

Feasibility Study of Isotope Ratio Analysis of Individual Uranium-Plutonium Mixed Oxide Particles with SIMS and ICP-MS

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Abstract: Isotope ratio analysis of nuclear materials in individual particles is of great importance for nuclear safeguards. Although secondary ion mass spectrometry (SIMS) and thermal ionization mass spectrometry (TIMS) are utilized for the analysis of individual uranium particles, few studies were conducted for the analysis of individual uranium-plutonium mixed oxide particles. In this study, we applied SIMS and inductively coupled plasma mass spectrometry (ICP-MS) to the isotope ratio analysis of individual U-Pu mixed oxide particles. In the analysis of individual U-Pu particles prepared from mixed solution of uranium and plutonium standard reference materials, accurate $^{235}\text{U}/^{238}\text{U}$, $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$ isotope ratios were obtained with both methods. However, accurate analysis of $^{241}\text{Pu}/^{239}\text{Pu}$ isotope ratio was impossible, due to the interference of the ^{241}Am peak to the ^{241}Pu peak. In addition, it was indicated that the interference of the ^{238}U peak to the ^{239}Pu peak has a possibility to prevent accurate analysis of plutonium isotope ratios. These problems would be avoided by a combination of ICP-MS and chemical separation of uranium, plutonium and americium in individual U-Pu particles.

Key words: SIMS, ICP-MS, Isotope ratio, Uranium, Plutonium

Introduction

Mass spectrometry has a crucial role in nuclear safeguards. Isotope ratio analysis of individual uranium particles in environmental samples taken at nuclear facilities is performed to verify the absence of undeclared nuclear activities related to uranium enrichment and production of nuclear weapons.¹⁻² For this purpose, two kinds of analytical techniques are mainly used, i.e., secondary ion mass spectrometry (SIMS) and thermal ionization mass spectrometry (TIMS) combined with a fission track method.³⁻¹² The SIMS allows us to analyze samples easily and rapidly. A main drawback in SIMS is molecular ion interferences by other elements in other particles. The interferences give inaccurate analytical results, especially for uranium minor isotopes (^{234}U and ^{236}U). In order to overcome this problem, a large geometry SIMS instrument with high mass resolution was used to separate peaks of uranium ions and molecular ions.⁷ As the result, accurate isotope ratio results were acquired in the analysis of swipe samples taken at nuclear facilities by using the instrument. As an alternative method, we developed a technique by a combination of particle manipulation under scanning electron microscope (SEM) and isotope ratio analysis with SIMS.⁵ The particle manipulation allowed us to transfer only uranium particles for subsequent

SIMS analysis, giving accurate isotope ratio results.

As well as uranium, plutonium is increasingly used as a uranium-plutonium mixed oxide fuel in commercial nuclear reactors. Although undeclared nuclear activities using plutonium should also be revealed, only a few studies were conducted to analyze isotope ratios of individual plutonium and uranium-plutonium mixed oxide particles.¹³⁻¹⁵ One of the reasons is the isobaric interference of the ^{241}Am peak to the ^{241}Pu peak in mass spectrometry. Americium-241 is formed by the decay of ^{241}Pu with the half life of 14.325 years,¹⁶ meaning that ^{241}Am and ^{241}Pu usually coexist in a single plutonium or uranium-plutonium mixed oxide particle. In a previous study,¹⁴ we developed an experimental technique for individual plutonium particles, which included particle manipulation, dissolution and chemical separation of plutonium and americium for subsequent isotope ratio analysis with inductively coupled plasma mass spectrometry (ICP-MS). Consequently, we could analyze isotope ratios accurately for individual plutonium particles.

In the present work, isotope ratio analysis of individual uranium-plutonium mixed oxide particles was performed by using SIMS and ICP-MS, and the applicability of these methods was discussed.

