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Rapid Column Extraction Method for Actinides and Sr-89/90 in Water Samples

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Abstract

The SRS Environmental Laboratory analyzes water samples for environmental monitoring, including river water and ground water samples. A new, faster actinide and strontium 89/90 separation method has been developed and implemented to improve productivity, reduce labor costs and add capacity to this laboratory. This method uses stacked TEVA Resin[®], TRU Resin[®] and Sr-Resin[®] cartridges from Eichrom Technologies (Darien, IL, USA) that allows the rapid separation of plutonium (Pu), neptunium (Np), uranium (U), americium (Am), curium (Cm) and thorium (Th) using a single multi-stage column combined with alpha spectrometry. By using vacuum box cartridge technology with rapid flow rates, sample preparation time is minimized. The method can be used for routine analysis or as a rapid method for emergency preparedness. Thorium and curium are often analyzed separately due to the interference of the daughter of Th-229 tracer, actinium (Ac)-225, on curium isotopes when measured by alpha spectrometry. This new method also adds a separation step using DGA Resin[®], (Diglycolamide Resin, Eichrom Technologies) to remove Ac-225 and allow the separation and analysis of thorium isotopes and curium isotopes at the same time.

Key Words

Water

Actinide analysis

Emergency preparedness

Extraction chromatography

Separations

Resin

Introduction

The analysis of actinides and strontium-89/90 in environmental water samples is an important analysis to meet environmental monitoring requirements at the Department of Energy's Savannah River Site (Aiken, South Carolina, USA). River water, drinking water and groundwater 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 assess actinides and strontium –89/90 levels in environmental samples for emergency preparedness reasons (1, 2). Rapid column extraction methods have been

used in the Savannah River Site Laboratory for several years for a variety of sample matrices (3, 4, 5).

The use of vacuum-assisted column extraction using cartridge technology is now employed by an increasing number of commercial and government laboratories in the USA to reduce analytical time and reduce labor costs. The new technology offers more rapid flow rates (5 times faster than gravity flow) and better separation efficiency (smaller elution bands) by using small particle size resin (50-100 micron). This approach also allows the operator to apply increased vacuum to any “stubborn” columns that do not flow as fast as others in the batch. Using gravity flow, one or more very slow columns can significantly increase the time it takes to process the entire batch.

This new method uses stacked TEVA Resin[®], TRU Resin[®] and Sr-Resin[®] cartridges from Eichrom Technologies (Darien, IL, USA) that allows the rapid separation of plutonium, neptunium, uranium, americium, curium and thorium using a single multi-stage column to separate actinide isotopes for alpha spectrometry. Strontium 89/90 is separated using Sr Resin and measured by gas proportional counting. Thorium and curium are often analyzed separately due to the interference of the daughter of Th-229 tracer, Ac-225, on curium isotopes when measured by alpha spectrometry. Ac-225 has alpha energies of 5.829 and 5.792 MeV, respectively. Francium (Fr) -221, the daughter of Ac-225, has alpha energies of 6.340 and 6.125 MeV. Cm-244 has alpha energies of 5.805, 5.763 and 5.633 MeV, while Cm-242 has alpha energies of 6.113, 6.070 and 5.949 MeV. Because of the interference of Th-229 daughter products on the measurement of Cm isotopes by alpha spectrometry, additional effort is required to prepare two separate sample aliquots so that thorium-229 daughter products do not interfere. In contrast, this

new method adds a separation step using DGA Resin ®, (Diglycolamide Resin, Eichrom Technologies) to remove Ac-225 and allow the separation and analysis of thorium isotopes and curium isotopes using the same sample preparation.

The new SRS water method is a rapid method that effectively separates actinides and strontium-89/90 for analysis for routine monitoring or emergency preparedness needs.

