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Determination of Pu and U isotopes in safeguard swipe sample with extraction chromatographic techniques

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ABSTRACT

A simple and reliable separation method of plutonium and uranium was developed using extraction chromatographic techniques. Using the separation method of plutonium and uranium developed in this study, recoveries of plutonium and uranium were compared with those by commercial separation methods of Pu and U. The redox reactions of hydrogen peroxide with plutonium in a nitric acid medium were investigated by UV–vis–NIR absorption spectroscopic techniques. The separation method of Pu and U isotopes with the UTEVA resin updated in this study could be effective to measure quantitatively nano- and picogram amounts of uranium and plutonium in swipe samples using isotope dilution thermal ionization mass spectrometry (ID-TIMS).

1. Introduction

To determine the activity concentration of radionuclides, the separation techniques based on the methods of anion exchange, liquid–liquid extraction or column extraction chromatography are frequently used in nuclear analytical applications [1–7]. Recently, novel extraction chromatographic resin has been developed by Horwitz and co-workers, which is capable of selective extraction of the actinides [8–10]. General separation of plutonium and uranium with extraction chromatographic techniques are focused on the environmental or radioactive waste samples. Also, the recoveries for Pu and U isotopes using the extraction chromatographic method sometimes vary depending on the sample matrix. For an effective extraction of Pu isotopes in the very low level of plutonium sample with UTEVA resin, the valence adjustment of Pu isotopes in the sample solution is required 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 picogram amounts of uranium and plutonium in the safeguard swipe samples.

Chemical yields of plutonium and uranium using an extraction chromatographic method of Pu and U developed in this study were compared with those by several separation methods for Pu and U generally used in the radiochemistry field [11–13]. Additionally, the redox reactions of hydrogen peroxide with plutonium in a nitric acid medium were investigated by the UV–vis–NIR absorption spectroscopic method. Based on a general extraction chromatography method with UTEVA resin, the separation method for nano- and picogram amounts of uranium and plutonium in swipe samples for nuclear safeguards was developed in this study.

2. Experimental

2.1. Reagents and instrument

40 pg of ^{242}Pu (NIST), 5 ng of ^{233}U (IRMM), 1 ng of ^{243}Am (NIST), 8 ng of ^{232}Th and 10 ng of ^{237}Np (Amersham) were used to prepare the simulated solution. The Pu stock solution was prepared by dissolving $^{242}PuO_2$ (ORNL, USA) with concentrated HNO_3 and HF in a glove box. The absorption spectrum of the Pu solution was measured (scanning speed: 600 nm/min) 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 0.02 mL of 30% hydrogen peroxide into 2 mL of Pu stock solution (0.3% H_2O_2) containing a mixture of Pu(IV) and Pu(VI), variation of its absorption spectrum was observed with standing time. After adding 1 mL of U(VI) into 1 mL of the Pu(IV) solution made by adding 0.5 M sodium nitrate into the Pu stock solution for adjusting the Pu oxidation state to Pu(IV) [14],

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Table 1
Recovery of ^{242}Pu and ^{233}U with various separation methods of Pu and U.

Separation method	Reference	Adjusting reagents of Pu and U isotopes	Stripping reagents of Pu isotopes	Stripping reagents of U isotopes	Chemical yield (%)	
					^{242}Pu[a]	^{233}U[a]
Anion exchange (Bio-rad)	[11]	0.2 M $NaNO_2$ in 8 M HNO_3 solution	0.37 M HCl/0.01 M HI	8 M HNO_3	88 ± 11[b]	86 ± 9
Anion exchange (Bio-rad)	[12]	0.1 M HNO_3 in 9 M HCl solution	0.1 M HI/9 M HCl	0.1 M HCl	90 ± 12	90 ± 7
UTEVA (EIchrom)	[13]	0.3% H_2O_2 in 8 M HNO_3 solution	0.002 M $NH_2OH{\cdot}HCl$ /0.002 M ascorbic acid	0.007 M $(NH_4)_2C_2O_4$	86 ± 7	96 ± 5
UTEVA (EIchrom)	This study	0.3% H_2O_2 in 8 M HNO_3 solution	0.02 M $NH_2OH{\cdot}HCl$ /0.02 M ascorbic acid	0.01 M HCl	94 ± 5	95 ± 6

[a] Number of aliquots analyzed is 3.
[b] Error is 1σ.

variation of its absorption spectrum was observed depending on the concentration of hydrogen peroxide.

