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Complete Simultaneous Analysis of Uranium Isotopes in NUSIMEP-7 Microparticles Using SEM-TIMS

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Abstract : Scanning electron microscopy combined with thermal ionization mass spectrometry (SEM-TIMS) was used to determine the precise isotope ratios of ultra-trace levels of uranium contained in individual microparticles. An advanced multiple ion counter system consisting of three secondary ion multipliers and two compact discrete dynodes was used for complete simultaneous ion detection. For verification purposes, using TIMS with complete simultaneous measurement, isotopes were analyzed in 5 pg of uranium of a certified reference material. A microprobe in the SEM was used to transfer individual particles from a NUSIMEP-7 sample to TIMS filaments, which were then subjected to SEM-TIMS and complete simultaneous measurement. The excellent agreement in the resulting uranium isotope ratios with the certified NUSIMEP-7 values shows the validity of SEM-TIMS with complete simultaneous measurement for the analysis of uranium isotopes in individual particles. Further experimental study required for investigation of simultaneous measurement using the advanced multiple ion counter system is presented.

Keywords : Thermal Ionization Mass Spectrometry, Uranium, SEM-TIMS, Particle analysis, Simultaneous measurement

Introduction

The monitoring of nuclear facilities requires highly accurate and precise determination of the isotope ratios of uranium (U).[1-2] In the bulk analysis of environmental samples, the total amount and averaged isotope ratios of uranium provide rough clues to abnormal nuclear activity.[3-5] Particle analysis, which determines the isotope ratios of uranium contained in individual microparticles, can provide clear evidence of undeclared nuclear activity in a facility.[2,6-10]

Thermal ionization mass spectrometry (TIMS) is one of the most accurate and precise techniques for isotope analysis, with high instrument sensitivity and negligible mass discrimination, matrix effect, and spectral interference.[6-7] Consequently, it is widely used for analyzing environmental samples, especially for individual particle analysis. Fission track (FT)-TIMS, which combines TIMS for isotope measurement with a FT technique for particle identification and screening, is the most reliable analytical method for particle analysis. However, FT-TIMS is not possible when neutron irradiation using a nuclear reactor is unavailable.

Unlike FT-TIMS, SEM-TIMS uses a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) for particle identification and screening. Although the sensitivity of SEM-EDS for particle identification is somewhat lower than that of FT, it does not require a nuclear reactor and is always operable. Furthermore, the combination with TIMS uses the main advantages of TIMS described above.[10]

Accurate determination of the uranium isotope ratios requires not only measuring the major isotopes, *i.e.*, ^{238}U and ^{235}U, but also accurate measurement of the minor isotopes ^{234}U and ^{236}U. In environmental samples, the abundances of ^{234}U, ^{235}U, and ^{236}U are at ultra-trace levels. This implies that the detection sensitivity of Faraday cups is insufficient, and ion counters are required. Furthermore, a multi-ion counter (MIC) system with multiple ion counters offers complete simultaneous measurement,

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which enables measurement of all four isotopes of uranium, *i.e.*, ^{234}U, ^{235}U, ^{236}U, and ^{238}U, simultaneously. Recently, the TIMS MIC system was upgraded by adopting three full-size secondary electron multipliers (SEMs) and two compact discrete dynodes (CDDs). It offers greater stability, repeatability, and precision than the older method using multiple continuous-type ion counters. The Korea Atomic Energy Research Institute (KAERI) has an advanced MIC system. Although KAERI is a member of the Network of Analytical Laboratories (NWAL) for particle analysis using FT-TIMS, the applicability of SEM-TIMS with such an MIC system to particle analysis has not been verified.

In this paper, the uranium isotope ratios in individual microparticles were determined at KAERI using SEM-TIMS. The advanced MIC system was used to measure the four uranium isotopes simultaneously. Before applying the proposed method to the analysis of individual microparticles, a preliminary isotope analysis of uranium reference materials with ultra-trace levels was performed to validate the complete simultaneous measurement method using the advanced MIC system. The micro-particles from a sample for NUSIMEP-7 (the 7th Nuclear Signatures Interlaboratory Measurement Evaluation Programme) was used for isotopic analysis.[11] The analytical results were compared with certified values of the NUSIMEP-7 sample to verify the ability of KAERI to perform SEM-TIMS analysis with the advanced MIC system.

