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Application of automated particle screening for effective analysis of individual uranium particles by thermal ionization mass spectrometry

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The isotope ratio analysis of individual uranium particles in environmental samples taken at nuclear facilities is important to clarify their origins for nuclear safeguards. Secondary ion mass spectrometry (SIMS) is often used for this purpose. An automated particle measurement (APM) screening software was recently developed for SIMS instruments, which enables us to obtain scanning ion images of uranium isotopes over the sample in short duration. The positions and approximate isotope ratios of each uranium particle can be determined from the images. This makes SIMS more effective because a few uranium particles with irregular isotopic compositions among thousands of uranium particles with normal isotopic compositions can be screened prior to precise isotope ratio analysis. However, the formation of molecular and/or hydride ions often leads to spectral interferences and inaccurate results in SIMS. In the present study, APM screening was applied to select uranium particles prior to precise isotope ratio analysis by thermal ionization mass spectrometry (TIMS). As a result, it was demonstrated that the APM-TIMS method eliminated molecular ion interferences in the uranium mass region in the analysis of real inspection samples, while higher and unreasonable ^{234}U and ^{236}U atomic ratios for some particles were obtained by APM-SIMS.

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Introduction

The isotope ratio analysis of individual micron-sized particles has been extensively studied in the field of nuclear safeguards.^{1–3} For the implementation of nuclear safeguards, environmental swipe samples are taken at nuclear facilities by inspectors of the International Atomic Energy Agency (IAEA) and the isotope ratios of uranium particles are measured to detect undeclared nuclear activities and facilities. Approximately 20 individual particles for one swipe sample are usually measured by mass spectrometry.

Thermal ionization mass spectrometry (TIMS) is often utilized for this purpose in combination with a particle screening technique using fission tracks.^{4–8} When the sample contains uranium particles, thermal neutron irradiation results in fission tracks in a nuclear track detector. The positions of each uranium particle are identified by observing the fission tracks. Furthermore, highly ^{235}U enriched uranium particles can be selectively sampled for subsequent isotope ratio analysis by TIMS because the number of fission tracks depends on the number of ^{235}U atoms in each particle. The detection of highly ^{235}U enriched uranium particles is critical to detect undeclared nuclear activities for nuclear safeguards. One drawback in the fission track-TIMS technique is that it requires a nuclear reactor to perform thermal neutron

irradiation. The other is “particle mixing”, due to which an average isotope ratio is obtained when two or more uranium particles are measured at one measurement. In a previous study, we overcame this particle mixing problem by adding a micro-sampling process to the fission track-TIMS procedure.⁸

Secondary ion mass spectrometry (SIMS) is also used for the isotope ratio analysis of individual uranium particles.^{9–11} Since individual uranium particles are randomly analyzed in a conventional SIMS technique without screening capability, it is difficult to detect and analyze a few uranium particles with undeclared isotopic compositions among thousands of uranium particles with normal isotopic compositions. The automated particle measurement (APM) screening software developed by Hedberg and Peres *et al.*^{12,13} significantly improves the SIMS performance and enables the selective analysis of particles of interest.^{14,15} In APM screening, scanning ion images of isotopes such as ^{235}U and ^{238}U are measured over the sample using a rastered primary ion beam (e.g., 500 μm). As a result, the positions and approximate isotope ratios of each particle are identified in short duration. Precise isotope ratio analysis is then performed for individual particles by SIMS using the instrument's microprobe mode. A drawback in SIMS is that the formation of molecular and/or hydride ions produces spectral interferences in the uranium mass region. For example, $^{207}\text{Pb}^{27}\text{Al}^+$ and $^{208}\text{Pb}^{27}\text{Al}^+$ molecular ions produce peaks at m/z 234 and 235, respectively.¹⁶ The separation of $^{207}\text{Pb}^{27}\text{Al}^+$ and $^{234}\text{U}^+$ ion peaks requires a mass resolution ($M/\Delta M$) of approximately

