Quantification and isotope ratio determination of uranium in particles of environmental samples using isotope dilution thermal ionization mass spectrometry

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1. Introduction

Highly accurate and precise quantitative and qualitative analysis of nuclear materials in environmental samples plays essential roles in monitoring undeclared nuclear activities of corresponding facilities [1]. The analyses are performed by largely two types of procedures; bulk analysis and particle analysis. The former focuses on the quantification of uranium (U) and plutonium (Pu) contained in a whole sample [2], while the latter enables us to acquire the isotopic ratios, which serve as the crucial basis to trace the nuclear histories of a facility.

However, the quantity of nuclear materials in a single-particle has not been acquired from the particle analysis, but has been estimated by the size of the particles. The adoption of the estimation is limited when the shape of a particle is not well defined, or a particle contains large amount of impurities.

This report is to describe the method developed to determine the quantity and the isotopic ratios of uranium in a micro-particle simultaneously. Complete dissolution of particle-spike mixture by repeated addition of nitric acid on a rhenium filament was performed to ensure the homogeneity of the mixture. Thermal ionization mass spectrometry (TIMS) was utilized to measure the U isotope ratios of the mixture with high accuracy. The isotopic ratios of the uranium in the particle sample were determined by mathematical deconvolution of U isotopic ratios of the mixture. Verification using particles of a certified reference material showed that the newly developed method can be used to quantify and to determine the isotopic ratios of U in a particle simultaneously.

2. Methods and Results

Particles of U030 with approximately 2 μm sizes were used to verify the method. All of the analytical processes were performed in a clean laboratory, which is maintained for ISO 5 class of cleanness.

2.1 Sample Preparation

The aluminum disk containing U030 particles was introduced into a scanning electron microscope (SEM, JSM-6610LV, JEOL) equipped with a three-axis micromanipulation system (MM3M-EM, Kleindiek Nanotechnik) to pick up particles and to load on zone-refined rhenium filaments as shown in Fig. 1. The uranium content was confirmed by an energy dispersive spectrometer (EDS, X-Max, Oxford) equipped in the SEM.

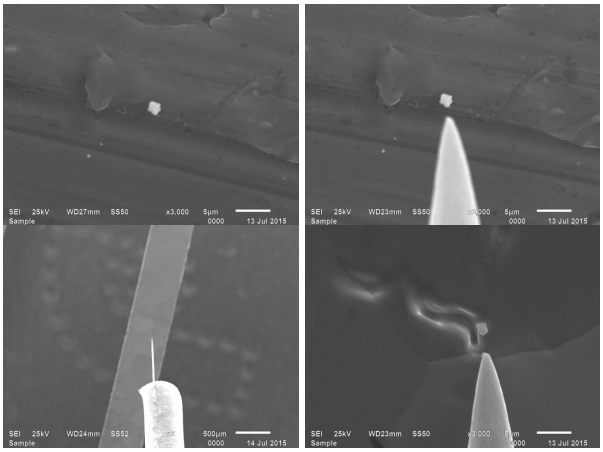

Fig. 1. Micro-manipulation of a U030 particle

2.2 Spiking and Dissolution

Known amounts of IRMM040a were added into each particle-loaded filament. Special care was paid for the droplets of solution to cover each particle. Once the solutions were dried, 2 μL of nitric acid (2M) were added into the spots of the mixtures of the particles and the spike followed by being dried with slight heat generated by 0.6 A of electrical current. Repeat of the dissolution process with nitric acid for five times resulted in complete dissolution of the particles and the spike, which ensure the physical and chemical homogeneity of the mixtures. The spiking and dissolution process was described in Fig. 2.

2.3 Isotopic Measurement by TIMS

TIMS was utilized for isotopic measurement using the continuous heating method [3, 4]. Mass bias correction of uranium isotopic ratios was carried out based on the isotopic measurements of U200. Simultaneous measurements were applied using three secondary electron multipliers and two compact

discrete dynode detectors to ensure high sensitivity of detection.