2.3. Separation of Pu and U on UTEVA resin

The UTEVA resin (100–150 µm, Eichrom Industries Inc.) was soaked in 1 M 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 8 M HNO_3 prior to its use. The flow rate was maintained at about 0.15 mL/min by a gravity elution. After conditioning the UTEVA column with 3 mL of 8 M HNO_3/0.3% H_2O_2, 2 mL of simulated sample solution was added into the column. After loading the sample solution, the column was washed with 1 mL of 8 M HNO_3. Plutonium was stripped from the column using 1 mL of 2 M HNO_3 containing 0.02 M hydroxylammonium chloride and 0.02 M ascorbic acid. The column was washed with 1 mL of 9 M HCl and 5 M HCl/0.05 M oxalic acid, respectively. Finally, uranium was eluted with 1 mL of 0.1 M HCl.

2.4. Recovery yield calculation

The recovery yields of the elements were calculated by quantifying the individual elements in the eluted solutions. A multi collector-inductively coupled plasma mass spectrometer (MC-ICPMS, NEPTUNE, Thermo Fisher Scientific) was utilized to measure the signal intensities of the elements followed by being quantified using the concentration calibration curve preset in a preliminary calibration. Diluted solutions of a certified isotopic reference material (IRMM-040a) with various concentrations were prepared to produce the concentration calibration curve from the correlation between the signal intensities of uranium measured by the MC-ICPMS, and the uranium concentrations of the solutions.

3. Results and discussion

3.1. Comparison of recoveries of Pu and U

Recoveries for ^{242}Pu and ^{233}U with various radiochemical separation methods of plutonium and uranium in a simulated sample solution are presented in Table 1. The recoveries for ^{242}Pu and ^{233}U with conventional exchange column methods [11,12] were lower than those with the UTEVA method developed in this study. The uncertainties of the chemical yield for ^{242}Pu and ^{233}U with the anion exchange method were higher than those with the UTEVA method developed in this study. This means that the UTEVA method of plutonium and uranium developed in this study has more reliable than the anion exchange method. Also, in the anion exchange method, it is necessary to purify uranium fraction eluted from the columns with an U stripping reagent (8 M HNO_3) once more, because Am was eluted with U without attaching the anion exchange resin in the 8 M HNO_3 solution. Also, a small amount of nuclides such as Am, Th and Pu were eluted with U in the anion exchange column methods [15].

The anion exchange method to determine the plutonium at the picogram level is less reliable than the UTEVA method, because the uncertainty in the recovery of the anion exchange method is larger than that of the UTEVA method. The recovery for ^{242}Pu with the UTEVA method reported by Morgenstern et al. [13] was lower than that of the UTEVA method developed in this study. In this study, the concentration of stripping reagents for plutonium increased 10 times compared with the UTEVA method reported by Morgenstern et al. was applied to separate plutonium, so that recovery of ^{242}Pu (this study: 94 ± 5%, Morgenstern's method: 86 ± 7%) increased. Additionally, the recovery for ^{233}U with the UTEVA method upgraded in this study (95 ± 6%) was similar to that