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2800. Although the separation is possible by narrowing the entrance and exit slits in small geometry SIMS (SG-SIMS) instruments, the resulting reduction in the signal intensity makes it impossible to perform precise isotope ratio analysis of uranium minor isotopes (^{234}U and ^{236}U) in a small particle. When large geometry SIMS (LG-SIMS) instruments are used, most of the molecular ion interferences can be eliminated due to the inherently higher transmission of secondary ions and higher mass resolution. However, the hydride ion interference of $^{235}\text{U}^+\text{H}^+$ on $^{236}\text{U}^+$ is still present even if LG-SIMS instruments are used. From this perspective, TIMS has an advantage because the molecular and hydride ion interferences are almost negligible.

In the present study, APM screening was combined with isotope ratio analysis using TIMS and applied to the analysis of quality control and real inspection samples. The APM screening was utilized for the selection of uranium particles to be analyzed. The selected particles were sampled using a scanning electron microscope (SEM) and measured by TIMS to determine precise isotope ratios. The analytical performance of the APM-TIMS was compared with that of the APM-SIMS through the analysis of real inspection samples.

Experimental

Samples

A quality control sample and multiple real inspection samples taken at nuclear facilities were used in this study. The quality control sample contained natural (0.72%), low ^{235}U enriched (3.8%) and highly ^{235}U enriched (61%) uranium particles with an approximate number ratio of 170 : 18 : 1. The particles in these samples were recovered onto glassy carbon planchets with a diameter of 25 mm (Hitachi Chemical Co. Ltd.) by a vacuum impactor technique¹⁷ for APM-SIMS analysis. And then, particles were also recovered from the same samples onto other planchets for APM-TIMS analysis. Here, the surface of each planchet was coated with 5 μL of a 1 : 1 mixture of eicosane and

nonadecane in hexane. After the particle recovery, the planchet was heated at 150 $^{\circ}\text{C}$ for 90 seconds. The NBL CRM U350 reference material was used to determine the mass fractionation factors in the SIMS and TIMS measurements.

Particle screening and sample preparation

To select uranium particles to be analyzed, APM screening was performed using an SG-SIMS instrument (IMS-6F, CAMECA). A focused O_2^+ primary ion beam with a current of 80 nA was rastered over an area of $500 \times 500 \mu\text{m}^2$. The $^{235}\text{U}^+$ and $^{238}\text{U}^+$ ion images were obtained for 20×20 areas (*i.e.*, $10 \times 10 \text{ mm}^2$). The measurement times of $^{235}\text{U}^+$ and $^{238}\text{U}^+$ were each set to 10 s. Prior to the measurement, each area was pre-sputtered by a primary ion beam with a current of 500 nA for 3 s. The total acquisition time for one sample was approximately 240 min. After the measurement, the center of each of the areas (X, Y) = (01, 01), (01, 20), (20, 01), and (20, 20) was marked with a primary ion beam with a current of 80 nA for 5 min. These marks were used to calculate the XY positions of each area in SEM instruments (JEOL, JSM-6700F and 7800F).

Fig. 1(a) shows $^{235}\text{U}^+$ and $^{238}\text{U}^+$ ion images with a raster size of $500 \mu\text{m}$ in an analytical area obtained by APM screening for an inspection sample. The presence of one uranium particle in the lower left position was indicated in these images. The CCD image of this area was obtained with a camera attached to the SIMS instrument as shown in Fig. 1(b). The sample was removed from the SIMS instrument and introduced into the SEM instrument. The positions of the analytical areas were calculated from the positions of the centers of areas (X, Y) = (01, 01), (01, 20), (20, 01) and (20, 20). By this calculation, the analytical positions were easily identified in SEM observation as shown in Fig. 1(c). The precision of the particle relocation was less than $10 \mu\text{m}$. Since the images in Fig. 1(a) and (c) are in mirror symmetry, it is expected that one uranium particle existed in the lower right position in Fig. 1(c). The backscattered electron image of the lower right position clearly indicated the

