



Original Article

Accurate determination of minor isotope ratios in individual plutonium–uranium mixed particles by thermal ionization mass spectrometry

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ABSTRACT

Isotopic analyses of plutonium and low-enriched uranium mixtures with particle sizes of 0.6–3.3 μm were performed using thermal ionization mass spectrometry with a continuous heating method to verify its effectiveness for the accurate analysis of minor isotopes without sample pretreatment. The mixed particles used in this study were prepared from a mixed solution of plutonium (SRM 947) and uranium (U010, ^{235}U 1% enriched) reference materials. The isotope ratios for plutonium in the individual mixed particles, including $^{238}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{239}\text{Pu}$ as well as $^{240}\text{Pu}/^{239}\text{Pu}$, and $^{242}\text{Pu}/^{239}\text{Pu}$, were in good agreement with the certified values despite the isobaric interference of ^{238}U and ^{241}Am . The isotope ratios for uranium in the mixed particles also agreed well with the certified values within the range of error. However, the isotope ratios for minor isotopes, such as ^{234}U and ^{236}U , in the particles with diameters of less than approximately 1.8 μm could not be measured because numbers of ^{234}U and ^{236}U atoms in analyzed particles are too low. These results indicate that thermal ionization mass spectrometry with a continuous heating method is applicable for the analysis of trace amounts of plutonium isotopes, including ^{238}Pu and ^{241}Pu , despite the presence of the respective isobars ^{238}U and ^{241}Am in the microsamples.

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1. Introduction

The International Atomic Energy Agency (IAEA) introduced the environmental sample analysis method, referred to as “environmental sampling”, into a strengthened safeguards system based on Programme 93 + 2, which is one of the key tools for detecting undeclared nuclear activity [1–3]. In this method, the isotopic compositions of trace amounts of uranium and plutonium in swipe samples taken by IAEA inspectors inside and outside of nuclear facilities are analyzed by IAEA-authorized Network of Analytical Laboratories members. These samples can be studied in two ways: by bulk analysis or particle analysis. Bulk analysis, in which the entire sample is dissolved and analyzed, provides information only about the average concentration and isotopic composition of the sample. In contrast, particle analysis, which measures the isotopic ratio of individual particles, provides more detailed information on

the nuclear activities at the inspected location. For example, low-enriched uranium (3–5% ^{235}U) is used as nuclear fuel for a typical commercial nuclear power plant. However, more than 90% enrichment is needed for the production of nuclear weapons. The presence of high-enriched uranium in a uranium enrichment facility suggests undeclared activities. In the process of enriching ^{235}U in an enrichment plant, ^{234}U is also enriched, and thus finding of enriched ^{234}U is indicative of the presence of an enrichment plant. On the other hand, ^{236}U is not contained in natural uranium and is produced by the $^{235}\text{U}(n,\gamma)^{236}\text{U}$ reaction in a nuclear reactor. Thus the presence of ^{236}U suggests the existence of a reprocessing plant. In general, swipe samples contain plutonium at femtogram (10^{-15} g) to picogram (10^{-12} g) levels and uranium at nanogram (10^{-9} g) levels. Thus, one of the main issues in environmental sampling is how to analyze ultra-trace concentrations of target elements. Furthermore, various impurities from the environment are also included in the swipe sample and influence the measurement accuracy and precision via isobaric and polyatomic interferences. To overcome the negative impact on measurement accuracy and precision resulting from these interferences, enable

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particle-level analysis, and analyze ultra-trace concentrations, a sophisticated analytical technique is needed.

