

## Rapid column extraction method for actinides in soil

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(Received April 17, 2006)

The determination of actinides in environmental soil and sediment samples is very important for environmental monitoring as well as for emergency preparedness. A new, rapid actinide separation method has been developed and implemented that provides total dissolution of large soil samples, high chemical recoveries and effective removal of matrix interferences. This method uses stacked TEVA Resin<sup>®</sup>, TRU Resin<sup>®</sup> and DGA-Resin<sup>®</sup> cartridges from Eichrom Technologies (Darien, IL, USA) that allows the rapid separation of plutonium, neptunium, uranium, americium, and curium using a single multi-stage column combined with alpha-spectrometry. The method combines a rapid fusion step for total dissolution to dissolve refractory analytes and matrix removal using cerium fluoride precipitation to remove the difficult soil matrix. By using vacuum box cartridge technology with rapid flow rates, sample preparation time is minimized.

### Introduction

The determination of actinides in environmental soil samples is an important analysis to meet environmental monitoring requirements at the Department of Energy's Savannah River Site (SRS) in Aiken, South Carolina, USA. Soil and sediment samples are analyzed at the Savannah River Site as part of a routine surveillance program. There is also a growing need to have available rapid methods to accurately assess actinides in environmental soil and sediment samples for emergency preparedness reasons.<sup>1,2</sup> A preconcentration method using Diphonix Resin<sup>®</sup> (Eichrom Technologies, Darien, IL, USA) for large soil samples was previously reported by this laboratory.<sup>3</sup> Although this method successfully removed soil matrix interferences, it required a microwave dissolution of the Diphonix Resin<sup>®</sup> to remove the actinides. The microwave dissolution steps could be time-consuming, depending on the performance of the microwave. Actinides can be removed from Diphonix Resin using 1-hydroxyethane-1, 1-diphosphonic acid (HEDPA) extractant. The HEDPA extractant can be destroyed via a manual hot plate digestion prior to further analysis, but this method generates a large amount of residual phosphate and often requires much larger extraction columns to separate the actinides.<sup>4</sup>

A new matrix removal technique was developed in the SRS Environmental Laboratory that is simpler and more effective than the Diphonix Resin methods. After a fusion technique to provide complete dissolution of the soil matrix and an iron hydroxide precipitation to collect the actinides, a novel cerium fluoride precipitation is used to effectively eliminate the soil matrix. This new method uses stacked TEVA Resin<sup>®</sup>, TRU Resin<sup>®</sup> and DGA-Resin<sup>®</sup> cartridges from Eichrom Technologies (Darien, IL, USA) that allows the rapid separation of

plutonium, neptunium, uranium, americium, and curium using a single multi-stage column to separate actinide isotopes for alpha spectrometry. DGA-Resin<sup>®</sup>, which has very strong retention for americium and curium, is used to enhance chemical recoveries of those analytes.<sup>5</sup>

The new SRS soil method is a rapid method that effectively separates actinides for analysis from large soil samples for routine environmental monitoring or for emergency response needs. It provides rapid, total dissolution of refractory actinides in soil samples and uses a stacked cartridge technology that allows for sequential actinides separations with minimal waste generation.

### Experimental

#### Reagents

The resins employed in this work are TEVA Resin<sup>®</sup> (Aliquat<sup>™</sup>336), TRU-Resin<sup>®</sup> (tri-n-butylphosphate (TBP) and N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)), DGA Resin (N,N,N',N' tetraoctyldiglycolamide), and Prefilter Resin (Amberchrome-CG-71) available from Eichrom Technologies, Inc., (Darien, Illinois). Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc.). All water was obtained from a Milli-Q2<sup>™</sup> water purification system. All other materials were ACS reagent grade and were used as received. Radionuclide tracers <sup>242</sup>Pu, <sup>243</sup>Am, and <sup>232</sup>U that were obtained from Analytix, Inc. (Atlanta, GA, USA) and diluted to the approximately 2 pCi/ml (0.074 Bq/ml) level using 3M HNO<sub>3</sub> were employed to enable yield corrections. Laboratory Control Standards (LCS) were analyzed using <sup>238</sup>Pu, <sup>235</sup>U, <sup>241</sup>Am and <sup>244</sup>Cm standards that were obtained from Analytix, Inc. (Atlanta, GA, USA) and diluted to approximately 2 pCi/ml (0.074 Bq/ml) in 3M HNO<sub>3</sub>.

