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Systematic Evaluation of Uranium Impurities in Process Blanks for Ultra-Trace Analysis on Environmental Safeguards Samples using MC-ICP-MS and Isotope Dilution Mass Spectrometry†

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Bulk analysis of environmental swipe samples is a very useful technique to determine the quantities and isotopic ratios of the elements of interest (uranium and plutonium in most cases) at ultra-trace levels. However, it involves tedious chemical procedures, leading to significant amounts of unexpected contaminants causing experimental errors and increasing degrees of uncertainty. Therefore, it is imperative to monitor and evaluate uranium impurities in process blanks to obtain the reliable analytical results at ultra-trace levels. In this work, we have separately estimated the amounts of uranium in a process blank by dividing the process into a chemical pre-treatment step (PB_{step1}) and chemical separation step (PB_{step2}) using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and isotope dilution mass spectrometry (IDMS) technique. In addition, uranium impurities from various possible routes such as chemical reagents and UTEVA resin for chemical separation have also been estimated. The average amount of uranium impurities was 8.73 ± 0.028 , 22.34 ± 0.073 and 27.25 ± 0.066 pg for PB_{step1}, PB_{step2} and PB_{total}, respectively. Although examinations of the optimization of sample pre-treatment and chemical separation conditions are still in progress, we have confirmed that the estimated values were constantly low and negligible for determining the isotopic ratios and amounts of uranium in environmental swipe samples.

Keywords: Bulk analysis, Uranium, Process blank, Environmental samples, MC-ICP-MS, Isotope dilution mass spectrometry.

INTRODUCTION

For over two decades, environmental swipe sample analysis introduced by the International Atomic Energy Agency (IAEA) based on the "Program 93+2" has played significant roles in detecting undeclared nuclear materials and activities within nuclear facilities¹. In most cases, the laboratories in the IAEA Network of Analytical Laboratories have performed this analysis with their own chemical procedures and measurement scheme². Broadly, there are two analysis methods which can be divided into particle and bulk analysis in the environmental swipe sample analysis¹⁻³. The particle analysis focuses on the uranium isotopic ratio of individual micrometer-sized particles, which is normally performed using fission track thermal ionization mass spectrometry (FT-TIMS)⁴, secondary ion mass spectroscopy (SIMS)⁵ and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)⁶. Alternatively, large geometry (LG)-SIMS improving the precision and accuracy of the uranium isotope measurements on small particles has been utilized in several laboratories⁷. On the other hand, a bulk

analysis provides the information on the average concentration and isotopic composition of uranium and plutonium in a whole sample. Most laboratories use thermal ionization mass spectrometry (TIMS)⁸ and inductively coupled plasma mass spectrometry (ICP-MS)⁹.

In bulk analysis, it is absolutely imperative to monitor and evaluate the uranium contents (or impurities) since uranium is ubiquitous. Moreover, a bulk analysis involves tedious chemical procedures that can introduce unexpected contaminants containing uranium, which may cause experimental errors and increase the degree of uncertainty. Therefore, an appropriate analytical methodology, a clean laboratory environment, ultra-high pure chemical reagents and strict management of standards along with proper quality assurance (QA) and quality control (QC) procedures are required to obtain reliable and accurate analytical results of an ultra-trace analysis for environmental safeguards samples.

As mentioned above, analyses of samples containing nuclear materials with ultra-trace levels require a special laboratory environment to prevent cross-contamination. A number

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of laboratories have established clean facilities¹⁰. For this purpose, Korea Atomic Energy Research Institute (KAERI) has also opened a new clean facility called "CLASS (Clean Laboratory for Analysis of Safeguards Sample)" supported by the Korea government in May of 2013. Various verification processes regarding the CLASS facility, instrumentation and analytical methodology have been performed to obtain more reliable results and conduct actual activities as a member of the Network of Analytical Laboratories (NWAL) for bulk analysis on environmental swipe samples. As a part of the verification processes, we have estimated the amounts and isotopic ratios of uranium impurities in a process blank during bulk analysis. In general, process blanks are good indicators for the cleanliness of an experimental environment, analytical instrumentation, chemical reagents and other labwares used in a routine analysis. Furthermore, such process blanks may have a strikingly effect on an analysis of the uranium isotopic ratios of the target samples containing ultra-trace amounts of uranium.