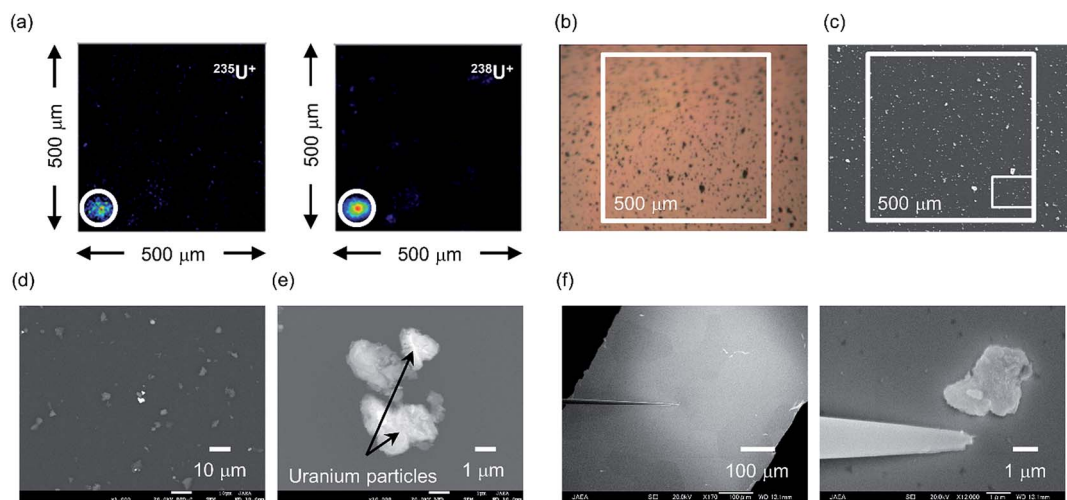


Fig. 1 (a) The $^{235}\text{U}^+$ and $^{238}\text{U}^+$ ion images in an analytical area obtained by APM screening for an inspection sample. (b) A CCD and (c) secondary electron image of the area. (d) A backscattered electron image of the area noted as a small square in (c), and (e) a secondary electron image of two uranium particles in the area. (f) Transfer of the large uranium particle in (e) onto a filament for isotope ratio analysis by TIMS.



presence of the particles containing heavy elements such as uranium as shown in Fig. 1(d). The secondary electron image with a high magnification of the particles and X-ray analysis (data are not shown) showed the presence of two uranium particles as shown in Fig. 1(e). One particle shown in Fig. 1(e) was then transferred onto a filament using a micromanipulator, as shown in Fig. 1(f), to avoid particle mixing. The micromanipulator has an ability to transfer particles with a diameter of around 0.5 μm .

Isotope ratio analysis

The isotope ratio analysis of individual uranium particles was performed by SIMS and TIMS. In SIMS, each uranium particle identified by APM screening was measured with a focused O_2^+ primary ion beam with a current between 0.5 and 5.0 nA and a raster size of 30 μm . The acquisition times of each cycle for $^{234}\text{U}^+$, $^{235}\text{U}^+$, $^{236}\text{U}^+$, $^{238}\text{U}^+$ and $^{238}\text{UH}^+$ were 4, 2, 4, 2 and 4 s, respectively. Here, the contributions of $^{235}\text{U}^{1\text{H}^+}$ ions to $^{236}\text{U}^+$ ions at m/z 236 were corrected using $^{238}\text{U}^{1\text{H}^+}/^{238}\text{U}^+$ intensity ratios in SIMS, although no hydride corrections were made in TIMS. Mass fractionation factors were determined for each isotope ratio by performing measurements on a sample of the NBL CRM U350 reference material.

