



Application of a continuous heating method using thermal ionization mass spectrometry to measure isotope ratios of plutonium and uranium in trace amounts of uranium–plutonium mixture sample

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ABSTRACT

A method for measuring isotope ratios of plutonium and uranium in plutonium or uranium–plutonium (Pu/U) mixture samples was developed by using a continuous heating method of thermal ionization mass spectrometry, which was previously shown to be effective in measuring isotope ratios of trace uranium. In this method, temperature of an evaporation filament is increased sequentially. This leads to measure the ratios of Pu and U at different temperatures in which each element is evaporated efficiently. Under optimal measurement conditions, the intensity of ^{239}Pu and the ratio of $^{240}\text{Pu}/^{239}\text{Pu}$ were measured down to sample amounts of 0.1 fg and 0.3 fg, respectively. In Pu/U mixture samples with pg-level masses and 0.01–10 Pu/U ratios, isotope ratios of $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{235}\text{U}/^{238}\text{U}$ were measured simultaneously without chemical separation of samples. The relative standard deviation of the isotope ratios of $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{235}\text{U}/^{238}\text{U}$ in the sample containing each 1 pg of plutonium and uranium were better than 2% and 4%, respectively. Moreover, $^{238}\text{Pu}/^{239}\text{Pu}$ ratios were obtained by using a correction in which the ^{238}U intensity was estimated from the ^{235}U intensity and the $^{235}\text{U}/^{238}\text{U}$ ratio. The results in this study suggest that the continuous heating method of thermal ionization mass spectrometry will be effective tool as a method for measuring isotope ratios in the Pu/U mixture samples.

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1. Introduction

Environmental sample analysis for safeguards (SG) is carried out by the International Atomic Energy Agency (IAEA) to find undeclared nuclear activities and detect nuclear materials. The environmental samples are mainly swipes taken by inspectors from the inside and outside of nuclear facilities. Isotope ratios in individual particles of nuclear materials on the swipe are measured. This is considered to be a useful tool because it provides information of past and present nuclear activities at the facility. These analyses are performed primarily using two methods, namely secondary ion mass spectrometry (SIMS) [1–4] and fission track-thermal ionization mass spectrometry (FT-TIMS) [5–7]. The SIMS method enables isotope ratios to be measured quickly. On the other hand, the FT-TIMS method is time-consuming compared to the SIMS method. However, FT-TIMS can analyze small particles below sub-micrometer size. These complementary methods have been used for routine analysis of uranium particles.

Recently, the number of facilities using plutonium and MOX (uranium–plutonium oxide) fuels has increased and this usage is expected to blossom in the near future. For this reason, measuring plutonium, in addition to uranium, is an important matter in environmental sample analysis for SG [8]. However, the SIMS method is problematic when measuring plutonium in Pu/U mixture particles, because the molecular monohydride ion of ^{238}U interferes with ^{239}Pu . The TIMS method has been used to measure plutonium particles in the past [9], but there is no report of TIMS measurement of a MOX particle. In general, chemical separation of plutonium and uranium is required in order to obtain accurate isotope ratios of plutonium and uranium in a Pu/U mixture sample [10]. However, the micrometer size of particles measured in environmental sample analysis for SG makes it difficult to subject these particles to chemical separation. Therefore, particle analysis is needed to measure plutonium and uranium simultaneously, without the need for chemical separation.

Walker et al. measured plutonium and uranium isotopes in Pu/U mixture samples at different temperatures using the TIMS method [11]. Plutonium and uranium were analyzed at 1450–1500 °C and 1700–1800 °C, respectively. However, using this approach required two heating steps, with the result that it took a long time to measure the isotope ratios. As the amount of sample available is often very small, the sample is largely consumed during conditioning to

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Table 1

Optimization for heating rate sequences of the EF current for measurement of plutonium sample and Pu/U mixture sample.

U^{131}		Pu		Pu/U	
EF current (mA)	Heating rate (mA/min)	EF current (mA)	Heating rate (mA/min)	EF current (mA)	Heating rate (mA/min)
0–800	200	0–800	200	0–800	200
800–1800	100	800–1800	150	800–1800	200
1800–2700	50	1800–3000	150	1800–2700	250
2700–4000	20	–	–	2700–5000	250

obtain suitable evaporation filament (EF) currents for measuring plutonium and uranium, or plutonium alone. This raises concerns that very small samples cannot be effectively measured by this technique. Ramakumar et al. reported that a Pu/U mixture solution was loaded on a filament and then the isotope ratios for both plutonium and uranium were measured at the same temperature [12]. This method can shorten the measurement time compared to the method using two heating steps. With this single-temperature method, however, it is impossible to employ optimum temperatures for measuring both plutonium and uranium.