In this study, we have focused on evaluating process blanks during chemical procedures, which can be divided into chemical pre-treatment and chemical separation. For a systematic estimation, we have separately performed quantification and isotopic measurements for each step using an IDMS technique and compared with those of entire procedures. We have also quantified and measured the isotope ratios of uranium impurities from other chemical reagents such as hydrochloric acid, stripping reagents and UTEVA resin for chemical separation.

EXPERIMENTAL

Chemical pre-treatment (ashing and acid digestion):

All reagents used were of analytical grade and used without further purification from commercial supplier. For dilution of reagents and samples, deionized and purified water with the Milli-Q system (Millipore, Germany, Resistivity: 18.2 MΩcm) was used. All labwares used in this work were made of Teflon (PTFE or PFA) and quartz and were thoroughly cleaned with ultra-high pure acids and Milli-Q water prior to use.

All of the analytical processes were conducted in a newly constructed clean facility (CLASS) and complied with the QA/QC system of KAERI. In particular, all chemical processes were performed in a Class 100 clean area and analytical instruments for isotopic measurements are installed in a Class 1000 area. Empty crucibles were separately placed on quartz plates in a high-temperature oven (Carbolite, UK). Each crucible was closed with a quartz lid to avoid cross-contamination and covered with a quartz beaker separately for protecting from additional contamination and then placed in the high-temperature oven. The ashing process was conducted in three steps: elevating the temperature to (1) 200 °C at a rate of 2.5 °C/min, (2) 400 °C at a rate of 2.5 °C/min and (3) finally 600 °C at a rate of 2.5 °C/min and held for 12 h. After several acid digestion steps, 10 mL of 8 M nitric acid was added followed by filtration to remove any insoluble matter. The resulting solution was accurately weighed.

The resulting solution was divided into three portions by weight corresponding to U-ID (40 wt. %), U-ISO (40 wt. %) and archive (20 wt. %), respectively. For isotope dilution mass

spectrometry (IDMS), ²³³U (IRMM 040a, Belgium) spike isotope reference material were added to the U-ID solution, where we simply referred the sample solutions as U-ID if the solution containing the spike and U-ISO if not. The spike amounts were determined by the results from the pre-screening and the resulting solutions were carefully weighted to calculate the spike quantities.

Chemical separation: UTEVA resin (Eichrom, 100-150 μm) was soaked in Milli-Q water prior to use. The slurry of UTEVA resin was poured into a disposable column (4.7 mm I.D., 60 mm H.) up to a bed volume of 0.6 mL. The UTEVA column was preconditioned with 8 M HNO₃. After conditioning the column with 2 mL of 8 M HNO₃/0.3 % H₂O₂, the previously prepared sample solution was loaded into the column. After loading the sample solution, the column was rinsed with 2 mL of 8 M HNO₃. The plutonium portion was stripped through the column with 2 mL of 8 M HNO₃/0.02 M ascorbic acid/0.02 M Hydroxylamine HCl followed by washing with 0.5 mL of 9 M HCl and 0.5 mL of 5 M HCl/0.05 M oxalic acid. Finally, the uranium portion was eluted into a conical PFA (Savillex) with 2 mL of 0.01 M HCl solution to determine the quantity and isotope ratios of uranium.

A Neptune Plus (Thermo Scientific Inc., Germany) double-focusing multi-collector inductively coupled mass spectrometer (MC-ICP-MS), equipped with nine Faraday collectors and five ion counters was used for the uranium measurements. The ion counters consist of three secondary electron multipliers (SEMs) and two compact discrete dynodes (CDDs). The multiple ion counter configurations used for the simultaneous measurements of the uranium isotopes in this study are shown in Table-1. The typical operating conditions of MC-ICP-MS and the desolvation system are summarized in Table-2.

