Radiochemical Analysis of Pu, U and Sr Isotopes in Soil Samples with Anion Exchange, UTEVA, Strontium Resin†

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This study presents a rapid and quantitative sequential radiochemical separation method for the Pu, U and Sr isotopes with an anion exchange resin, UTEVA resin and Sr resin in soil samples. After the radionuclides were leached from samples with 8M HNO_3, the Pu, U and Sr isotopes were sequentially adsorbed on the anion exchange column, UTEVA column connected with Sr Spec column. The Pu isotopes were purified from other nuclides through the anion exchange column and the uranium isotopes were separated from other nuclides through the UTEVA column. Also, ^{90}Sr was separated from other hindrance elements with the Sr Spec column. After a source preparation for the purified Pu and U with the micro-coprecipitation method, the Pu and U were measured by an α-spectrometry. Strontium-90 was measured by a low level liquid scintillation counter. The radiochemical procedure for Pu, U and Sr nuclides investigated in this study has been validated by application to IAEA reference soils.

Key Words: Pu, U, Sr, Soil samples, Anion exchange, UTEVA resin, Sr resin.

INTRODUCTION

Recently, several studies have reported on combined procedures for the determination of radionuclides in soils or sediment samples with extraction chromatographic materials such as the TRU, Sr and TEVA Spec resins[1-4]. These methods are somewhat difficult to apply for very low levels of fallout radionuclides without using large amounts of extraction chromatographic resin. Therefore, it is necessary to develop improved determination methods for actinides with lower detection limits, faster turnaround time and reduced analysis costs. It is also desirable that the method does not generate any appreciable amount of mixed waste or hazardous wastes. In order to meet these challenges, a procedure has been developed to provide sequential determination of plutonium, uranium and radiostrontium in soil samples. By sequentially analyzing the entire sample, it is possible to avoid repeating the extra and unnecessary digestion/dissolution processes, which are quite time consuming and costly. Minimum detectable activity (MDA) is also achieved by analyzing the whole sample, rather than dividing it into small subsamples for each individual analysis[5].

In order to reduce the analysis cost and turnaround time in conventional methods, a sequential determination for Pu, U and Sr nuclides in environmental and radioactive waste samples has become increasingly important. The aim of this study was to develop a rapid and sensitive analytical procedure for the sequential determination of critical man-made radio-isotopes in environmental and radioactive waste samples based on the α-spectrometry following radiochemical separation by ion exchange and extraction chromatography after decomposition of sample matrix. The sequential analytical method for Pu, U and ^{90}Sr nuclides investigated in this study has been validated by application to IAEA reference materials.

EXPERIMENTAL

Most of the radiochemical protocols follow three main steps *i.e.*, sample decomposition, radiochemical separation and source preparation before measurement. A flow chart of the analytical procedure for Pu, U and ^{90}Sr isotopes in the nitric acid medium is shown in Fig. 1.

Sample decomposition: After soil or sediment (10-30 g) was weighed into a porcelain dish and ashed in a muffle furnace with a gradual heating program up to 550 ºC to eliminate organic matter, the sample was transferred to a Teflon beaker. A strontium carrier (about 1 ppm) and spikes of ^{242}Pu and ^{232}U tracers (about 0.1 Bq) were added to ensure isotopic equilibrium with the analyte nuclides. In the acid leaching method,

the ashed samples were dissolved in 30 mL of 8 M HNO_3 with a stirring on a hot plate. In the total decomposition method, the ashed samples were dissolved in 10 mL of concentrated HNO_3 and 10 mL of HF (48 %) and evaporated to a dryness. Dissolution in HNO_3/HF was repeated and the sample was evaporated again to a dryness.
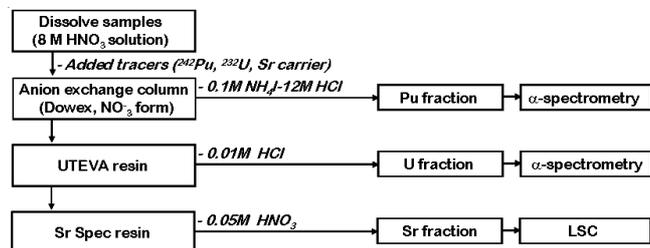

Fig. 1. Separation scheme of the Pu, U and Sr isotopes in soil samples

The residue was dissolved with 30 mL of 8 M HNO_3. The sample solution was filtered through a membrane filter (0.2 µm pore size). About 2 mL of 0.5 M $NaNO_2$ was added into the solution to adjust the oxidation state of the Pu(IV).

