

Preliminary Mass Spectrometric Analysis of Uranium on Environmental Swipe Materials

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1. Introduction

It is well-known that uranium and plutonium isotopic compositions of safeguards samples are very useful to investigate the history of nuclear activities [1,2]. To strengthen the capabilities of environmental sampling analysis in the ROK through MOST/DOE collaboration, round robin test for uranium and plutonium was designed in 2003. As the first round robin test, a set of dried uranium-containing solutions (~35ng and ~300ng) was distributed to the participating laboratories in November of 2003, with results reported in April of 2004. The KBSI (Korea Basic Science Institute) and ORNL (Oak Ridge National Laboratory) are currently in the process of analyzing uranium on cotton swipes for the second round robin test. As a preliminary test for the second round, KBSI intends to analyze home-made swipe samples into which international uranium standards are added. Here we describe technical steps of sample preparation and mass spectrometry at KBSI, and report some results of the preliminary test.

2. Methods

Two sets of duplicate samples, each spiked with c. 100ng of U015 and U005A standard solutions were prepared, along with one blank swipe and one procedure blank.

2.1 Sample Preparation

The test swipe samples were ashed twice using 12 steps-programmed Isotemp® Muffle Furnace. Ashes were transferred into Teflon vials with 6ml 4M HNO₃. After heating during overnight, the solutions were cooled and evaporated. The solutions were treated with 6ml 4M HNO₃ and 2ml mixed acids (HClO₄:HF=1:10), and then were divided into the small split (for U concentration measurement by isotope dilution) spiked with calibrated ²³³U isotopic tracers and the large split (for U isotopic ratio measurement). The small split was dried again to ensure an isotopic equilibration of the sample with the tracer.

The uranium for both isotope dilution and isotopic ratio measurements was separated using Eichrom TRU-Spec resin [3]. The resin was cleaned by passing 0.2M HCl and an HCl-HF mixture, and then preconditioned with 1.5M HNO₃. After the sample solutions in 1.5M HNO₃ were loaded onto the resin bed, the columns were washed with 1.5M HNO₃. Uranium was eluted with an

acid mixture containing 0.1M HCl and 0.3M HF. The chemical yields were better than 95% for uranium and Th/U ratio was less than 0.1 in the uranium cut. All the experiments were done in a clean room (CLASS-1000) with laminar flow benches. Acid and water used were double distilled with quartz still or Teflon two-bottle method. The level of experimental uranium blank was less than 100pg.

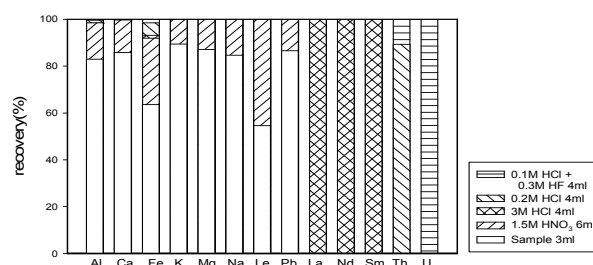


Figure 1. Elution pattern of uranium and other selected elements during the separation of a standard solution with the chemical technique utilizing TRU-Spec resin.

2.2 Mass Spectrometry

Two kinds of analytical instruments for measuring uranium isotopic composition are installed at KBSI; thermal ionization mass spectrometer (TIMS, GV Isoprobe-T) and multiple collectors inductively coupled plasma mass spectrometer (MC ICP-MS, VG AXIOM). We run the samples with the TIMS, considering its better abundance sensitivity. The TIMS used here is equipped with nine Faraday buckets and an axial Daly ion counting system, together with a secondary energy filter (WARP). Abundance sensitivity of ion counting system with the WARP filter of the Isoprobe-T is less than 20 ppb at mass 237 relative to a mass 238, which is negligible for measuring ultra-trace levels of ²³⁴U and ²³⁶U. A liquid nitrogen cold trap was always used on the mass spectrometer source to keep the pressure <2×10⁻⁸ mbar for improving the abundance sensitivity and extending the lifetime of filaments [4].

