

Determination of low level of plutonium and uranium isotopes in safeguard swipe sample

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1. Introduction

For the determination of radionuclides, the separation techniques based on the principles of anion exchange, liquid-liquid extraction or column extraction chromatography are frequently used in nuclear analytical applications [1-2]. Recently, a novel extraction chromatographic resin has been developed by Horwitz and co-workers, which are capable of selective extraction of the actinides [3-4]. General separation of plutonium and uranium with extraction chromatographic techniques are focused on the environmental or radioactive waste samples. Also, the chemical yields for Pu and U isotopes with extraction chromatographic method sometimes are variable. For effective extraction of Pu isotopes in the very level of plutonium sample with UTEVA resin, the valence adjustment of Pu isotopes in the sample solution requires due to instability in the oxidation state of Pu isotopes during separation step. Therefore, it is necessary to develop a simple and robust radiochemical separation method for nano- or pico gram amounts of uranium and plutonium in safeguard swipe samples.

Chemical yields of plutonium and uranium with extraction chromatographic method of Pu and U upgrades in this study were compared with several separation methods for Pu and U generally used in the radiochemistry field. Also, the redox reactions of hydrogen peroxide with plutonium in the nitric acid media were investigated by UV-Vis-NIR absorption spectroscopy. Based on general extraction chromatography method with UTEVA resin, the separation method of nano- and picogram amounts of uranium and plutonium in safeguard swipe samples was developed in this study.

2. Methods

2.1 Reagents and instrument

Picogram level of ^{242}Pu (NIST) and ^{243}Am (NIST), and nanogram level of ^{233}U (IRMM), ^{232}Th and ^{237}Np were used to prepare the simulated solution. Thermal ionization mass spectrometry (TIMS, TRITON, Thermo Scientific) and MC-ICP-MS was used for a measurement of the individual isotopes in the eluates. The absorption spectra of the Pu solutions A Pu stock solution prepared by dissolving $^{242}\text{PuO}_2$ (ORNL, USA) with concentrated HNO_3 and HF in a glove box were measured with a high-resolution UV-Vis-NIR

spectrophotometer (CARY5, Varian), using a 1.0 cm semi-micro quartz cell (Hellma).

2.2 Valence control of plutonium

After adding 0.3% hydrogen peroxide onto Pu stock solution containing a mixture of Pu(IV) and Pu(VI), variation of its absorption spectrum was measured with standing time. After adding aliquot U(VI) onto the Pu(IV) solution made by adding 0.5M sodium nitrate onto the Pu stock solution, variation of its absorption spectrum was measured with 0.3% hydrogen peroxide.

2.3 Separation of Pu and U on UTEVA resin

The UTEVA resin (100-150 μm , Eichrom Industries Inc.) was soaked in 1M HNO_3 for one day. Aliquots of the slurry were then poured into a disposable column (4.7 mm I.D., 60 mm H.) up to a bed volume of about 0.6 mL. The UTEVA column was preconditioned with 8M HNO_3 prior to its use. The flow rate was maintained at about 0.15 mL/min by a gravity elution.

3. Results and discussion

3.1 Comparison of chemical yields of Pu and U

The chemical yield for ^{233}U stripped with 8M HNO_3 from the anion exchange column was lower than those with other uranium separation methods. This means that a lot of uranium eluted with plutonium, when Pu was stripped from the anion exchange column with 0.37M $\text{HCl}/0.01\text{M HF}$. The anion exchange method for determining plutonium in picogram level is less reliable than the UTEVA method, because uncertainty in the chemical yield of the anion exchange method is bigger than that of the UTEVA method. Also, the chemical yield for ^{242}Pu with the UTEVA method reported by Morgenstern et al. was lower than the UTEVA method developed in this study. In this study, concentration of stripping reagents for plutonium increased ten times compared with common UTEVA method was applied for separating plutonium that high chemical yield of ^{242}Pu was obtained. Also, the chemical yield for ^{233}U with the the UTEVA method upgraded in this study was similar to that with UTEVA method used commercially. However, it is necessary to decompose ammonium oxalate used for eluting U from the UTEVA column with concentrated nitric acid before loading onto filament for TIMS analysis, while U fraction purified with stripping reagent (0.01M HCl) of isotope used in this study makes it possible to load onto filament without pretreating the U fraction with concentrated nitric acid. Therefore, the radiochemical separation

method upgraded in this study has been effective to achieve quantitative extraction of nano or pico gram amounts of uranium and plutonium by the UTEVA resin using ID-TIMS.