Experimental

Reagents

The resins employed in this work are TEVA Resin® (Aliquat TM336), TRU-Resin® (tri-n-butylphosphate (TBP) and N,N-diisobutylcarbamoymethylphosphine oxide (CMPO)), Sr-Resin® (4, 4', (5') di-t-butylcyclohexane-18-crown-6), 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-Q2TM water purification system. All other materials were ACS reagent grade and were used as received. Radiochemical isotope tracers Pu-242, Am-243, U-232 and Th-229 that were obtained from Analytix, Inc. (Atlanta, GA, USA) and diluted to the approximately 2 pCi/mL level were employed to enable yield corrections. U-232 tracer was prepared to be self-cleaning, removing its Th-228 daughter using barium sulfate precipitation (6). A solution of 20.0 mg/mL stable strontium was used to determine strontium carrier recovery. The strontium carrier solution was standardized gravimetrically using a strontium carbonate precipitation technique. Laboratory Control Standards (LCS) were analyzed using Pu-238, U-235, Am-241 and Th-230 that were obtained from Analytix, Inc. (Atlanta, GA, USA) and diluted to the

approximately 2 pCi/mL level. Sr-90 standard from Analytix, Inc was diluted to approximately 80 pCi/mL for use as an LCS.

Procedures

Column preparation. TEVA, TRU, SR, DGA Resin columns were obtained as cartridges containing 2 mL of each resin from Eichrom Technologies, Inc.. Small particle size (50-100 micron) 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 Preparation. Water samples were obtained and preserved by adjustment to approximately pH 2 using nitric acid upon sample collection. For river and drinking water samples, 1 liter samples are typically analyzed, but for groundwater samples only 200 mL sample aliquots were required. After samples are aliquoted, tracers are added and 2 mL of 3.2M calcium nitrate and 5 mL of 3.2M ammonium hydrogen phosphate are added to each sample. Five milligrams of barium as barium chloride was added to precipitate carbonate, to reduce heating times previously required to remove carbonate as carbon dioxide. For 200 mL samples, the aliquoting and the above reagent additions were performed in a 225mL centrifuge tube to save time. For 1 liter samples, some heating is required to facilitate settling of the calcium phosphate precipitate. The pH was adjusted to pH 10 with concentrated ammonium hydroxide using a phenolphthalein endpoint. The groundwater samples can be centrifuged immediately at 3000 rpm for 5 minutes, while the 1liter samples required some heating and settling before pouring off the supernate and transferring to 225 mL centrifuge tubes and centrifuging in the same way. After

discarding the supernate, the precipitate was rinsed once with 10 mL of water and centrifuged at 3000 rpm for 5 minutes. The rinse was discarded and the precipitate dissolved in 8 mL of 6M HNO₃ and 8 mL of 2M Al(NO₃)₃. The final load solution contains 16 mL of 3M HNO₃ and 1M Al(NO₃)₃. 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 at ~10 mL per minute. The column was prepared from a water slurry of the resin.

Column separation. TEVA, TRU, and SR Resin cartridges were stacked on the vacuum box from top to bottom, in that order. 50 mL centrifuge tubes were used to collect 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 with a three minute wait step, followed by 1 mL of 3.5M sodium nitrite. After the valence adjustment, the sample solution was loaded onto the stacked column at approximately 1 drop per second. After the sample was loaded, a beaker rinse of 3 mL of 3M HNO₃ was transferred to the stacked column and a rinse of 5 mL of 3M HNO₃ was added directly to the column. The TRU Resin and Sr-Resin cartridges were removed and the TEVA cartridges were kept on the vacuum box. The TEVA cartridge was rinsed with 15 mL of 3M nitric acid to remove matrix components. To elute thorium from TEVA Resin, 23 mL of 9M hydrochloric acid were added. If Th isotope analysis were required, a Prefilter Cartridge was placed below TEVA Resin to remove any extractant that bleeds off TEVA Resin while Th was being stripped with 23 mL of 9M HCL. If the thorium was discarded, no Prefilter Cartridge was needed. If Th

analysis was required, the 9M HCl solution was diluted to a total volume of 45 mL with water to reduce the acidity. Fifty micrograms of cerium as cerium nitrate was added, along with 5 mL of concentrated hydrofluoric acid (49%). After waiting 30 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene filters (Resolve filter-Eichrom Technologies) and counted by alpha spectrometry.