Experimental procedure

Samples

Uranium-plutonium mixed oxide particles were prepared from

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mixed solution of standard reference materials (SRM 947, National Bureau of Standards (NBS), USA and CRM U-500, New Brunswick Laboratory (NBL), USA). Purification for the SRM 947 plutonium solution was carried out to remove americium by using an anion exchange method on July 14, 2008. The 10 μL of the mixed solution was pipetted onto a quartz glass and heated at 800 $^{\circ}\text{C}$ to produce U-Pu mixed oxide particles. Then, the obtained particles were suspended in n-dodecane and pipetted onto a Si planchet with a diameter of 25 mm (Nihon Exceed Co. Ltd., Japan).

Sample preparation for SIMS

The Si planchet containing U-Pu particles and a glassy carbon planchet (25 mm ϕ , Hitachi Chemical Co. Ltd., Japan) were introduced into the main chamber of a scanning electron microscope (JSM-6700F, Jeol Co. Ltd., Japan). Each U-Pu particle was picked up 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 (PC-10, Narishige Co. Ltd., Japan) and thinly coated with gold.

Sample preparation for ICP-MS

Si chips with a dimension of 5 \times 5 mm (Semitec Co. Ltd., Japan) were cleaned, in sequence, with 40% HNO_3 , 2% HNO_3 (TAMA-pure, Tama Chemicals Co. Ltd., Japan) and deionized Milli-Q water (resistivity : 18 $\text{M}\Omega\cdot\text{cm}$). The Si chips and the Si planchet containing U-Pu particles were introduced into a chamber of the SEM instrument. Individual U-Pu particles on the Si planchet 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 U-Pu 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. The 2 mL of HNO_3 solution was then added to the bottle and evaporated to dryness to dissolve the particle. This dissolution process was repeated twice. The sample was finally adjusted to 5% HNO_3 solution.

Instrumentation

A secondary ion mass spectrometer (IMS-6f, Cameca, France) was used for measuring isotope ratios in individual U-Pu particles. In SIMS analysis, an O_2^+ focused beam of 15 keV with a current of 4-15 nA was rastered over a 50 \times 50 μm area. Positive secondary ions emitted from a particle were accelerated through 5 keV. Transfer optics of 150 μm and a field aperture of 1,800 μm were used. An energy slit was adjusted for a band pass of 50 eV. The mass resolution was set at 300. Secondary ions 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.

A high resolution ICP-MS model ELEMENT 1 (Thermo

Fisher Scientific, USA), having an ICP ion source with Guard Electrode and a double-focusing mass spectrometer, was used for isotope ratios analysis. The instrument was operated in electric scanning (E-scan) modes with a mass resolution ($M/\Delta M$) of 300. An Apex-Q desolvation system (Elemental Scientific Inc., USA) was used for sample introduction to the ICP-MS instrument. This system consisted of a heated cyclonic spray chamber, a Peltier cooled condenser and an ACM Naflon fluoropolymer membrane desolvation module, allowing high efficient sample introduction. The operating condition of the ICP-MS instrument is listed in Table 1. The mass bias factor assuming the following equation was determined using 5.14 pg/mL NBS SRM 947 standard solution:

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

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.

Results and Discussion

SIMS analysis

Fig. 1 shows the SEM image and the energy dispersive X-ray (EDX) spectrum of a U-Pu particle on a Si planchet. In the EDX spectrum, U-M α (3.18 keV), U-M β (3.37 keV), Pu-M α (3.37 keV), Pu-M β (3.55 keV) and O-K α (0.53 keV) peaks were observed. The peaks assigned to carbon and silicon

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 $^{\circ}\text{C}$
Condenser temperature	2 $^{\circ}\text{C}$
Nitrogen flow	1.5 mL/min.
Additional gas (Ar)	0.08-0.15 L/min.

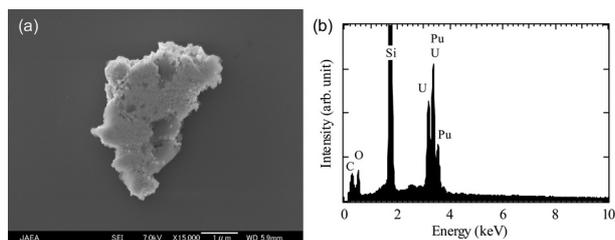


Fig. 1. (a) SEM image and (b) EDX spectrum of a uranium-plutonium mixed oxide particle.

