Development of Resonance Laser-Assisted Sputtered Neutral Mass Spectrometry for Uranium Isotope Measurement

Jinkyu Park [a*], Sang Ho Lim [a], Chi-Gyu Lee [a], Sun Ho Han [a]
[a]*Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, 34057, Republic of Korea*

1. Introduction

These days, mass spectrometric techniques play major roles in the fields of nuclear safeguards and nuclear forensics, providing essential information to monitor illegal nuclear activities. Most of all, resonance laser-assisted sputtered neutral mass spectrometry (RL-SNMS) is rarely applied and a challenging technique, which is useful for the selective analysis of an element in the presence of mass-interfering species [1]. For instance, ^{238}U mass interferes with ^{238}Pu, and ^{241}Pu does the same with ^{241}Am. Common mass spectrometric techniques such as secondary ion mass spectrometry cannot mass resolve those elements because it requires extremely high mass resolving power ($m/dm > 10^5$).

Here we developed a RL-SNMS consisting of a wavelength-tunable laser system and a time-of-flight mass spectrometer (TOF-MS) equipped with a liquid metal ion gun, for selectively analyzing uranium isotope ratio in the presence of isobaric elements. Uranium standard material was analyzed with this system and the resultant major isotope ratio was in good agreement with the certified value.

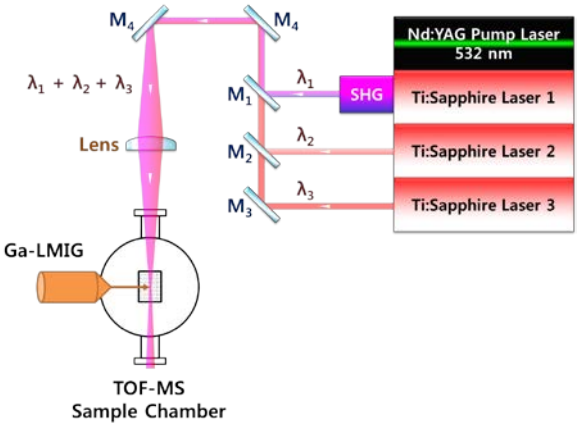

Fig. 1. A schematic diagram of RL-SNMS system at KAERI. SHG (second harmonic generator) for frequency doubling.

2. Methods and Results

2.1 Instrumentation

Galium (Ga) liquid metal ion gun (LMIG) from Ionoptika was employed to generate primary ion beam (15 ~ 25 keV) for sputtering samples. The sputtered neutrals above the sample surface are ionized by laser beams from 3-color wavelength-tunable laser system (Photonics Industries International, Inc.). The laser system consists of three Titanium:Sapphire lasers pumped by a Nd:YAG laser with high repetition rate (4 ~ 10 kHz). To selectively ionize uranium neutrals, wavelengths were tuned to 436. 3 and 735.8 nm (2-color scheme) or 415.5, 829.1 and 722.2 nm (3-color scheme), respectively, which are known to excite uranium neutrals to an autoionizing state [2]. The laser-induced uranium ions were analyzed by TOF-MS (Kore Technology Ltd.). TOF cycles were adjusted to match with the repetition rate of laser pulses.

2.2 Sample Preparation

Three different types of uranium materials were used to prepare samples. NIST (National Institute of Standards and Technology, USA) SRM (Standard Reference Material) U020, U050 (U_3O_8) and uranium dioxide (depleted uranium, DU) powder were deposited onto vitreous carbon planchets by vacuum-suction impaction method [3]. Briefly, a minimal amount of uranium material was smeared on a cotton swipe and an impactor assembly installed with a vacuum pump was moved around over the swipes to collect uranium particles by vacuum suction. Inside the impactor assembly, a planchet coated with sticky grease was placed to trap the incoming particles. Finally, the planchet with uranium particles was dried at 500 °C for 10 min to remove the grease material and ready for the measurement.

2.3 Detection of Laser-Induced Uranium Ions

First of all, DU powder was used for RL-SNMS experiment to avoid spectral complexity and focus mainly on ^{238}U-originated peaks. 2-Color excitation scheme was chosen to simplify beam alignment process. Wavelengths of Laser 1 with second harmonic generator and Laser 3 were tuned to 436.3 and 735.8 nm, respectively and collinearly focused. With laser off, we observed secondary ion peaks mainly from uranium hydrocarbide (UCH_x^+, x = 1 - 3), and uranium oxide (UO^+) and hydroxide (UOH^+) ions. With laser on, a new broad peak appeared between 254 and 255 m/z, which is probably due to laser-induced UO^+. The Laser-induced UO^+ might originate from the recombination of laser-ionized U and adventitious O, the ionization of UO neutrals or the breakdown of UO_2^+.

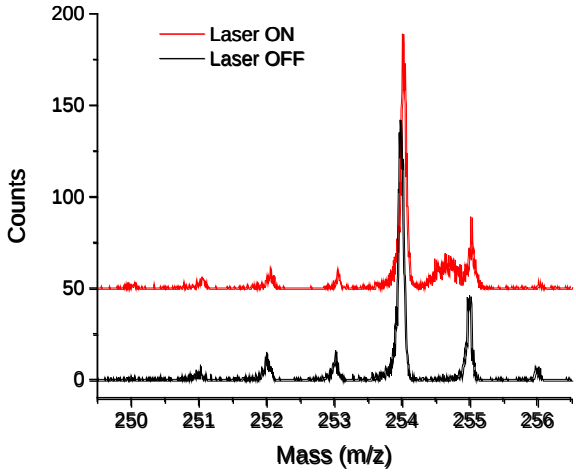

Fig. 2. Mass spectra obtain from DU sample using RL-SNMS.

Use of 3-color excitation scheme, spot-beam mode of the primary ion beam and adjustment of retardation voltage of the TOF tube increased the intensity of laser-induced uranium peaks and minimized secondary ion signals.

2.4 Measurement of Uranium Isotope Ratio

Mass spectra of NIST SRM U020, U050 and DU samples were obtained using RL-SNMS and major isotope ratio ($^{235}U/^{238}U$) was measured from laser-induced uranium peaks. The results were in good agreement with certified or reference value. Relative errors for U020 and U050 were 1.7 and 0.9%, respectively. Relative error for DU was 16% because of its low ^{235}U fraction; however, the experimental and reference values were consistent within the uncertainties.

3. Conclusions

Half home-built RL-SNMS system was successfully applied for uranium isotope measurement. Although the system requires optimization in many aspects such as laser beams focusing and wavelength stabilization, the current system is useful to measure major isotope ratio of uranium even for depleted uranium. The next step is to test its applicability for uranium samples mixed with other interfering elements.

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