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Ultra-trace analysis of plutonium by thermal ionization mass spectrometry with a continuous heating technique without chemical separation

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ABSTRACT

Thermal ionization mass spectrometry (TIMS) with a continuous heating technique is known as an effective method for measuring the isotope ratio in trace amounts of uranium. In this study, the analytical performance of thermal ionization mass spectrometry with a continuous heating technique was investigated using a standard plutonium solution (SRM 947). The influence of the heating rate of the evaporation filament on the precision and accuracy of the isotope ratios was examined using a plutonium solution sample at the fg level. Changing the heating rate of the evaporation filament on samples ranging from 0.1 fg to 1000 fg revealed that the influence of the heating rate on the precision and accuracy of the isotope ratios was slight around the heating rate range of 100–250 mA/min. All of the isotope ratios of plutonium (SRM 947), $^{238}Pu/^{239}Pu$, $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$, were measured down to sample amounts of 70 fg. The ratio of $^{240}Pu/^{239}Pu$ was measured down to a sample amount of 0.1 fg, which corresponds to a PuO_2 particle with a diameter of 0.2 μm. Moreover, the signals of ^{239}Pu could be detected with a sample amount of 0.03 fg, which corresponds to the detection limit of ^{239}Pu of 0.006 fg as estimated by the 3-sigma criterion. ^{238}Pu and ^{238}U were clearly distinguished owing to the difference in the evaporation temperature between ^{238}Pu and ^{238}U. In addition, ^{241}Pu and ^{241}Am formed by the decay of ^{241}Pu can be discriminated owing to the difference in the evaporation temperature. As a result, the ratios of $^{238}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ as well as $^{240}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ in plutonium samples could be measured by TIMS with a continuous heating technique and without any chemical separation processes.

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1. Introduction

The accurate determination of plutonium isotopes plays an important role in various fields, such as nuclear safeguards, nuclear forensics, and environmental science. Plutonium isotopes, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu with half-lives of 87.7 yr, 24,110 yr, 6561 yr, 14.35 yr and 373,000 yr, respectively, are the most frequently studied. After the Fukushima Daiichi nuclear power plant (DNPP) accident, the atmospheric release of plutonium isotopes into the environment as a result of this accident emerged [1,2]. The amounts, isotopic ratios, and distribution of the released plutonium on the ground have been studied using alpha-spectrometry (AS), inductively coupled plasma-sector field mass spectrometry (SF-ICP-MS) with a high efficiency sample introduction system (APEX) and accelerator mass spectrometry (AMS) to provide a scientific basis with which to estimate the radiation doses and predicts the behavior of these isotopes. The $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ atom ratios found in litter samples ranged from 0.303 to 0.330 and 0.103 to 0.135 [1], respectively, which were significantly higher than those of a global fallout, at 0.180 ± 0.007 for $^{240}Pu/^{239}Pu$ and 0.00194 ± 0.00014 for $^{241}Pu/^{239}Pu$ [3], indicating a new Pu inflow from the Fukushima DNPP accident. Because fine particles, including small amounts of plutonium, can be easily inhaled into the human body, there is a risk of radiation exposure. Therefore, accurate determinations of the plutonium isotopic composition provide important information when attempting to estimate rates of internal radiation exposure.

In addition, the isotope ratios of plutonium are used as a fingerprint to identify the source, such as nuclear fuel reprocessing, nuclear weapon tests, and reactor accidents, as the isotopic composition of plutonium varies depending on the type of nuclear reactor, the nuclear fuel burn-up characteristics and the type of nuclear weapon. The $^{240}Pu/^{239}Pu$ ratio is a good indicator for distinguishing different types of sources. The ratios of $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ can also provide information on the production processes of a nuclear material [4]. The determination of ^{238}Pu is one

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of the most important factors for deducing the reactor type from an analysis of the isotope ratios in plutonium recovered from spent fuels. In order to determine the origin of plutonium in nuclear forensics, plutonium isotope ratios have been measured using thermal ionization mass spectrometry [5–7]. In particular, an accurate $^{241}Pu/^{239}Pu$ ratio is important for determining the age of plutonium. Accurate determinations of plutonium isotopes are of interest for nuclear safeguards [8]. In analyses of environmental samples for nuclear safeguards, isotope ratio measurements of both the uranium and plutonium contained in the particles from MOX fuels need to be performed [9,10].

Highly sensitive analytical techniques are needed to measure the isotope ratios accurately due to the low amounts of plutonium and uranium in environmental samples and sub-micrometer plutonium-containing particles. Isotopes in plutonium have routinely been measured by mass spectrometric methods such as ICP-MS, TIMS, AMS, and radiometric methods such as alpha spectrometry. Alpha spectrometry is commonly used for determining actinides in environmental samples owing to the simplicity of these methods and to their low cost and compatibility with radio-tracers. However, alpha spectrometry cannot distinguish between ^{239}Pu and ^{240}Pu owing to their very similar alpha energies (5.16 MeV and 5.17 MeV for ^{239}Pu and ^{240}Pu, respectively); thus, the sum of ^{239}Pu and ^{240}Pu was obtained in that the ratio of $^{240}Pu/^{239}Pu$ cannot be measured directly by alpha spectrometry. In contrast, mass spectrometric methods enable a highly precise and accurate analysis. AMS has very short analysis times, high sensitivity, and enables measurements of ^{241}Pu. It also offers the ability to discriminate ^{239}Pu from ^{240}Pu [11,12]. However, it is not yet possible to determine ^{238}Pu due to the interference of ^{238}U. Thus far, AMS combined with an alpha-spectrometry system has been required to measure the ratio of $^{238}Pu/^{239}Pu$. On the other hand, ICP-MS is fast, highly sensitive, and capable of providing individual concentrations of ^{239}Pu and ^{240}Pu; however, the determination of ^{238}Pu is hindered by the presence of even minute amounts of ^{238}U. Therefore, the chemical separation of solution samples is conducted to provide accurate isotope ratios. However, for particulate samples, dissolution, purification, and chemical separation are difficult, and all increase the background.