The presence of plutonium in the environment is mainly attributed to artificial factors, such as reactor accidents, nuclear fuel reprocessing, and nuclear weapon tests, as plutonium does not exist naturally to any meaningful extent. Because the isotopic composition of plutonium varies with the type of nuclear reactor, nuclear fuel burnup, and nuclear weapon, the isotope ratios of plutonium can be used as fingerprints to identify its source [4–6]. The analysis of Pu-containing particles recovered from inside hot cells can yield important information about the activities conducted there. In particular, the handling of irradiated reactor fuel should produce particles in which the ratio of uranium and plutonium depends on the irradiation conditions. For example, high levels of plutonium in a particle may indicate chemical separation activities. Furthermore, the amount of americium (Am) in a particle relative to the amount of Pu can provide an indication of the age of the material. The ^{241}Pu in a plutonium sample undergoes beta decay with a half-life of 14.325 years to produce ^{241}Am ; thus, the amount of ^{241}Am in a plutonium sample increases with time. For these reasons, the accurate measurement of the ^{241}Pu and ^{241}Am ratio is of interest in nuclear forensics, especially for determining the origin of plutonium [5]. The accurate determination of ^{238}Pu in plutonium recovered from spent fuels is also important for deducing the reactor type [7]. The accurate analysis of uranium minor isotopes, such as ^{234}U and ^{236}U , is essential for nuclear safeguards and nuclear forensics. The detection of ^{236}U suggests that the investigated nuclear facility may have handled reprocessed uranium at some point. Meanwhile, samples containing ^{234}U above the nominal concentration may indicate that enrichment activities were conducted at the facility.

Thermal ionization mass spectrometry (TIMS) is a high-sensitivity method for precisely measuring the isotopic abundances of the major and minor isotopes of plutonium and uranium. There are several TIMS techniques for measuring isotopic compositions in plutonium and uranium: the total evaporation (TE) method [8,9], modified total evaporation (MTE) method [10], and continuous heating method [11]. In the TE method, the signals for each isotope are integrated simultaneously from beginning of analysis until the entire sample has been exhausted, with the result that the effects of mass fractionation can be minimized. The TE method enables high-precision measurement of major isotopes, but minor isotope signal intensities are biased due to peak tailing contributions from the significantly more abundant isotopes. This major drawback has been overcome by the MTE method which routinely stops the TE process to allow measurement of backgrounds, internal yield calibration of the scanning electron microscopy (SEM) detector, and ion beam focusing. These interruptions are mainly useful for improving the accuracy of the minor isotope ratio measurements without degrading the quality of the major isotope ratio. Thus far, TE-TIMS and MTE-TIMS, which are commonly used for determining the isotopic compositions of plutonium and uranium, are generally not used for the determination of the $^{238}\text{Pu}/^{239}\text{Pu}$ isotope ratio due to the isobaric interference of ^{238}U . To overcome this problem, it has been necessary to conduct chemical separation of the solution sample before mass spectrometry measurements [12,13]. However, in the case of particulate samples, chemical processes such as dissolution, purification, and separation are difficult and increase the background level. In addition, to measure the isotope ratios of ultra-trace amounts of samples with high accuracy and precision, the development of a sophisticated detection system and analytical technique is desirable because such measurements become increasingly difficult as the total sample concentration available for analysis decreases.

In previous works, the interference of ^{238}U and ^{241}Am in ^{238}Pu and ^{241}Pu measurements, respectively, was successfully overcome by using TIMS with a continuous heating method, without the need for any chemical separation [11,14]. We have shown that the isotope ratios of mixed particles of plutonium and high-enriched uranium (U500, ^{235}U 50% enriched) can be measured by TIMS with a continuous heating method without any chemical separation [15]; all minor isotopes, including ^{238}Pu and ^{241}Pu , were accurately measured. To extend the effectiveness of the continuous heating method, it is necessary to verify the process under conditions in which the amount of ^{238}U is comparatively large. In this study, the effectiveness of TIMS with a continuous heating method for the accurate determination of isotope ratios under the coexistence of an isobar was verified by measuring the isotope ratios in mixed particles of plutonium and low-enriched uranium.

