Feasibility Study of the Single Particle Analysis of Uranium by Laser Ionization Time-of-Flight Mass Spectrometry

Yeong-Keong Ha,[a] Sun-Ho Han,[a] Hyung-Yeol Pyo,[a] Yong-Joon Park,[a] Kyuseok Song [b]
a Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Dukjin-dong, Yuseong, Daejeon, 305-353, Korea, nykha@kaeri.re.kr
b Laboratory for Quantum Optics, Korea Atomic Energy Research Institute, Dukjin-dong, Yuseong, Daejeon, 305-353, Korea

1. Introduction

The control of activities in nuclear facilities worldwide is one of the most important tasks of nuclear safeguard. To meet the needs for nuclear safeguard, International Atomic Energy Agency (IAEA) strengthened the control of nuclear activities to detect these activities earlier. Thus, it is very important to develop analytical techniques to determine the isotopic composition of hot particles from swipe samples. The precise measurement of the $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ ratios is important because it provides information about the initial enrichment of reactor uranium, core history, and post accident story.

Because conventional α-spectrometry is not sufficiently sensitive for the determination of long-lived radionuclides in environmental samples, several analytical techniques, such as SNMS (Sputtered Neutral Mass Spectrometry)[1], RIMS (Resonance Ionization Mass Spectrometry)[1,2], AMS (Accelerator Mass Spectrometry)[3] etc., have been proposed for uranium isotope measurements. In case of microparticles, analytical techniques such as SIMS (Secondary Ion Mass Spectrometry)[4] have been applied for the isotopic characterization. The aim of this work was the development of a sensitive analytical technique for determination of isotopic ratio of uranium in swipe samples. In this work, feasibility of LIMS (Laser Ionization Mass Spectrometry) for the determination of such particles has been evaluated using a reference material of natural uranium.

2. Methods and Results

The LIMS system developed in the laboratory for quantum optics at KAERI were used for the particle analysis. The experimental setup was described in detail elsewhere.[5]

2.1 Experimental setup

It consisted of a Nd:YAG laser and a linear time-of-flight mass spectrometer. The Nd:YAG laser (532 nm) was used as light source for ionization of the sample and the incident angle was about 45 degree. The laser was operated with a pulse repetition rate of 10 Hz, and a pulse energy of 0.8mJ. Ions were extracted into the time-of-flight mass spectrometer by applying a voltage to the electrode. The ions were detected by a dual microchannel plate.

The sample was prepared by attaching a natural uranium metal particle of 70 ㎛ in diameter to a carbon tape (1x1 mm) on a 1.5x2 ㎝ zircaloy plate. It is observed that U metal particle was oxidized during preparation. The prepared uranium particle was shown in Fig. 1. The prepared sample was installed by metal clip under vacuum condition.

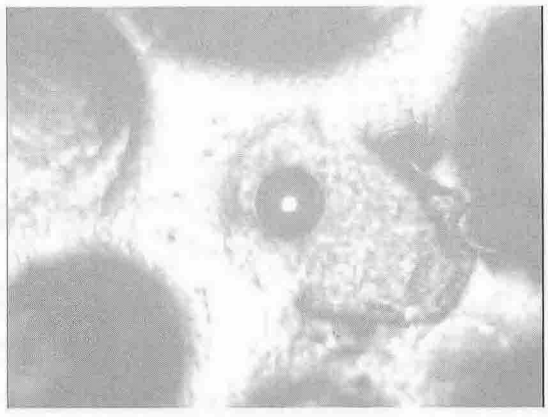

Figure 1. Optical microscopy of a uranium metal particle of 70 ㎛ in diameter on a 1x1 mm carbon tape

2.2 Determination of isotopic ratio of uranium, $^{235}U/^{238}U$

In order to determine the isotopic ratio of the natural uranium particle, mass spectra was collected and analyzed. As the spot size was ca. 200 ㎛ in diameter, this system ionize components in the carbon tape as well, in addition to a natural uranium particle.

The strongest signals were observed on the UO^+ (m/z 254) and UO_2^+ (m/z 270) mass, while that of U^+ (m/z 238) showed weak signal, indicating the uranium particle was oxidized. In Fig. 2, we can see the time-of-flight mass spectra of UO^+ (m/z 235, 251) and UO_2^+ (m/z 267, 270). It showed that laser ionization time-of-flight mass spectrometry can be used for the determination of isotope ratio of uranium particle. However, the resolution was not sufficient to resolve m/z 235, 236, 237 and 238, and the peak intensity was too low to detect ^{234}U or ^{236}U.

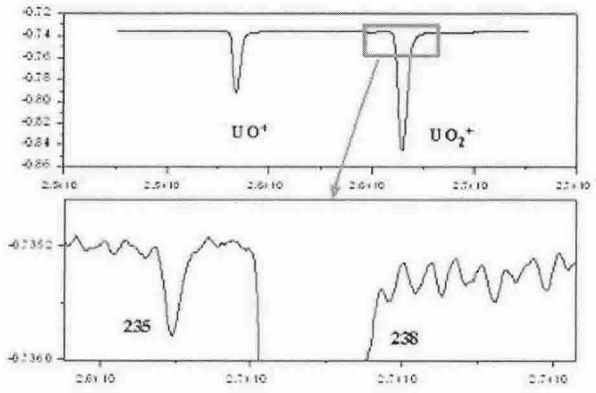

Figure 2. Time-of-flight mass spectra of a uranium particle

2.3 Reproducibility of isotopic ratio measurements of uranium

To evaluate the reproducibility of isotopic ratio of uranium, five measurements of $^{235}U/^{238}U$ were performed. The reproducibility of uranium isotopic ratio, $^{235}U/^{238}U$ was ca. 40 % (RSD). The preliminary results obtained in this work deviated from the value of a reference material, but the improvement of the S/N and isotope ratio can be achievable if some experimental parameter can be optimized. In addition, the merit of quick response and micro sampling for laser ablation TOF-MS technology may open a possibility to use this system to a particle analysis.

3. Conclusion

The laser ionization time-of-flight mass spectrometry was applied to the determination of isotope ratio of a uranium particle. At the present stage with preliminary investigation, the resolution and the peak intensity was sufficient to detect $^{235}U/^{238}U$, but not sufficient to detect ^{234}U and ^{236}U. Further investigation on laser ablation mass spectrometry may enable to detect and quantify the fractions of uranium isotope in particle samples.

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