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Technical note

Isotopic analysis of single uranium and plutonium particles by chemical treatment and mass spectrometry

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ABSTRACT

The isotopic composition of single uranium and plutonium particles was measured with an inductively coupled plasma mass spectrometer (ICP-MS) and a thermal ionization mass spectrometer (TIMS). Particles deposited on a carbon planchet were first analyzed with an energy dispersive X-ray spectrometer (EDX) attached to a scanning electron microscope (SEM) and then transferred on to a silicon wafer using a manipulator. The particle on the silicon wafer was dissolved with nitric acid and the isotopic ratios of U and Pu were measured with ICP-MS and TIMS. The results obtained by both methods for particles of certified reference materials showed good agreement with the certified values within the expected uncertainty. The measurement uncertainties obtained in this study were similar for both mass spectrometric methods. This study was performed to establish the method of particle analysis with SEM, EDX, the particle manipulation and chemical preparation technique, and the measurement of isotopic ratios of U and Pu in a single particle by mass spectrometry.

1. Introduction

The analytical methods applied to environmental samples for nuclear safeguards can be roughly classified into two types: bulk analysis and particle analysis. The results of bulk analysis provide the average isotopic composition of the elements U and Pu in the whole sample. On the other hand, particle analysis involves the measurement of individual particles in samples thus giving more detailed information, although it is usually not possible to identify and analyze all of the particles in a sample [1,2]. A common method used for analysis of U particles is secondary ion mass spectrometry (SIMS). This method can be rapid for particle analysis but has the disadvantage that minor isotopes such as ^{234}U and ^{236}U are not measured with high precision enough, although recent applications of ultra-high sensitivity SIMS [3–6] improved such problems dramatically. SIMS also has difficulty measuring Pu isotopes because of isobaric interference from ^{238}UH on ^{239}Pu and from ^{241}Am on ^{241}Pu. A more precise method for particle analysis involving a combination of the fission track and thermal ionization mass spectrometry (FT-TIMS), can be mentioned [7–9]. This method provides precise U and Pu isotope ratio measurements for particles at lower detection limits than by SIMS. However FT-TIMS require a reactor facility, a high level of experience for the analyst and is a time consuming method.

A systematic analysis of radioactive particles coming from a nuclear weapon related accident in Palomares, Spain (1996) was performed using SEM–X-ray analysis, gamma-ray-, alpha-, liquid scintillation spectrometry, SIMS and inductively coupled plasma mass spectrometry (ICP-MS). In this study, the quantitative and isotopic analysis of U, Pu and Am in soil samples were performed [10]. The results of isotopic measurements obtained with ICP-MS and SIMS showed, however, significant differences, and the authors proposed that this was an analytical artifact or could reflect possible inhomogeneities of isotopic composition. They concluded that their study highlighted the importance of using different complementary methods in particle analysis.

Plutonium-containing particles collected from Marshall Islands soil in the northern Marshall Islands were characterized and studied using various non-destructive analytical and microanalytical methods [11]. The results of Pu isotopic ratio measurements, ^{137}Cs, ^{241}Am/^{239}Pu and the other matrix elements were used for the conclusions about the source of the particles. Detailed study of individual U particles from reference materials (NBL CRM U050 and U350) has been reported [12]. The measurement of U isotopic ratios from single particles was performed with ICP-MS showing that the results with the dimension between 0.5 and 3.9 μm were consistent with the certified value. The analysis of Pu was not performed in this work.

In the present study, a combination of particle analysis and chemical analysis was demonstrated for particles of the reference materials NBS U-500 for U and NBS 947 for Pu. It involved the picking-up of particles using a manipulator attached to a SEM, followed by U and Pu measurement with ICP-MS and TIMS after chemical

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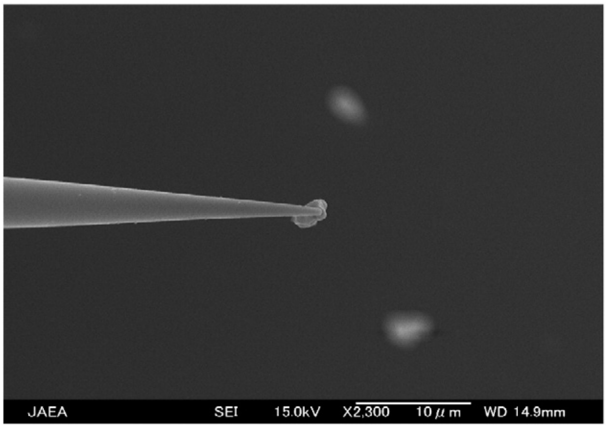

Fig. 1. Picking up a uranium particle with a quartz needle coated with evaporated gold and carbon.

decomposition of the particles. The results obtained by both mass spectrometric methods were compared. Although particle analysis is commonly used for safeguards measurements, the combination of particle and chemical analysis for U and Pu in a single particle is not yet a routine method. The chief advantages of this technique, “particle-chemical analysis”, is that the isotopic ratios of the elements can be analyzed separately from a single specimen, the quantitative analysis is possible using isotope dilution mass spectrometry, and the separation to remove isobars, e.g., ^{238}U on ^{238}Pu and ^{241}Am on ^{241}Pu . As for the first step of the particle-chemical analysis, this work was performed to assist the development of a particle manipulation technique and as a preliminary study for further chemical separation of U, Pu and Am in a single particle to obtain more accurate and detailed information. The results of further studies on chemical analysis of particles for age determination of Pu in single particles will be published elsewhere [13].