A TIMS instrument (TRITON; Thermo Fisher Scientific, USA) and zone-refined rhenium double filaments were used for isotope ratio measurements. In the measurement, each uranium particle identified by APM screening was transferred onto the filament with a micromanipulator. Here, no treatment was carried out to fix the particle on the filament. The evaporation filament current was continuously increased during each measurement. The measurement procedure has been described in detail previously.¹⁸ The current was increased to 5000 mA at a rate of 100 mA min^{-1} . The acquisition times of each cycle for $^{234}\text{U}^+$, $^{235}\text{U}^+$, $^{236}\text{U}^+$, and $^{238}\text{U}^+$ were 4, 4, 4, and 2 s, respectively. Mass fractionation factors were determined for each isotope ratio by performing measurements on a sample of the CRM U350 reference material. The uncertainties in the results were estimated considering measurement variability, the certified values for the reference material, and mass fractionation corrections, following the principles described in the Guide to the Expression of Uncertainty in Measurements (GUM).¹⁹ The analytical performance of the TIMS measurement for individual uranium particles was confirmed by using an NBL CRM U050 reference material in a previous study.⁸

Results and discussion

Analysis of a quality control sample

A quality control sample with a mixture of natural, low ^{235}U enriched, and highly ^{235}U enriched uranium particles was measured by SIMS, APM-SIMS and APM-TIMS. A result of APM screening is shown in Fig. 2. The ^{238}U signal intensities were plotted against the $^{235}\text{U}/^{238}\text{U}$ isotope ratios. Main populations of the $^{235}\text{U}/^{238}\text{U}$ isotope ratios at 0.0072 and 0.038 were observed for 904 uranium particles found. The maximum $^{235}\text{U}/^{238}\text{U}$

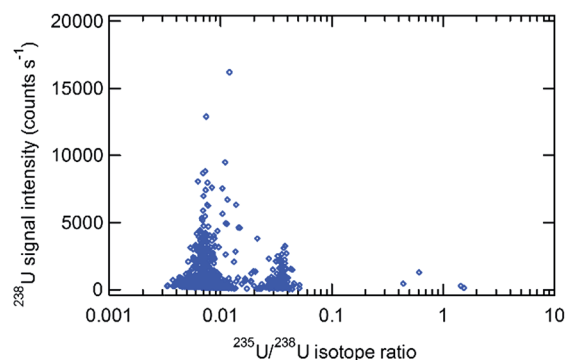


Fig. 2 An APM screening result measured for a quality control sample with a mixture of natural, low ^{235}U enriched, and highly ^{235}U enriched uranium particles. The ^{238}U signal intensities of 904 uranium particles were plotted against the $^{235}\text{U}/^{238}\text{U}$ isotope ratios. The data with ^{235}U signal intensities below 1 count per s were filtered.

isotope ratio was 1.54, which corresponded to approximately 61% ^{235}U enriched uranium.

Fig. 3(a) shows the ^{234}U , ^{235}U and ^{236}U atomic ratios measured by APM-SIMS for the quality control sample. In the analysis of 12 individual particles, 7 natural uranium, 2 low ^{235}U enriched uranium, and 2 highly ^{235}U enriched uranium particles were found. Furthermore, one particle with a ^{235}U atomic ratio of 1.1226(44) was observed, which suggested the mixing of some uranium particles with different atomic ratios. The ^{236}U atomic ratios for natural uranium were slightly different from the reference value, probably due to the insufficient sensitivity. In the measurement by APM-TIMS, 4 natural, 6 low ^{235}U enriched, and 2 highly ^{235}U enriched uranium particles were detected as shown in Fig. 3(b). No particle mixing effects were observed because of the microsampling of individual uranium particles prior to the isotope ratio analysis by TIMS. No highly ^{235}U enriched uranium particles were detected in SIMS without APM screening as shown in Fig. 3(c). These results indicated the excellent performance of APM screening for the detection of a smaller number of particles of interest.