Suzuki et al. developed the 'continuous heating method' to measure isotope ratios in a uranium particle [13]. The temperature of the EF was increased sequentially and the data in the temperature region with highest intensities during the measurement were used to calculate the isotope ratios. This method made it possible to measure isotope ratios in uranium particles with high precision, essentially independent of sample amounts as well as the operator's experience and skill. With this method, signal intensities of relevant masses are recorded while the sample evaporates. When measuring Pu/U mixture samples, it is expected that data obtained at optimum temperatures which plutonium and uranium evaporate can be used to calculate the isotope ratios of plutonium and uranium, providing results with high precision. Moreover, this method presents the possibility for correcting interference between isobaric ^{238}U and ^{238}Pu using different evaporation behavior of each isotope.

In this study, the continuous heating method was applied to measure isotope ratios of plutonium and uranium in Pu/U mixture samples by TIMS. At first, measurement conditions for the plutonium sample were optimized, as this method has previously been used only to measure uranium. After this optimization, the method was used to measure the isotopes of Pu/U mixture samples. The interference between ^{238}U and ^{238}Pu and a new correction method for this interference are also discussed.

2. Experimental

A TIMS (TRITON, Thermo Fisher Scientific) was used to measure isotope ratios. A double filament assembly made of zone-refined Re was used. This was prepared by degassing for 20 min with a 4.5 A current under a vacuum better than 5×10^{-6} mbar. The instrument was equipped with seven Faraday detectors and a secondary electron multiplier (SEM). The SEM with peak-jumping sequence was used in this study because the amounts of plutonium and uranium were very small. When measuring the plutonium samples, the integration time and idle time for each plutonium isotope were 4 s and 1 s, respectively. For the Pu/U mixture sample, masses of 239 and 240 for plutonium were measured in addition to masses of 235 and 238 for uranium. The integration times of the masses of 238 and 239 for measuring major isotopes of ^{238}U and ^{239}Pu were 2 s, while those of masses of 235 and 240 were 4 s. The idle time was 0.5 s. As the peak-jumping sequence was used, correction of a time dependent effect of measurement of different masses was needed. Each intensity of ^{238}U and ^{239}Pu at measurement of the masses of ^{235}U and ^{240}Pu was calculated by linear approximation using intensities

of ^{238}U and ^{239}Pu measured before and after the measurement of the masses of ^{235}U and ^{240}Pu .

Isotope standard reference materials, SRM 947 (National Bureau of Standards, USA) for plutonium and CRM U350 (35% ^{235}U enriched, New Brunswick Laboratory, USA) for uranium were used. Plutonium in the SRM 947 was purified from decay products such as americium and uranium using an anion exchange separation procedure [14]. The method in the previous study included two steps of plutonium separation, as the samples were sediments containing a large amount of impurities. In this study, only one separation step was used, due to the small amount of impurities in the SRM 947. The purified SRM 947 solution and CRM U350 solution were diluted with 1 M HNO_3 solution to the specified concentrations for determining isotope ratios and then were mixed according to need.

The plutonium solution or Pu/U mixed solution was loaded onto the filament and then heated with 1.5 A for 15 s or 2.0 A for 30 s, respectively, before commencing the measurement.

3. Results and discussion

3.1. Optimization of measurement conditions

Before the optimization of measurement conditions for measuring plutonium isotope ratios, the evaporation behavior of plutonium was observed using the heating rate sequence for measuring uranium (Table 1). A profile of the ^{239}Pu signal while measuring the solution sample containing 4 pg of plutonium is shown in Fig. 1. A profile of the ^{238}U signal in a solution sample containing 4 pg of uranium is also shown for comparison. The intensities of ^{239}Pu and ^{238}U exhibited maxima at EF currents of 1900 mA and 2700 mA, respectively. The integrated ^{238}U intensity was much lower than the ^{239}Pu intensity. This is probably due to differences in the type of ion species and ionization efficiency of uranium and plutonium.

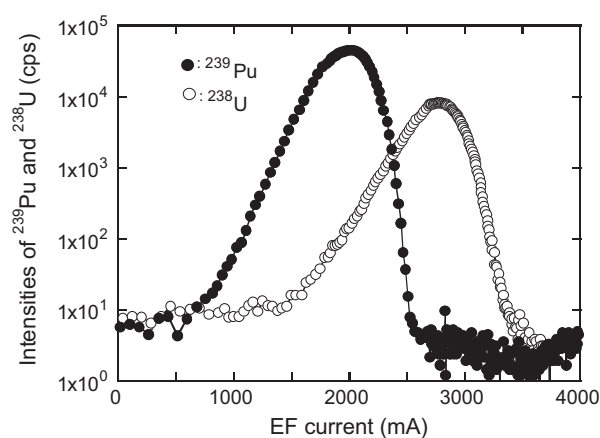


Fig. 1. Intensities of ^{239}Pu and ^{238}U as a function of the EF current. Heating rate was used for the measurement of uranium (see Table 1). Quantities of 4 pg each of plutonium or uranium were loaded on the filament.

