

## A SIMPLE AND QUANTITATIVE DETERMINATION OF PU ISOTOPES IN SOIL SAMPLES

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**Abstract** - An accurate and simple analytical technique for low levels of fallout Pu in the environment was developed using an anion exchange resin. To develop the reliable determination of Pu isotopes in soil samples, decomposition of soil matrix, plutonium oxidation state adjustment on the anion exchange column and source preparation of Pu isotopes have been carried out. The optimum method of Pu isotopes with an anion exchange has been validated by application to IAEA-Reference soils.

### INTRODUCTION

A determination of plutonium isotopes in soil samples is generally complicated, because chemical recoveries are variable due to interference from major salt ions, the so-called "matrix effects". Also, Pu isotopes have no stable counterparts and exist simultaneously in several valences ( $\text{Pu}^{3,4,5,6+}$ ) in the environment.

The determination of low levels of fallout Pu isotopes requires lengthy and tedious chemical processes, which include techniques such as ion exchange[1], a liquid-liquid extraction[2], precipitation[3] and adsorption[4] for separating and preconcentrating the nuclides. Recently, a novel extraction chromatographic resin (TRU and TEVA Spec resin) has been developed by Horwitz and co-workers capable of selective extraction of the actinides[5]. However, TRU Spec resin is expensive, so that it is not suitable to determine Pu isotopes for routine environmental samples.

Among the analytical methods of Pu, the anion exchange method is commonly used for separation of plutonium from other hindrance

elements. Before loading the solution containing Pu isotopes on an anionic exchanger, the Pu species in the leaching solution extracted from soil sample with 8 M  $\text{HNO}_3$  can exist in up to four oxidation states such as Pu (III), Pu (IV), Pu (V) and Pu (VI) at one time. Among the oxidation states of Pu,  $\text{Pu}^{4+}$  are strongly absorbed on the anion exchange resin as anionic complexes ( $\text{Pu}(\text{NO}_3)_6^{2-}$ ,  $\text{Pu}(\text{Cl})_6^{2-}$ ) in the nitric and hydrochloric acid media. Therefore, it is important to adjust and maintain the valences of Pu through the anionic exchange step for a quantitative and reliable separation of Pu from other nuclides. In this study, a simple and reliable determination method of Pu isotopes using an anion exchange resin was developed and validated by application to IAEA-Reference soils.

### EXPERIMENTAL METHODS

#### 1. Radiochemical separation

A flow chart of the determination of Pu isotopes is shown in Fig. 1.

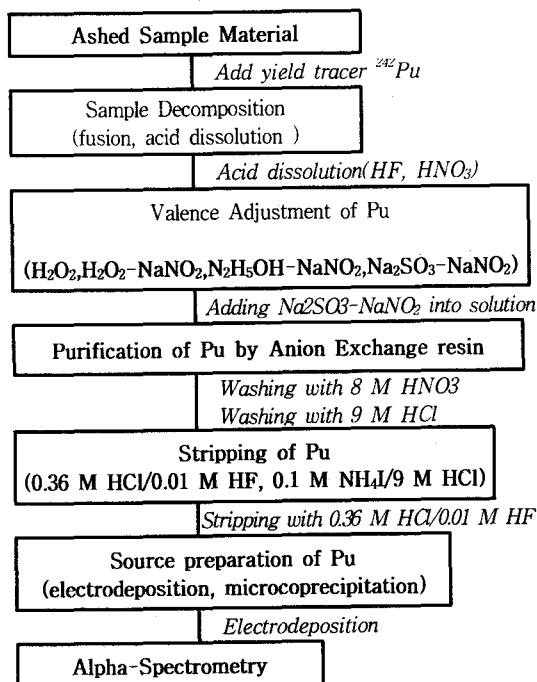


Fig. 1. Analytical procedure for separation of Pu isotopes

### 1-1. Sample decomposition

A total of 50 g of soil was weighed into a porcelain dish and ashed in a muffle furnace with a gradual heating program up to 600 °C to eliminate organic matter. To compensate chemical recovery,  $^{242}\text{Pu}$  standard solution as a yield tracer was added into the soil sample. In this study two decomposition methods such as fluoride-pyrosulfate fusion[6] and acid dissolution method[7] were compared.