TABLE-1
CUP CONFIGURATION DESIGNED FOR THE
SIMULTANEOUS MEASUREMENT OF U ISOTOPES

| Line | IC#4 | IC#3 | IC#2 | IC#1 | IC#5 |
|-----------------|------------------|------------------|------------------|------------------|------------------|
| Uranium isotope | ²³³ U | ²³⁴ U | ²³⁵ U | ²³⁶ U | ²³⁸ U |

TABLE-2
OPTIMIZED INSTRUMENTAL CONDITIONS OF
MC-ICP-MS AND DESOLVATION SYSTEM

| | |
|----------------------------|-------------------------|
| RF power | 1200 W |
| Cooling gas flow rate | 15 L/min |
| Auxiliary gas flow rate | 1.0 L/min |
| Mass resolution (ΔM/M) | 400 |
| Number of spectra acquired | 10 × 3 |
| Scan type | Static multi-collection |
| Solution uptake rate | 50 μL/min |
| Spray chamber temperature | 110 °C |
| Membrane temperature | 160 °C |
| Ar flow rate | 3.7 L/min |
| N ₂ flow rate | 5 mL/min |

TABLE-3
AMOUNT AND ISOTOPIC RATIOS OF URANIUM
MEASURED WITH MC-ICP-MS IN PB_{step1}, PB_{step2} AND PB_{total}

| | PB _{step1} | PB _{step2} | PB _{total} |
|--------|---------------------|---------------------|---------------------|
| U [pg] | 8.73 ± 0.028 | 22.34 ± 0.073 | 27.25 ± 0.066 |

TABLE-4
AMOUNT OF URANIUM IN STRIPPING REAGENTS DURING CHEMICAL SEPARATION MEASURED WITH MC-ICP-MS

| | 8 M HNO ₃ | Pu eluent | Th eluent | Np eluent | U eluent | UTEVA |
|--------|----------------------|-------------|-------------|-------------|---------------|--------------|
| U [pg] | 2.61 ± 0.02 | 4.91 ± 0.05 | 3.23 ± 0.10 | 2.34 ± 0.03 | 0.342 ± 0.003 | 2.99 ± 0.003 |

RESULTS AND DISCUSSION

In order to examine a suitable nitric acid, we have taken three candidates from different commercial suppliers referred as nitric acid #1 (Seastar's baseline, Canada, 67-70 wt. %, all metal impurities under 10 ppt), nitric acid #2 (TAMA-Pure-AA-10, Japan, 55 wt. %) and nitric acid #3 (Merk's Suprapur grade, Germany, 65 wt. %) and determined the concentration of uranium based on the MC-ICP-MS measurement combined with IDMS technique. The concentration of uranium impurities in each nitric acid is lower than 1 ppt (0.4 ppt for Seastar and TAMA and 1 ppt for Merk), indicating that it does not matter if any nitric acid from these companies is used during bulk analysis. For consistent analytical results, we have chosen the nitric acid #1 for all case.

The chemical procedures for environmental swipe samples in bulk analysis can be generally divided into chemical pre-treatment and chemical separation. For a systematic estimation how much portions of uranium impurities come from each step, quantification and isotopic measurements for each step were separately performed. Then, the analytical results of the chemical pre-treatment step (PB_{step1}, where PB is the abbreviation of "process blank") and chemical separation step (PB_{step2}) have been compared with those of the entire procedures (PB_{total}). As shown in Table-3, the sum of uranium contents in PB_{step1} and PB_{step2} is slightly smaller than the amount of uranium in PB_{total}. This difference (3.7 pg) may be attributed to the combination of the cleanliness of the CLASS facility and taflon/quartz labwares as well as the errors by weight measurement during IDMS. However, one thing we can say is that major portions of the uranium impurities were stemmed from PB_{step2} involving complicated chemical separation steps rather than PB_{step1}.

For more detailed information about the uranium impurities in chemical separation step, we have also investigated the amount of uranium for each stripping reagent and UTEVA resin. The amounts of uranium contained in each chemical reagent and UTEVA resin are shown in Table-4. The total

amount of uranium impurities (16.42 ± 0.23 pg) listed in Table-4 was quite different from the amount of uranium in PB_{step2}. The difference (6 pg) may also be originated mostly from errors in the weight measurement during the IDMS and the cleanliness of the CLASS and labwares.

Conclusion

In the present work, a systematic evaluation of uranium impurities for individual steps involved in chemical procedures was conducted using MC-ICP-MS and IDMS. Although sufficient long-term evaluations of process blank are still needed to obtain reliable analytical results for the bulk analysis on environmental swipe samples performed in CLASS, negligible and constantly low amounts of background uranium in process blank can verify the quality assurance of the bulk analysis performed in CLASS. To further lower the process blank levels and improve analytical capabilities obtained along with the CLASS's QA/QC program, related works such as a purification of the stripping reagents, adopting a new chemical separation scheme are underway.

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