Table 2
Isotope ratios of $^{238}\text{Pu}/^{239}\text{Pu}$, $^{240}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$ in the SRM947 sample containing 1 pg of plutonium measured by the continuous heating method with plutonium heating rate.

Sample	$2\sigma^a$			
	$^{238}\text{Pu}/^{239}\text{Pu}$	$^{240}\text{Pu}/^{239}\text{Pu}$	$^{241}\text{Pu}/^{239}\text{Pu}$	$^{242}\text{Pu}/^{239}\text{Pu}$
1	$(3.0 \pm 0.4) \times 10^{-3}$	$(2.42 \pm 0.03) \times 10^{-1}$	$(1.02 \pm 0.04) \times 10^{-2}$	$(1.6 \pm 0.1) \times 10^{-2}$
2	$(3.2 \pm 0.6) \times 10^{-3}$	$(2.40 \pm 0.03) \times 10^{-1}$	$(1.04 \pm 0.06) \times 10^{-2}$	$(1.6 \pm 0.2) \times 10^{-2}$
3	$(2.9 \pm 0.6) \times 10^{-3}$	$(2.41 \pm 0.03) \times 10^{-1}$	$(1.04 \pm 0.07) \times 10^{-2}$	$(1.6 \pm 0.1) \times 10^{-2}$
Certified value	2.9×10^{-3}	2.41×10^{-1}	1.02×10^{-2}	1.6×10^{-2}

^a Uncertainty (2σ) shows variability of 5 ratios obtained in the measurement of a sample.

Measurement conditions were optimized in the EF current range from 800 mA to 3000 mA in which plutonium signals were detected. Specifically, data were acquired at several heating rates (20, 50, 70, 100, 150, 200 and 250 mA/min) in order to optimize the heating rate in the current ranges of 800–1800 mA and 1800–3000 mA. The highest ^{239}Pu intensity was observed at a heating rate of 150 mA/min for both current ranges. To measure the Pu/U sample, the optimal measurement condition was determined in the same way. Optimal heating rates for measuring plutonium and Pu/U mixture samples are summarized in Table 1. The heating rate at the EF current of more than 1800 mA for measuring the Pu/U mixture sample were faster than those for measuring the U sample. This condition was selected to measure a small amount of sample and led to higher intensities than those used by the previous rate [13] because amount of evaporation of uranium increased per unit of time.

3.2. Determination of isotope ratios in plutonium sample

Isotope ratios in the SRM 947 sample containing 1 pg of plutonium were measured using the optimal heating rate, as discussed in Section 3.1 (Table 1). The results are shown in Table 2. All of the ratios are in good correspondence with the certified values. Relative standard deviations (2σ) of the ratios were less than 1% for $^{240}\text{Pu}/^{239}\text{Pu}$ ratio and those of the other ratios were 20%, 7% and 13% for $^{238}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$ ratios, respectively.

The minimum amount that can be measured by this continuous heating method was estimated. Amounts of plutonium used were varied from 0.1 fg (10^{-16} g) to 1 pg (10^{-12} g). In each case, three samples with the same amount were measured. Fig. 2 shows averages of the ^{239}Pu maximum intensity and the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio obtained from measurements of each set of three samples. The ^{239}Pu signal could be detected for the sample of only 0.1 fg;

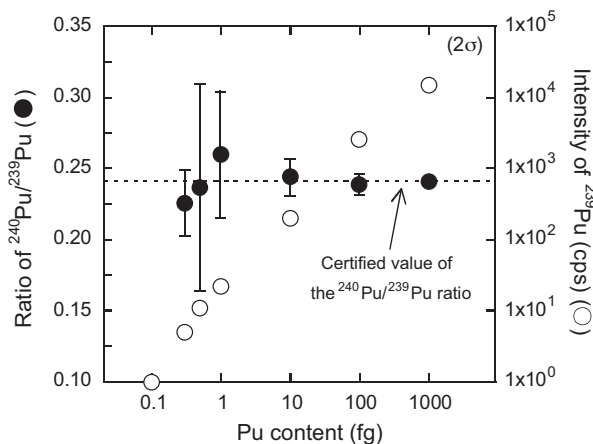


Fig. 2. Ratios of $^{240}\text{Pu}/^{239}\text{Pu}$ and the maximum intensity of ^{239}Pu ($n = 3$, n is a number of measured samples) with amounts of sample. The uncertainties of the maximum intensities are not shown to enhance viewability.