A 5 mL volume of 3M HNO₃ 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 mLs of 0.1M hydrochloric acid-0.05M hydrofluoric acid -0.03M titanium chloride. A 0.5 mL volume of 30 wt% hydrogen peroxide was added that will oxidize any residual uranium to U+6 as a precaution. 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 micron 25 mm polypropylene and counted by alpha spectrometry .

The TRU cartridges were placed on a separate vacuum box. If Th and Cm isotopes were needed, a DGA Resin cartridge was placed below each TRU Resin cartridge for further separation. If Th and Cm isotopes were not being analyzed, a Prefilter Cartridge was placed below TRU Resin to remove any extractant that typically bled off TRU Resin while Am was being stripped with 4M HCL. The Prefilter Cartridge eliminated the need to evaporate and wet ash this solution to remove organics and improve alpha peak resolution.

If Th and Cm isotopes were analyzed and Th-229 tracer was added, DGA cartridges are placed below the TRU cartridges to remove the Th-229 daughter, Ac-225. The Am and Cm are stripped from TRU Resin onto DGA Resin using 15 mL of 3M

HCL. The TRU cartridge is removed and the DGA cartridge was rinsed with 5 mL of 1M HNO₃, followed by 15 mL of 0.1M HNO₃ to remove Ac-225. Am and Cm were stripped from DGA using 15 mL of 0.25M HCl. 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 micron 25 mm polypropylene filters and counted by alpha spectrometry.

If Prefilter Resin was used below TRU Resin instead of DGA Resin (Th and Cm were not analyzed together), Am and Cm were stripped from TRU Resin with 15 mL of 4M HCl. This solution was diluted to a total volume of 30 mL to reduce the acidity. Fifty micrograms of cerium as cerium nitrate was added, along with 3 mL of concentrated hydrofluoric acid (28M). After waiting 30 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene filters (Resolve filter-Eichrom Technologies) and counted by alpha spectrometry.

TRU Resin was rinsed with 12 mL of 4M HCL-0.2M HF to remove any residual thorium that may have passed through TEVA and been retained on TRU Resin. Uranium was stripped from TRU Resin using 15 mL of 0.1M ammonium bioxalate. A 0.5mL volume of 20wt% titanium chloride was added to reduce U to U +4. This solution was diluted with water to a total volume of 30 mL to reduce the acidity. 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 micron 25 mm polypropylene filters (Resolve® filter-Eichrom Technologies) and counted by alpha spectrometry.

The SR Resin cartridges were placed on a vacuum box and rinsed with 10 mL of 8M HNO₃. The Sr-89/90 was stripped from the Sr Resin using 10 mL of 0.05M HNO₃ into 50 mL tubes. This solution was transferred to preweighed planchets and evaporated on a hot plate to dryness. A 3 mL volume of 8M HNO₃ was used to rinse each tube and then was transferred to each planchet and dried. The dried planchets were allowed to cool and then were weighed to determine gravimetric carrier recovery. The planchets were counted by gas proportional counting.

Figure 1 shows the vacuum box apparatus and the stacked TEVA, TRU and Sr 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. Figure 2 shows TRU Resin cartridges moved to the second box and stripped with either DGA Resin below the TRU cartridges (when Cm and Th isotopes are required) or Prefilter Cartridges when Ac-225 removal was not needed. Sr Resin cartridges were set aside until they could be processed or handed off to another technician to continue processing on a separate vacuum box.

Apparatus

Plutonium, thorium, americium, curium and uranium measurements were performed by alpha-particle pulse-height measurements using surface barrier silicon 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.