The continuous heating technique was developed to determine the isotope ratios in ultra-trace amounts of uranium and plutonium samples as a new method of thermal ionization mass spectrometry [13]. In particular, the ratios of $^{238}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ in the mixed sample of uranium and plutonium can be measured accurately even isobaric interference such as ^{238}U and ^{241}Am, based on different evaporation behavior of each isotope in this method [10,14]. In this study, an analytical performance of the thermal ionization mass spectrometry with a continuous heating technique was examined as a means of measuring the isotope ratios using a plutonium solution sample at the fg level.

Table 1
Integrated and idle times of TIMS for measurement of plutonium.

Step	Mass (m/z)	Integrated time (s)	Idle time (s)
1	238	4	0.5
2	239	2	0.5
3	240	2	0.5
4	241	4	0.5
5	242	4	0.5

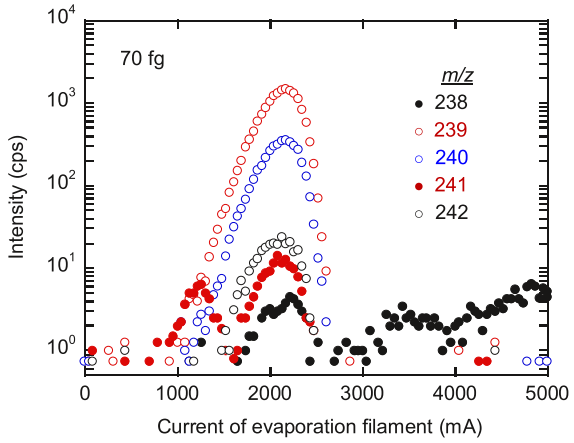

Fig. 1. Signal profiles of m/z 238, 239, 240, 241 and 242 in 70 fg of Pu (SRM 947) as measured by TIMS with a heating rate of 100 mA/min.

2. Experimental

2.1. Materials

The isotope standard reference material SRM 947 (plutonium sulfate tetrahydrate, National Bureau Standards, USA) was used in this study. Plutonium in the SRM 947 was purified from the decay

Table 2
Ratios of $^{238}Pu/^{239}Pu$, $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ measured by TIMS with a heating rate of 100 mA/min. The average intensities of ^{239}Pu are also given in this table. Isotope ratios and average intensities are the mean value of three measurements.

Sample amount (fg)	$^{238}Pu/^{239}Pu$	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$	Average intensity of ^{239}Pu (cps)
	Ratio ± 1SD	Ratio ± 1SD	Ratio ± 1SD	Ratio ± 1SD	
1000	$(2.89 \pm 0.02) \times 10^{-3}$	$(2.41 \pm 0.01) \times 10^{-1}$	$(9.05 \pm 0.42) \times 10^{-3}$	$(1.55 \pm 0.01) \times 10^{-2}$	74,048
500	$(2.81 \pm 0.03) \times 10^{-3}$	$(2.39 \pm 0.01) \times 10^{-1}$	$(8.42 \pm 0.31) \times 10^{-3}$	$(1.58 \pm 0.01) \times 10^{-2}$	9952
100	$(2.91 \pm 0.10) \times 10^{-3}$	$(2.42 \pm 0.01) \times 10^{-1}$	$(8.46 \pm 0.23) \times 10^{-3}$	$(1.52 \pm 0.06) \times 10^{-2}$	2104
70	$(2.57 \pm 0.68) \times 10^{-3}$	$(2.40 \pm 0.06) \times 10^{-1}$	$(8.59 \pm 1.27) \times 10^{-3}$	$(1.57 \pm 0.13) \times 10^{-2}$	1448
10		$(2.31 \pm 0.11) \times 10^{-1}$	$(9.11 \pm 2.88) \times 10^{-3}$	$(1.77 \pm 0.15) \times 10^{-2}$	151
5		$(2.45 \pm 0.05) \times 10^{-1}$	$(8.05 \pm 3.95) \times 10^{-3}$	$(1.45 \pm 0.30) \times 10^{-2}$	71
1		$(2.38 \pm 0.27) \times 10^{-1}$			17
0.5		$(2.59 \pm 0.30) \times 10^{-1}$			8.4
0.3		$(2.45 \pm 0.40) \times 10^{-1}$			8.0
0.1		$(2.60 \pm 0.15) \times 10^{-1}$			3.1
0.03					0.7
Certified value[a]	2.87×10^{-3}	2.41×10^{-1}	8.99×10^{-3}	1.56×10^{-2}	

The blank spaces show that the isotope ratios were not able to be measured.

[a] Corrected value considering decay of each isotope on measurement date (November 17, 2011).

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