Analysis of inspection samples

Three inspection samples (A, B, and C) from nuclear facilities were measured by APM-SIMS and APM-TIMS. The ^{234}U and ^{236}U atomic ratios were plotted against the ^{235}U atomic ratios in Fig. 4–6. The average value of the $^{238}\text{U}^{1\text{H}^+}/^{238}\text{U}^+$ intensity ratios for these samples was 1.6×10^{-3} in APM-SIMS. The contribution of $^{235}\text{U}^{1\text{H}^+}$ signals on signals at m/z 236 for each particle was estimated to be 55% as the average. An apparent correlation between the ^{234}U and ^{235}U atomic ratios in sample A was observed for both techniques (Fig. 4). The linear relationship between ^{234}U and ^{235}U is typical for samples taken at uranium enrichment facilities. However, one particle had relatively high ^{234}U (0.1196(16)) and ^{236}U (0.0818(59)) atomic ratios based on the APM-SIMS results. This was presumably due to the spectral interferences by molecular ions, which would be produced from the elements in neighbouring particles. Such unreasonable ratios were not observed in APM-TIMS, indicating that this



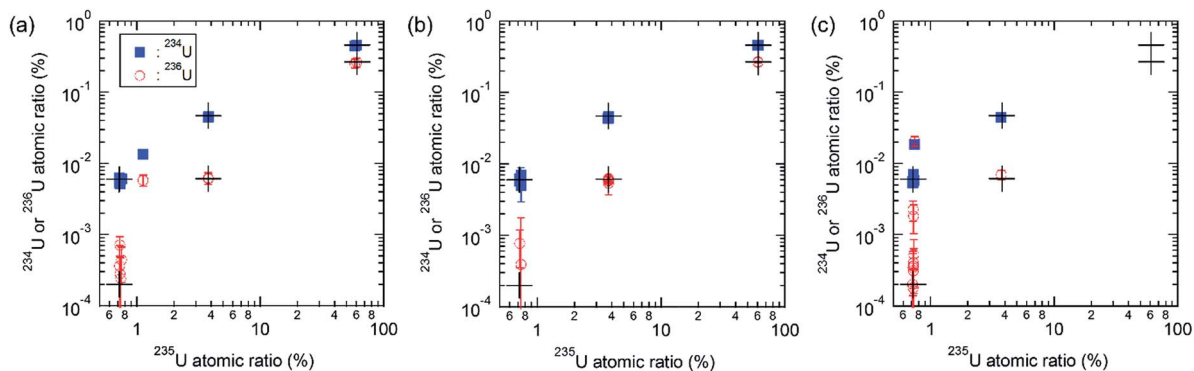


Fig. 3 Uranium atomic ratios of individual particles in a quality control sample with a mixture of natural, low ^{235}U enriched, and highly ^{235}U enriched uranium particles measured by (a) APM-SIMS, (b) APM-TIMS and (c) SIMS without APM screening. The intersections of the crossed lines represent the reference values of each particle. The error bars represent the expanded uncertainties with a coverage factor of $k = 2$.

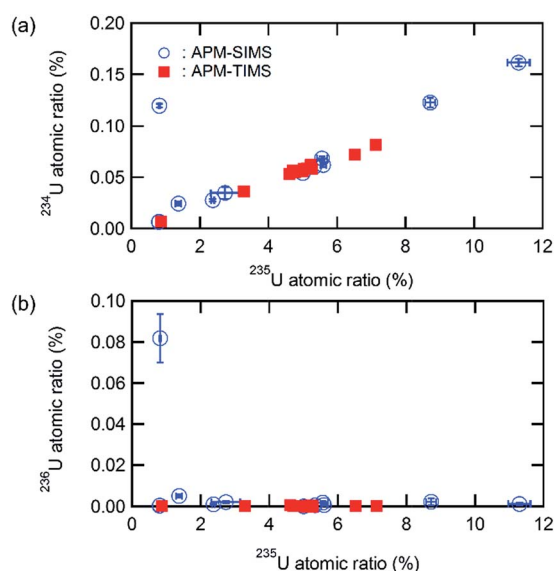


Fig. 4 The uranium atomic ratios of individual particles in the inspection sample A measured by APM-SIMS and APM-TIMS. The (a) ^{234}U and (b) ^{236}U atomic ratios are plotted against the ^{235}U atomic ratios. The error bars represent the expanded uncertainties with a coverage factor of $k = 2$.