2. Material and methods

2.1. Sample preparation

Mixed particles of plutonium and uranium were prepared from the respective isotopic standard reference solutions: SRM 947 (NBL, USA) for plutonium and CRM U010 (^{235}U 1% enriched, NBL, USA) for uranium. On July 14, 2008, chemical separation of plutonium solution was performed using anion exchange to remove americium and uranium. Equal amounts of plutonium and uranium solution were used to prepare the mixed particles. 27 μL of the purified plutonium solution (15 μg of Pu) and 150 μL of the purified uranium solution (15 μg of U) were pipetted into a 1-mL round-bottom flask made of silica glass and then evaporated to form a pinpoint dried residue. The flask containing the pinpoint dried residue was heated at 800 $^{\circ}\text{C}$ for 20 s to produce the oxide. After cooling, 10 μL of *n*-dodecane was added to the flask, and the dried residue was crushed with a silica glass rod to form particulate samples. An additional 90 μL of *n*-dodecane was added to the flask, which was then placed in an ultrasonic bath for 20 min to prevent particle agglomeration. The *n*-dodecane solution containing the crushed particles was pipetted onto a 25-mm-diameter silicon planchet. Next, *n*-dodecane was evaporated by heating to obtain the particulate mixed samples. The elemental composition of the prepared mixed particles was checked by energy-dispersive X-ray (EDX) measurements to ensure that the particles contained both plutonium and uranium. A SEM image and EDX spectrum of a prepared mixed particle are shown in Fig. S1. The EDX spectrum features peaks assigned to plutonium, uranium, and oxygen, implying that the particle consists of a mixture of plutonium and uranium as an oxide. ^{241}Pu and ^{241}Am formed through the decay of ^{241}Pu are also present in the mixed particles because of the time elapsed since the purification of the plutonium solution sample. Individual particles were picked up and transferred onto the center of each filament using a micro-manipulator attached to the SEM.

2.2. Isotope ratio measurements

A TIMS (TRITON, Thermo Fisher Scientific, USA) with continuous heating was utilized to measure the isotope ratios of plutonium and uranium for individual particles. The instrument is equipped with a secondary electron multiplier in ion counting mode. A double-filament assembly composed of zone-refined rhenium was used for the isotope ratio measurements. The filaments were degassed twice to reduce the background from the filament. First, degassing was performed using a filament bake-out device (Thermo Finnigan), in which the filaments were subjected to a heating routine for degassing for 20 min at 4500 mA under a vacuum of less than 5×10^{-6} mbar. The degassed filaments were then mounted in the

TIMS sample magazine, and the filament current was increased to 5000 mA to provide a second degassing.

The ionization filament was heated until the ^{187}Re intensity, read on the Faraday detector, reached 100 mV, after which the ion lens system was optimized to maximize the intensity. After the ^{187}Re intensity had been readjusted to 100 mV, the measurement process was commenced using the secondary electron multiplier detector. The evaporation filament was gradually raised to 5000 mA (ca. 2000°C) to evaporate the sample. The intensities of each isotope were measured with a peak-jumping sequence. The optimized integrated and idle times are shown in Table 1. In the continuous heating method, the temperature of the evaporation filament was increased linearly at a heating rate of 100 mA/min, and the data in the temperature region with the highest intensities during the measurement were used to calculate the isotope ratios. One of the main features of this method is its ability to analyze uranium and plutonium, even in the case of ultra-trace, subpicogram amounts [11]. Mass bias was corrected using certified reference materials: CRM U-350 (35% ^{235}U enriched, NBL, USA) for uranium and SRM 947 (NBL, USA) for plutonium.

3. Results and discussion

3.1. Determination of isotope ratios in a mixed particle of uranium and plutonium

The presence of plutonium and uranium in each of the mixed particles of plutonium and uranium prepared from the solution sample was confirmed by SEM-EDX before the isotope ratio measurement of the mixed particles. Fig. 1 shows the signal profiles obtained by continuous heating method of all isotopes in a mixed particle with a diameter of approximately 1.8 μm . In these profiles, the peaks corresponding to plutonium and uranium in the mixed particle are observed at currents of approximately 1950 mA (Fig. 1B) and 3100 mA (Fig. 1A), respectively.

The results of the isotope ratio measurements in the individual mixed particles with diameters of 0.6–3.3 μm are shown in Fig. 2, with the isotope ratios of uranium and plutonium shown in Fig. 2A and 2B, respectively. The isotope ratios of plutonium and uranium in the mixed particles were in good agreement with the certified values, even for submicrometer-sized particles.

When using conventional methods, such as TE-TIMS, the ratio of $^{241}\text{Pu}/^{239}\text{Pu}$ in a plutonium sample may exceed the certified value because beta decay of ^{241}Pu produces ^{241}Am in the time elapsed since chemical purification. Thus, chemical separation of americium from plutonium is usually employed when attempting to accurately measure ^{241}Pu . However, the influence of ^{241}Am on the ratio of $^{241}\text{Pu}/^{239}\text{Pu}$ can be avoided without chemical separation by utilizing the continuous heating method used in this study. As shown in Fig. 1B, the peak for an evaporation filament current of approximately 1000 mA at $m/z = 241$ represents the ^{241}Am formed

Table 1

Integrated and idle times of TIMS for measurement of the mixed particles of plutonium and uranium.

