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Isotope Ratio Analysis of Individual Plutonium and Uranium–Plutonium Mixed Oxide Particles by Thermal Ionization Mass Spectrometry with a Continuous Heating Method

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Isotope ratio analysis of individual plutonium and uranium–plutonium mixed oxide (MOX) particles was performed using a combination of single particle transfer and thermal ionization mass spectrometry (TIMS) with a continuous heating method, namely the particles were measured without any chemical treatment. Accurate values were obtained for all isotope ratios of the individual particles prepared from standard solution. As a consequence, it is confirmed that the combination method is useful for isotope ratio analysis of individual plutonium and MOX particles.

Plutonium is an artificial nuclide and has various isotopic compositions reflecting nuclear activities. Therefore, accurate determination of plutonium isotopic composition is of great importance for nuclear safeguards, nuclear forensics, and so on. In particular, analyzing plutonium isotope ratios of individual particles gives detailed information on their origins. Isotope ratio analysis of solution samples containing a small amount of plutonium was performed by mass spectrometry such as inductively coupled plasma mass spectrometry (ICP-MS) and thermal ionization mass spectrometry (TIMS).[1–4] Although isotope ratio analysis of individual plutonium particles was also carried out,[5,6] the analytical procedure was considerably complicated, because individual plutonium particles had to be dissolved prior to the measurement. In addition, chemical treatments such as dissolution may cause contamination by ^{238}U existing in the environment, which gives isobaric interference to ^{238}Pu. This makes it difficult to obtain accurate ^{238}Pu/^{239}Pu isotope ratios.

In the present work, as a novel approach for the isotope ratio analysis of individual plutonium particles, an analytical method by a combination of single particle transfer[7] and TIMS with a continuous heating method[8,9] was examined for individual plutonium particles. In addition, the technique was applied to the analysis of individual uranium–plutonium mixed oxide (MOX) particles. The effect of isobaric interferences on the results of the isotope ratio analysis without any chemical treatments is also discussed.

Plutonium and MOX particles used in this work were produced from isotopic reference material solution, Pu (SRM-947, National Bureau of Standards, USA) and U (CRM U500, New Brunswick Laboratory, USA). The brief procedure of the production of particles is mentioned below, for details, refer to the previous paper.[10] Plutonium was purified with an anion exchange method to remove americium and uranium. The solution containing approximately 10 µg plutonium was pipetted into a quartz glass flask, and dried. Then, the dried residue was heated at 800 °C to produce plutonium oxides. After cooling, *n*-dodecane was added to the flask, and the dried residue was crushed with a quartz-glass rod to form particles. Hence, the particles had various shapes and sizes. The particles suspended in *n*-dodecane in the flask were pipetted onto a Si planchet with a diameter of 25 mm (Nihon Exceed Co., Ltd., Japan). The MOX particles were also produced with the same procedure by using CRM U500 and SRM-947 mixed (1.17:1 wt % ratio) solution.

Individual particles were picked up and transferred onto the center of each evaporation filament (EF) by a manipulator attached to a scanning electron microscope (JSM-6700F, JEOL, Japan).[7] In this work, each particle with a diameter of around 1 µm was selected for analysis because the measurement of such small particles is necessary in nuclear safeguards and nuclear forensics. Isotope ratio measurements were performed with the continuous heating method[8,9] by using a TIMS instrument (TRITON, Thermo Fisher Scientific, USA) equipped with a secondary electron multiplier in an ion-counting mode. In this work, the EF current was gradually increased to 4000 mA with a heating rate of 150 mA min^{-1} for plutonium particles and 5000 mA with a heating rate of 100 mA min^{-1} for MOX particles, respectively. The signal intensities of each isotope were measured with a peak-jumping sequence. The details of the isotope-ratio calculation have been described in previous papers.[8,9] Mass fractionation factors were determined by four measurements of isotopic reference material solution, CRM U350 (New Brunswick Laboratory, USA) for uranium and SRM-947 for plutonium, respectively.