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### Procedures

*Column preparation:* TEVA, TRU, and DGA Resin columns were obtained as cartridges containing 2 ml of each resin from Eichrom Technologies, Inc. Small particle size (50–100  $\mu\text{m}$ ) resin was employed, along with a vacuum extraction system (Eichrom Technologies). Flow rates of 1–2 ml/min were typically used, much faster than the 0.25 ml/min gravity flow rates typically observed. Sample loading and column stripping steps were performed at ~1 drop/second, while column rinse steps were usually performed at 1 to 2 drops per second.

*Sample preparation:* Soil samples were dried at 110 °C and blended prior to taking sample aliquots. Five-gram sample aliquots were taken for soil samples that were more clay-like in texture and ten-gram aliquots were taken for sandy soil and sediment samples with high silicon content. After samples were aliquoted into 50 ml glass beakers, tracers were added and the samples were placed in a furnace at 550 °C for 4 hours or more. Samples were transferred to 250 ml teflon beakers, rinsing the glass beakers with hot concentrated nitric acid. Five milliliters of concentrated hydrochloric acid and 10 ml of concentrated hydrofluoric acid were added. The samples were ashed to dryness on a hotplate. For emergency response samples which require faster turnaround, the furnace step can be eliminated if ~2 ml of 30 wt.% hydrogen peroxide is also added during each of the following ashing steps. Five ml of concentrated nitric acid and 5 ml of concentrated hydrofluoric acid were added and the samples were ashed to dryness on a hotplate. This step was repeated once more. Any residual fluoride was volatilized by adding 5 ml of concentrated nitric acid and heating to dryness on a hot plate twice. Silicon was volatilized during the ashing steps with hydrofluoric acid as  $\text{SiF}_6$ . After ashing, the residual solids were transferred to 250 ml zirconium crucibles (Metal Technology, Inc., Albany, OR, USA). The beakers were rinsed with concentrated nitric acid, transferred to the crucible and the crucible contents were evaporated on a hot plate to dryness.

After removing the crucibles and allowing them to cool, 15 grams of sodium hydroxide were added to each crucible. The crucibles were covered with a zirconium lid and placed into a furnace at 600 °C for 20 minutes. Smith et al have also applied sodium hydroxide fusion to soil samples.<sup>6</sup>

After removing the crucibles from the furnace, they were transferred to a hot plate and water was added to transfer the solids to 225-ml centrifuge tubes. The residual solids were removed from the crucibles by adding water and heating the crucibles on the hot plate as needed. One hundred and twenty-five milligrams of iron were added as ferric nitrate to each sample. Five milliliters of 20% titanium chloride were added to each

