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Secondary ion mass spectrometry combined with alpha track detection for isotope abundance ratio analysis of individual uranium-bearing particles

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ABSTRACT

Secondary ion mass spectrometry (SIMS) was used in combination with alpha track detection for the efficient analysis of uranium-bearing particles with higher ^{235}U abundances in environmental samples. A polycarbonate film containing particles was prepared and placed in contact with a CR-39 plastic detector. After exposure for 28 days, the detector was etched in a NaOH solution and each uranium-bearing particle was identified through observation of the alpha tracks recorded in the detector. A portion of the film containing each uranium-bearing particle was cut out and put onto a glassy carbon planchet. The films on the planchet were decomposed through plasma ashing for subsequent uranium abundance ratio analysis with SIMS. The alpha track-SIMS analysis of 10 uranium-bearing particles in a sample taken from a nuclear facility enabled $n(^{235}U)/n(^{238}U)$ abundance ratios in the range 0.0072–0.25 to be detected, which were significantly higher than those obtained by SIMS without alpha track detection. The duration of the whole analytical process for analysis of 10 particles was about 32 days. The detection efficiency was calculated to be 27.1 ± 6.5%, based on the analysis of the particles in uranium reference materials. The detection limits, defined as the diameter of the particle which produces alpha tracks more than one for a 28-days exposure, were estimated to be 0.8, 0.9, 1.1, 2.1 and 3.0 μm for the particles having the same uranium abundance ratios with NBL CRM U850, U500, U350, U050 and U010 reference materials, respectively. The use of alpha track detection for subsequent SIMS analysis is an inexpensive and an efficient way to measure uranium-bearing particles with higher ^{235}U abundances.

1. Introduction

Since the discovery by Young [1] and Silk et al. [2] in the late 1950s of nuclear tracks recorded in solids, solid-state nuclear track detectors (SSNTDs) have been studied and used in various research fields. In the environmental sciences, for instance, SSNTDs have been used to detect radionuclides in contaminated soil and aerosol samples [3,4], and to determine concentration levels of radon in the environment [5]. Recently, this technique has been applied successfully to the analysis of individual uranium-bearing particles in environmental samples for nuclear safeguards [6–10]. Here, environmental samples are taken from nuclear facilities by inspectors of the International Atomic Energy Agency, and the isotope abundance ratios of individual uranium-bearing particles are measured to detect undeclared nuclear materials and activities. For the identification of uranium-bearing particles, the samples placed in contact with fission track detectors such as Lexan and Makrofol are irradiated with thermal neutrons in a nuclear reactor. Uranium-bearing particles are then identified by observing the fission tracks recorded in the detectors, and are measured by using thermal ionization mass spectrometry (TIMS) to reveal the uranium isotope abundance ratios. The number of fission tracks depends on the amount of ^{235}U atoms in the particle. Therefore, uranium-bearing particles with high ^{235}U abundances can be selectively identified, prior to the isotope abundance ratio analysis. This fact is significantly important for nuclear safeguards. Since fission tracks are induced by the irradiation of uranium with thermal neutrons, a neutron source such as a nuclear reactor is necessary, which limits the availability of this technique.

Secondary ion mass spectrometry (SIMS) is also a powerful tool to measure isotope abundance ratios of uranium-bearing particles [11,12]. The recent development of an automated particle measurement (APM) software has allowed us to perform rapid screening measurement over a sample [13,14]. Here, the exact locations and rough $^{235}U/^{238}U$ abundance ratios of individual particles can be determined by obtaining $^{235}U^+$ and $^{238}U^+$ secondary ion images. The detection capability of uranium-bearing particles with high ^{235}U abundances has been significantly improved, owing to the development of this software. However, this software can be used only for CAMECA IMS-series SIMS instruments.

In a previous paper [15], we combined a fission track technique with SIMS, and demonstrated the effectiveness of this approach

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for nuclear safeguards. The number of fission tracks being proportional to the number of fissionable ^{235}U atoms in each particle, uranium-bearing particles with the highest ^{235}U abundances can be detected selectively through observation of the fission tracks. This is particularly advantageous in the identification of undeclared nuclear materials and activities related to nuclear weapon programs. As mentioned above, fission tracks are induced by the irradiation of uranium with thermal neutrons. Therefore, a neutron source such as a nuclear reactor is necessary. In this work, we performed alpha track detection to identify uranium-bearing particles for subsequent isotope abundance ratio analysis with SIMS. Since alpha track detection is based on the decays of radionuclides through alpha emission, no neutron sources are necessary. In addition, the detectors are inexpensive, allowing us to perform the analysis more easily. Although Vlasova et al. [16] used SIMS for the analysis of a zircon particle containing natural uranium after alpha track detection, only $^{235}U^+$ and $^{238}U^+$ secondary ion signals were detected. We applied this method to the analysis of certified reference materials and environmental samples taken from nuclear facilities to confirm its effectiveness for nuclear safeguards.

