Sequential Isotopic Determination of Plutonium, Thorium, Americium, Uranium, and Strontium in Air-Filter Sample

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Abstract. A procedure has been developed to provide sequential analysis of $^{238}$Pu, $^{230}$Th, $^{241}$Am, $^{238}$U, and $^{90}$Sr in NRIP glass-fiber filter samples. Tracers and/or carriers ($^{242}$Pu, $^{229}$Th, $^{243}$Am, $^{232}$U, and stable strontium) are added into the samples as chemical yield monitors, and then digested and extracted with nitric acid and hydrogen peroxide. Plutonium, thorium, strontium, americium, and uranium are sequentially separated and purified by Dowex ion-exchange resin, EiChroM Sr-resin, EiChroM TRU-resin, and Chelate-100 resin, respectively. The radioactivities of $^{90}$Sr and the actinides are measured using the liquid scintillation counter and alpha-particle spectrometer, respectively. This method is verified through comparing with the results of the U.S. National Institute of Standard and Technology NRIP2003 glass-fiber filters samples. The analytical results of $^{241}$Am, $^{238}$Pu, $^{230}$Th, $^{238}$U, and $^{90}$Sr agree with the NIST values within -2.1%, -3.6%, +0.7%, -0.6% and -1.8%, respectively. According to the traceability limits defined in ANSI N42.22, the ability (capability) has been demonstrated to be well below the criteria, i.e., 30%, 27%, 30%, 29% and 37% for $^{241}$Am, $^{238}$Pu, $^{230}$Th, $^{238}$U, and $^{90}$Sr, respectively.

1. Introduction

Radioisotopes of plutonium, thorium, americium, strontium and uranium in the environmental samples (such as soil, vegetation, water and air-filter) are frequently analyzed for both emergency and routine radiation monitoring. Health physicists use the analytical results to estimate the amount of radioactive material present in the environment and human body, calculating its burden for the radiological workers and the general public.

Chu, et al.[1] and several other investigators [2,3] have reported on the methods of individual analysis for isotopes of strontium, plutonium, americium, and uranium in environmental samples. Bakhtiar, et al.[4] have reported a method for simultaneous determination of strontium, thorium, plutonium, uranium, and americium in environmental samples. The method involved the addition of tracers and/or carriers as chemical yield monitors, and finally, the activities of strontium-90 and actinides were measured by gas proportional counting and alpha-particle spectrometry.

The radioisotopes are found in our routine air-filter samples at extremely low concentration. It takes much more time and costs in our laboratory for individual analysis of the radioisotopes in the air-filter samples. Therefore, an emerging need in our laboratory is to develop a improved method to provide rapid analytical results, with reduced analysis cost and fast turnaround time for emergency and routine works. To meet this challenge, a procedure is developed to provide sequential analysis of plutonium, thorium, americium, strontium and uranium in a single air-filter sample. In this study, one set of U.S. National Institute of Standard and Technology Radiochemical Intercomparison Program (NRIP) performance evaluation (PE) samples (5 spiked and 3 blank glass-fiber filter samples) which can be traceable to NIST primary standards were analyzed to validate the validation of this sequential analysis method.

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2. Experimental

2.1. Sample matrix

Five spiked and three blank NRIP2003 glass-fiber filter samples were analyzed in this study. There are five certified radionuclides in each matrix ($^{241}$Am, $^{239}$Pu, $^{230}$Th, $^{238}$U, and $^{90}$Sr), and the certified activity level range from 0.03-0.3 Bq per sample.[5,6] Additionally, some radionuclides ($^{226}$Ra, $^{237}$Np, $^{133}$Ba, $^{134}$Cs, $^{137}$Cs, $^{57}$Co, $^{58}$Co, $^{54}$Mn, and $^{65}$Zn) were also added into the samples as potential interferences.

2.2. Sample preparation

To determine the typical radiometric and gravimetric yields, the tracers ($^{242}$Pu, $^{229}$Th, $^{243}$Am, $^{232}$U) and carriers ($^{90}$Sr, $^{44}$Ca) were added into the samples. The samples combined with concentrated nitric acid were heated to boiling for 2 hours, and then filtered. The filtrates were heated to dryness. The sequential analysis flowchart is shown in Figure 1.