Step	Mass (m/z)	Related nuclides	Integrated time (s)	Idle time (s)
1	234	^{234}U	4	0.5
2	235	^{235}U	2	0.5
3	236	^{236}U	4	0.5
4	238	^{238}U (^{238}Pu)	2	0.5
5	239	^{239}Pu	2	0.5
6	240	^{240}Pu	2	0.5
7	241	^{241}Pu (^{241}Am)	4	0.5
8	242	^{242}Pu	4	0.5

TIMS, thermal ionization mass spectrometry.

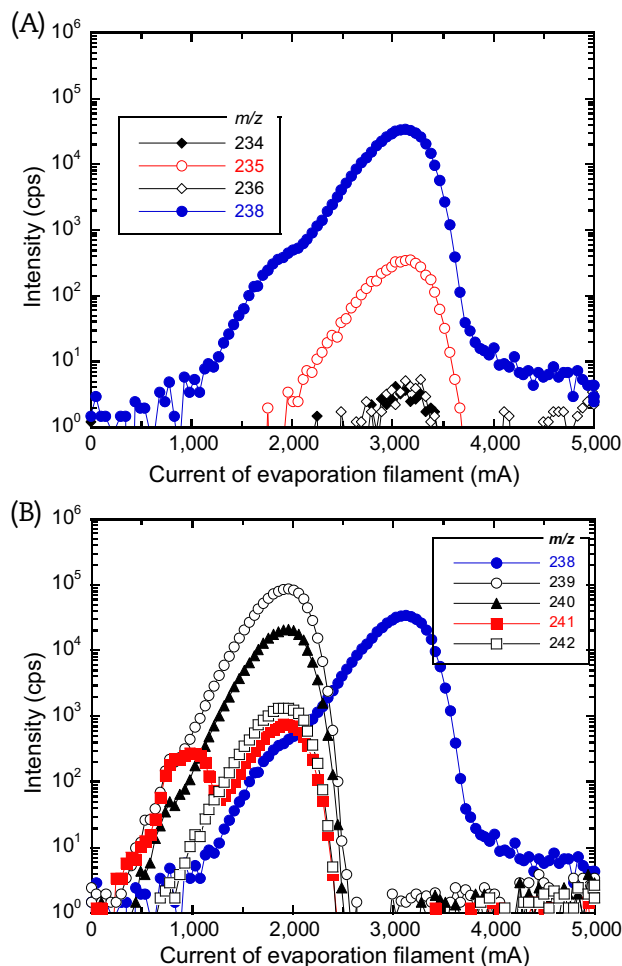


Fig. 1. TIMS signal profiles of a plutonium–uranium mixed particle with a size of approximately 1.8 μm . (A) $m/z = 234$ –238. (B) $m/z = 238$ –242. TIMS, thermal ionization mass spectrometry.

by the beta decay of ^{241}Pu . Thus, TIMS measurement with continuous heating method enables ^{241}Am and ^{241}Pu to be distinguished, as shown in the signal profile of $m/z = 241$. For the mixed particle with a diameter of 0.6 μm , which corresponds to a plutonium particle with a diameter of approximately 0.49 μm , the ratio of $^{241}\text{Pu}/^{239}\text{Pu}$ can be accurately measured, as shown in Fig. 2B. Despite the ultra-trace amount of the sample, an accuracy of 3.5% and relative standard deviation (2RSD) of 10.2% are achieved.

3.2. Measurement of ^{238}Pu

For the isotope ratio measurements of the mixed sample of plutonium and uranium, one of the key challenges is the measurement of ^{238}Pu . The ratio of $^{238}\text{Pu}/^{239}\text{Pu}$ in a sample of plutonium including uranium cannot be measured by TE-TIMS due to the isobaric interference of ^{238}U in ^{238}Pu . Several methods for correcting the ^{238}U interference at the mass to charge ratio of ^{238}Pu in the mixed sample of plutonium and uranium have been reported [14–16]. In Fig. 1, the shoulder at approximately 1950 mA in the signal profile of $m/z = 238$ is attributed to ^{238}Pu , that is, the continuous heating method for TIMS measurement used herein permits the discrimination of ^{238}U and ^{238}Pu in this signal profile. In this study, the signal intensity of ^{238}Pu in this signal profile of $m/z = 238$ was calculated by the fitting method [15]. It was possible to estimate the net intensity of the ^{238}Pu peak in the signal profile of $m/z = 238$ by deducting the ^{238}U background of the ^{238}Pu peak, in

