Determination of plutonium, uranium and americium/curium isotopes in environmental samples with anion exchange, UTEVA, Sr and DGA resin

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(Received December 15, 2009; accepted in revised form November 12, 2010)

Actinides / Strontium / Environmental samples / Anion exchange / Extraction chromatography

Summary. This study presents a quantitative sequential radiochemical separation method for the Pu, U, Sr and Am/Cm isotopes with an anion exchange resin, UTEVA resin, Sr resin and DGA resin in environmental samples. After the radionuclides were leached from samples with 8 M HNO₃, the Pu, U, Sr and Am/Cm isotopes were sequentially adsorbed on the anion exchange column, UTEVA column connected with Sr Spec column and DGA 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, ⁹⁰Sr was separated from other hindrance elements such as Ca²⁺, Ba²⁺ and Y³⁺ with the Sr Spec column. Finally, Am/Cm fractions were purified with the DGA and anion exchange resins. After a source preparation for the purified Pu, U and Am/Cm isotopes with the micro-coprecipitation method, the Pu, U and Am/Cm isotopes were measured by an alpha spectrometry. Strontium-90 was measured by a low level liquid scintillation counter. The radiochemical procedure for Pu, U and Am nuclides investigated in this study has been validated by application to IAEA Reference soils.

1. Introduction

The major nuclear weapon tests conducted in the 50s and early 60s caused worldwide contamination. The determination of radionuclides resulting from global fallout and discharges from nuclear facilities is obviously important in view of the public health and public concern about the hazards of radionuclide pollutants in the environment. For obtaining reliable data for the activity concentration of radionuclides, the analysis of plutonium, uranium, americium, curium and radiostrontium at extremely low levels in the environment requires a large amount of samples. The methods of analysis of radionuclides have always been time consuming regarding sample treatment and the radiochemical separation procedures of large amounts of sample material. In an emergency situation a rapid and reliable analytical method of radionuclides is desirable.

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, americium, curium and radiostrontium in environmental and radioactive waste 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, Sr and Am 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 radioisotopes in environmental and radioactive waste samples based on the alpha spectrometry following radiochemical separation by ion exchange and extraction chromatography after decomposition of sample matrix. The sequential analytical method for Pu, U, ⁹⁰Sr and ²⁴¹Am nuclides investigated in this study has been validated by application to IAEA Reference materials.

2. Method development

Most of the radiochemical protocols follow three main steps: sample decomposition, radiochemical separation, and source preparation before measurement. A flow chart of the analytical procedure for Pu, U, ⁹⁰Sr and ²⁴¹Am isotopes in the nitric acid medium is shown in Fig. 1.
2.1 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 °C to eliminate organic matter, the sample was transferred to a Teflon beaker. A strontium carrier (about 1 ppm) and spikes of $^{242}$Pu, $^{232}$U, and $^{243}$Am 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.

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).

2.2 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, Sr and Am radionuclides were sequentially purified with UTEVA [4, 8], Sr and DGA resins [9, 10] 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/minute. The column was then washed with 20 mL of 8 M HNO$_3$ to remove U isotopes. The effluent (passing and washing solution) was reserved for sequential separation of U, Sr and Am 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$_3$I – 12 M HCl.

The UTEVA, Sr and DGA 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. The UTEVA, Sr and DGA 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 Np 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 the Sr Spec column was separated from the stacked columns, it was washed with 10 mL of 3 M HNO$_3$ – 0.5 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 HNO$_3$.

The DGA columns were rinsed with 3 mL of 1 M HNO$_3$, followed by 10 mL of 0.1 M HNO$_3$ to remove interferences. The DGA columns were stripped with 15 mL of 0.25 M HCl to elute americium and curium. The residue was dissolved in 20 mL of 1 M HNO$_3$ – 93% CH$_3$OH with gentle heating and stirring. The column for removing rare earth elements (REEs) was prepared from Bio Rad AG 1 × 4 resin (mesh; 100–200, inner diameter; 1 cm, column length; 1.2 cm). The column was conditioned with 100 mL of 1 M HNO$_3$ – 93% methanol. Samples were loaded onto the column followed by washing with 50 mL of 1 M HNO$_3$ – 93% methanol. Americium is adsorbed on the column together with REEs and traces of Pb and U, etc., while any remaining traces of Fe pass through the column. The column was washed with
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80 mL of 0.1 M HCl – 0.5 M NH₄SCN – 80% methanol to remove REEs and traces of U isotopes. A wash with 20 mL of 1 M HNO₃ – 93% methanol was performed. Am was stripped with 20 mL of 0.5 M HCl.

2.3 Source preparation of Pu, U, Am and Sr nuclides
A tracer level (about 1 Bq) of ²³²Pu, ²³³U, ²⁴³Am and ²⁴⁴Cm was used for comparing properties of electrodeposition and micro-coprecipitation. After electrodeposition [11, 12] and micro-coprecipitation [13–15], the ²³²Pu, ²³³U, ²⁴³Am and ²⁴⁴Cm isotopes were measured by alpha spectrometry.