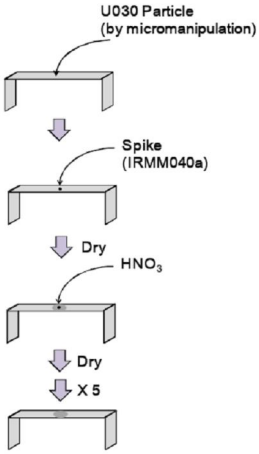

Fig. 2. Flow diagram of the chemical treatment for bulk analysis of swipe samples

The amounts of uranium in the samples were determined by isotope dilution mass spectrometry (IDMS) using the following equation [5];

$$c(^{238}U,x)=\frac{R_y-R_b}{R_b-R_x}\cdot\frac{1}{R_y}\cdot\frac{m_y}{m_x}\cdot c(^{233}U,y) \quad (1)$$

where,
R_b : amount ratio n(^{233}U)/n(^{238}U) in the blend
R_x : amount ratio n(^{233}U)/n(^{238}U) in the sample
R_y : amount ratio n(^{233}U)/n(^{238}U) in the spike
m_x : mass of the sample
m_y : mass of the spike
$c(^{238}U,x)$: amount content of ^{238}U kg^{-1} in the sample
$c(^{233}U,y)$: amount content of ^{233}U kg^{-1} in the spike

U isotope ratios of each U030 particles were calculated by the U isotope ratios of the mixtures and the certified value of the spike material (IRMM040a). To avoid additional isotopic measurement of the particles, which is not possible as the particles were completely consumed, a reasonable assumption that the particles samples do not contain any ^{234}U content was made.

2.4 Analytical Results

The analytical results were summarized in Table 1. The uncertainty was estimated in compliance with GUM (Guide to the expression of Uncertainty in Measurement).

Although n(^{234}U)/n(^{238}U) deviated from the corresponding certified value due to the large content of ^{234}U in the spike, good agreements of n(^{235}U)/n(^{238}U) and n(^{236}U)/n(^{238}U) with certified values showed the validity of the newly developed method for determination of quantity and the isotope ratios of a single uranium particle simultaneously by ID-TIMS.

Table 1: Analytical Results of U amout and isotopic ratios of U030 determined by ID-TIMS

	n(^{235}U)/n(^{238}U) ($\times 10^{-2}$)	n(^{236}U)/n(^{238}U) ($\times 10^{-4}$)	U amount (pg)
Cert.	3.143[±0.003]	2.10[±0.01]	-
Meas.#1	3.12[±0.41]	2.39[±0.84]	25.4[±1.8]
Meas.#2	3.14[±0.32]	2.6[±1.1]	21.0[±1.1]

3. Conclusions

The development of a method for simultaneous determination of the quantity and the isotope ratios of uranium contained in particles by isotope dilution thermal ionization mass spectrometry (ID-TIMS) was described. For homogeneity of the mixture of particles and spike, repeated dissolution using nitric acid for five times was performed. The consistent agreement of n(^{235}U)/n(^{238}U) and n(^{236}U)/n(^{238}U) with certified values and the reasonable estimation of uranium amounts in the particles verified the applicability of the newly developed method using ID-TIMS to quantification and isotopic ratio determination of uranium in micro-particles.

REFERENCES

[1] D. L. Donohue, Strengthening IAEA Safeguards through Environmental Sampling and Analysis, Journal of Alloys and Compounds, Vol.271-273, p.11, 1998.
[2] J.-H Park, S. Lee, Y.-G. Ha, S. A. Lee, K. Jeong, M. Lee, K. Song, Bulk analysis of a simulated environmental sample in natural abundance performed in KAERI for nuclear safeguards, J. Randioanal. Nucl. Chem. Vol. 303, P.1297, 2015.
[3] J.-H. Park, K. Jeong, K. Song, Isotopic Analysis of Uranium and Plutonium at Ultra Trace Levels using Thermal Ionization Mass Spectrometry with Simultaneous Measurements, Asian Journal of Chemistry, Vol. 25, p. 7061, 2013.
[4] D. Suzuki, Y. Saito-Kokubu, S. Sakurai, C.-G. Lee, M. Magara, K. Iguchi, T. Kimura, A New Method for Isotope Ratio Measurement of Uranium in Trace Amount by Thermal Ionization Mass Spectrometry: The Continuous Heating Method, International Journal of Mass Spectrometry, Vol. 294, p. 23, 2010.
[5] K.G.Heumann, International Journal of Mass Spectrometry and Ion Physics, Vol. 45, p. 87, 1982., Vol. 294, p. 23, 2010.