Results and Discussion

Table 1 shows tracer/carrier recoveries for a batch of twenty groundwater samples using an aliquot of 200 mL for each sample. In this test, thorium isotopes were not analyzed so DGA Resin was not used. The results for a Laboratory Control Standard (spiked blank) analyzed along with this batch of groundwater samples is also shown in Table 1. The measured values for Pu-238, Am-241, U-235 and Sr-90 are well within the QC guidelines of 75%-125% of the known values. If individual Sr-89 and Sr-90 results are required, a second count measured after 7-10 days can be used to differentiate Sr-89 and Sr-90. There are also Čerenkov counting techniques for more rapid determination of Sr-89 and Sr-90 (7). The sample preparation to determine strontium gravimetric recovery did not add significant time to the procedure, approximately an hour or so to evaporate the column strip solutions and weigh on planchets. Table 2 shows tracer recoveries for groundwater samples using an aliquot of 200 mL each when Th-229 tracer was added and DGA Resin was used to remove Ac-225. Figure 2 shows an example of the alpha spectra for the plutonium isotopes when Pu-242 is used as the tracer. The Pu-242 tracer recovery was 103% and the Full Width Half Maximum (FWHM) was 36, showing excellent alpha peak resolution. If electrodeposition were desired instead of cerium fluoride microprecipitation to prepare the alpha mounts, rongalite (sodium formaldehyde sulfoxylate) can be used as a reductant instead of titanium chloride in the Pu strip solution. In contrast to titanium chloride, rongalite does not interfere with electrodeposition. Figure 3 shows an example of spectra for the Am/Cm isotopes. Note that there are no extraneous alpha peaks from Ac-225 and its daughter, Fr-221, in this

spectrum. Cm-isotopes can be measured accurately without interference. The DGA removal of Ac-225 is simple, effective and eliminates the need to prepare a separate aliquot for thorium analysis. Figure 4 shows an example of the uranium isotope spectra and Figure 5 shows an example of the thorium isotope spectra. Table 1 also shows results obtained when known amounts of standards were spiked into blank samples (LCS) and analyzed along with the groundwater samples.

The addition of barium to precipitate any carbonate present in the water samples was effective based on the high recoveries observed, indicating soluble actinide carbonate complexes were not present in significant amounts. For water sample aliquots of 200 mL or less, this eliminated the heating step typically used to remove carbonate as carbon dioxide. A short heating step to facilitate aggregation and settling of the precipitate in large samples was still required. Dissolving the calcium phosphate precipitate directly into the load solution also saved time. Time-consuming ashing of the calcium phosphate precipitate with concentrated nitric acid before dissolving in the column load solution as is sometimes done was not required. The time required to prepare a batch of samples has been reduced to 1 to 2 hours instead of 3 to 4 hours. The column work usually takes about 5 to 6 hours for all the actinides and strontium-89/90 to be separated and purified. This allows for actinide and strontium results in less than 6 to 8 hours if a short count is employed. In the event of a radiological emergency, a short count may suffice to meet initial environmental assessment needs.

In addition to environmental water samples, this stacked cartridge technology has been applied to the analysis of air filters used for environmental and stack air monitoring at the Savannah River Site. The glass fiber filters are dissolved and wet-ashed using nitric

acid and hydrofluoric acid and the redissolved into the same load solution as is used in the water method. The column separation steps are identical.

Conclusions

The new stacked cartridge method developed in the SRS Environmental Laboratory is a rapid method for actinides and Sr-89/90 that can be used for routine or emergency analyses of environmental water samples. This method has high tracer recoveries, effectively removes interferences and combines the sample preparation for a large number of actinides and Sr-89/90 into a single column extraction method. It provides a DGA removal step that eliminates the interference of Ac-225 on curium isotopes and allows thorium and curium isotopes to be analyzed together by alpha spectrometry even when Th-229 tracer is used.