For destroying soil matrix with fluoride-pyrosulfate fusion, ash samples were transferred into platinum dish and evaporated to dryness with 50 ml of 65 % HNO<sub>3</sub> and 30 ml of 48 % HF and then fused with fluoride with 40 g of anhydrous potassium fluoride at 850°C. The cooled fluoride melt was transposed with 20 ml of concentrated sulfuric acid and heated until SO<sub>3</sub> fumes were emitted. The residue was fused with 40 g of sodium sulfate at 700 - 800 °C to ensure complete dissolution of any remaining insoluble materials. Also, for using acid dissolution method, calcined samples were transferred into Teflon beaker and 50 ml of 48 % HF were added. The mixture was stirred and

boiled gently to promote dissolution and removal silica. When the mixture had been evaporated to a paste, a second addition of 50 ml of 48 % HF was made and the evaporation was repeated. Then 50 ml of 65 % HNO<sub>3</sub> were added and the mixture was again evaporated to a paste. This evaporation was repeated two more times.

### 1-2. Plutonium separation by anion exchange

The residue was dissolved with 50 ml of 8 M HNO<sub>3</sub>. The solution was centrifuged and filtered through a 0.2 μm pore size filter. To accomplish valence adjustment of plutonium in nitric solution, four methods such as H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> - NaNO<sub>2</sub>[8], N<sub>2</sub>H<sub>5</sub>OH - NaNO<sub>2</sub>[9] and Na<sub>2</sub>SO<sub>3</sub> - NaNO<sub>2</sub>[10] were carried out. After adjusting Pu<sup>4+</sup>, the sample solution was passed through a pre-conditioned anion exchange column with 8 M HNO<sub>3</sub> at the rate of 1 ml/minute. The column was then washed with 120 ml of 8 M HNO<sub>3</sub> for removing hindrance nuclides. Columns were washed with 250 ml of 9 M HCl. Finally, Pu is stripped with 20 ml of 0.36 M HCl/0.01 M HF or 50 ml of 0.1 M NH<sub>4</sub>I/9 M HCl solution.

### 2. Source preparation of Pu isotopes

The purified Pu fraction was evaporated to dryness. The residue was dissolved in 2 ml of concentrated HCl for destroy any organic and evaporated to dryness. Pu isotopes was electroplated on stainless steel platelets[11]. Also, Pu isotopes was microcoprecipitated with NdF<sub>3</sub> on the 0.1 μm membrane filter[12].

### 3. Measurement of Pu isotopes

Pu isotopes were measured by alpha-spectrometry. The alpha spectrometer (OASIS, OXFORD) was equipped with eight 450 mm<sup>2</sup> Canberra PIPS (passivated ion implanted planar silicon) detectors. The alpha peak detection efficiencies were 23 to 28 %. Typical alpha resolution (FWHM) was 21 keV at 5.486 MeV of  $^{241}\text{Am}$ .

## RESULTS AND DISCUSSION

### 1. Decomposition of soil matrix

Complete decomposition of soil matrix is important for radiochemical analysis in environmental samples, because destruction of soil matrix make it possible to help isotopic exchange and convert the nuclides to an ionic form that can undergo chemical reactions. As presented in Table 1, the chemical recovery of acid leaching was similar to that of fluoride-pyrosulfate fusion. However, even if the fusion procedure is a proven decomposition method, it is time consuming, requires expensive platinum dishes and is relatively dangerous, especially for an inexperienced analyst. Therefore, though the acid dissolution procedure is not as powerful as the fusion, acid leaching is very convenient decomposition method for routine environmental samples. However, with only strong mineral acid (HCl, HNO<sub>3</sub>), Pu isotopes is effectively extracted from soil component into acidic solution in the determination of global fallout Pu in environmental samples[10].