Table 1 shows the results of isotope ratio measured for three individual plutonium particles. The certified values were corrected by the time elapsed after plutonium purification. All isotope ratios were consistent with the certified values. In particular, accurate values were obtained for the ^{238}Pu/^{239}Pu isotope ratio, indicating that the isobaric interference of ^{238}U to ^{238}Pu was negligible in this analysis. For the plutonium particles, the time elapsed after plutonium purification was approximately 1.3 years. Therefore, ^{241}Am coexisted in the individual particles due to the β decay of ^{241}Pu to ^{241}Am. In fact, an ICP-MS

Table 1. Isotope ratios in individual plutonium particles

Particle (µm)[a]	Isotope ratio (±uc[b])			
	^{238}Pu/^{239}Pu	^{240}Pu/^{239}Pu	^{241}Pu/^{239}Pu	^{242}Pu/^{239}Pu
P-1 (1.30)	0.0029	0.241	0.0096	0.0154
	(±0.0003)	(±0.003)	(±0.0006)	(±0.0004)
P-2 (1.51)	0.0029	0.241	0.0096	0.0154
	(±0.0001)	(±0.001)	(±0.0004)	(±0.0005)
P-3 (1.71)	0.0029	0.241	0.0097	0.0158
	(±0.0002)	(±0.005)	(±0.0001)	(±0.0005)
Certified value[c]	0.0029	0.241	0.0095	0.0156

[a]Particle diameter means the average value between the lengths of the major and minor axes. [b]Uncertainty (coverage factor $k = 2$). [c]Certified values as of November 11, 2009.

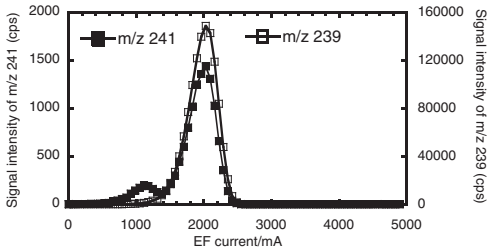

Figure 1. The profiles of m/z 239 and m/z 241 signal intensities measured for a plutonium particle by TIMS with the continuous heating method.

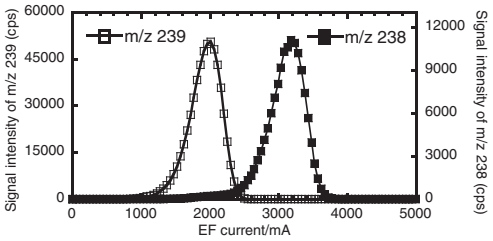

Figure 2. The profiles of m/z 239 and m/z 238 signal intensities measured for a MOX particle by TIMS with the continuous heating method.

Table 2. Isotope ratios in individual MOX particles produced from mixed CRM U500 and SRM-947 solution

Particle (μm)[a]	Isotope ratio (±uc[b])						
	$^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{236}U/^{238}U$	$^{238}Pu/^{239}Pu$	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$
M-1 (1.20)	0.0101	1.01	0.0017	0.0029	0.239	0.0090	0.0153
	(±0.0008)	(±0.03)	(±0.0003)	(±0.0003)	(±0.005)	(±0.0006)	(±0.0007)
M-2 (1.05)	0.0104	1.00	0.0017	0.0029	0.239	0.0087	0.0154
	(±0.0006)	(±0.02)	(±0.0002)	(±0.0007)	(±0.005)	(±0.0003)	(±0.0009)
M-3 (1.28)	0.0105	1.00	0.0017	0.0029	0.239	0.0089	0.0154
	(±0.0011)	(±0.03)	(±0.0004)	(±0.0006)	(±0.004)	(±0.0003)	(±0.0003)
Calculated value[c]	0.0105	1.00	0.0016	0.0029	0.241	0.0090	0.0156

[a]Particle diameter means the average value between the lengths of the major and minor axes. [b]Uncertainty (coverage factor $k = 2$). [c]Calculated values as of February 18, 2011. Uranium isotope ratios were calculated by taking into account the increases of each isotope due to the α decay of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{242}Pu.