tube, followed by 1 ml of 10% barium nitrate to complex any carbonate present. Seven milligrams of cerium were typically added as cerium nitrate to each tube, however, only 1 mg of cerium was added to soil standards such as MAPEP laboratory soil standards that contain higher levels of rare earth elements. The tubes were centrifuged at 3500 rpm for 5 minutes and the supernate was poured off. The remaining solids were dissolved in a total volume of 60 ml of 1.5M HCl. This solution was diluted to 170 ml with 0.01M HCL. Two milligrams of cerium as cerium nitrate were added to each sample. To ensure no actinides were in the hexavalent state and facilitate complete precipitation, ten milliliters of 20% titanium chloride were added to each sample. Twenty-two milliliters of 28M hydrofluoric acid were added to each sample. The samples were placed on ice for ~10 minutes to reduce solubility and centrifuged for 20 minutes at 3500 rpm. The supernate was removed and the residual solids containing the actinides were dissolved in 5 ml of warm 3M  $\text{HNO}_3$ –0.25M boric acid, 6 ml of 7M  $\text{HNO}_3$  and 7.5 ml of 2M aluminum nitrate. The solids were transferred to 100 ml teflon beakers during this step and warmed to redissolve the solids. The aluminum nitrate was previously scrubbed to remove trace uranium by passing approximately 250 ml of 2M aluminum nitrate through a large column (Environmental Express, Mount Pleasant, SC, USA) containing 7 ml of UTEVA Resin (Eichrom Technologies) at ~10 to 15 ml per minute. The columns were prepared from a water slurry of the UTEVA Resin.

*Column separation:* TEVA, TRU, and DGA Resin cartridges were stacked on the vacuum box from top to bottom, in that order. Fifty milliliter centrifuge tubes were used to collect the rinse or final purified fractions.

A valence adjustment was performed by adding 0.5 ml of 1.5M sulfamic acid and 1.25 ml of 1.5M ascorbic acid. After a three-minute wait step, one milliliter of 3.5M sodium nitrite (freshly prepared) to adjust plutonium to  $\text{Pu}^{4+}$ . After the valence adjustment, the sample solution was loaded onto the stacked column at approximately 1 drop per second. Column reservoirs may be replaced and/or TEVA cartridge frits removed if any solids form in the load solution and affect column flow. After the sample was loaded, a beaker rinse of 3 ml of 6M  $\text{HNO}_3$  was transferred to the stacked column. At this point the TRU and DGA cartridges were removed and the DGA Resin cartridges were placed on a second vacuum box. Five milliliters of 0.25M nitric acid were added to each DGA column to remove any residual uranium that may have been retained on the DGA cartridges. This rinse was collected and set aside for later addition to TRU Resin. The TEVA Resin was rinsed with 7 ml of 3M  $\text{HNO}_3$  to remove residual uranium, which was also collected in clean tubes and set aside for later addition to TRU Resin. The TEVA cartridge was rinsed with 10 ml of 5M nitric acid and

then 10 ml of 3M nitric acid to remove matrix components. To elute thorium from TEVA Resin, 23 ml of 9M hydrochloric acid were added.

A 5 ml volume of 3M HNO<sub>3</sub> was added to TEVA Resin (and discarded) to reduce the amount of any residual extractant before stripping the plutonium from the resin. The plutonium was stripped from TEVA Resin with 20 ml of 0.1M hydrochloric acid – 0.05M hydrofluoric acid – 0.03M titanium chloride (freshly prepared). A 0.5 ml volume of 30 wt.% hydrogen peroxide was added to each Pu strip solution to oxidize any residual uranium to U<sup>6+</sup> as a precaution to prevent coprecipitation. Fifty micrograms of cerium as cerium nitrate was added, along with 1 ml of concentrated hydrofluoric acid (49%). After waiting 30 minutes, the solutions were filtered onto 0.1 μm 25 mm polypropylene and counted by alpha-spectrometry.