2.3. Plutonium and thorium separation

Each dried sample was dissolved in 3:2 nitric acid (100ml) and then introduced into an anion exchange column (Dowex 1x8, Cl-form, 100-200 mesh, SIGMA Chemical Co., U.S.A.) to affect isolation of plutonium and thorium. The column was rinsed with a further aliquot of 3:2 nitric acid (120ml) and the combined effluent (solution A) retained for strontium, americium and uranium isolation. The anion exchange column was washed with 5:1 hydrochloric acid (300ml) to remove the thorium species; plutonium was then removed from the column by reduction with a freshly prepared mixture of ammonium iodide [5%(w/v)] and conc. hydrochloric acid (29:71 by volume). The collected fractions of thorium and plutonium were heated to incipient dryness, treated with nitric and perchloric acid, and then electrolyzed for 2 hours with a platinum as an anode and a stainless steel plate as a cathode.

2.4. Strontium separation

Oxalic acid (20 g) was added to the retained fraction(solution A) from the plutonium and thorium separation, and the pH of the solution was adjusted to 4.2 to form the precipitation of oxalate. The oxalate was filtered through a Whatman 42 filter paper, and the filtrate(solution B) retained for americium and uranium isolation. The oxalate was dissolved in 8M nitric acid (10 ml), transfer to a Sr.Resin extraction chromatography column (EIChoM Industries Inc., U.S.A.), and then rinsed with a further aliquot of 8M nitric acid (15 ml). Twenty milliliter of water was added to the column to afford strontium removal. The effluent was collected and heated to dryness, and the strontium nitrate was then weighed to calculate the gravimetric yields of strontium. The strontium nitrate was dissolved in 8M nitric acid (20 ml), transfer to a polyethylene low-diffusion liquid-scintillation vial.

2.5. Americium separation

Carrier (Ca$^{2+}$, 100 mg), Oxalic acid (5 g) and ammonium oxalate (5 g) was added to the retained americium and uranium fraction (solution B), the pH of the solution was adjusted to 1.5, and the precipitation of oxalate is formed. The oxalate was filtered through a Whatman 42 filter paper, and the filtrate (solution C) retained for uranium isolation. The oxalate combined with the filter paper was ashed at 550 ℃ for 4 hours. The ashed samples were dissolved in the solution of 1 M Al(NO$_3$)$_3$ in 3 M HNO$_3$ (10 ml), and then transfer to a TRU.Resin extraction chromatography column (EIChoM Industries Inc., U.S.A.). Sequentially rinse the column with 2 M nitric acid (5 ml) and 0.5 M nitric acid (5 ml), and the effluent was discarded. Stripped the americium with 9 M hydrochloric acid (3 ml) and 4 M hydrochloric acid (15 ml). The eluate of hydrochloric acid was heated to incipient dryness, treated with nitric and perchloric acid, and then electrolyzed for 2 hours with a platinum as an anode and a stainless steel plate as a cathode.
2.6. Uranium separation

The retained uranium fraction (solution C) was heated to boiled for 10 minutes, and cooled to room temperature. Adjusted the pH value of solution to 3.0, and 10 ml of chelating resin (Chelex-100, Na-form; 50-100 mesh, SIGMA Chemical Co., U.S.A.) was added to the solution. Stirred for 2 hours, the uranium was adsorbed on the resin. The resin was filtered through a Whatman 42 filter paper, and the uranium was then desorbed by ammonium carbonate solution [3%(w/v)]. The collected ammonium carbonate solution was heated to dryness, treated with nitric and perchloric acid, and then electrolyzed for 2 hours with a platinum as an anode and a stainless steel plate as a cathode.