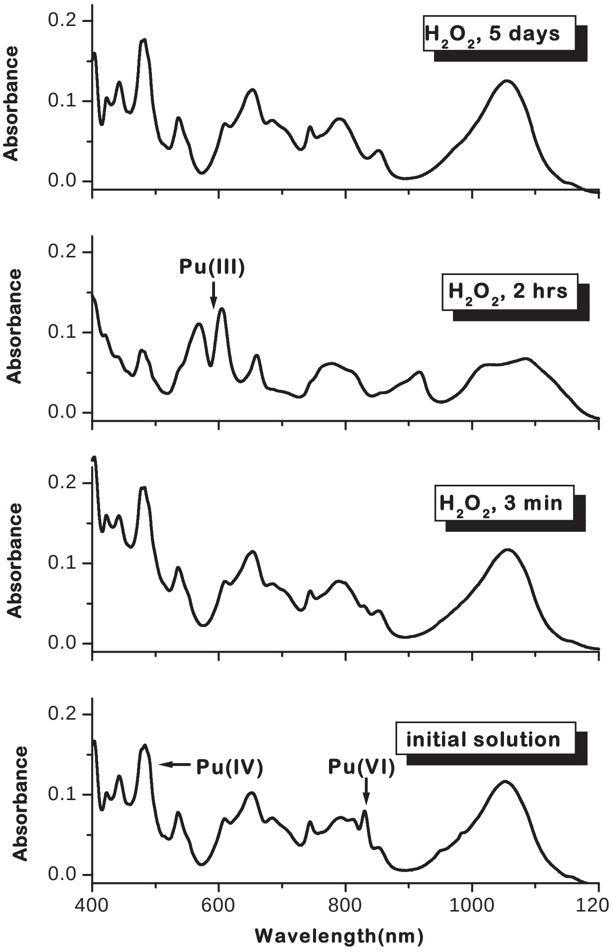

Fig. 1. Variation of absorption spectra of a Pu solution in 8 M HNO_3 solution versus standing time after addition of 0.3% H_2O_2: [Pu(IV)] = 3.73 mM, [Pu(VI)] = 0.47 mM.

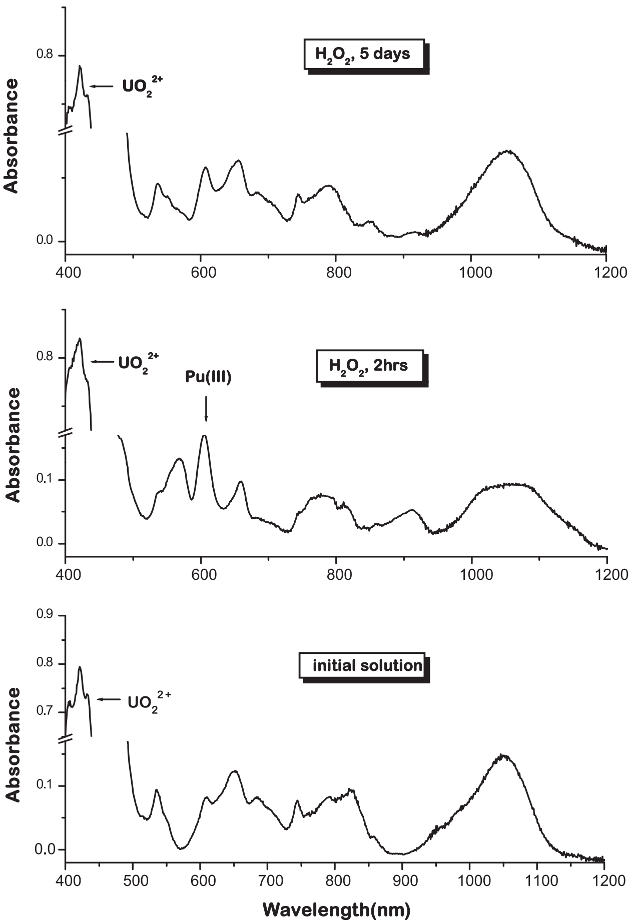

Fig. 2. Variation of absorption spectra of Pu(IV) and UO_2^{2+} in 8 M HNO_3 solution versus standing time after adding 0.3% H_2O_2: [Pu(IV)] = 5.50 mM, [UO_2^{2+}] = 55 mM.

with the UTEVA method reported by Morgenstern et al. (96 ± 5%). But, it is necessary to decompose the ammonium oxalate used for eluting U from the UTEVA column with concentrated nitric acid before loading onto a filament for TIMS analysis. However, the U fraction purified with a stripping reagent (0.01 M HCl) of U isotope used in this study makes it possible to load onto a filament without pretreatment of the U fraction with concentrated nitric acid. Therefore, the upgraded radiochemical separation method in this study has been effective for achieving quantitative extraction of nano or picogram 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 medium

Hydrogen peroxide is a reducing reagent [16] and has been used for adjusting the oxidation states of Pu in the radiochemical separation method [17]. It has been reported that 80% of plutonium is reduced to a trivalent state within a few minutes while about 20% remains in a tetravalent state after the addition of 0.3% hydrogen peroxide [13]. Therefore, it is necessary to check the redox reaction of hydrogen peroxide with plutonium before applying it for separating plutonium. To investigate the redox reactions of Pu with hydrogen peroxide, 8 M nitric acid solutions containing 5.5 mM of Pu were analyzed by UV–vis-NIR absorption spectroscopy before and after the addition of hydrogen peroxide. After 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 min, as shown in Fig. 1. After standing for 2 h the typical absorption peaks of Pu(III) at 565- and 602 nm appeared due to reducing Pu(IV) to Pu(III). However, after keeping the nitric acid solution 5 days, Pu(III) finally returned to Pu(IV), since hydrogen peroxide decomposes slowly in 8 M HNO_3 solution. Krot and Shuiskaya reported that the rate of H_2O_2 decomposition in a 8 M HNO_3 solution was less than 1.5% per hour under conditions without any catalytic impurity [18]. From this result, it is inferred that Pu(III) re-oxidizes Pu(IV) due to 8 M HNO_3 as a result of decomposition of hydrogen peroxide after 5 days.