Radiochemical separation: To shorten the radiochemical separation steps of the conventional analysis of Pu and Sr isotopes, an anion exchange column was connected with a Sr Spec column[6,7]. In this study, U and Sr radionuclides were sequentially purified with UTEVA and Sr resin[4,8] after purifying Pu isotopes with anion exchange resin.

The sample solution with an 8 M HNO_3 medium was passed through a pre-conditioned anion exchange resin (Bio-Rad, 100-200 Mesh) column (inner diameter; 10 mm, resin bead length; 120 mm) with 8 M HNO_3 at the rate of 0.5 mL/min. The column was then washed with 20 mL of 8 M HNO_3 to remove the hindrance nuclides. The effluent (passing and washing solution) was reserved for sequential separation of U and Sr radionuclides. Columns were washed with 20 mL of 9 M HCl to desorb the Th. Finally, Pu isotopes were eluted with 20 mL of 0.1 M NH_4I-12 M HCl.

UTEVA and Sr resin columns were obtained as cartridges containing 1 g of each resin from Eichrom company. Small particle size (50-100 µm) resin was employed, along with a vacuum extraction system. UTEVA and Sr resin cartridges were stacked on the vacuum jar from top to bottom, in that order. The resins were conditioned with 10 mL of 8 M HNO_3. The sample solution eluted from the anion exchange column was then loaded onto the cartridge at a rate of 0.5 mL/min. Beakers and columns were washed with 2 × 5 mL of 8 M HNO_3.

After this step, the cartridges were separated. The UTEVA column containing U isotopes was washed with 5 mL of 8 M HCl. This rinse converted the resin to the chloride system and removed a small amount of neptunium isotopes. To remove neptunium and thorium isotopes, 20 mL of 5 M HCl-0.05 M oxalic acid was added into the column. The uranium isotopes were eluted with 15 mL of 0.01 M HCl.

After Sr Spec columns were separated from stacked columns on the vacuum bottle, the Sr Spec column was washed with 10 mL of 3 M HNO_3-0.05 M oxalic acid for removing the trace levels of Pu and Np isotopes passed from the front columns. The columns were washed with an additional 5 mL of 8 M HNO_3 to remove the alkaline earth metal interferences such as K^+, Ca^{2+} and Ba^{2+}. Finally, Sr was stripped with 10 mL of 0.05 M M HNO_3.

Source preparation of Pu, U, Am and Sr nuclides: A tracer level (about 1 Bq) of ^{242}Pu and ^{233}U was used for comparing properties of electrodeposition and micro-coprecipitation. After electrodepositing[9,10] and micro-coprecipitating[11-13] them, the ^{242}Pu and ^{233}U isotopes were measured by α-spectrometry.

The purified Pu and U fractions were evaporated to dryness. The residue was dissolved in 1 mL of concentrated HNO_3 and evaporated to dryness. The purified isotopes were coprecipitated with neodymium fluoride[13]. After source preparation, the Pu and U isotopes were measured by α-spectrometry.

For a chemical yield of ^{90}Sr, 1 mL was taken from the purified Sr solution and the concentration of stable Sr element with an ICP-AES was measured. The remaining the purified Sr solution was transferred to low diffusion polyethylene vial and mixed with 11 mL of liquid scintillation cocktail. Strontium-90 was analyzed by liquid scintillation counting[14].

RESULTS AND DISCUSSION

Decomposition of sample matrix: Complete decomposition of the soil matrix is important for radiochemical analysis in environmental samples, because destruction of soil matrices makes it possible to help isotopic exchange and convert the nuclides to an ionic form that can undergo chemical reactions. As presented in Tables 1 and 2, the activity concentrations of $^{239,240}Pu$ and ^{238}U with total decomposition method were close to the recommended value reported by the IAEA. However, the activity concentrations of $^{239,240}Pu$ and ^{238}U with an acid leaching method were a little lower than the recommended

TABLE-1
ACTIVITY CONCENTRATIONS OF $^{239,240}Pu$ IN THE IAEA-375 REFERENCE MATERIALS

Separation method	Decomposition method	Sequential determination	Activity concentration of $^{239,240}Pu^a$ (Bq/kg)		Chemical yield (%)
			Recommended values	Mean concentration	
Anion exchange (Bio-rad) [Ref. 15]	Acid leaching (8M HNO_3)	Possible	0.30	0.27 ± 0.10^b	74 ± 5^b
Anion exchange (Bio-rad)^c	Total decomposition (con. HNO_3 + HF)	Possible	0.30	0.33 ± 0.09	77 ± 4
Extraction chromatography (TEVA)[Ref. 16]	Total decomposition (con. HNO_3+HF)	Possible	0.30	0.29 ± 0.06	73 ± 5
Solvent extraction (TOPO)[Ref. 17]	Total decomposition (con. HNO_3+HF)	Difficult	0.30	0.35 ± 0.08	65 ± 7