The purified Pu, U and Am fractions were evaporated to dryness. The residue was dissolved in 1 mL of concentrated HNO₃ and evaporated to dryness. The purified isotopes were coprecipitated with neodymium fluoride [15]. After source preparation, the Pu, U and Am isotopes were measured by alpha spectrometry.

Table 1. Activity concentrations of ²³⁹,²⁴⁰Pu in the IAEA-375 reference materials.

<table>
<thead>
<tr>
<th>Separation method</th>
<th>Decomposition method</th>
<th>Sequential determination</th>
<th>Recommended values</th>
<th>Mean concentration</th>
<th>Chemical yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion exchange (Bio-Rad) [17]</td>
<td>Acid leaching (8 M HNO₃)</td>
<td>Possible</td>
<td>0.30</td>
<td>0.27 ± 0.10⁶</td>
<td>74 ± 5b</td>
</tr>
<tr>
<td>Anion exchange (Bio-Rad)⁵</td>
<td>Total decomposition (con. HNO₃ + HF)</td>
<td>Possible</td>
<td>0.30</td>
<td>0.33 ± 0.09</td>
<td>77 ± 4</td>
</tr>
<tr>
<td>Extraction chromatography (TEVA) [18]</td>
<td>Total decomposition (con. HNO₃ + HF)</td>
<td>Possible</td>
<td>0.30</td>
<td>0.29 ± 0.06</td>
<td>73 ± 5</td>
</tr>
<tr>
<td>Solvent extraction (TOPO) [19]</td>
<td>Total decomposition (con. HNO₃ + HF)</td>
<td>Difficult</td>
<td>0.30</td>
<td>0.35 ± 0.08</td>
<td>65 ± 7</td>
</tr>
</tbody>
</table>

a: Number of aliquots analyzed is 3; b: Error is 1σ; c: This paper.

Table 2. Activity concentrations of ²³⁸U in the IAEA-375 reference materials.

<table>
<thead>
<tr>
<th>Separation method</th>
<th>Decomposition method</th>
<th>Sequential determination</th>
<th>Recommended values</th>
<th>Mean concentration</th>
<th>Chemical yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction chromatography (UTEVA)⁵</td>
<td>Acid leaching (8 M HNO₃)</td>
<td>Possible</td>
<td>24.4</td>
<td>20.3 ± 1.5c</td>
<td>81 ± 6c</td>
</tr>
<tr>
<td>Extraction chromatography (UTEVA)⁵</td>
<td>Total decomposition (con. HNO₃ + HF)</td>
<td>Possible</td>
<td>24.4</td>
<td>25.2 ± 1.6</td>
<td>78 ± 4</td>
</tr>
<tr>
<td>Anion exchange (Bio-Rad) [20]</td>
<td>Total decomposition (con. HNO₃ + HF)</td>
<td>Possible</td>
<td>24.4</td>
<td>26.4 ± 1.9</td>
<td>72 ± 4</td>
</tr>
<tr>
<td>Solvent extraction (TBP) [21]</td>
<td>Total decomposition (con. HNO₃ + HF)</td>
<td>Difficult</td>
<td>24.4</td>
<td>26.9 ± 2.1</td>
<td>78 ± 6</td>
</tr>
</tbody>
</table>

a: Number of aliquots analyzed is 3; b: This paper; c: Error is 1σ.

For a chemical yield of ⁸⁰Sr, 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 [16].

3. Results and discussion
3.1 Decomposition of sample matrix
Complete decomposition of the soil matrix is important for radiocchemical 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 ²³⁹,²⁴⁰Pu and ²³⁸U
Table 3. Activity concentrations of 90Sr in the IAEA-375 reference materials.

<table>
<thead>
<tr>
<th>Separation method</th>
<th>Decomposition method</th>
<th>Sequential determination</th>
<th>Recommended values</th>
<th>Mean concentration</th>
<th>Chemical yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr Spec</td>
<td>Acid leaching (8 M HNO3)</td>
<td>Possible</td>
<td>108</td>
<td>115 ± 11.4&lt;sup&gt;c&lt;/sup&gt;</td>
<td>79 ± 7&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Sr Spec</td>
<td>Total decomposition (con. HNO3 + HF)</td>
<td>Possible</td>
<td>108</td>
<td>103 ± 9.4</td>
<td>74 ± 5</td>
</tr>
</tbody>
</table>

<sup>a</sup>: Number of aliquots analyzed is 3;  
<sup>b</sup>: This paper;  
<sup>c</sup>: Error is 1σ.

Table 4. Activity concentrations of 241Am in the IAEA-375 reference materials.

