procedure without particles. Table 2 shows the count rates on the masses 239, 240, 241 and 242 in procedural blank solution measured by ICP-MS with and without desolvation. Slight increases in the count rates on the masses 239, 240 and 242 are observed, when the desolvation system is applied. However, all count rates of the procedural blank are considerably low (less than 0.7 cps). The procedural blank values are much lower than those in the case of uranium analysis, for example, 115.8 cps for ^{238}U [12].

3.3. Analysis of individual plutonium particles by ICP-MS with desolvation

We measured the count rates on the masses 239, 240, 241 and 242 in SRM-947 standard solution with the concentration of 5.14 ppt by ICP-MS with and without desolvation. By using the desolvation system, the count rates about six times increase as shown in Table 3. The sensitivities are calculated to be 1700 and 10,600 cps/ppt for the measurement without and with desolvation, respectively. These results indicate that the use of desolvation system in ICP-MS is suitable for the present study.

Plutonium isotope ratios in individual particles were measured by ICP-MS without desolvation and are shown in Fig. 4(a). Here, the particles with the diameter ranging from 0.53 to 2.86 μm were measured. Since hydride formation was negligible, no correction for the interference by hydride ions was made in the measurement. As shown in Fig. 4(a), the ^{240}Pu/^{239}Pu isotope ratios are consis-

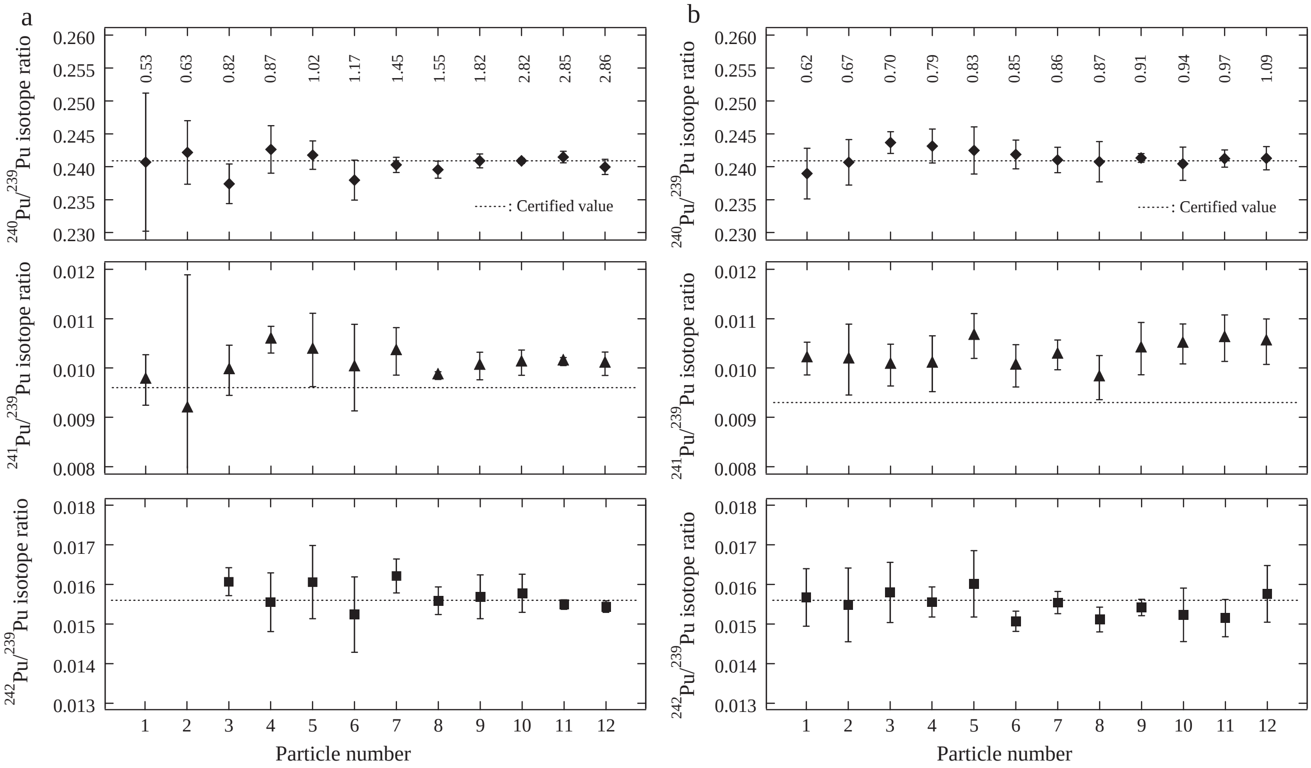

Fig. 4. Plutonium isotope ratios in individual particles measured by ICP-MS without (a) and with (b) desolvation sample introduction. The error bar represents the uncertainty, which corresponds to one standard deviation. The dotted line represents the certified value. The diameters (μm) of individual particles are noted. The measurement dates were (a) September 9, 2009 and (b) June 14, 2010.