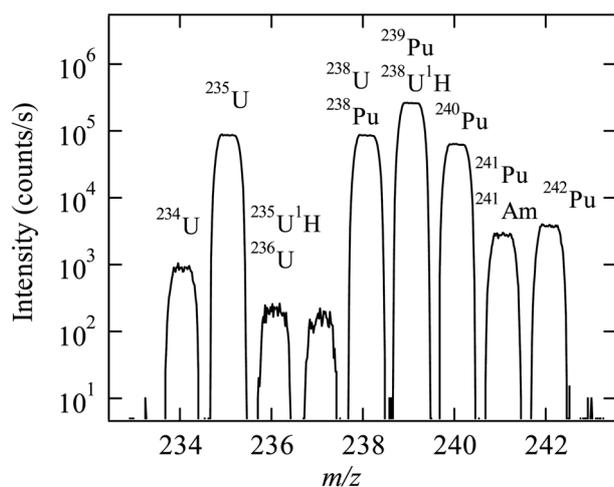


Fig. 2. Mass spectrum of a uranium-plutonium mixed oxide particle measured with SIMS.

are due to surface contaminants and the planchet material, respectively.

Fig. 2 displays the mass spectrum of a U-Pu particle measured with SIMS. The peaks related to uranium ions were observed on the masses of 234, 235, 236, 238 and 239. The ²³⁵UH peak overlapped with the ²³⁶U peak and the ²³⁸U peak was interfered by the ²³⁸Pu peak. The peaks related to plutonium ions were observed on the masses of 238, 239, 240, 241 and 242. The ²⁴¹Pu peak was overlapped with the ²⁴¹Am peak. The formation of ²⁴¹Am is due to the decay of ²⁴¹Pu. The ²³⁹Pu peak was interfered by the ²³⁸UH peak. According to the previous studies,^{6,15} the hydride formation rate (²³⁸UH/²³⁸U) in SIMS analysis was in the range from 3 × 10⁻³ to 4 × 10⁻⁴. In the analysis of uranium particles, the hydride formation rate is determined for each particle by measuring ²³⁸UH/²³⁸U ratio. However, this can not be applied to the analysis of U-Pu particles because of the presence of the ²³⁹Pu peak. Thus, it is difficult to estimate the contribution of the ²³⁸UH peak to the ²³⁹Pu peak in SIMS analysis.

For two individual U-Pu mixed oxide particles, the isotope ratios of ²³⁵U/²³⁸U, ²⁴⁰Pu/²³⁹Pu, ²⁴¹Pu/²³⁹Pu and ²⁴²Pu/²³⁹Pu were measured and are summarized in Table 2. The isotope ratios of ²⁴⁰Pu/²³⁹Pu, and ²⁴²Pu/²³⁹Pu were in good agreement with the certified values, respectively. The isotope ratio of

Table 2. Uranium and plutonium isotope ratios of individual uranium-plutonium mixed oxide particles measured with SIMS.

Particle No.	²³⁵ U/ ²³⁸ U	²⁴⁰ Pu/ ²³⁹ Pu	²⁴¹ Pu/ ²³⁹ Pu	²⁴² Pu/ ²³⁹ Pu
1	1.00±0.02*	0.238±0.006	(1.03±0.06) × 10 ⁻²	(1.52±0.15) × 10 ⁻²
2	0.988±0.008	0.240±0.002	(1.01±0.02) × 10 ⁻²	(1.54±0.03) × 10 ⁻²
Certified value	1.00	0.241	0.900 × 10 ⁻²	1.56 × 10 ⁻²

*Uncertainty, which corresponds to two standard deviations.

Table 3. Uranium and plutonium isotope ratios of individual uranium-plutonium mixed oxide particles measured with ICP-MS.