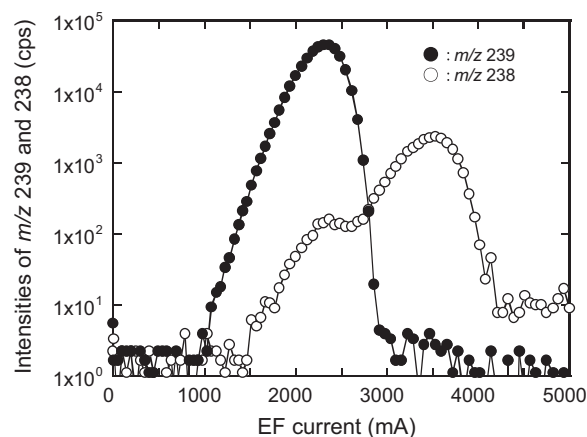


Fig. 3. Profiles of intensities of m/z 238 and 239 in mixed solution of SRM 947 and CRM U350 (Pu:U = 1 pg:1 pg).

however, the ^{240}Pu signal could not be detected below 0.3 fg. Therefore the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio could only be measured down to a sample size of 0.3 fg. This amount corresponds to a spherical PuO_2 particle with a diameter of $\sim 0.04 \mu\text{m}$. These results clearly suggest that this method permits the measurement of plutonium isotope ratios in particles relevant to environmental sample analysis for SG.

3.3. Determination of plutonium and uranium isotope ratios in Pu/U mixture sample

Profiles of the intensities of m/z 238 and 239 in a Pu/U mixture sample containing 1 pg of each plutonium and uranium are shown in Fig. 3. Isotope ratios in Pu/U mixture samples with varying ratios of Pu/U were measured to estimate interference of each isotope in plutonium and uranium. Environmental sample analysis for SG requires the measurement of isotope ratios in particles with various Pu/U ratios formed in the manufacturing processes of MOX fuels and the reprocessing of spent fuels. In this study, samples with Pu/U ratios of 0.01, 0.1, 1 and 10 were measured (Table 3). Fig. 4 shows the $^{235}\text{U}/^{238}\text{U}$, $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{238}\text{Pu}/^{239}\text{Pu}$ ratios in the Pu/U mixture samples. The measured ratios of $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{235}\text{U}/^{238}\text{U}$ were in good correspondence with the certified values. The relative standard deviation of the isotope ratios of $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{235}\text{U}/^{238}\text{U}$ in the sample containing each 1 pg of plutonium and uranium (Pu/U ratio = 1) were less than 2% and 3–4%, respectively. The relative standard deviations in the sample with Pu/U ratios of 0.01,

Table 3
Amounts of plutonium and uranium in Pu/U mixture samples.

