International Journal of Mass Spectrometry 310 (2012) 52–56

Contents lists available at SciVerse ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

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

Yoko Saito-Kokubu*, Daisuke Suzuki, Chi-Gyu Lee, Jun Inagawa, Masaaki Magara, Takaumi Kimura

Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

ARTICLE INFO

Article history:
Received 6 September 2011
Received in revised form
16 November 2011
Accepted 16 November 2011
Available online 25 November 2011

Keywords:
Thermal ionization mass spectrometry
Continuous heating method
Uranium
Plutonium
Isotope ratios

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}Pu/^{239}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}Pu/^{239}Pu and ^{235}U/^{238}U were measured simultaneously without chemical separation of samples. The relative standard deviation of the isotope ratios of ^{240}Pu/^{239}Pu and ^{235}U/^{238}U in the sample containing each 1 pg of plutonium and uranium were better than 2% and 4%, respectively. Moreover, ^{238}Pu/^{239}Pu ratios were obtained by using a correction in which the ^{238}U intensity was estimated from the ^{235}U intensity and the ^{235}U/^{238}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.

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

---

* Corresponding author at: 959-31 Jorinji, Izumi-cho, Toki-shi, Gifu 509-5102, Japan. Tel.: +81 572 53 0211; fax: +81 572 53 0180.
E-mail address: kokubu.yoko@jaea.go.jp (Y. Saito-Kokubu).

1387-3806/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2011.11.008

Table 1
Optimization for heating rate sequences of the EF current for measurement of plutonium sample and Pu/U mixture sample.

U[13]		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 peck-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.

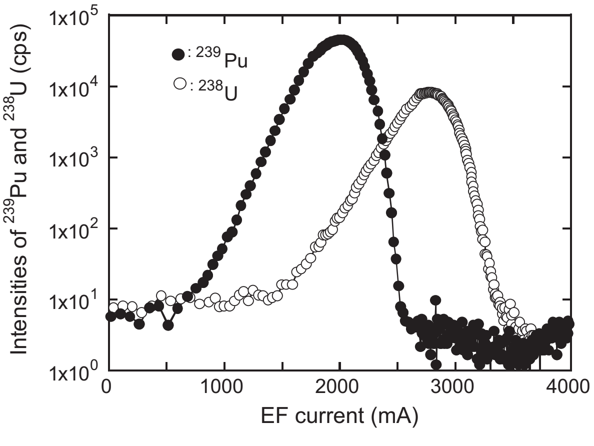

Fig. 1. Intensities of ^{239}Pu and ^{238}U as a function of the EF current. Heating rate was used for the measurement of uranium (see Table 1). Quantities of 4 pg each of plutonium or uranium were loaded on the filament.