^{a}Number of aliquots analyzed is 3; ^{b}Error is 1σ; ^{c}This paper

TABLE-2
ACTIVITY CONCENTRATIONS OF ^{238}U IN THE IAEA-375 REFERENCE MATERIALS

Separation method	Decomposition method	Sequential determination	Activity concentration of ^{238}U^a (Bq/kg)		Chemical yield (%)
			Recommended values	Mean concentration	
Extraction chromatography (UTEVA)^b	Acid leaching (8 M HNO$_3$)	Possible	24.4	20.3 ± 1.5^c	81 ± 6^c
Extraction chromatography (UTEVA)^b	Total decomposition (con. HNO$_3$ + HF)	Possible	24.4	25.2 ± 1.6	78 ± 4
Anion exchange (Bio-rad) [Ref. 18]	Total decomposition (con. HNO$_3$ + HF)	Possible	24.4	26.4 ± 1.9	72 ± 4
Solvent extraction (TBP) [Ref. 19]	Total decomposition (con. HNO$_3$ + HF)	Difficult	24.4	26.9 ± 2.1	78 ± 6

^{a}Number of aliquots analyzed is 3; ^{b}This paper; ^{c}Error is 1σ

TABLE-3
ACTIVITY CONCENTRATIONS OF ^{90}Sr IN THE IAEA-375 REFERENCE MATERIALS

Separation method^b	Decomposition method	Sequential determination	Activity concentration of ^{90}Sr^a, (Bq/kg)		Chemical yield (%)
			Recommended values	Mean concentration	
Sr Spec	Acid leaching (8 M HNO$_3$)	Possible	108	115 ± 11.4^c	79 ± 7^c
Sr Spec	Total decomposition (con. HNO$_3$ + HF)	Possible	108	103 ± 9.4	74 ± 5

^{a}Number of aliquots analyzed is 3; ^{b}This paper; ^{c}Error is 1σ

value reported by the IAEA, though the variation of the activity concentrations of ^{239,240}Pu with the acid leaching method and the recommended value is allowable, considering uncertainty of the determination of ^{239,240}Pu. This means that the acid leaching method is not enough to completely leach the oxides of plutonium and uranium in the soil matrix. Therefore, to analyze Pu and U isotopes in the soil, total depomposition method must be used, though the total depomposition method is time consuming and requires expensive Teflon beakers. However, the activity concentrations of ^{90}Sr with the acid leaching method were close to the recommended value reported by the IAEA, as shown in Table-3. Also, the activity concentrations and chemical yields of ^{90}Sr with the acid leaching method were similar to those with the total decomposition method. This means that with 8 M HNO$_3$, ^{90}Sr isotopes were easily leached into acid solution from the soil matrix.

Separation of Pu, Sr and U isotopes: Activity concentrations of ^{239,240}Pu in the IAEA-375 reference material with different separations method were presented in Table-1. Activity concentrations of ^{239,240}Pu in the IAEA-375 reference material with the anion exchange, the extraction chromatography and solvent extraction method were close to the recommended value reported by the IAEA. However, the analytical cost of the anion exchange method is cheaper than the extraction chromatography method. Also, it is difficult to determine sequentially activity concentrations for Pu, U and Sr isotopes with the solvent extraction method.

As presented in Table-2, activity concentrations of ^{238}U in the IAEA-375 reference material with different separations method were close to the recommended value reported by the IAEA, except for those with the acid leaching method. For the samples contaminated with high activity concentration of Pu and Am isotopes, the determination of uranium isotopes with the anion exchange method or solvent extraction method is insufficient to completely separate U isotopes from Pu and Am isotopes[15]. Therefore, to obtain precise and accurate data on the U isotopes in highly contaminated samples, it is

necessary to completely separate the uranium isotopes from transuranium elements with the extraction chromatography method.

