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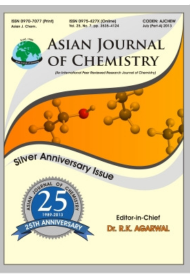

Minimization of Uranium Process Blank During Chemical Treatments of a Swipe Sample†

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A uranium background derived from the chemical treatment of a swipe sample was determined using multi-collector inductively coupled plasma mass spectrometry. Prior to the mass spectrometric analysis, sequential acid digestion and chemical separation can be utilized to avoid polyatomic ion interference. This chemical process may increase the amount of uranium in the process blank, which has an effect on an accurate isotopic measurement of uranium in the sample. As a result of a uranium background analysis, a significant portion of uranium in process blank was provided from a plutonium elute solution used for chemical separation. Careful treatments for cleaning bottles and using pure reagents reduce the amount of uranium in the process blank. Additionally, the uranium background can be controlled by checking the amount of uranium in each process. An isotope dilution mass spectrometry technique was utilized to determine ultra-trace uranium (pico-gram level) in the process blank. An isotopic analysis was also performed by varying the concentration of HNO_3 (DI, 3 % and 5 % of HNO_3) used to dissolve the sample for mass spectrometric measurements.

Key Words: Ultra-trace uranium, Isotopic analysis, Isotope dilution mass spectrometry, Inductively coupled plasma mass spectrometry.

INTRODUCTION

An isotopic analysis of uranium in swipe samples has been particularly useful in monitoring undeclared nuclear activities for safeguards and nuclear forensics[1-3]. Due to the high sensitivity of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), this technique has emerged as a powerful method to determine the isotopic ratios for nuclear materials at ultra-trace levels[4-6]. Simultaneous detection of several isotopes using the MC-ICP-MS technique allows a rapid and accurate isotopic measurement with a minimum amount of sample. However, an isotopic analysis with MC-ICP-MS is still challenging due to the interference effect of polyatomic ions ($^{195}Pt^{40}Ar^+$, $^{198}Pt^{40}Ar^+$, $^{207}Pb^{16}O_2^+$ and $^{208}Pb^{16}O_2^+$), which are combinations of one heavy element like Pb, Hg, W, Ir, Pt, *etc.*, with some of the most abundant atoms, such as O, N, H, Cl and Ar, in the plasma[7]. To avoid polyatomic ion interference, chemical treatments including sample ashing, acid digestion and chemical separation need to be performed prior to the mass spectrometric measurement.

The chemical process may increase the amount of uranium, which also has an effect on the isotopic ratios for the sample only. Several factors such as the lab environment, separation methods and chemical equipment influence on the amount of uranium in the process blank, which has become a critical issue for an accurate determination of isotopic ratio at ultra-trace levels. We observed a variation of uranium in the process blanks derived from the chemical treatments. In this study, we obtained the minimized and controlled process background of uranium after a careful chemical treatment. The amount of uranium in the process blank was determined according to an isotopic dilution mass spectrometry (IDMS) approach[8]. Finally, a mass spectrometric analysis with MC-ICP-MS was performed to determine the isotopic ratios. To investigate the solvent effect for isotopic measurements, standard reference material (SRM) U-005 (0.5 % ^{235}U) solutions dissolved in different concentrations of HNO_3 were analyzed through MC-ICP-MS.

EXPERIMENTAL

Sample preparation: Ultrapure reagents (HNO_3 and HCl) were purchased from Seastar Chemicals Inc. (Sydney, BC, Canada) and used for chemical separation and mass spectrometric analysis. All labware was cleaned by soaking in 8 M HNO_3 and rinsing with Milli-Q deionized water (~18 MΩ cm). Process blanks were prepared by processing the same procedure for a swipe sample analysis without a sample. An empty crucible was placed in the furnace for ashing of the process

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blank. After the ashing step, 2 mL of conc. HNO_3 was added to the sample. The solution was evaporated to dryness. The acid digestion was repeated three times. The sample was dissolved in 10 mL of 8 M HNO_3 and was spiked with a certified isotopic reference material (IRMM-040a, 98 % ^{233}U). Then, uranium was extracted using the previously described separation method[9]. Briefly, the UTEVA resin (100-150 μm, Eichrom Technologies LLC, IL, USA) was used to pack the column up to a bed volume of about 0.6 mL. After conditioning the UTEVA column, it was washed with 8 M HNO_3. After a series of elutions for americium, plutonium, thorium and neptunium, uranium was eluted with 2 mL of 0.1 M HCl from the column. The eluted uranium was heated to dryness and dissolved in 3 % HNO_3 for an isotopic measurement.