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Table Captions

Table 1 Performance of Stacked Cartridge Method on Groundwater Samples

Table 2. Performance of Stacked Cartridge Method on Groundwater Samples (Th and Cm included)

Figure Captions

Figure 1. Vacuum Box System with Stacked Cartridges

Figure 2 Cartridges Split Apart: Am/Cm Removal from TRU Resin

Figure 3. Alpha Spectrometry Spectra showing Pu Isotopes

Figure 4. Alpha Spectrometry Spectra showing Am Isotopes

Figure 5. Alpha Spectrometry Spectra showing U Isotopes

Figure 6. Alpha Spectrometry Spectra showing Th Isotopes

Table 1. Performance of Stacked Cartridge Method on Groundwater Samples

N=20

Tracer/carrier	Avg. Recovery	RSD	LCS Recovery
Pu-242	104%	4.9%	98.5% (Pu-238)
Am-243	92.6%	6.0%	109% (Am-241)
U-232	85.6%	5.4%	104% (U-235)
Sr carrier	98.1%	3.9%	99.1% (Sr-90)

Table 2. Performance of Stacked Cartridge Method on Groundwater Samples (Th and

Cm included)

N=4

Tracer	Avg. Recovery	RSD	LCS Recovery
Pu-242	95.1%	4.9%	98.4% (Pu-238)
Am-243	100.4%	4.5%	92.3% (Am-241) 105.8% (Cm-244)
U-232	82.2%	1.2%	104% (U-235)
Th-229	82.4 %	4.4%	97.7% (Th-230)