The TRU cartridges were placed above the DGA cartridges and 15 ml of 4M HCl was used to strip Am and Cm from TRU Resin onto the DGA Resin. After removal of the TRU cartridges, the DGA cartridges were stripped with 10 ml of 0.25M HCl. These strip solutions were transferred to 50 ml glass beakers using ~3 ml of concentrated nitric acid and 0.05 ml of 1.8M sulfuric acid was added to enhance destruction of any extractant in this solution. The Am/Cm strip solutions were evaporated to dryness on a hotplate. These fractions were ashed once time using 2 ml of concentrated nitric acid and 2 ml of 30 wt.% hydrogen peroxide to remove any residual extractant that may have bled off the resin. The samples were redissolved in 5 ml of 4M ammonium thiocyanate – 0.1M formic acid, warming gently as needed. These solutions were loaded onto a TEVA cartridge to remove rare earths present, which interfere with alpha-spectrometry peak resolution. The TEVA cartridges were rinsed with 10 ml of 1.5M ammonium thiocyanate – 0.1M formic acid to remove rare earths, and the americium and curium were stripped using 20 ml of 1M HCl. The original load solution beaker was rinsed with 5 ml of warm 1M HCl to ensure all the americium and curium was removed from this beaker. This solution, followed by 15 ml of 1M HCl also used to rinse the beaker, was passed through the TEVA Resin to remove the americium and curium. Fifty micrograms of cerium as cerium nitrate was added, along with 2 ml of concentrated hydrofluoric acid (49%). After waiting 30 minutes, the solutions were filtered onto 0.1 μm 25 mm polypropylene and counted by alpha-spectrometry.

Three milliliters of concentrated HNO<sub>3</sub> was added to each 3M HNO<sub>3</sub> rinse volume from TEVA resin that was set aside and added to TRU Resin to recover any residual amount of uranium from TEVA Resin. The 0.25M HNO<sub>3</sub> rinse from DGA Resin was also added to TRU Resin after 4 ml of concentrated HNO<sub>3</sub> was added to increase the acidity of this solution to ~7M HNO<sub>3</sub>.

The higher nitric acid concentration increases the retention of uranium on TRU Resin and selects against retention of any <sup>210</sup>Po. TRU Resin was rinsed with ~20 ml of 4M HCl–0.2M HF to remove any residual thorium that may have passed through TEVA and been retained on TRU Resin. A 3 ml volume of 3M HNO<sub>3</sub> was added to TRU Resin (and discarded) to reduce the amount of any residual extractant before stripping the uranium from the resin. Uranium was stripped from TRU Resin using 15 ml of 0.1M ammonium bioxalate. A 0.5 ml volume of 20 wt.% titanium chloride was added to reduce U to U<sup>4+</sup>. Fifty micrograms of cerium as cerium nitrate was added, along with 1 ml of concentrated hydrofluoric acid (49%). After waiting 30 minutes, the solutions were filtered onto 0.1 μm 25 mm polypropylene filters (Resolve<sup>®</sup> filter-Eichrom Technologies) and counted by alpha-spectrometry.

Figure 1 shows the vacuum box apparatus and the stacked TEVA, TRU and DGA Resin cartridges. The second vacuum box in the picture was used after the cartridges were split apart so that the cartridges could be processed on two boxes for enhanced productivity. DGA and TRU Resin cartridges were moved to the second box and stripped as described above.

### Apparatus

Plutonium, americium, curium and uranium measurements were performed by alpha-particle pulse-height measurements using passivated implanted planar silicon (PIPS) detectors. Polycarbonate vacuum boxes with 24 positions and a rack to hold 50 ml plastic tubes were used. Two boxes were connected to a single vacuum source by using a T-connector and individual valves on the tubing to each box.

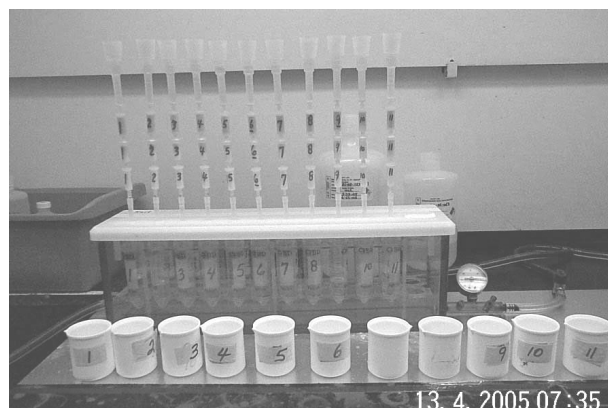


Fig. 1. Vacuum box system with stacked cartridges (TEVA+TRU+DGA Resin)