analysis of the plutonium particles confirmed that the ^{241}Am coexisted in the individual particles.[6] Figure 1 shows typical profiles of the signal intensity of plutonium particles, measured with the continuous heating method. As can be seen in Figure 1, the profile of the signal intensity of m/z 239 showed only one peak, though that of m/z 241 displayed two peaks at around 1200 (ca. 800 °C) and 2000 mA (ca. 1300 °C). Here, the former peak is assigned to ^{241}Am and the latter peak is attributed to ^{241}Pu. As a result, accurate $^{241}Pu/^{239}Pu$ isotope ratios were obtained in this work, owing to the separation of Pu and Am during measurement.

Table 2 shows the results of isotope ratio analysis for three individual MOX particles. Since the time elapsed after plutonium purification was about 2.3 years, the amounts of uranium isotopes ^{234}U, ^{235}U, ^{236}U, and ^{238}U in individual MOX particles increased by the α decays of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{242}Pu. Therefore, certified values of uranium isotope ratios were calculated by using the time elapsed after plutonium purification. As a consequence, all uranium and plutonium isotope ratios were in good agreement with the calculated values. Figure 2 shows typical profiles of the signal intensities measured for a MOX particle. The peaks of m/z 239 and m/z 238 appeared at around 2000 and 3200 mA (ca. 1600 °C), respectively. Here, the peak at around 2000 mA is assigned to Pu and that at around 3200 mA is attributed to U. The signal intensity of m/z 238 at around 2000 mA assigned to ^{238}Pu was slightly affected by the tail of the peak attributed to ^{238}U at around 3200 mA. However, by subtracting the ^{238}U contribution calculated using the $^{235}U/^{238}U$ isotope ratio and the ^{235}U signal intensity from the signal intensity of m/z 238,[9] the $^{238}Pu/^{239}Pu$ isotope ratio could be determined accurately as shown in Table 2.

In conclusion, this proposed analytical method by a combination of single particle transfer and TIMS with the continuous heating method is a useful tool for the accurate isotope ratio analysis of plutonium and MOX particles without any chemical treatments.

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References

1 C.-S. Kim, C.-K. Kim, P. Martin, U. Sansone, *J. Anal. At. Spectrom.* **2007**, *22*, 827.
2 F. Pointurier, P. Hémet, A. Hubert, *J. Anal. At. Spectrom.* **2008**, *23*, 94.
3 M. L. D. P. Godoy, J. M. Godoy, L. A. Roldão, L. Tauhata, *J. Environ. Radioact.* **2009**, *100*, 613.
4 R. Jakopič, S. Richter, H. Kühn, L. Benedik, B. Pihlar, Y. Aregbe, *Int. J. Mass Spectrom.* **2009**, *279*, 87.
5 T. Shinonaga, F. Esaka, M. Magara, D. Klose, D. Donohue, *Spectrochim. Acta, Part B* **2008**, *63*, 1324.
6 F. Esaka, M. Magara, D. Suzuki, Y. Miyamoto, C.-G. Lee, T. Kimura, *Talanta* **2010**, *83*, 569.
7 F. Esaka, K. T. Esaka, C.-G. Lee, M. Magara, S. Sakurai, S. Usuda, K. Watanabe, *Talanta* **2007**, *71*, 1011.
8 D. Suzuki, Y. Saito-Kokubu, S. Sakurai, C.-G. Lee, M. Magara, K. Iguchi, T. Kimura, *Int. J. Mass Spectrom.* **2010**, *294*, 23.
9 Y. Saito-Kokubu, D. Suzuki, C.-G. Lee, J. Inagawa, M. Magara, T. Kimura, *Int. J. Mass Spectrom.*, in press. doi:10.1016/j.ijms.2011.11.008.
10 C.-G. Lee, D. Suzuki, F. Esaka, M. Magara, T. Kimura, *Talanta* **2011**, *85*, 644.