### 2. Plutonium oxidation state adjustment

Many reducing and oxidizing reagents such as H<sub>2</sub>O<sub>2</sub>, NaNO<sub>2</sub>, Fe(NH<sub>2</sub>SO<sub>3</sub>)<sub>2</sub>, Na<sub>2</sub>SO<sub>3</sub> and hydrazinium hydroxide (N<sub>2</sub>H<sub>5</sub>OH) have been used to stabilize Pu (IV). In this study, four valence adjustment methods of Pu were

conducted and presented in Table 1. The chemical yields of plutonium with H<sub>2</sub>O<sub>2</sub> were found to be lower than other the redox-systems. Therefore, only H<sub>2</sub>O<sub>2</sub> without NaNO<sub>2</sub> is not sufficient to stabilize Pu oxidation state (IV), because the oxidation state of Pu is not stable during the separation step with anion exchange column. Also, Qingjiang reported that the traces of <sup>238</sup>U and <sup>234</sup>U were detected in the purified Pu fraction, using H<sub>2</sub>O<sub>2</sub> to adjust Pu valence state (IV)[10]. The high chemical yields of plutonium using redox-systems such as H<sub>2</sub>O<sub>2</sub> - NaNO<sub>2</sub>, N<sub>2</sub>H<sub>5</sub>OH - NaNO<sub>2</sub> and Na<sub>2</sub>SO<sub>3</sub> - NaNO<sub>2</sub> were obtained in the IAEA Reference soil. However, when H<sub>2</sub>O<sub>2</sub> - NaNO<sub>2</sub> is applied for valence adjustment of plutonium, it needs a standing time after adding H<sub>2</sub>O<sub>2</sub> - NaNO<sub>2</sub> to the sample solution, as the Pu (III) is rapidly oxidized by H<sub>2</sub>O<sub>2</sub> - NaNO<sub>2</sub>; but the Pu (V, VI) are rather slowly reduced to Pu (IV)[13]. Also, valence adjustment of Pu with N<sub>2</sub>H<sub>5</sub>OH - NaNO<sub>2</sub> is somewhat tedious and complicated, though the reaction is more powerful and effective than other reagents. It was reported that Pu<sup>4,5,6+</sup> was easily reduced by Na<sub>2</sub>SO<sub>3</sub> and then the Pu<sup>2+</sup> was oxidized to Pu<sup>4+</sup> by NaNO<sub>2</sub>, using Na<sub>2</sub>SO<sub>3</sub> - NaNO<sub>2</sub>. Therefore, Na<sub>2</sub>SO<sub>3</sub> and NaNO<sub>2</sub> agents are recommendable for adjusting Pu<sup>4+</sup>, because oxidation and reduction of Pu are fast and quantitative.

### 3. Separation of plutonium from other elements

Table 1. Comparison of the chemical yield of plutonium in soils by deposition method, redox-systems and stripping agent

Deposition Method	oxidizing Agent	Reducing Agent	Stripping Agent	Chemical yield <sup>242</sup> Pu(%)
Acid leaching		H <sub>2</sub> O <sub>2</sub>	0.01M HF/0.36M HCl	67.2±7.4
Acid leaching	H <sub>2</sub> O <sub>2</sub> or NaNO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub> or NaNO <sub>2</sub>	0.01M HF/0.36M HCl	82.7±5.7
Acid leaching	NaH <sub>5</sub> OH	NaNO <sub>2</sub>	0.01M HF/0.36M HCl	85.8±9.0
Acid leaching	NaH <sub>5</sub> OH	NaNO <sub>2</sub>	0.1M NH <sub>4</sub> I/9M Hcl	84.7±6.0
Fusion	NaH <sub>5</sub> OH	NaNO <sub>2</sub>	0.01M HF/0.36M HCl	83.9±7.5
Acid leaching	Na <sub>2</sub> SO <sub>3</sub>	NaNO <sub>2</sub>	0.01M HF/0.36M HCl	86.2±6.8
Acid leaching	Na <sub>2</sub> SO <sub>3</sub>	NaNO <sub>2</sub>	0.01M HF/0.36M HCl	83.7±7.5
Fusion	Na <sub>2</sub> SO <sub>3</sub>	NaNO <sub>2</sub>	0.01M HF/0.36M HCl	85.2±7.2

**Table 2.** Comparison of resolutions and chemical with different source preparation, and concentrations of  $^{239,240}\text{Pu}$  in the IAEA-Reference soil with anion exchange resin method