## Results and discussion

Table 1 shows tracer recoveries for a typical batch of soil samples using an aliquot of 5 grams for each sample. The results for a Laboratory Control Standard (spiked blank) analyzed along with this batch of soil samples is also shown in Table 1. The measured values for  $^{238}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$  and  $^{235}\text{U}$  are well within the QC guidelines of 75%–125% of the known values. Table 2 shows results in Bq/kg for the analysis of the soil standard MAPEP-05-S13 (Department of Energy (DOE), Radiological and Environmental Sciences Laboratory (RESL), Idaho Falls, ID, USA). The measured values are within 5% of the MAPEP reference values, indicating excellent method performance. SILL and SILL<sup>7</sup> have emphasized the need for total dissolution soil methods. Total dissolution allows accurate measurement of refractory particles and the large sample size makes accurate measurement of lower levels quantities possible, as shown by the accurate measurement of the  $^{238}\text{Pu}$  isotope at the  $\sim 0.5$  Bq/kg level. Table 3 again shows excellent performance on a DOE-QAP soil standard 0903 (DOE-EML, Environmental Measurements Laboratory, New York, NY, USA) versus reference values. If incomplete dissolution had occurred on refractory samples, results would have been low.  $^{210}\text{Po}$  (5.30 MeV) has an unresolvable alpha-energy from  $^{232}\text{U}$  (5.26, 5.32 MeV). If  $^{210}\text{Po}$  had not been removed effectively,  $^{232}\text{U}$  tracer values would have been biased high and  $^{234}\text{U}$  and  $^{238}\text{U}$  measured values would have been biased low. Figure 2 shows a typical spectra for the plutonium isotopes when  $^{242}\text{Pu}$  is used as the tracer. The  $^{242}\text{Pu}$  tracer recovery was 99.5% and the full width half maximum (FWHM) was 55 keV, showing good alpha-peak resolution. Figure 3 shows an example of spectra for the Am/Cm isotopes. The  $^{243}\text{Am}$  tracer recovery was 105.5% and the FWHM was 48.6 keV. Figure 4 shows an example of the spectra for uranium isotopes. The  $^{232}\text{U}$  tracer recovery was 108.8% and the FWHM was 38.3 keV. If  $^{236}\text{Pu}$  tracer is used instead of  $^{242}\text{Pu}$ , neptunium can also

be measured.<sup>8,9</sup> To facilitate Np reduction to  $\text{Np}^{4+}$  in the column load solution, a small amount of iron ( $\sim 1$  to 2 mg) may be added along with the ascorbic acid in the column load solution.

After initial drying, blending and heating at 550 °C for 4 hours, the time required to prepare a batch of soil samples is about 5 hours. The column work usually takes about 5 to 6 hours for all the actinides to be separated and purified. The new method is much faster than the previous method of soil analysis used in the SRS Environmental Laboratory.

Table 1. Performance of the method on typical soil samples ( $N=7$ )

Tracer	Average recovery, %	RSD, %	LCS recovery, %
$^{242}\text{Pu}$	104	4.4	96.2 ( $^{238}\text{Pu}$ )
$^{243}\text{Am}$	105.2	5.3	88.0 ( $^{241}\text{Am}$ )
$^{232}\text{U}$	98.4	13	95 ( $^{235}\text{U}$ )

Table 2. Performance on MAPEP-05-S13 Soil Standard (in Bq/kg)

Analyte	Measured	Reference	Ratio
$^{238}\text{Pu}$	0.48	0.48	1.00
$^{239}\text{Pu}$	84.1	89.5	0.95
$^{241}\text{Am}$	101	109	0.93
$^{234}\text{U}$	64.9	62.5	1.04
$^{238}\text{U}$	252	249	1.01

5 gram sample analyzed.