Figure 1 Vacuum Box System with Stacked Cartridges

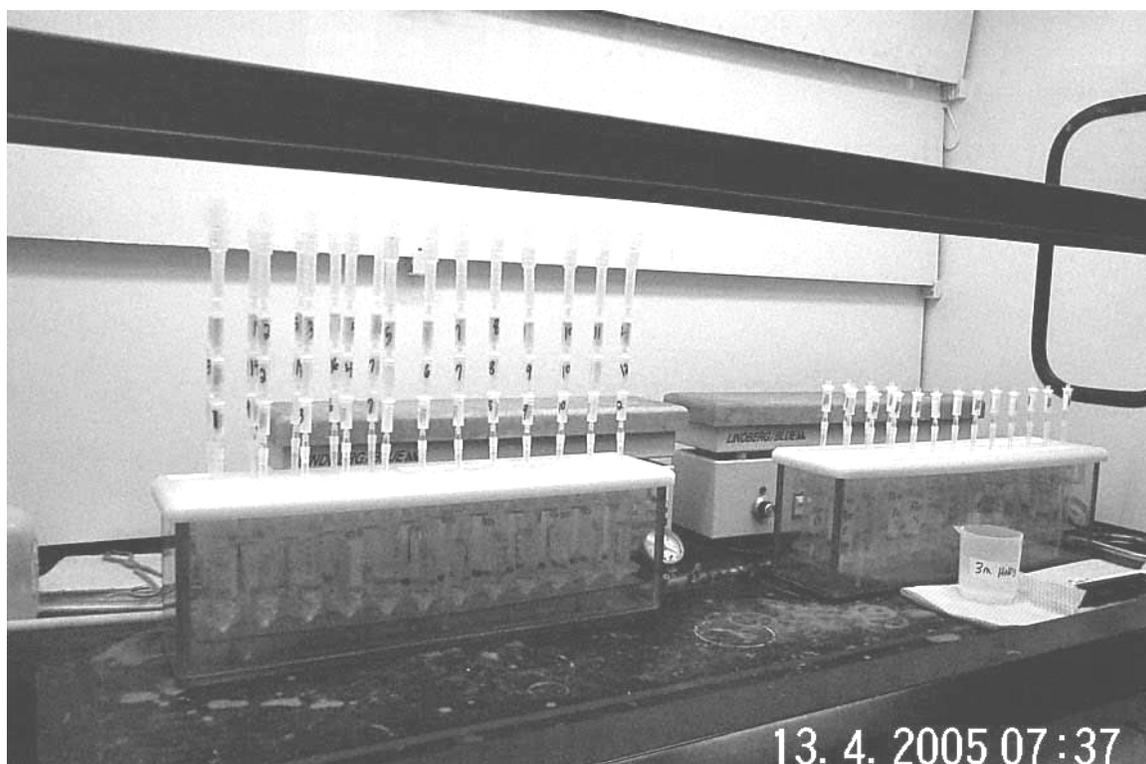
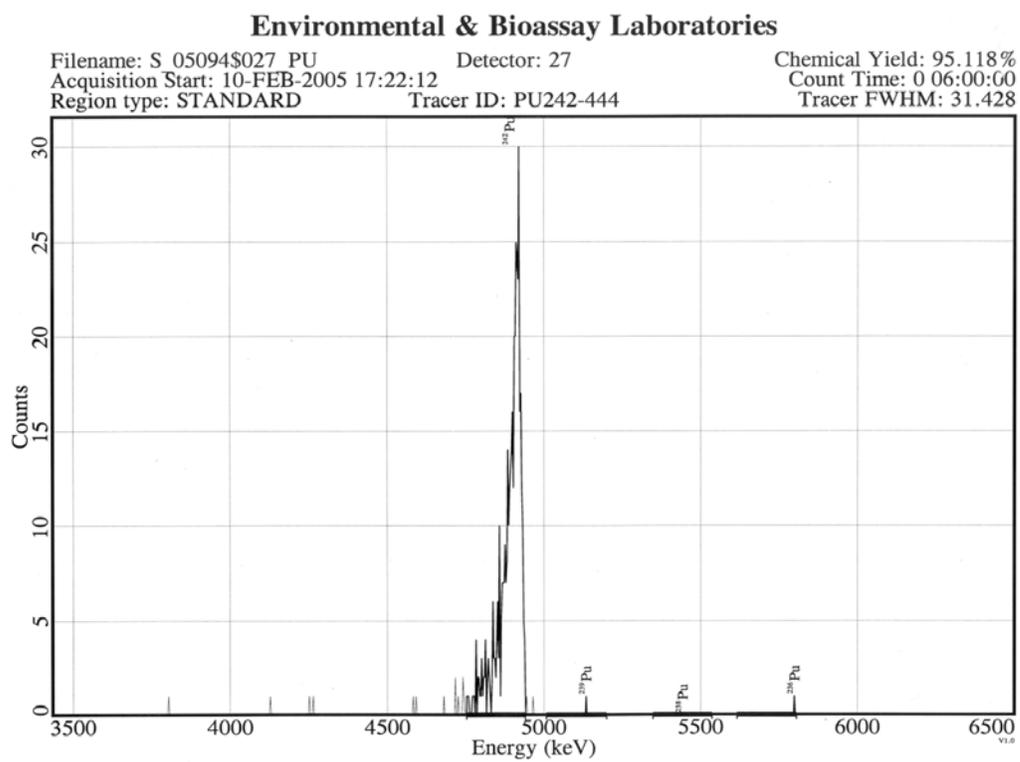