	Source preparation	FWHM $^{239,240}\text{Pu}$ (KeV)	Chemical yield $^{242}\text{Pu}$ (%)	Concentration of $^{239,240}\text{Pu}$ (Bq/kg)	
				Recommended value	Anion exchange method
IAEA-SOIL-6	Electrodeposition	22.1	84.8±9.8	1.04	0.91±0.20
IAEA-SOIL-6	Microcoprecipitation	53.4	86.3±8.4	1.04	0.89±0.14
IAEA-375	Electrodeposition	24.8	85.1±7.4	0.30	0.34±0.05
IAEA-375	Microcoprecipitation	55.4	83.8±5.2	0.30	0.28±0.04

Pu (IV) and Th (IV) are strongly sorbed on the resin as anionic nitrate complexes while U (VI) is only weakly sorbed. Also, Am (III) and Sr (II) as well as Fe (II), Ca (II), Mg (II), Al (III), Ti (IV), REEs and other soil matrix components are not retained on the anion resin column and therefore pass completely through it. The column was then washed with 100 ml of 8 M  $\text{HNO}_3$  for removing hindrance nuclides such as traces of U isotopes weakly sorbed on the column. Thorium was desorbed from the column by passing through 200 ml of 9 M HCl. Plutonium (IV) is retained by the column as anionic chloride complexes. Finally plutonium was stripped from the column by passing through 20 ml of 0.36 M HCl/0.01 M HF solution or 50 ml of 0.1 M  $\text{NH}_4\text{I}$ /9 M HCl solution. HF or  $\text{NH}_4\text{I}$  reduces Pu (IV) to Pu (III), which does not form an anionic chloride complex. As presented Table 1, the chemical yields with 0.36 M HCl/0.01 M HF were similar to those with 0.1 M  $\text{NH}_4\text{I}$ /9 M HCl. However, in the stripping Pu isotopes, 0.36 M HCl/0.01 M HF is preferable due to small volume (20 ml) of 0.36 M HCl/0.01 M HF (0.1 M  $\text{NH}_4\text{I}$ /9 M HCl; 50 ml).

#### 4. Source preparation of Pu isotopes

The recoveries and resolutions of for the electrodeposition and microcoprecipitation are shown in Table 2. The resolution of electrodeposition was better than that of microcoprecipitation,

though the chemical recoveries were similar. Especially, measuring very low activity of fallout Pu prepared by microcoprecipitation, it is difficult to distinguish the peaks of Pu isotopes such as  $^{242}\text{Pu}$ ,  $^{239,240}\text{Pu}$  and  $^{238}\text{Pu}$  due to bad resolution. Therefore, electrodeposition method can be used as a sample preparation for low activity of fallout Pu due to excellent peak resolution, even if this method is time consuming and required elaborate electroplating system.

#### 5. Validation of the anion exchange method

The determination of Pu isotopes with an anion exchange resin was validated by its application to IAEA-Reference samples. As shown in Table 2, the concentrations of  $^{239,240}\text{Pu}$  in the IAEA-SOIL 6 and IAEA-375 samples were consistent with the reference values reported by the IAEA. Therefore, the anion exchange resin method investigated in this study make it possible to be used for determining low levels of fallout Pu in the environment.

## CONCLUSIONS

In this work, decomposition of soil matrix, plutonium oxidation state adjustment on the anion exchange column and source preparation

of Pu isotopes have been investigated. From this investigation, the following conclusions are drawn.

1. Acid leaching method is convenient for decomposition of soil matrix in the routine environmental samples.
2.  $\text{Na}_2\text{SO}_3$  and  $\text{NaNO}_2$  agents are recommendable for adjusting  $\text{Pu}^{4+}$ .
3. 0.36 M HCl/0.01 M HF is suitable for stripping Pu isotopes from the anion exchange column.
4. Electrodeposition method can be used as a sample preparation for low activity of fallout Pu due to excellent peak resolution.
5. The concentrations of  $^{239,240}\text{Pu}$  in the IAEA Reference samples using the optimum method of Pu isotopes with an anion exchange were consistent with the reference values reported by the IAEA.
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