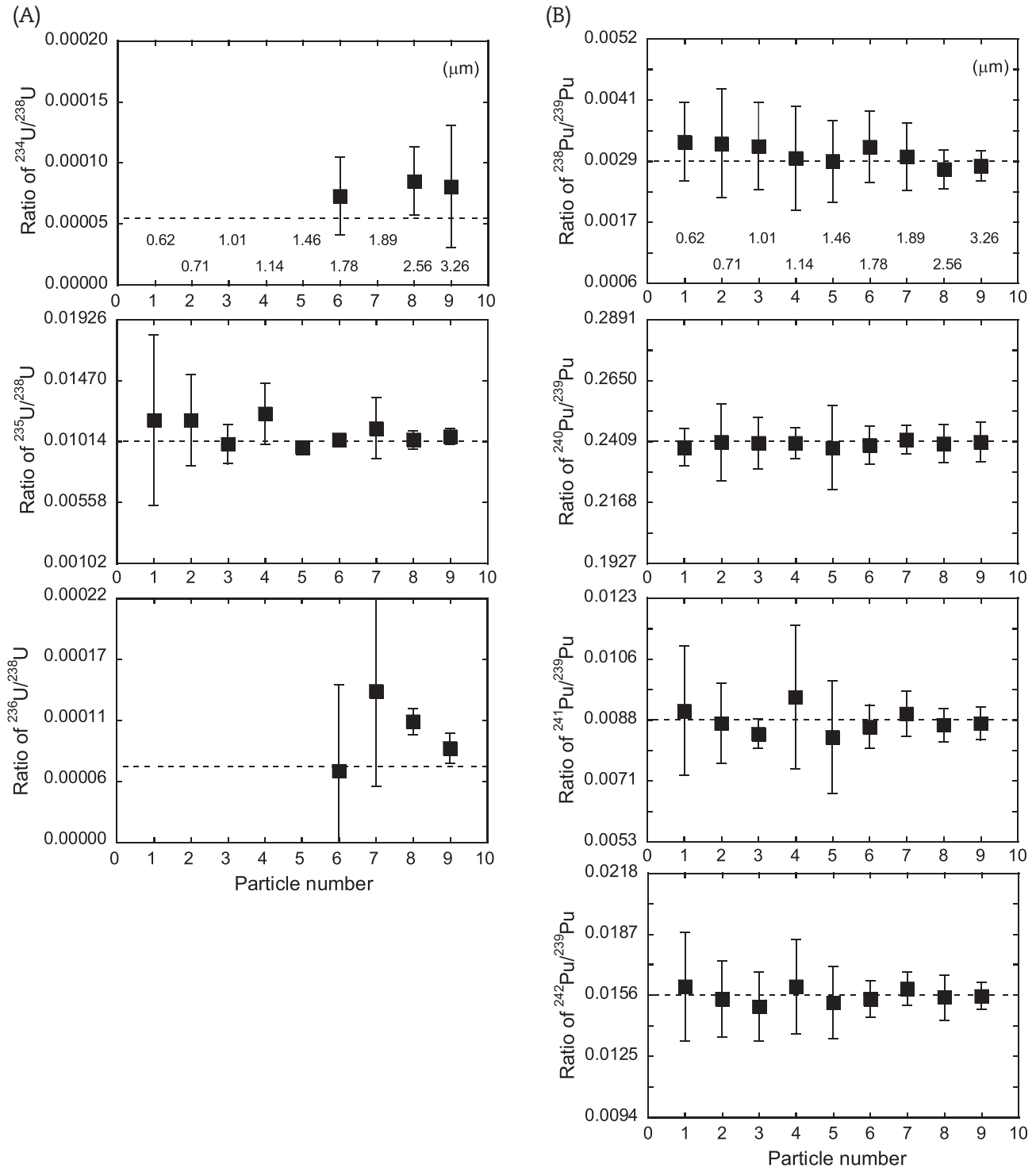


Fig. 2. Uranium and plutonium isotope ratios in individual mixed particles prepared from the mixed solution of plutonium (SRM 947) and uranium (U010). (A) Uranium isotope ratios. (B) Plutonium isotope ratios. The sizes of the particles are shown in the figure. The certified value of $^{241}\text{Pu}/^{239}\text{Pu}$ was corrected by the measurement date. The dotted lines represent the certified values. Error bars present the 2SD. SD, standard deviation.