2.7. Radioactivity determination

After electrolyzed on a stainless steel plate, the radioactivities of actinides were alpha-counted with an Ortec surface barrier detector assembly (EG&G Ortec, U.S.A.). Besides, the strontium purified with Sr. spect. column was transferred to a liquid-scintillation vial with 20 ml 8M nitric acid. After 14 days later, the vial was subjected to Cerenkov counting on a Packard 2260TR liquid-scintillation counter (Packard Instrument Company, U.S.A.), and the radioactivity of $^{90}$Sr($^{90}$Y) was determined. Furthermore, the result and its combined standard uncertain for each measurement; and the mean activity concentration value and the total combined standard uncertainty of the mean were calculated.[7,8]

Figure 1. The flowchart of sequential procedure for isotopic analysis of plutonium, thorium, americium, uranium and strontium.
3. Results and Discussions

3.1. Radioactivity determination

All the measurement results were expressed as massic activity (Bq/g) with the corrected mass obtained from NIST. The massic activities of glass-fiber filter samples analyzed in this study are listed in Table II. Upon completion of each analysis, for the measurement, the radiometric and gravimetric yields, and minimum detectable activities (MDA) were then calculated. The recoveries of actinides and strontium-90 in the process of analysis are measured by radiometric and gravimetric yields of the tracers ${}^{242}$Pu, ${}^{229}$Th, ${}^{243}$Am, ${}^{232}$U and carrier (Sr) spiked in the samples, respectively. The minimum detectable activities values were calculated using the formula: [9]

$$\text{MDA} = \frac{(4.65Sb + 2.7)}{(T \times E \times R \times S \times F)}$$

(1)

Where:

- $Sb$ = Standard deviation in the total number of counts of the blank in the total counting time interval.
- $T$ = Sample counting time.
- $E$ = Counting efficiency.
- $R$ = Trace/Gavimetric yield.
- $S$ = Sample size.
- $F$ = Unit conversion factor.

The typical radiometric and gravimetric yields, and minimum detectable activities (MDA) attained from the present study are listed in Table II. The typical radiometric and gravimetric yields of the ${}^{238}$Pu, ${}^{230}$Th, ${}^{90}$Sr, ${}^{241}$Am and ${}^{238}$U are ranging from 42%-85%. The great differences of the yields between these nuclides are coming from the sequential order of the analysis and the individual analysis method of the nuclide used in this study. The MDA values of glass-fiber filter samples are 0.004-0.006 and 0.059 Bq/sample for the actinides and strontium-90 in this study, respectively. The MDA values calculated from the present study can well meet the requirements of the emergency and routine radiation monitoring.

3.2. Performance evaluation

The traceability per ANSI N42.22[10] for Environmental measurement were evaluated. The traceability limits per ANSI N42.22 for measurements can be calculated by the following equation:

$$\left| V_R - V_N \right| \leq 3 \times \sqrt{\sigma_R^2 + \sigma_N^2}$$

(2)

Where:

- $V_R$ = Reported value.
- $V_N$ = NIST value.
- $\sigma_R$ = 1 sigma total uncertainty of reported value.
- $\sigma_N$ = 1 sigma total uncertainty of NIST value.
- $3\times\sqrt{\sigma_R^2 + \sigma_N^2} = $ Traceability limit.

Traceability evaluation of the glass-fiber filter samples analyzed in this study are listed in Table II. A comparison of analyzed mean values with NIST values shows that the ${}^{241}$Am, ${}^{238}$Pu, ${}^{230}$Th, ${}^{238}$U and ${}^{90}$Sr values agree with the NIST value within -2.1%, -3.6%, +0.7%, -0.6% and -1.8%, respectively.
According to the traceability limits defined in ANSI N42.22, the $^{241}$Am, $^{239}$Pu, $^{238}$U and $^{90}$Sr values of the glass-fiber filter samples analyzed in this study have met the ANSI N42.22 criteria and measurement traceability for low-level radionuclides of ±30%, ±27%, ±30% and ±37%, respectively.