Results are average of 3 replicates.

Table 3. Performance on DOE-EML Soil Standard 0903 (in Bq/kg)

Analyte	Measured	Reference	Ratio
$^{238}\text{Pu}$	31.2	30.4	1.02
$^{239}\text{Pu}$	15.0	14.6	1.03
$^{241}\text{Am}$	17.5	18.4	0.95
$^{234}\text{U}$	125.0	127.3	0.98
$^{238}\text{U}$	126.4	127.1	0.99

5 gram sample analyzed.

Results are average of 2 replicates.

**Environmental & Bioassay Laboratories**

Filename: S\_500001888\$300068092\_PU Detector: 6 Chemical Yield: 99.530%  
Acquisition Start: 31-OCT-2005 14:49:47 Count Time: 0 16:00:00  
Region type: MANUAL Tracer ID: PU242-444 Tracer FWHM: 55.056

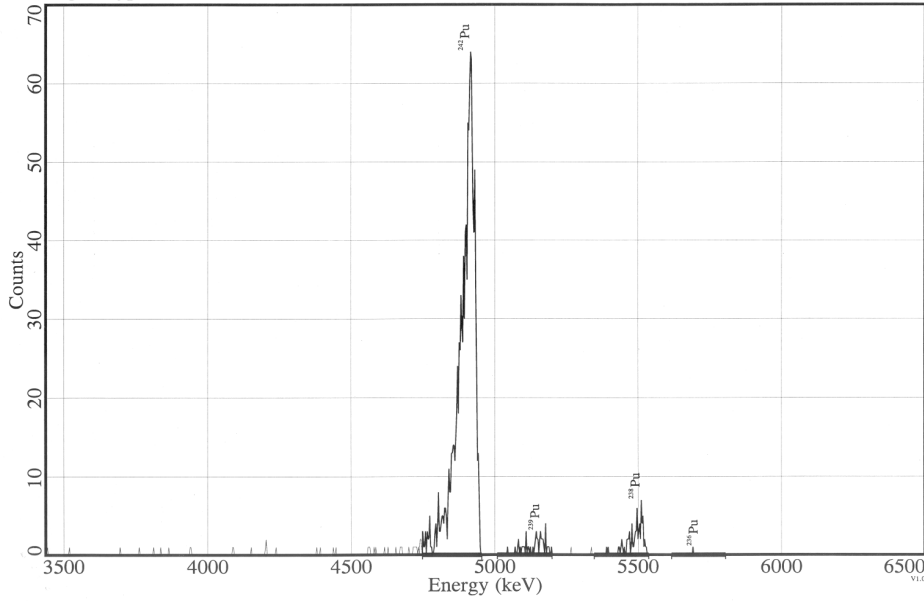


Fig. 2. Alpha-spectra showing Pu isotopes

**Environmental & Bioassay Laboratories**

Filename: S\_500001889\$300068001\_AM Detector: 29 Chemical Yield: 105.56%  
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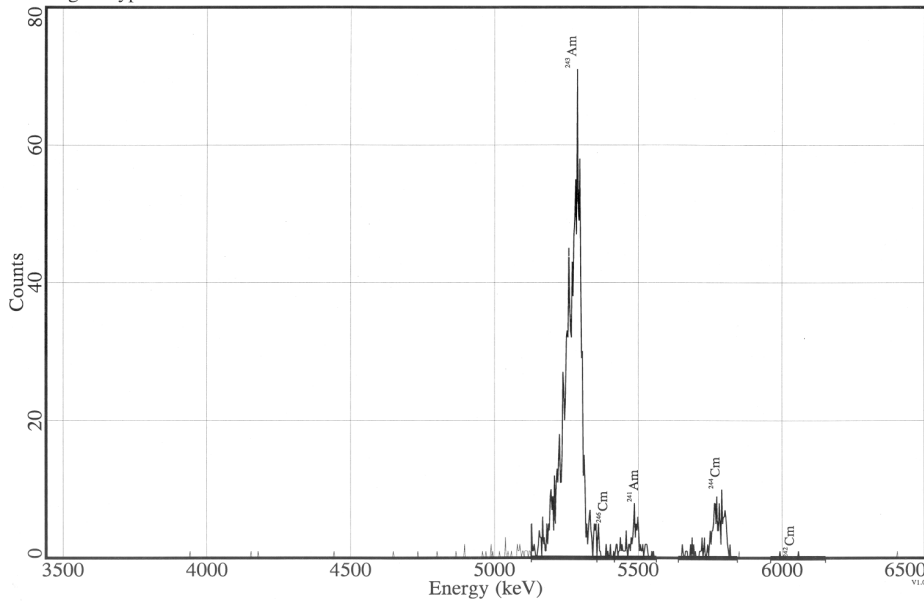