Figure 2 Cartridges Split Apart: Am/Cm Removal from TRU Resin

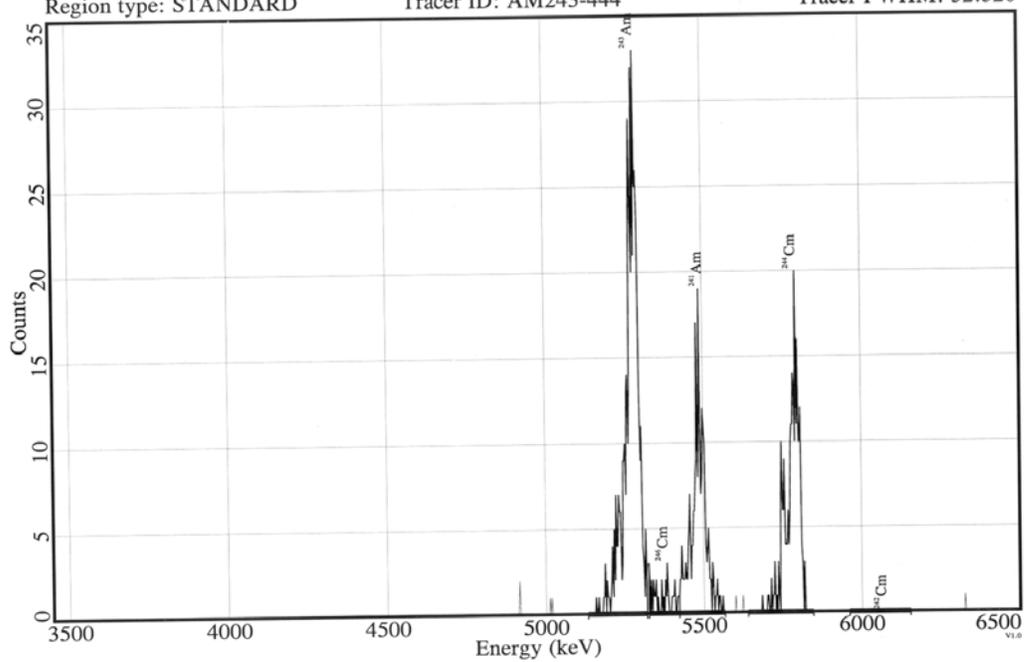


Figure 3. Alpha Spectrometry Spectra showing Pu Isotopes Resin



Environmental & Bioassay Laboratories

Filename: C_05093\$050_AM Detector: 50 Chemical Yield: 106.46%
Acquisition Start: 10-FEB-2005 17:23:42 Count Time: 0 06:00:00
Region type: STANDARD Tracer ID: AM243-444 Tracer FWHM: 32.526



Environmental & Bioassay Laboratories

Filename: S_05091\$083_TU Detector: 83 Chemical Yield: 98.842%
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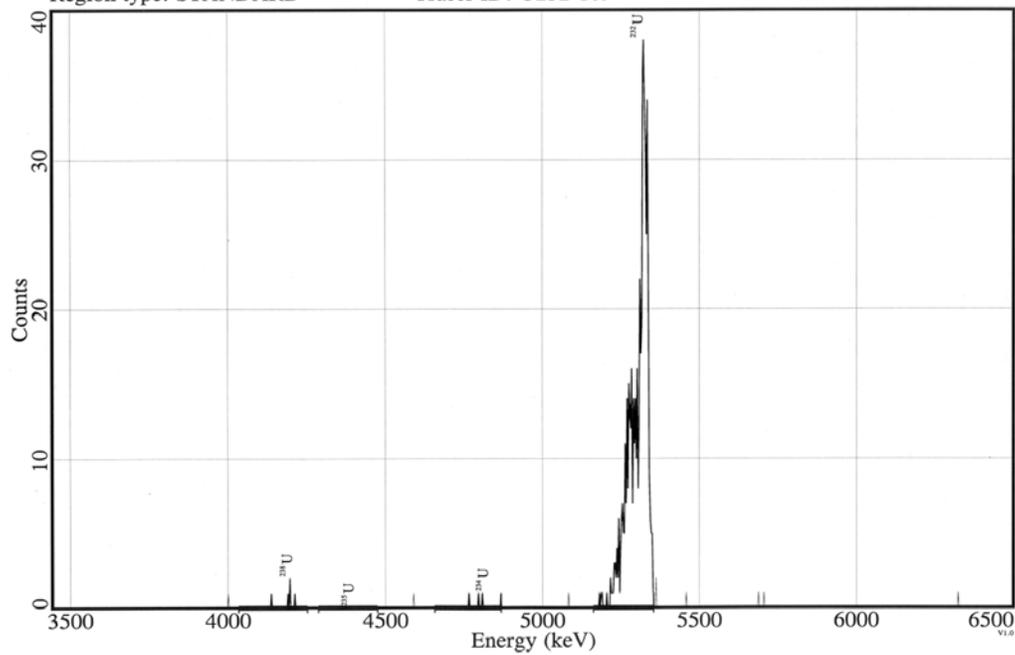


Figure 6. Alpha Spectrometry Spectra showing Th Isotopes