Experimental

A nitric acid solution of a certified reference material (U030, National Bureau of Standards, USA) was used as the uranium sample. Approximately 5 pg of uranium from the U030 solution was loaded on a background minimized zone-refined rhenium filament and then dried with a current of 0.6 A and fixed at 1.8 A for 30 s.

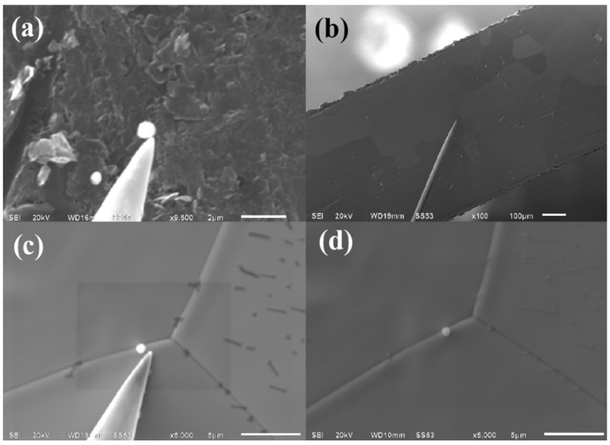

Figure 1. Micromanipulation of a particle of NUSIME-7. Particle pickup from the planchet (a), transfer (b) and loading (c) to a rhenium filament. SEM image after fixing (d).

The particle identification and manipulation procedure used to transfer individual particles to the TIMS filaments was performed as described elsewhere.[10] The NUSIMEP-7 sample is a planchet-type sample containing uranium microparticles. Fig. 1 shows the procedure used to transfer a particle from the NUSIMEP-7 sample to a filament using a microprobe on a three-axis micromanipulator system (MM3M-EM, Kleindiek Nanotechnik). Five particles approximately 1 µm in diameter were transferred and numbered P1 to P5.

The experimental setup for the isotope measurements using TIMS (TRITON Plus, Thermo Fisher Scientific, Bremen, Germany) with the continuous heating method has been described in detail elsewhere. [12-15] For complete simultaneous detection of uranium ions, three SEMs and one CDD were used, as described in Table 1. During each cycle, the ion signals were integrated for 4 s and 300 cycles were repeated for each measurement until the current of the evaporating filament reached 5,000 mA.

The detector yield was calculated by sequentially introducing approximately 300,000 cps of ^{187}Re^{+} signal into each ion counter. Approximately 50 pg of U200 (National Bureau of Standards, USA) was used for mass bias correction, which was negligible in this study.

The uncertainty, which was originated mostly from the random error of TIMS measurements, was estimated according to the Guide to the Expression of Uncertainty in Measurement in compliance with ISO/IEC Guide 98-3.[16-17] All of the analytical processes were performed in a clean facility controlled to ISO5 and ISO6 levels to avoid sample contamination.

Results and Discussion

Complete simultaneous measurement of isotopic ratios of uranium in a ultra trace level

The uranium isotope ratios were determined for four replicated U030 samples (S1, S2, S3, and S4), each containing approximately 5 pg of uranium, as summarized in Figure 2 and Table 2. The isotope ratios of n(^{234}U)/n(^{238}U) and n(^{235}U)/n(^{238}U) were consistent with the corresponding certified values, with respective accuracies of 1.5% and -0.16%. The relative standard deviation (RSD) of the three analytical results for n(^{234}U)/n(^{238}U) and n(^{235}U)/n(^{238}U) was 2.6% and 0.36%, respectively, which demonstrates that there was considerable precision.

For n(^{236}U)/n(^{238}U), a consistent positive bias was observed. The accuracy of the mean value and the

Table 1. Detector configuration of TIMS.

Isotope	^{234}U	^{235}U	^{236}U	^{238}U
Detector (Type)	IC3 (SEM)	IC2 (SEM)	IC1 (SEM)	IC5 (CDD)