which it was possible to evaluate the background of ^{238}U in ^{238}Pu by the fitting of the ^{238}U signal to the region of the ^{238}Pu peak. As shown in Fig. 2B, the ratios of $^{238}\text{Pu}/^{239}\text{Pu}$ in the mixed particles corrected by the fitting method agreed well with the certified value for all particles used in this study. The 2RSD values for $^{238}\text{Pu}/^{239}\text{Pu}$, $^{240}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{239}\text{Pu}$, and $^{242}\text{Pu}/^{239}\text{Pu}$ in the mixed particle with

diameter of 1.14 μm were estimated at 16.8%, 1.3%, 10.9%, and 7.5%, respectively. However, the accurate determination of the ratios of $^{238}\text{Pu}/^{239}\text{Pu}$ in the mixed sample of plutonium and uranium, that is, discrimination of ^{238}U and ^{238}Pu , relies entirely on the quantitative ratio of uranium and plutonium included in the mixed sample. Recently, the ratio of $^{238}\text{Pu}/^{239}\text{Pu}$ has been determined in a mixed

sample of plutonium and uranium using the samples with various ratios of plutonium and uranium, where the ratio of $^{238}\text{Pu}/^{239}\text{Pu}$ in a mixed sample could not be measured in a sample with a low $^{238}\text{Pu}/^{238}\text{U}$ ratio [17]. This limitation requires pretreatment, such as chemical separation, before analysis of the isotope ratios by TIMS to obtain accurate isotope ratios for samples with low $^{238}\text{Pu}/^{238}\text{U}$ ratio.

3.3. Measurement of uranium minor isotopes

All the uranium isotope ratios in the mixed particles with diameters greater than 1.78 μm can be measured; the 2RSD values of the $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$ ratios for the particles with diameter of 1.78 μm were 19.3%, 1.6%, and 51.8%, respectively. However, the minor isotopes, such as ^{234}U and ^{236}U , could not be measured in the particles with diameters less than approximately 1.8 μm , as shown in Fig. 2A. This is because the enrichment of the uranium (UO10, 1% ^{235}U enriched) used in this study is very low, and the uranium in a mixed particle is therefore present in ultra-trace amounts. Each mixed particle contains half plutonium and half uranium. As shown in Fig. S1, the morphology of the mixed particle prepared from the solution sample of plutonium and uranium is not a perfect sphere; therefore, it contains fewer components than would a perfectly spherical particle with the diameter calculated in this study. Thus, a sophisticated analytical technique may be needed to analyze the isotope ratios in samples with ultra-trace amounts. For this purpose, it would be interesting to use a TIMS equipped with a multiple-ion counting detection system.

4. Conclusions

This study demonstrates the effectiveness of TIMS with a continuous heating method for the accurate determination of ^{238}Pu and ^{241}Pu despite coexistence of their respective isobars ^{238}U and ^{241}Am . This approach was successfully applied for the determination of isotope ratios in mixed particles with an ultra-trace amount of plutonium and low-enriched uranium. The $^{238}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ ratios as well as the $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$ ratios in the mixed particles were accurately measured under isobaric interference from ^{238}U and ^{241}Am . The minor isotope ratios of uranium, $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$, could not be measured in particles smaller than 1.8 μm ; however, this limitation could be mitigated somewhat by using a multi-ion counting detection system.

Novelty statement

This study demonstrates the effectiveness of TIMS with a continuous heating method for the accurate determination of isotope ratios under the coexistence of an isobar. The $^{238}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ ratios as well as the $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$ ratios in the plutonium and low-enriched uranium mixed particles were accurately measured without any chemical separation under isobaric interference from ^{238}U and ^{241}Am .

Conflicts of interest

All authors have no conflicts of interest to declare.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.net.2017.10.010>.

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