Fig. 3. Alpha-spectra showing Am isotopes

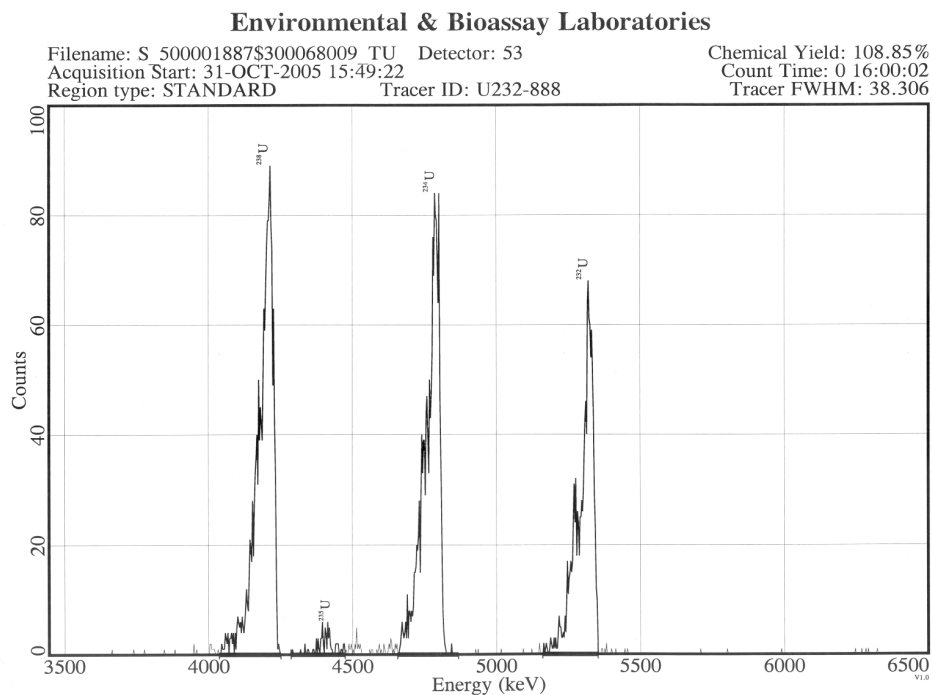


Fig. 4. Alpha-spectra showing U isotopes

## Conclusions

The new procedure developed in the SRS Environmental Laboratory is a rapid method for actinides that can be used for routine or emergency analyses of environmental soil samples. This method has high tracer recoveries, effectively removes interferences and combines the sample preparation for a large number of actinides into a single multi-stage column extraction method. The method provides total dissolution and effective removal of soil matrix interferences to allow rapid, accurate determination of actinides in relatively large soil samples.

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This work was performed under the auspices of the Department of Energy, DOE Contract No. DE-AC09-96SR18500. The authors wish to acknowledge Gene COOKE, Martha HOLMES, Becky CHAVOUS and Jack HERRINGTON for their assistance in testing this method.

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