2. Experimental procedure

2.1. Samples

Uranium-bearing particles in certified reference materials (CRM U050, U350 and U500, New Brunswick Laboratory (NBL), USA) were used for alpha track detection. The certified ^{235}U abundances of the U050, U350 and U500 materials were 5.010, 35.190 and 49.696%, respectively. In addition, three environmental samples taken from nuclear facilities by wiping particles with pieces of high-purity cotton cloth ($10 \times 10\ cm^2$, TX304, ITW Texwipe Co. Ltd., USA) were used for the identification and analysis of uranium-bearing particles. The NBL CRM U350 material was used for mass bias correction in mass spectrometry. For alpha track detection, CR-39 detectors (Baryotrak-P, Nagase-Landauer Co. Ltd., Japan) based on polyallyldiglycol carbonate ($C_{12}H_{18}O_7$) were used.

2.2. Sample preparation

Uranium-bearing particles with diameters of approximately 1, 3 and 5 μm from each standard reference material (U050, U350 or U500) were transferred onto Si wafers ($5 \times 5\ mm^2$, Semitec. Co. Ltd., Japan) by using a micro-manipulator under scanning electron microscope observation. The particles were then covered with a polycarbonate solution made through the dissolution of polycarbonate membrane filters (diameter: 25 mm; pore size: 0.2 μm; Toyo Roshi Kaisha Ltd., Japan) in a mixture of 1,2-dichloroethane and dichloromethane. These samples were placed in contact with CR-39 detectors and exposed for 7, 14, 21 and 28 days. After exposure the detectors were removed and etched for 3 h in a 7 M NaOH solution at 70 °C. A digital microscope (VHX-200, KEYENCE Co. Ltd., Japan) and a scanning electron microscope (JSM-7800F, JEOL Co. Ltd., Japan) were used for observation and counting of the alpha tracks.

Particles in the environmental samples taken from nuclear facilities were used for isotope abundance ratio analysis. These sample were recovered through filtration and collected on polycarbonate membrane filters by vacuum pumping [7]. The filter containing particles was placed in a 1-mL volumetric flask, and a mixture of 1,2-dichloroethane and dichloromethane was added. The mixture was then stirred until the filter was dissolved completely. The polycarbonate solution containing particles was poured onto a clean silica glass plate and dried to form a thin polycarbonate film containing particles. The films containing the particles in environmental samples were placed in contact with CR-39 detectors and exposed for 28 days. Here, four locations of the film and the detector were marked with a laser beam. After exposure the detectors were etched for 3 h in 7 M NaOH solution at 70 °C. The four marks of the film and the detector were carefully superimposed and uranium-bearing particles were then identified through observation of the alpha tracks with the microscope. A portion of the film containing each uranium-bearing particle (with dimensions of approximately $150 \times 150\ \mu m^2$) was cut out with a Leica AS LMD laser-microdissection system (Leica Microsystems Ltd., Germany) and transferred onto a glassy carbon planchet (diameter: 25 mm; Hitachi Chemical Co. Ltd., Japan). Prior to SIMS analysis, the films on the planchet were ashed at a power of 300 W for 30 min with a plasma asher (PR-31, Yamato Scientific Co. Ltd., Japan).

2.3. Instruments

A secondary ion mass spectrometer (IMS-6 f, Cameca Co. Ltd., France) was used for isotope abundance ratio analysis. The pressure of the main chamber was less than 9×10^{-8} Pa. Each particle was irradiated with an O_2^+ beam of 15 keV. The current of the primary ion beam was between 6 and 18 nA. The mass to charge ratios of $^{234}U^+$, $^{235}U^+$, $^{236}U^+$, $^{238}U^+$ and $^{238}U^1H^+$ were counted sequentially in automatic peak jumping mode with acquisition times of 4, 2, 4, 2 and 4 s, respectively. Secondary ions were detected using an electron multiplier with a dead time of 30 ns. Other parameters were described in a previous paper [15].

The secondary ion signals vary with time in SIMS measurement. The signal drift was corrected by aligning the time series of isotopes through a linear interpolation approach [17]. Mass bias corrections were conducted by measuring isotope abundance ratio of a certified uranium reference material (NBL CRM U350) and the mass bias correction factor was calculated by using the true ratio divided by the measured ratio. The average value was calculated to be 0.45% per atomic mass unit. The hydride formation of uranium was determined by measuring the $^{238}UH/^{238}U$ ratio for each particle [18].

Uncertainties were estimated according to the principles described in the Guide to the Expression of Uncertainty in Measurements (GUM) [19,20]. Here, the contributions arising from the certified values of the reference material, the measured isotope ratios after time correction, and mass bias and hydride corrections were taken into account.

3. Results and discussion

3.1. Detection of alpha tracks created by particles in certified reference materials

Fig. 1 displays scanning electron images of NBL CRM U500, U350 and U050 particles with diameters of approximately 3 μm and their alpha tracks after exposure for 28 days. By careful observation of various images taken for these tracks using the SEM and the optical microscope, the numbers of alpha tracks for U500, U350 and U050 particles were determined to be 46, 20 and 2, respectively. Fig. 2 shows the numbers of alpha tracks of particles with diameters of approximately 1, 3, and 5 μm plotted against exposure time (7, 14, 21 and 28 days), together with their linear fit lines. Here, no alpha tracks were observed for the U050 particle with a diameter of 0.9 μm, which suggests that such a small particle with a ^{235}U abundance of less than 5% is difficult to