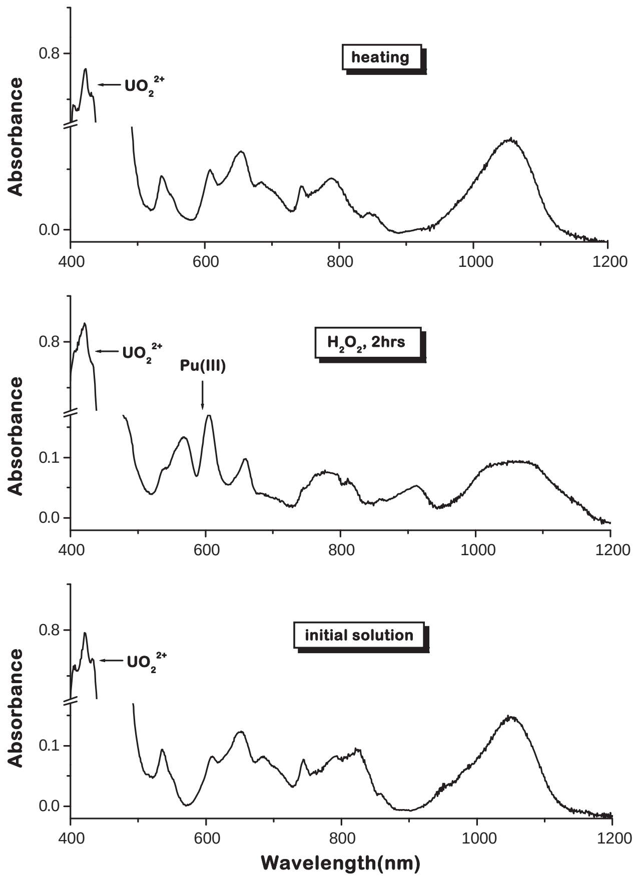

Fig. 3. Variation of absorption spectra of Pu(IV) and UO_2^{2+} in 8 M HNO_3 solution after adding 0.3% H_2O_2 and heating: [Pu(IV)] = 5.50 mM, [UO_2^{2+}] = 55 mM.

In the presence of uranium(VI), the redox reactions between plutonium and hydrogen peroxide were also investigated. As shown in Figs. 2 and 3, for the sample solution after standing for 2 h, typical absorption peaks of Pu(III) at 565 and 602 nm appeared due to reducing Pu(IV) to Pu(III), as mentioned previously, while the oxidation state of U(VI) remained unchanged independent of the standing time. However, after heating the sample solution, which containing hydrogen peroxide, at 80 °C for 20 min and then cooling the sample solution for 10 min, Pu(III), which was reduced from Pu(IV) due to hydrogen peroxide, changed to Pu(IV), as shown in Fig. 3. This means Pu(III) had rapidly re-oxidized to Pu(IV) due to the thermal decomposition of hydrogen peroxide. Therefore, in the adjustment process of Pu oxidation, it is necessary to heat the sample solution containing Pu(III) prior to separation of Pu from other nuclides with the UTEVA resin after adding the hydrogen peroxide.

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

The separation method of plutonium and uranium modified the extraction chromatographic procedure proposed by Morgenstern