Mass spectrometry: Isotopic measurements were performed on a multi-collector inductively coupled plasma mass spectrometer (NEPTUNE plus, Thermo scientific Inc., Germany). A detailed description of the MC-ICP-MS instrument used for this study can be found elsewhere[10]. Briefly, the instrument is comprised of an ion source, an electrostatic analyzer, a magnetic sector and variable multicollectors with nine faraday cups and five ion counters. For a sample introduction, a membrane desolvator system (Aridus II, CETAC, NE, USA) was incorporated with an ICP-MS instrument. The sweep Ar flow was set to 4.5-4.6 L/min and N_2 gas was introduced at 7-8 mL/min. The temperatures of the spray chamber and the membrane desolvator were set to 110 and 160 °C, respectively. The flows of the cool gas, auxiliary gas and sample gas for the argon plasma were operated at 15, 0.97 and 0.77 L/min, respectively. All measured isotopic values presented in this study were recorded for a total of *ca*. 5 min (about 10 cycles).

RESULTS AND DISCUSSION

Uranium background after chemical treatments: Sequential chemical treatments including sample ashing, acid digestion and chemical separation are required to extract and isolate individual nuclear elements from a cotton swipe sample. The amount of uranium may increase through the chemical process due to any uranium contained in the chemicals and labware. Fig. 1 shows the amount of ^{238}U in the process blanks. Isotopic dilution mass spectrometry technique was applied to determine uranium concentrations. Without careful washing of the bottles and equipment such as the column and pipette tips, the amount of ^{238}U in the process blanks (PB1, PB2 and PB3 in the Fig. 1) significantly changed for an individual process (133, 245 and 89 pg of ^{238}U in 10 mL of process blanks, respectively). Although the uranium background was at the picogram-level, the increased amount of uranium can have an effect on an accurate isotopic measurement of ultra-trace levels of uranium in the sample only.

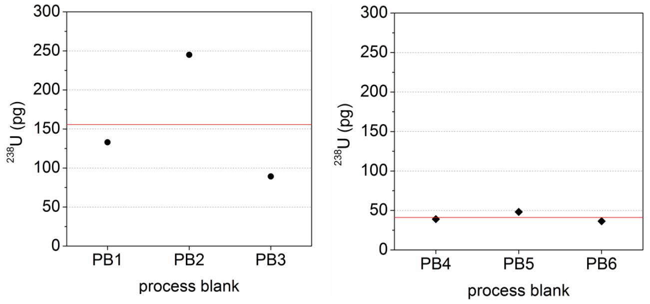

Fig. 1. Amount of uranium (^{238}U) in the process blanks before (PB1, PB2 and PB3) and after (PB4, PB5 and PB6) careful treatment of cleaning bottles and using pure reagents

All labware was carefully cleaned with 8 M HNO_3 and deionized water to minimize the uranium background. The solutions (Table-1) used for acid digestion and chemical separation were freshly made before each chemical process. After careful treatment, the uranium background was dropped to one-third compared to that before careful treatment. As shown in Fig. 1, three process blanks, PB4, PB5 and PB6, show a small variation of uranium (39, 48 and 36 pg of ^{238}U, respectively). The minimized and controlled process background of uranium is very important in the measurement of accurate isotopic values and consequently in determination of ultra-trace amounts of uranium in the sample only.