Particle No.	²³⁵ U/ ²³⁸ U	²⁴⁰ Pu/ ²³⁹ Pu	²⁴¹ Pu/ ²³⁹ Pu	²⁴² Pu/ ²³⁹ Pu
3	1.00±0.02*	0.244±0.006	(1.05±0.05) × 10 ⁻²	(1.61±0.15) × 10 ⁻²
4	0.998±0.004	0.240±0.004	(1.02±0.05) × 10 ⁻²	(1.53±0.10) × 10 ⁻²
Certified value	1.00	0.241	0.900 × 10 ⁻²	1.56 × 10 ⁻²

*Uncertainty, which corresponds to two standard deviations.

²³⁵U/²³⁸U measured for the particle No. 2 was slightly lower than the certified value, while that measured for the particle No.1 corresponded to the certified value. The isotope ratios of ²⁴¹Pu/²³⁹Pu were higher than the certified value, which is due to the contribution of the ²⁴¹Am peak to the ²⁴¹Pu peak. In SIMS analysis, the separation of ²⁴¹Pu and ²⁴¹Am peaks is impossible, even if high mass resolution is used in the measurement. This is a limitation of SIMS for isotope ratio analysis of individual U-Pu particles.

As shown in Table 2, accurate ²⁴⁰Pu/²³⁹Pu isotope ratios were obtained, though no correction for the interference of the ²³⁸UH peak to the ²³⁹Pu peak was made. If the particle has higher ²³⁸U/²³⁹Pu ratio, the ²³⁹Pu peak would be strongly interfered by the ²³⁸UH peak, which makes it impossible to determine plutonium isotope ratios accurately. This is another limitation of SIMS for isotope ratio analysis of U-Pu particles.

ICP-MS analysis

The application of ICP-MS to the isotope ratios analysis of individual U-Pu particles was also examined in this study. The isotope ratios of ²³⁵U/²³⁸U, ²⁴⁰Pu/²³⁹Pu, ²⁴¹Pu/²³⁹Pu and ²⁴²Pu/²³⁹Pu were measured and are summarized in Table 3. The isotope ratios of ²⁴¹Pu/²³⁹Pu were higher than the certified value. This is due to the contribution of the ²⁴¹Am peak to the ²⁴¹Pu peak. The isotope ratios of ²⁴⁰Pu/²³⁹Pu were in good agreement with the certified value. As well as SIMS analysis, the ²³⁹Pu peak is interfered by the ²³⁸UH peak in ICP-MS analysis. In a previous study,⁶ the hydride formation rate (²³⁸UH/²³⁸U) in ICP-MS analysis was estimated to be

about 5×10^{-5} , which is at least one order of magnitude lower than that in SIMS analysis. Therefore, even if the particle has higher $^{238}\text{U}/^{239}\text{Pu}$ ratio, the interference of the ^{238}U peak to the ^{239}Pu peak may be avoided to a certain extent.

In contrast to SIMS, ICP-MS has a potential to avoid these spectral interferences caused by uranium hydride and americium ions. In a previous study, we performed chemical separation of plutonium and americium in individual plutonium particles and successfully determined the $^{241}\text{Pu}/^{239}\text{Pu}$ isotope ratios with ICP-MS.¹⁴ The combination of chemical separation and ICP-MS analysis would overcome these problems and enable us to perform accurate isotope ratio analysis for individual U-Pu particles, though further study is necessary.

Conclusions

In the present work, analytical techniques using SIMS and ICP-MS were applied to the isotope ratio analysis of individual U-Pu mixed oxide particles prepared from the mixed solution of SRM 947 and CRM U-500 standard reference materials. The isotope ratios of $^{235}\text{U}/^{238}\text{U}$, $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$ were accurately determined with both methods. However, accurate analysis of $^{241}\text{Pu}/^{239}\text{Pu}$ isotope ratio was impossible in both techniques, due to the interference of the ^{241}Am peak to the ^{241}Pu peak. In order to overcome this problem, ICP-MS would be appropriate because the method can be combined with chemical separation of uranium, plutonium and americium in individual U-Pu particles.

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