<table>
<thead>
<tr>
<th>Separation method</th>
<th>Decomposition method</th>
<th>Sequential determination</th>
<th>Recommended values</th>
<th>Mean concentration</th>
<th>Chemical yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction chromatography (DGA + AE)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Acid leaching (8 M HNO3)</td>
<td>Possible</td>
<td>0.13</td>
<td>0.15 ± 0.02&lt;sup&gt;d&lt;/sup&gt;</td>
<td>82 ± 6&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Extraction chromatography (DGA + AE)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Total decomposition (con. HNO3 + HF)</td>
<td>Possible</td>
<td>0.13</td>
<td>0.12 ± 0.01</td>
<td>85 ± 5</td>
</tr>
<tr>
<td>Extraction chromatography (TRU + AE)&lt;sup&gt;[6]&lt;/sup&gt;</td>
<td>Total decomposition (con. HNO3 + HF)</td>
<td>Possible</td>
<td>0.13</td>
<td>0.14 ± 0.01</td>
<td>79 ± 6</td>
</tr>
</tbody>
</table>

<sup>a</sup>: Number of aliquots analyzed is 3;  
<sup>b</sup>: Anion exchange resin;  
<sup>c</sup>: This paper;  
<sup>d</sup>: Error is 1σ.

with total decomposition method were close to the recommended value reported by the IAEA. However, the activity concentrations of 238U with an acid leaching method were a little lower than the recommended value reported by the IAEA. This means that the acid leaching method is not enough to completely leach the uranium in the soil matrix. Therefore, to analyze U isotopes in the soil, total decomposition method must be used, though the total decomposition method is time consuming and requires expensive Teflon beakers.

The activity concentrations of 90Sr and 241Am with the acid leaching method were close to the recommended value reported by the IAEA, as shown in Tables 3 and 4. Also, the activity concentrations and chemical yields of 90Sr and 241Am with the acid leaching method were similar to those with the total decomposition method. This means that with 8 M HNO3, 90Sr and 241Am isotopes which is decay product from 241Pu, were easily leached into acid solution from the soil matrix.

### 3.2 Separation of Pu, Sr, U and Am isotopes

Activity concentrations of 239, 240Pu 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, Sr and Am isotopes with the solvent extraction method.

As presented in Table 2, activity concentrations of 238U 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 [22]. 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.

The separation of the actinides from environmental samples, especially those in the trivalent state like 241Am has been a complicated and time-consuming task. Recently, the chromatographic resins for extraction such as TRU,
UTEVA, and Diphonix resins have given an opportunity to develop fast and simple separation methods for many radionuclides [23–25]. The Diphonix resin shows high affinity towards Am(III), however, its elution is not as easy as with DGA Resin. The TRU and DGA resins have been reported as being suitable for separation of Am(III) with a high retention factor. The activity concentrations of 241Am using extraction chromatographic method with DGA and TRU resins were close to the recommended value reported by the IAEA, as shown in Table 4. Also, the chemical yield for 241Am with the DGA resin was close to that with the TRU resin, though the retention factor for Am(III) on the DGA resin in 8 M HNO3 medium is higher than that on the TRU [26]. In spite of the Am isotopes are purified from other hindrance nuclides such as Pu and U isotopes with the DGA or TRU resins in the soil sample, it is necessary to remove REEs in the Am fraction with the anion exchange resin or TEV A resin. In this study, the REEs were removed with the anion exchange resin, since the cost of the anion exchange resin is cheaper than that of the TEVA resin. However, with a radioactive waste sample that contains very low level of the rare earth elements, it is sufficient to purify the Am isotopes with DGA or TRU resins.

3.3 Source preparation for measuring Pu, U and Am isotopes

There are a number of α source preparation methods, such as direct evaporation, electrodeposition, and microcoprecipitation; this paper compares the electrodeposition method and the microcoprecipitation method. As shown in Fig. 2, recoveries of the actinides (242Pu, 232U, 243Am, 244Cm) with electrodeposition methods and microcoprecipitation methods were over 90%. Recoveries of the actinides with Talvitie’s method (Electrodep-1) [11] were similar to those with Lee’s method (Electrodep-2) [12]. However, for preparation of an α source, Lee’s method is more convenient than Talvitie’s method, because Talvitie’s method requires accurate control of pH and that the deposition solution is free of iron and organic materials. Also, recoveries of the actinides with the Nd coprecipitation method were similar to those with the Ce and La coprecipitation 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 alpha peaks, so that it is difficult to use for α source preparation. However, though the α-peak resolution with Nd or Ce coprecipitation method is over 30 keV, the peak of 241Am was distinguished from 243Am and 244Cm, as shown in Fig. 4. Also, for analyzing 241Pu by a LSC or 239Pu and 240Pu by thermal ionization mass spectrometry (TIMS) after measuring alpha 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 microcoprecipitation 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.

4. Conclusions

In this study, we developed a quantitative sequential separation method for Pu, U, Sr and Am/Cm 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 $^{238}\text{U}$ 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 $^{90}\text{Sr}$ and $^{241}\text{Am}$ with the acid leaching method were close to the recommended value reported by the IAEA.

Activity concentrations of $^{239,240}\text{Pu}$, $^{238}\text{U}$, $^{90}\text{Sr}$ and $^{241}\text{Am}$ 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 $\alpha$ source preparation methods, recoveries of the actinides such as $^{241}\text{Pu}$, $^{235}\text{U}$, $^{243}\text{Am}$ and $^{244}\text{Cm}$ with electrodeposition methods were similar to those with micro-coprecipitation methods. Though the $\alpha$-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 $\alpha$ source preparation.

Acknowledgment. This study was carried out under the Nuclear R&D program by Ministry of Education, Science and Technology of Korea.

References