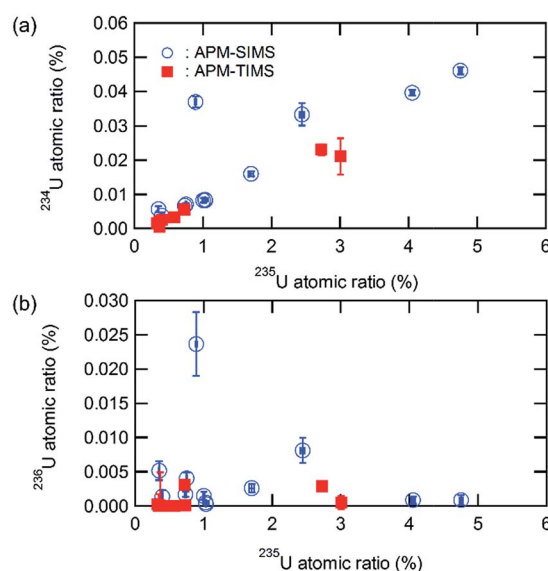


Fig. 5 The uranium atomic ratios of individual particles in the inspection sample B measured by APM-SIMS and APM-TIMS. The (a) ^{234}U and (b) ^{236}U atomic ratios are plotted against the ^{235}U atomic ratios. The error bars represent the expanded uncertainties with a coverage factor of $k = 2$.

technique can provide data without molecular ion interferences. The highest ^{235}U atomic ratio in APM-TIMS was lower than that in APM-SIMS. This would be due to the sample preparation, because the particles for APM-SIMS measurement were first recovered from the sample. The results obtained from sample B also showed an apparent correlation between the ^{234}U and ^{235}U abundance ratios for both techniques (Fig. 5). Similarly, some particles produced relatively high and unreasonable ^{234}U and ^{236}U atomic ratios in APM-SIMS. The ^{236}U atomic ratios obtained for sample C by APM-SIMS (Fig. 6) were relatively higher than the ratios obtained for sample A by APM-SIMS (Fig. 4). The SEM-EDX analysis confirmed that most of the uranium particles in sample C contained uranium, oxygen, and other impurities such as Na, Mg, Al, Si, S, Cl, Ca, Ti, Fe and Zn, whereas the uranium particles in samples A mainly comprised

only uranium and oxygen. Therefore, the impurities in each uranium particle were considered to have produced molecular ions that resulted in higher ^{236}U atomic ratios in APM-SIMS. Most of the measured particles produced reasonably low ^{236}U atomic ratios in APM-TIMS, while one particle produced a higher ^{236}U abundance ratio (0.0248(29) in Fig. 6(b)). The reason for the high ^{236}U atomic ratio was unclear. Since the uranium particle mainly comprised uranium and oxygen (Fig. 7), the result suggested that the high atomic ratio was due to molecular ion interferences by organic compounds or impurity elements in the TIMS filament.

In the present study, an SG-SIMS instrument was used for the isotope ratio analysis of individual uranium particles. Ranebo *et al.* compared the analytical performance between SG-SIMS and LG-SIMS instruments.¹⁶ They reported that the LG-



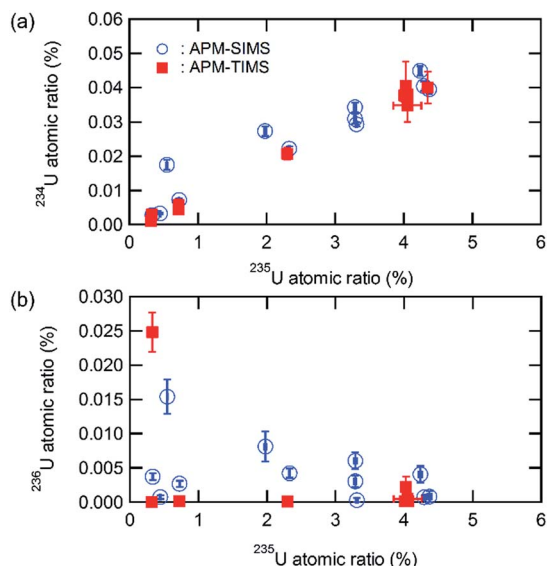


Fig. 6 The uranium atomic ratios of individual particles in the inspection sample C measured by APM-SIMS and APM-TIMS. The (a) ^{234}U and (b) ^{236}U atomic ratios are plotted against the ^{235}U atomic ratios. The error bars represent the expanded uncertainties with a coverage factor of $k = 2$.