The separated uranium was loaded on a carefully cleaned Re-Re-Re triple filament with an aquadag carbon. Table 1 shows the collector configurations of mass spectrometer. First the Daly-Faraday gain was measured on the sample filament at around 10 mV of ²³⁸U, and the ²³⁵U and ²³⁸U intensities were measured by the Daly and Faraday detectors, respectively. Ionizing filament current was then increased to the higher intensity of ²³⁸U (typically 100-300 mV) for multi-static

analysis in which ^{234}U and ^{236}U intensities were counted by the Daly system and ^{235}U and ^{238}U intensities by the Faraday buckets.

This multi-static method is insensitive to ion beam growth or decay but is very sensitive to inter-collector gain variability. Therefore it is strongly recommended that the gain be monitored carefully. The gain variability of ^{232}Th with the Isoprobe-T at KBSI is less than 0.5%/hour as shown in Figure 2.

The $^{233}\text{U}/^{238}\text{U}$ ratios for the isotope dilution were measured by using the Daly system, and the results were externally calibrated with reference to the U500 data.

Table 1. Collector configurations for mass spectrometry.

Step	L 2	Daly	H 1	H 2	H 3	H 4
D-F Gain	1	234	235	236		238
	2	238				
$^{235}\text{U}/^{238}\text{U}$	1	235				238
Multistatic	1	234	235			238
	2	235	236		238	

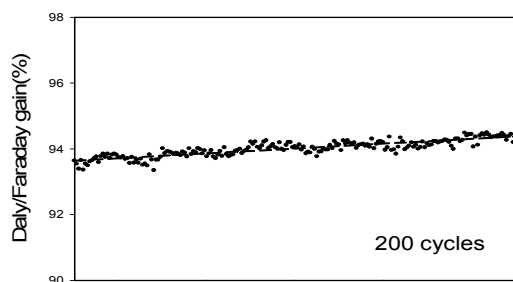


Figure 2. Faraday/Daly gain variability of ^{232}Th during 200 cycles run (integration time / 1 cycle = 10 s).

3. Results

As shown in Figure 3, all the measured uranium isotopic compositions for c. 40ng of the U015 standard are well agreed with the recommended values within error ranges, while the test swipe samples give clearly different values. This discrepancy is easily ascribed to the addition of uranium in the swipe matrix. We found that the blank swipe contains considerable amounts of uranium (6.8 ng/10cm x 10cm) whose $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios are much lower than the U015 standard. Mass balance calculations between uranium in the added standards and the swipe matrix yield consistent results with the measured data. The isotope dilution results match well with initially added weight, considering matrix uranium in the swipes.

4. Conclusion

We showed that the sample preparation system and thermal ionization mass spectrometry at KBSI gave reliable results for measuring uranium isotopic

compositions on environmental swipe materials. This capability is potentially very important for promoting international cooperation with regard to the nuclear transparency and nonproliferation.

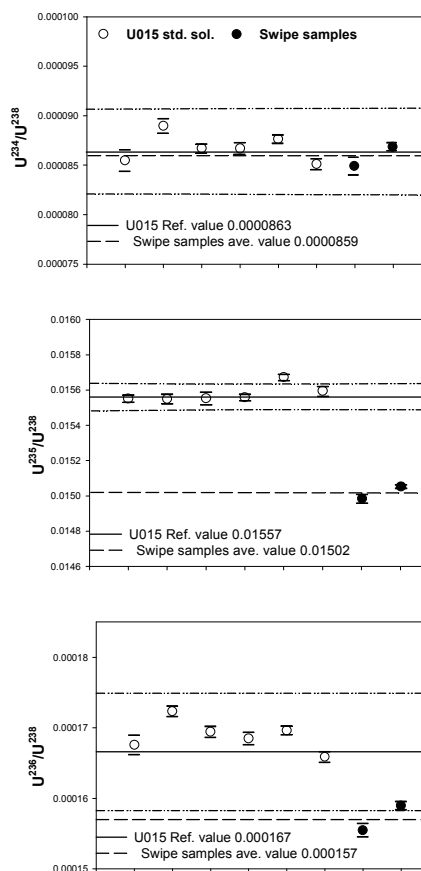


Figure 3. Uranium isotopic ratios measured in the U015 standard and test swipes.

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