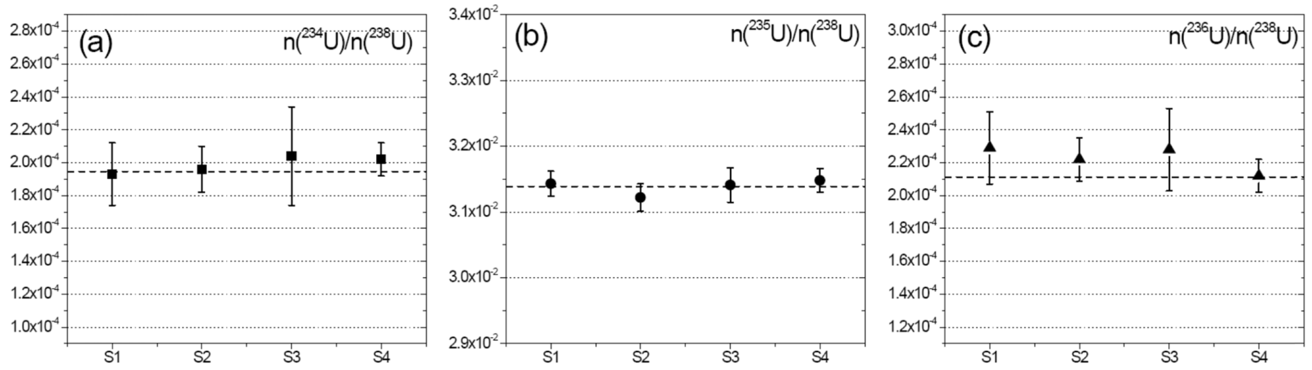

Figure 2. The isotopic ratios of uranium in U030 samples by SEM-TIMS with simultaneous measurement. (a) n(^{234}U)/n(^{238}U), (b) n(^{235}U)/n(^{238}U), and (c) n(^{236}U)/n(^{238}U).

Table 2. The isotopic ratios of uranium in U030 samples by SEM-TIMS with simultaneous measurement.

	Isotopic Ratio		
	n(^{234}U)/n(^{238}U) (× 10^{-4})	n(^{235}U)/n(^{238}U) (× 10^{-2})	n(^{236}U)/n(^{238}U) (× 10^{-4})
Certified Value	1.961[±0.010]	3.143 0[±0.003 0]	2.105[±0.010]
S1	1.93[±0.19]	3.148[±0.019]	2.29[±0.22]
S2	1.96[±0.14]	3.123[±0.016]	2.22[±0.13]
S3	2.04[±0.30]	3.141[±0.026]	2.28[±0.25]
S4	2.02[±0.10]	3.148[±0.018]	2.12[±0.10]
Mean Value	1.99	3.138	2.23
Accuracy (%)	1.5	-0.16	5.9
RSD (%)	2.6	0.36	3.5

*The numbers in parentheses indicate expanded uncertainty, $Ue = k \cdot u_c$, where u_c is the combined uncertainty and $k = 2$ with an approximately 95 % confidence level.

*Accuracy is defined as (Mean measured value - Certified value)/(Certified value)*100.

precision of the three measurements were 5.9% and 3.5%, respectively. This is thought to result from the peak tail contribution of ^{238}U to the intensity of ^{236}U, which is typical in TIMS measurements unless a retarding potential quadrupole (RPQ) is installed or a correction method is applied.[18]

The results demonstrated that complete simultaneous measurement using the advanced MIC system could be applied to the analysis of uranium in individual particles because the estimated amount of uranium contained in a ca. 1-μm particle was approximately 4 pg, as in the NUSIMEP-7 sample.

Application of SEM-TIMS with complete simultaneous measurement to isotopic analysis of uranium in individual particles

SEM-TIMS with complete simultaneous measurement using the advanced MIC system was applied to the analysis of uranium isotopes in individual NUSIMEP-7 microparticles; the results are summarized in Table 3. The NUSIMEP-7 sample contained two types (type 1 and 2) of particles with different isotope ratios of uranium, which are shown in Table 3 as ‘certified values 1 and 2’, respectively.

The analytical results for P1 and P2 were in excellent agreement with the certified value 1. The average accuracies of n(^{234}U)/n(^{238}U), n(^{235}U)/n(^{238}U), and n(^{236}U)/n(^{238}U) were 2.0%, 0.25%, and 20%, respectively. This satisfies the accuracy requirements for particle analysis for nuclear safeguards, which are lower than 20% for n(^{234}U)/n(^{238}U) and n(^{236}U)/n(^{238}U), and 2% for n(^{235}U)/n(^{238}U) when a particle is 1 μm in diameter.[19] A consistent positive bias resulting from the peak tail contribution of ^{238}U$^+$ on ^{236}U$^+$ was observed.