Pu/U	Pu (pg)	U (pg)
0.01	0.5	50
0.1	1	10
1	1	1
10	5	0.5

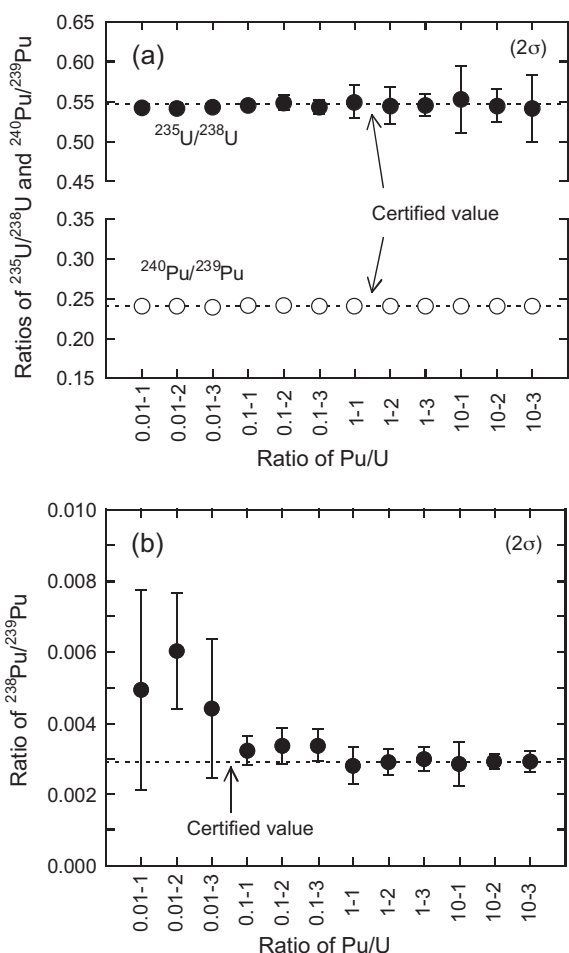


Fig. 4. Ratios of $^{235}\text{U}/^{238}\text{U}$, $^{240}\text{Pu}/^{239}\text{Pu}$ (a) and $^{238}\text{Pu}/^{239}\text{Pu}$ (b) in the Pu/U mixture samples with varying ratios of Pu/U. Three samples of each ratio were measured, and amounts of Pu and U in each ratio were presented in Table 3.

0.1 and 10 were less than 2% and 8% for the ratios of $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{235}\text{U}/^{238}\text{U}$, respectively. These results indicate that the continuous heating method makes it possible to measure isotope ratios regardless of Pu/U ratio in a Pu/U mixture sample containing trace amounts of plutonium and uranium without the need for chemical separation. As the samples analyzed in the environmental samples for SG are very small, it is difficult to effectively perform chemical separation, and this new method will be effective for analyzing the SG samples containing plutonium and uranium.

An attempt was also made to estimate the $^{238}\text{Pu}/^{239}\text{Pu}$ ratio. As can be seen from Fig. 3, Pu starts evaporating already the EF currents of 1000 mA, while uranium ions are observed only at currents above 1500 mA. Measurable Pu ion currents are still observed at filament currents of about 2200 mA. Hence, in the range between 1500 mA and 2500 mA both uranium and plutonium ions are observed. For this reason, it is possible that an isobar, ^{238}U , can present interference in the detection of ^{238}Pu when measuring the $^{238}\text{Pu}/^{239}\text{Pu}$ ratio. Aggarwal et al. reported that ^{238}U was estimated from ^{235}U measured in enriched uranium (93 at% of ^{235}U) added to a plutonium sample in order to measure ^{238}Pu in the plutonium sample, and then $^{238}\text{Pu}/^{239}\text{Pu}$ ratio was corrected from the result [15]. As the samples in the present study were measured for uranium, such an addition of enriched uranium would interfere with the determination of accurate uranium isotope ratios. Moreover this method cannot be applied for a particle sample because of no isotope exchange reaction between the sample and the enriched uranium. Accordingly, the ^{238}U intensity during evaporation of

plutonium was estimated using the ^{235}U intensity and the $^{235}\text{U}/^{238}\text{U}$ ratio obtained from the measurements. Hence, the ^{238}Pu intensity was calculated by subtracting the estimated ^{238}U intensity from the measured intensity at mass position 238. The results of the $^{238}\text{Pu}/^{239}\text{Pu}$ ratio shown in Fig. 4(b) were in reasonable agreement with the certified value for Pu/U ratios of 0.1 or greater. In measurements of uranium-rich samples in which the Pu/U ratio was less than 1, the $^{238}\text{Pu}/^{239}\text{Pu}$ ratio, and its standard deviation, tended to be high and large. These results were due to the small amount of ^{238}Pu and the underestimated ^{238}U intensity, calculated from poor ^{235}U intensity during the evaporation of plutonium. A future goal will be to find a solution to this flaw in the method. For example, the ^{238}Pu intensity will be estimated from peak fitting of the ^{238}U intensity.

4. Conclusions

The continuous heating method was applied to measure isotope ratios in plutonium and Pu/U mixture samples by TIMS. Optimization of measurement conditions enabled us to measure plutonium isotope ratios accurately in samples down to the fg-level. The method was successfully established as an analyzing method for measuring simultaneously plutonium and uranium isotope ratios in Pu/U mixture samples without chemical separation before the measurement. The relative standard deviation of the isotope ratios in the sample of Pu/U ratio = 1 were less than 2% for $^{240}\text{Pu}/^{239}\text{Pu}$ and 3–4% for $^{235}\text{U}/^{238}\text{U}$. Moreover, the method allowed us to measure $^{238}\text{Pu}/^{239}\text{Pu}$ ratio using the ^{235}U intensity and the $^{235}\text{U}/^{238}\text{U}$ ratio obtained from the measurements. The results of this study indicate that the continuous heating method of TIMS allow us to analyze plutonium and MOX particles at sub-micrometer sizes, which is hard to accomplish using other methods in the environmental sample analysis for SG. In the near future, this method will be extended to measure isotope ratios of samples containing minor isotopes such as ^{234}U , ^{236}U , ^{241}Pu and ^{242}Pu .

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