3.2 Redox reactions of Pu and U isotopes with hydrogen peroxide in nitric acid media

Hydrogen peroxide is reducing reagent and has been used for adjusting oxidation states of Pu in the radiochemical separation method. It has been reported that 80% of plutonium were reduced to the trivalent state within a few minutes while about 20% remained in the tetravalent state after addition of 0.3% hydrogen peroxide. Therefore, it is necessary to check redox reaction of hydrogen peroxide with plutonium before adding hydrogen peroxide into the sample solution before applying it for separating plutonium. For investigating the redox reactions of Pu with hydrogen peroxide, 8M nitric acidic solutions containing millimolar concentrations of Pu were analyzed by UV-Visible absorption spectroscopy before and after addition of hydrogen peroxide. Adding 0.3% hydrogen peroxide to the nitric acid solution the typical absorption peak of Pu(VI) at 830 nm disappeared after standing for 3 minutes. After standing for 2 hrs the typical absorption peaks of Pu(III) at 565- and 602 nm appeared due to reducing Pu(IV) to Pu(III). However, after standing the nitric acid solution 5 days, Pu(III) finally returned to Pu(IV), since hydrogen peroxide decomposes slowly in 8M HNO₃ solution. Krot et al. reported that the rate of a H₂O₂ decomposition in 8M HNO₃ solution was less than 1.5% per hour under the conditions without any catalytic impurity. From this result, it is inferred that Pu(III) re-oxidizes Pu(IV) due to 8M HNO₃ as a result of decomposition of hydrogen peroxide after 5 days.

3.3 Optimization method for separating Pu and U isotopes with UTEVA resin

After conditioning the UTEVA column with about 5 bed volumes of 8M HNO₃/0.3% H₂O₂, the simulated sample solution (2 mL) containing about 5 ng for uranium and 40 pg for plutonium in 8M HNO₃/0.3% H₂O₂ was added onto the column. After loading the sample solution the column was washed with 2 mL of 8M HNO₃ to remove americium and fission products. Plutonium was stripped from the column using 2 mL of 2M HNO₃ containing 0.02M hydroxylammonium chloride and 0.02M ascorbic acid. The column was washed 1 mL of 9M HCl and 5M HCl/0.05M oxalic acid to remove thorium and neptunium, respectively. Uranium was eluted with 2 mL of 0.007M ammonium oxalate. The recoveries were found to be 94 ± 7% for plutonium and 95 ± 5% for uranium. The chromatogram of sequential separation procedure is summarized in Fig. 1. Most of plutonium and uranium were eluted from the UTEVA column with 1mL of the stripping reagent for Pu and U, respectively. Also, plutonium and uranium was completely separated from other nuclides.

Therefore, since the reagents used for stripping plutonium and uranium are relatively simple compounds, plutonium or uranium was loaded easily onto filaments for TIMS analysis, after decomposing the stripping reagents with concentrated nitric acid.

4. Conclusions

The extraction chromatography method with a UTEVA column developed in this study makes it possible to separate completely plutonium and uranium in nitric acid media. The chemical yields with the extraction chromatography method with a UTEVA column were found to be 94 ± 7% for plutonium and 95 ± 5% for uranium. From spectroscopic investigation with a UV-Vis-NIR spectrophotometer, the addition of hydrogen peroxide to the sample solution in 8M HNO₃ was found to be an efficient for the valency adjustment of uranium and plutonium. The separation method of Pu and U isotopes with the UTEVA resin updated in this study makes it possible to be used for determining Pu and U isotopes in the safeguard swipe samples with isotope dilution thermal ionization mass spectrometry (ID-TIMS).

References

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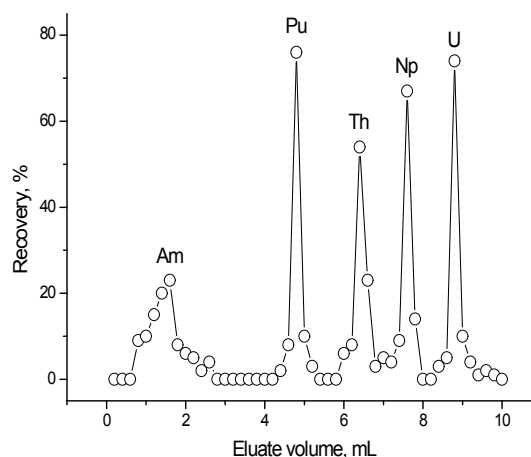


Fig. 1. Elution sequence of the simulated solution containing Pu, U, Am, Th and Np isotopes from the UTEVA resin column