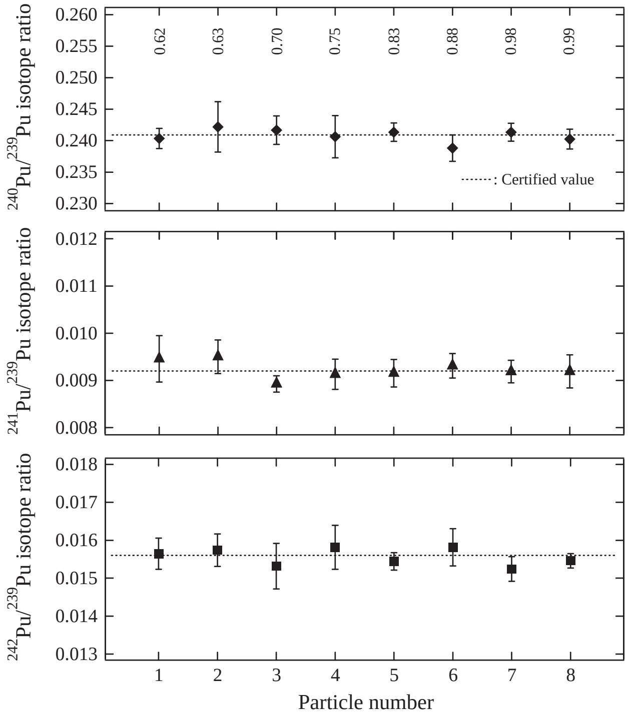

Fig. 5. Plutonium isotope ratios in individual particles measured by ICP-MS with desolvation sample introduction after chemical separation of plutonium and americium. The error bar represents the uncertainty, which corresponds to one standard deviation. The dotted line represents the certified value. The diameters (μm) of individual particles are noted. The measurement date was August 17, 2010.

tent with the certified value. However, the uncertainty increases with decreasing particle size. For example, the uncertainty of the $^{240}Pu/^{239}Pu$ isotope ratio measured for the particle with the diameter of 0.53 μm is 4.4%. The $^{242}Pu/^{239}Pu$ isotope ratios also give results with inferior precision for the particles with the diameter less than 1 μm. The $^{242}Pu/^{239}Pu$ isotope ratios for the particles with the diameter of 0.53 and 0.63 μm, which are 0.021 and 0.019, are not plotted in Fig. 4(a).

Fig. 4(b) displays the plutonium isotope ratios in individual particles measured by ICP-MS with desolvation. Here, we focus on the analysis for sub-micrometer particles. Compared to the result measured without desolvation, the uncertainty is much improved. For example, the uncertainty of the $^{240}Pu/^{239}Pu$ isotope ratio for the particle with the diameter of 0.62 μm is 1.6%. These results confirm that ICP-MS with desolvation enables to perform precise plutonium isotope ratio analysis of individual sub-micrometer particles. The $^{241}Pu/^{239}Pu$ isotope ratios are higher than the certified value, which is due to the contribution of ^{241}Am as mentioned before.

3.4. Analysis of individual plutonium particles by ICP-MS with chemical separation

One remaining problem is the accuracy of the $^{241}Pu/^{239}Pu$ isotope ratios. The average value (0.0103) of the $^{241}Pu/^{239}Pu$ isotope ratios was 12% higher than the certified value in Fig. 4(b), which is close to the $(^{241}Pu + ^{241}Am)/^{239}Pu$ ratio (0.0102) estimated by considering the in-growth of ^{241}Am from the purification date to the measurement date. As shown in Figs. 3 and 4, accurate analysis of $^{241}Pu/^{239}Pu$ isotope ratios in individual particle is difficult in SIMS and ICP-MS without chemical separation, due to the interference by ^{241}Am coexisting in the particle. In order to overcome this problem, a process of chemical separation is added to the analytical procedure. Fig. 5 shows the plutonium isotope ratios measured for individual sub-micrometer particles after chemical separation. Here, the desolvation system was used for sample introduction. Consequently, accurate $^{241}Pu/^{239}Pu$ isotope ratios are successfully obtained. The average value (0.0092) of the $^{241}Pu/^{239}Pu$ isotope ratios is in good agreement with the certified value. The $^{240}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ isotope ratios also correspond to the certified values. The uncertainties are less than 1.6% for $^{240}Pu/^{239}Pu$ isotope ratios, 5.2% for $^{241}Pu/^{239}Pu$ isotope ratios and 3.9% for $^{242}Pu/^{239}Pu$ isotope ratios, respectively. For the analysis for nuclear safeguards, the uncertainty within 5% is required for $^{240}Pu/^{239}Pu$ isotope ratios in individual particle measured with SIMS. The results in this work indicate that the proposed method is effective to perform isotope ratio analysis of individual plutonium particles precisely and accurately.

4. Conclusions

In the present work, an analytical technique by a combination of chemical separation and inductively coupled plasma mass spectrometry (ICP-MS) using a desolvation sample introduction system is developed and applied to isotope ratio analysis of individual sub-micrometer plutonium particles. The ICP-MS results for individual plutonium particles prepared from a standard reference material (NBL SRM-947) indicate that the use of the desolvation system for sample introduction improves the precision of isotope ratios. In addition, the accurate $^{241}Pu/^{239}Pu$ isotope ratios can be obtained by addition of a chemical separation process. The performance of the proposed ICP-MS technique for the analysis of individual plutonium particles is greater than that of the conventional SIMS technique. Therefore, the proposed method will become a powerful tool for nuclear safeguards.

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