2. Materials and methods

2.1. Reference materials of U and Pu and sample preparation for particle analysis

The reference materials of U and Pu used in this study were NBS U-500 (uranium oxide) [14] and NBS 947 (plutonium sulfate tetrahydrate) [15].

Particles of these materials were transferred onto a polished graphite planchet by the vacuum impactor method [16] prior to SEM analysis. The particles on the planchet were fixed with a n-eicosan (Wako Chemicals, Co. Ltd.) coating followed by heating the planchet to evaporate the organic coating. The chemical treatment was performed in an ISO Class 5 (US Federal Standard: Class-100) area both in the JAEA CLEAR Laboratory, Tokai Japan and the IAEA Clean Laboratory, Seibersdorf Austria. High purity nitric acid (Tama Chemicals Co. Ltd. and Seastar Chemicals Inc.) and 18.2 MΩ (Milli-Q Element) de-ionized water were used for the chemical treatments.

A standard solution of ^{233}U (IRMM-CRM057) [17] was used for the quantitative analysis of U in the blank materials.

2.2. Scanning electron microscope and manipulator

The particles on the graphite planchet were observed by a SEM (JEOL JSM-6700 F) in the CLEAR Laboratory. The particle pick-up was performed using a manipulator system in the sample chamber of the SEM. The planchet with particles was held in the SEM stage along with nine silicon wafers as shown in Fig. 1 and each particle was transferred from the planchet onto a separate silicon wafer [18]. One or two silicon wafers were used for the blank.

The primary electron accelerating voltage of the scan was 7 keV for the study of particle morphology with SEM and 20 kV for energy dispersive X-ray analysis (EDX). The acquisition time for EDX analysis was 300 s.

2.3. ICP-MS measurement

The ICP-MS instrument used in this study was a ThermoElectron Element 1 with double focusing magnetic sector field. The condition of the measurements was: plasma RF power: 1148 W, sample gas flow: 0.98–1.05 l/min, sample uptake rate: 0.17–0.22 l/min, sampling time per isotope: 50 ms, scans per replicate: 400, number of replicates: 5 and resolution ($M/\Delta M$): 300 [19]. A PFA micro-flow nebulizer (self-aspirating mode) was used in combination with a Scott-type double pass spray chamber cooled to 4 °C. The sensitivity for ^{238}U was 2.5 Mcps/(ng/ml). Procedural blank obtained by performing the same chemical procedure without particles was also measured every time for subtracting the count rates. The method for dead time correction was described in detail in a previous paper [20].

The mass dependent bias was estimated by measuring a 160 ppt solution of NBS U-500 standard ($^{235}\mathrm{U}/^{238}\mathrm{U}=0.9997$) and the bias correction factor (BCF) was calculated from a set of 10 measurements using the following formula [21].

$$\mathrm{BCF}=\frac{\left(\frac{\mathrm{N238}\times R^{235/238}_{\mathrm{Re}\,f}}{\mathrm{N235}}-1\right)}{\Delta M^{235/238}} \tag{1}$$

where N235 and N238 are the average count rates from a scan for ^{235}U and ^{238}U, $R^{5/8}_{\mathrm{Re}\,f}$ is the certified $^{235}\mathrm{U}/^{238}\mathrm{U}$ isotopic ratio and $\Delta M^{5/8}$ is the mass difference ($\Delta M^{235/238}=235-238=-3$ for $^{235}\mathrm{U}/^{238}\mathrm{U}$). The calculated BCF was equal to −0.002 amu^{-1} and was not statistically different from zero.

2.4. TIMS measurement

The isotopic ratios of U and Pu were measured with a ThermoElectron Triton instrument using ion counting detection with a secondary electron multiplier and peak jump measurement scheme. The final fraction of U and Pu was dried on a rhenium single-filament along with graphite powder. The temperature used for the measurements was 1680 °C for U and 1440 °C for Pu. Three to ten blocks (10 scans per block) of measurements were performed for each sample.

The mass dependent bias was corrected by measuring 1 ng of NBS U-500 standard ($^{235}\mathrm{U}/^{238}\mathrm{U}=0.9997$) and the bias correction factor

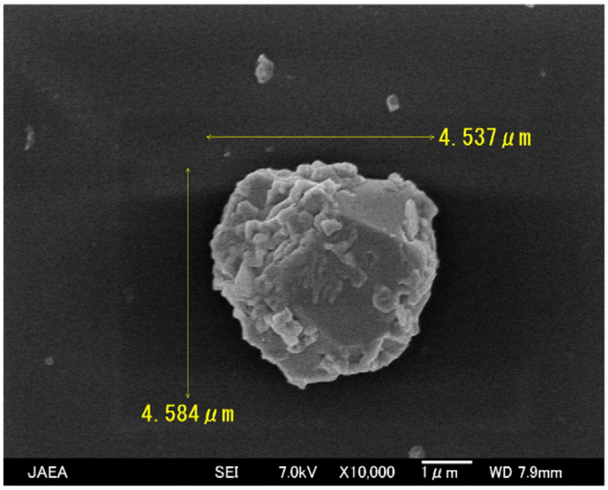

Fig. 2. SEM image of a uranium particle (NBS U500) on a silicon wafer.