Table I. The massic activities of soil, water, filter, synthetic urine, and synthetic feces samples analyzed in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ID</th>
<th>$^{241}$Am (Bq/g)</th>
<th>$^{238}$Pu (Bq/g)</th>
<th>$^{238}$U (Bq/g)</th>
<th>$^{90}$Sr (Bq/g)</th>
<th>$^{230}$Th (Bq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter</td>
<td>05</td>
<td>0.26 ± 0.06</td>
<td>0.24 ± 0.05</td>
<td>1.08 ± 0.23</td>
<td>1.03 ± 0.28</td>
<td>0.42 ± 0.09</td>
</tr>
<tr>
<td>(NRIP03)</td>
<td>75</td>
<td>0.26 ± 0.06</td>
<td>0.24 ± 0.05</td>
<td>1.11 ± 0.24</td>
<td>1.18 ± 0.33</td>
<td>0.45 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>76</td>
<td>0.26 ± 0.06</td>
<td>0.24 ± 0.05</td>
<td>1.14 ± 0.25</td>
<td>1.00 ± 0.27</td>
<td>0.42 ± 0.09</td>
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<tr>
<td></td>
<td>89</td>
<td>0.31 ± 0.07</td>
<td>0.23 ± 0.05</td>
<td>1.10 ± 0.24</td>
<td>0.97 ± 0.28</td>
<td>0.42 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>102</td>
<td>0.30 ± 0.07</td>
<td>0.26 ± 0.05</td>
<td>1.10 ± 0.24</td>
<td>1.24 ± 0.36</td>
<td>0.44 ± 0.10</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>0.28 ± 0.03</td>
<td>0.24 ± 0.02</td>
<td>1.11 ± 0.11</td>
<td>1.08 ± 0.14</td>
<td>0.43 ± 0.04</td>
</tr>
</tbody>
</table>

Table II. Typical radiometric and gravimetric yields, minimum detectable activities and evaluation per ANSI N42.22 for air-filter samples analyzed in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nuclide</th>
<th>Yields(1)</th>
<th>MDA (2)</th>
<th>Analyzed (Bq/g)</th>
<th>NIST (Bq/g)</th>
<th>Diff. (%)</th>
<th>per ANSI N42.22 Limit(%)</th>
<th>Traceable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter</td>
<td>$^{241}$Am</td>
<td>42%-65%</td>
<td>0.006</td>
<td>0.28 ± 0.03</td>
<td>0.284 ± 0.001</td>
<td>-2.1</td>
<td>30</td>
<td>Yes</td>
</tr>
<tr>
<td>(NRIP03)</td>
<td>$^{238}$Pu</td>
<td>61%-85%</td>
<td>0.004</td>
<td>0.24 ± 0.02</td>
<td>0.251 ± 0.001</td>
<td>-3.6</td>
<td>27</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>$^{238}$U</td>
<td>56%-73%</td>
<td>0.005</td>
<td>1.11 ± 0.11</td>
<td>1.112 ± 0.004</td>
<td>-0.6</td>
<td>29</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>$^{90}$Sr</td>
<td>67%-83%</td>
<td>0.059</td>
<td>1.08 ± 0.14</td>
<td>1.100 ± 0.004</td>
<td>-1.8</td>
<td>27</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>$^{230}$Th</td>
<td>64%-83%</td>
<td>0.004</td>
<td>0.43 ± 0.04</td>
<td>0.426 ± 0.001</td>
<td>+0.7</td>
<td>30</td>
<td>Yes</td>
</tr>
</tbody>
</table>

(1) Yields = Radiometric and Gravimetric Yields  
(2) MDA = Minimum Detectable Activities (Bq/sample)

4. Conclusions

A combination of different radiochemical processes has been developed to provide sequential analysis of $^{238}$Pu, $^{230}$Th, $^{241}$Am, $^{238}$U, and $^{90}$Sr in air-filter samples. In this way, sequential radionuclide analysis of a single sample avoids the cumbersome task of dividing the sample into subsamples for each analysis required. And, the sample pretreatment and dissolution, and wastes generated from the laboratory, are minimized. Therefore, the total sample analysis turnaround time, as well as the amount of laboratory waste generated, are reduced significantly, because it is necessary to perform sample concentration and/or digestion/dissolution only once for all requested analyses. Furthermore, by using a larger sample size for each radionuclide analysis, will result in much lower minimum detectable activity measurements.

5. References