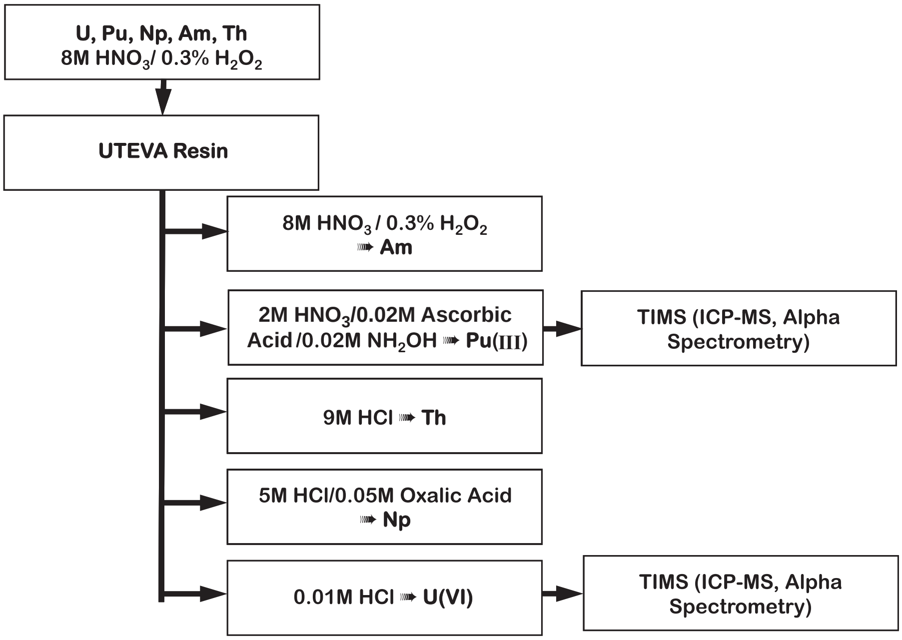

Fig. 4. Separation scheme for the separation of Pu, U, Th and Np with extraction chromatographic method.

et al. is shown in Fig. 4. After conditioning the UTEVA column with about 5 bed volumes of 8 M HNO_3/0.3% H_2O_2, 2 mL of simulated sample solution was added into the column. After loading the sample solution, the column was washed with 2 mL of 8 M HNO_3 to remove americium and fission products. Plutonium was stripped from the column using 2 mL of 2 M HNO_3 containing 0.02 M hydroxylammonium chloride and 0.02 M ascorbic acid. The column was washed with 1 mL of 9 M HCl and 5 M HCl/0.05 M oxalic acid to remove thorium and neptunium, respectively. Uranium was eluted with 2 mL of 0.1 M HCl. A chromatogram of the sequential separation procedure is summarized in Fig. 5. The plutonium and uranium were completely separated from other nuclides such as Am, Th and Np isotopes. In this study, the volume of stripping reagent for Pu and U was fixed to 1 mL, respectively, because most of the plutonium and uranium were eluted from the UTEVA column with 1 mL of the stripping reagent for Pu and U. Also, since the reagents used for stripping plutonium and uranium are relatively decomposable compounds, plutonium or uranium was loaded easily onto filaments for TIMS analysis, after decomposing the stripping reagents with concentrated nitric acid.

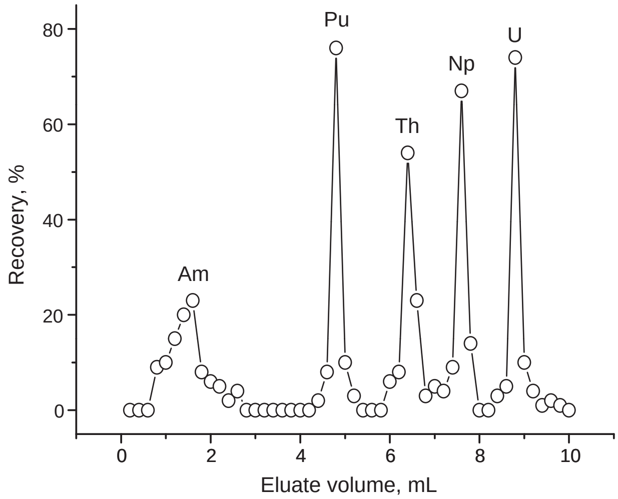

Fig. 5. Elution sequence of the simulated solution containing Pu, U, Am, Th and Np isotopes from the UTAVA resin column.

4. Conclusions

For determining very low levels of Pu and U in a swipe sample, an extraction chromatography method with a UTEVA column was developed in this study. The recoveries with the extraction chromatography method with a UTEVA column were found to be 94 ± 7% and 95 ± 5% for plutonium and uranium, respectively. From a spectroscopic investigation with a UV–vis–NIR spectrophotometer, the addition of hydrogen peroxide into the sample solution in a nitric medium was found to be 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 safeguard swipe samples with isotope dilution thermal ionization mass spectrometry (ID-TIMS).

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