The isotope ratios of n(^{234}U)/n(^{238}U) and n(^{235}U)/n(^{238}U) for P3 and P4 agreed with the corresponding certified value 2. In comparison, considerable deviation in the measured values of n(^{236}U)/n(^{238}U) from the certified value were observed. The estimated ^{236}U$^+$ intensity should have been approximately 0.2 cps for the analytical results to coincide with the certified value because the ^{238}U$^+$ intensity in the analyses of P3 and P4 was approximately 30,000 cps. However, this is below our limit of detection because

Table 3. The isotopic ratios of uranium in individual NUSIMEP-7 particles determined by SEM-TIMS with simultaneous measurement.

	Isotopic Ratio		
	n(^{234}U)/n(^{238}U) (× 10^{-4})	n(^{235}U)/n(^{238}U) (× 10^{-2})	n(^{236}U)/n(^{238}U) (× 10^{-4})
Certified Value 1	3.451[±0.002]	3.415[±0.002]	1.032 7[±0.0.000 7]
Certified Value 2	0.743 6[±0.000 6]	0.907 2[±0.000 5]	0.080 21[±0.000 07]
P1	3.62[±0.13]	3.422[±0.016]	1.23[±0.10]
P2	3.42[±0.23]	3.425[±0.034]	1.25[±0.19]
P3	0.84[±0.23]	0.911[±0.013]	0.75[±0.19]
P4	0.80[±0.14]	0.904[±0.012]	0.20[±0.21]
P5	1.62[±0.12]	1.673[±0.013]	0.469[±0.071]

*The numbers in parentheses indicate expanded uncertainty, $Ue = k \cdot u_c$, where u_c is the combined uncertainty and $k = 2$ with an approximately 95% confidence level.

our preliminary study indicated that the background in the mass range of $^{236}U^+$ is at the level of 0.5 cps. Furthermore, the peak tail of $^{238}U^+$ must have contributed to the deviation. Further study on improving the sensitivity of TIMS reduce the limit of detection.

The observed isotope ratios of uranium of P5 were between the two certified values, implying that the two types of particles were mixed. The observed uranium isotope ratio, R_{obs}, is determined as follows:

$$R_{\text{obs}} = a \cdot R_1 + (1-a) \cdot R_2 \qquad (1)$$

where R_1 and R_2 are the certified values 1 and 2, respectively, and a is the portion of type 1 in the mixture. Based on Eq. (1), the measured uranium isotope ratios of P5 imply that P5 was a mixture of 30% type 1 and 70% type 2.

Further study

In particle analysis using SEM-TIMS and FT-TIMS, it is important to ensure analytical reliability, including accuracy and precision, which are critically dependent on the detector configuration. The TIMS multi-collector system consists of the advanced MIC system described above, and nine Faraday cups. It offers dynamic, multi-dynamic, and static modes.

In dynamic mode, only one SEM is used for the sequential detection of ion signals. In multi-dynamic mode, combinations of one SEM and Faraday cups are used to measure multiple ion signals simultaneously; however, it is necessary to change the magnetic field when more than one isotope is not sufficiently abundant to be detected by the Faraday cups. The determination of uranium isotope ratios can be included in such cases. The abundances of ^{234}U, ^{235}U, ^{236}U, and even ^{238}U in some cases, in environmental samples are usually too low for Faraday cups to be used. Isotope measurement in static mode uses the advanced MIC system, and does not require a change in magnetic field for sequential detection. The adoption of the appropriate measurement mode based on the sample size is essential for efficient, reliable analysis of environmental samples, because the three measurement modes each have advantages and disadvantages.

Experimental comparison of the three modes in terms of accuracy, precision, and uncertainty level is required according to the amount of uranium.

Conclusions

Four replicated U030 samples containing ultra-trace levels of uranium and five individual particles from a NUSIMEP-7 sample were analyzed to determine the uranium isotope ratios using SEM-TIMS. The advanced MIC system was used for the complete simultaneous measurement of four uranium isotopes. The excellent agreement of n(^{234}U)/n(^{238}U), n(^{235}U)/n(^{238}U), and n(^{236}U)/n(^{238}U) with certified values verified the applicability of SEM-TIMS with complete simultaneous measurement using the advanced MIC system to analyze uranium isotopes in individual microparticles. Further study should compare the effectiveness of the three measurement modes according to the amount of uranium.

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