TABLE-1
MEASUREMENTS OF URANIUM (^{238}U) IN REAGENTS USED FOR CHEMICAL PROCESS

Reagents	^{238}U (cps)	^{238}U (pg)
18 mL of 8 M HNO_3	7.9×10^4	2.0
2 mL of Am elute solution (8 M HNO_3 + 0.3 % H_2O_2)	4.7×10^4	1.2
0.5 mL of Th elute solution (9 M HCl)	7.4×10^4	1.9
0.5 mL of Np elute solution (5 M HCl + 0.5 M oxalic acid)	2.4×10^5	6.2
2 mL of U elute solution (0.1 M HCl)	1.6×10^3	0.02
2 ml of Pu elute solution (0.02 M NH_2OH/HCl + 0.02 M ascorbic acid)	1.2×10^6	31.0

Uranium background in reagents used for chemical treatments: Diluted solutions used for acid digestion and chemical separation were analyzed to examine the amount of uranium. The signal intensities shown in Table-1 are calculated values with the measured intensities on the basis of the degree of dilution and the use of the solution for each process. During the chemical process, a lot of high concentrated acid was used. However, the total amount of uranium derived from the acid solution was very low (few pico-gram of ^{238}U) due to its high purity. A large portion of uranium in the process blank was obtained from the plutonium elute solution used for the chemical separation. In this case, the uranium carried with plutonium elute solution can be remained in the UTEVA resin. Because uranium was eluted after the plutonium extraction, the additional uranium from the plutonium elution can be eluted with the original uranium from the sample only. The detailed uranium background analysis accounts for the origin of uranium increase in the process blank. It can be expected to lower the uranium background by using a higher purity of ascorbic acid for plutonium elution.

Solvent effect for isotopic measurements: After the chemical treatments, the eluted uranium in 0.1 M HCl was heated to dryness and then dissolved in 3 % of HNO_3 for an isotopic measurement. It is of interest to consider whether or not a different concentration of HNO_3 solvent can influence the measured isotopic values. An isotopic analysis for SRM U-005 (100 ppt) was performed by varying the concentration of HNO_3 (0, 3 and 5 % of HNO_3) used to dissolve the dried uranium for mass spectrometric measurements. As shown in Fig. 2, consistent isotope ratios of $^{235}U/^{238}U$ were obtained regardless of the concentration of HNO_3 solvent. The measured isotopic values were in good agreement with the certified values ($^{235}U/^{238}U$ ratio corresponds to 4.9194×10^{-4}). Because the ultrapure HNO_3 contains a small amount of uranium (Table-1), the variation of the solvent concentration does not have an effect on an accurate isotopic measurement of uranium in the sample only.

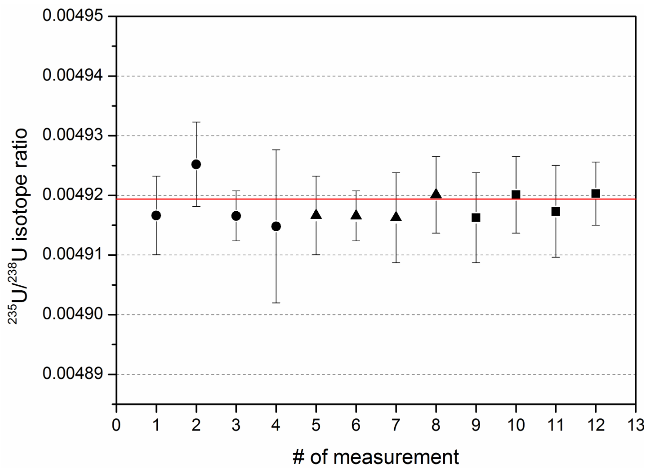

Fig. 2. $^{235}U/^{238}U$ isotope ratios measured for SRM U-500 solutions (100 ppt) dissolved in different concentrations of HNO_3 (0, 3 and 5 % corresponding to circles, triangles and squares, respectively)

Conclusion

The amount of uranium in the process blank needs to be minimized for an accurate isotopic measurement at ultra-trace levels. After chemical treatment, the uranium background in a process blank was analyzed using MC-ICP-MS. The lab environment, reagents and chemical equipment influence the total amount of uranium. The plutonium elute solution used for the chemical separation was a major source of uranium increase in the process blank. After careful treatments involved in cleaning the bottles and using ultra-pure reagents, a reduced and controlled uranium background was obtained (pico-gram level). The isotopic values of SRM U-005 solutions (100 ppt-level) dissolved in different concentrations of HNO_3 were examined using MC-ICP-MS. The $^{235}U/^{238}U$ isotope ratios have shown a good agreement with the certified values. This means an accurate isotopic measurement can be obtained with a variation of HNO_3 concentration of 0 to 5 %.

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