Source preparation for measuring Pu and U isotopes: There are a number of a source preparation methods, such as a direct evaporation, an electrodeposition and a micro-coprecipitation, this paper compares the electrodeposition method and the micro-coprecipitation method. As shown in Fig. 2, recoveries of the actinides (^{242}Pu, ^{233}U) with electrodeposition methods and micro-coprecipitation methods were over 90 %. Recoveries of the actinides with Talvitie's method (Electrodep-1)[9] were similar to those with Lee's method (Electrodep-2)[10]. However, for preparation of a source, Lee's method is more convenient than Talvitie's method, because Talvitie's method requires accurate control of pH adjustment and free of iron and organic materials in the deposition solution. Also, recoveries of the actinides with the Nd coprecipitation method were similar to those with the Ce and La coprecipitation methods.
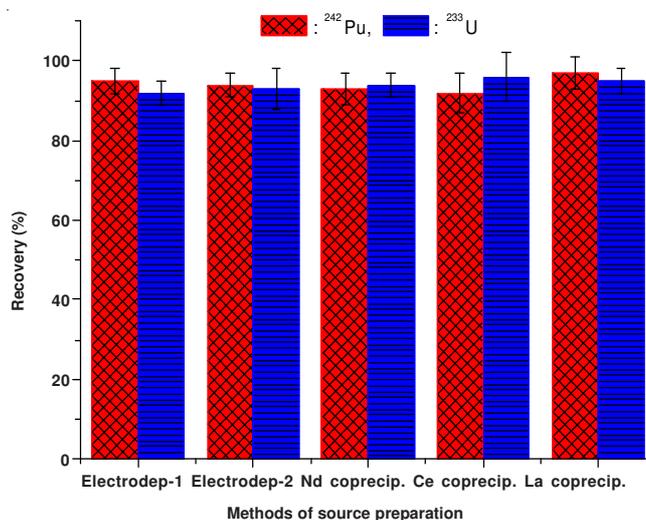

Fig. 2. Recoveries using electrodeposition and microcoprecipitation methods

As shown in Fig. 3, the α-peak resolution for the actinides with the electrodeposition methods was found to be in the range of 20 keV to 30 keV. The α-peak resolution for the actinides with the electrodeposition methods was better than that with micro-coprecipitation methods. Especially, the α-peak resolution for the actinides with La coprecipitation method was too large to distinguish α-peaks, so that it is difficult to use for a source preparation. However, for analyzing ^{241}Pu by a LSC or ^{239}Pu and ^{240}Pu by a TIMS after measuring α-peaks by alpha spectrometry, in the electrodeposition method, it is necessary to remove Fe or Ni ions dissolved from an electroplating plate with an ion exchange resin. However, in the micro-coprecipitation method, the Pu isotopes are measured directly by a LSC or a TIMS after dissolving the Pu isotopes from the membrane filter. Therefore, the micro-coprecipitation method with the Nd and Ce element is more useful for the alpha source preparation than the electrodeposition method, because electrodeposition requires rather elaborate equipment which is difficult to maintain and is plagued with problems, such as current fluctuations and pH changes during an electrodeposition.
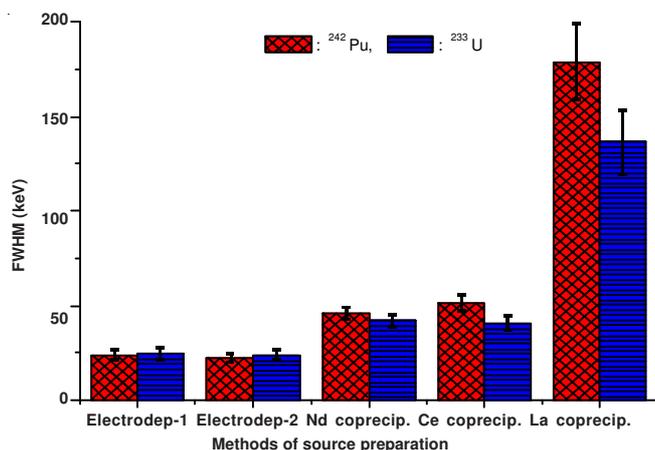

Fig. 3. Energy resolutions using electrodeposition and microcoprecipitation methods

Conclusion

In this study, we developed a rapid and quantitative sequential separation method for Pu, U and Sr isotopes in an environmental sample and validated the method by application to the IAEA reference soil. Regarding the destruction of the sample matrix, the acid leaching method was compared with the total decomposition method. The activity concentrations of ^{239,240}Pu and ^{238}U in the IAEA-375 reference soil with an acid leaching method were a little lower than the recommended value reported by the IAEA, while the activity concentrations of ^{90}Sr with the acid leaching method were close to the recommended value reported by the IAEA.

Activity concentrations of ^{239,240}Pu, ^{238}U and ^{90}Sr in the IAEA-375 reference material with sequential separation methods such as the anion exchange method and the extraction chromatographic methods were close to the recommended value reported by the IAEA.

After comparing a source preparation methods, recoveries of the actinides such as ^{242}Pu and ^{233}U with electrodeposition methods were similar to those with micro-coprecipitation methods. Though the α-peak resolution for the actinides with the electrodeposition methods was better than that with micro-coprecipitation methods, the micro-coprecipitation methods are useful for the alpha source preparation, because the micro-coprecipitation method is simple for a source preparation.

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