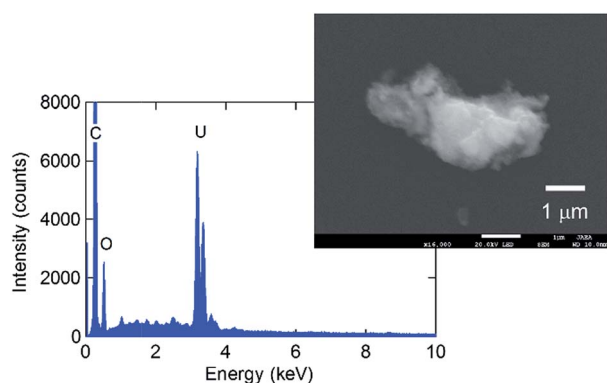


Fig. 7 A scanning electron microscopy image and an EDX spectrum of a uranium particle in the inspection sample C. This particle had a high ^{236}U atomic ratio (0.0248(29)) in APM-TIMS as shown in Fig. 6(b).

SIMS instrument produces excellent quality analytical data due to the resolution of almost all molecular ion interferences. Therefore, most of the molecular ion interferences observed in Fig. 4–6 could potentially be avoided if an LG-SIMS instrument was applied to the measurements. Ranebo *et al.* also compared the performance between LG-SIMS and TIMS instruments and reported that analyses using the LG-SIMS instrument had a limitation in the detection limit of ^{236}U at higher enrichments due to the necessity for a hydride correction.¹⁶ The lack of a hydride correction requirement in TIMS analysis is a clear advantage compared to analysis with LG-SIMS instruments.

Particle mixing was observed in the APM-SIMS analysis of the quality control sample in Fig. 3(a). The process of micro-sampling each uranium particle under SEM observation (as shown in Fig. 1(e) and (f)) helped to avoid particle mixing in

APM-TIMS. The distance between two uranium particles was only 3 μm in Fig. 1(e). It should be noted that it would be difficult to avoid particle mixing in this case even if a focused primary ion beam is used for the analysis using SG-SIMS or LG-SIMS instruments.

As mentioned above, reliable data from the analysis of individual uranium particles can be efficiently obtained by APM-TIMS. However, there was a disadvantage because additional work was required for the microsampling of individual particles under SEM observation. Typically, one day is the adequate time required to analyze the isotope ratios of 20 individual uranium particles by SIMS in the microprobe mode after APM screening. In APM-TIMS, one or two days are necessary to first identify the positions of each uranium particle and then to transfer the particles onto each filament after APM screening. Three additional days are then necessary to perform the isotope ratio analysis of 20 individual particles by TIMS. Therefore, the proposed method should be applied only to the analysis of samples containing a large number of uranium particles, which may have caused particle mixing. The analysis by APM-SIMS is effective for the samples containing a smaller number of uranium particles, which has a lower probability of particle mixing. The APM screening results can provide information on which method would be appropriate for each sample.

Conclusions

The screening by APM was performed prior to the isotope ratio analysis of individual uranium particles by TIMS. The results indicated that a few uranium particles of interest among many uranium particles were able to be selected prior to the analysis by TIMS. Furthermore, molecular ion interferences were almost completely avoided using a TIMS instrument instead of an SG-SIMS instrument. Therefore, the results showed that APM-TIMS was effective for the isotope ratio analysis of individual particles. Since the screening by APM required no thermal neutron irradiation in a nuclear reactor, particles that contained no fissile materials can be identified. Therefore, APM-TIMS as well as APM-SIMS can be applied to the analysis of various elements in individual particles in the environment, which will open up new research fields in environmental sciences.

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