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Rapid Analysis of Emergency Urine and Water Samples

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Abstract

There is a need for fast, reliable methods for the determination of actinides and Sr-89/90 analysis on environmental and bioassay samples in response to an emergency radiological incident. The SRS (Savannah River Site) Environmental Laboratory participated in the National Institute of Standards and Technology Radiochemistry Intercomparison Program (NRIP-06) and analyzed water and urine samples within 8 hours of receipt. The SRS Environmental Laboratory was the only lab that participated in the program that analyzed these samples for both actinides and Sr-89/90 within an eight hour turnaround time. A rapid actinide and strontium-89/90 separation method was used for both urine and water samples. 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), and americium (Am), curium (Cm) and thorium (Th) using a single multi-stage column combined with alpha spectrometry. Vacuum box cartridge technology with rapid flow rates was used to minimize sample preparation time. This paper discusses the technology and conditions employed for both water and urine samples and presents the SRS performance data on the NRIP-06 samples.

Introduction

There is also a growing need to have rapid methods available 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 (SRS) Laboratory for several years for a variety of sample matrices (3, 4, 5). A new method was reported by this laboratory for rapid analysis of actinides and Sr-89/90 in water (6). This method has also been applied successfully at SRS to emergency urine samples with slight modifications. The National Institute of Standards and Technology Radiochemistry Intercomparison Program (NRIP-06) sent samples to six labs with only one day notice in an effort to test the capability of selected labs to perform rapid analyses and to help improve the efficiency and effectiveness of radioanalytical methods for emergency response.

This labs that participated were the SRS Environmental Laboratory (Aiken, SC, USA), Fluor Daniel (Hanford Site, Richland,WA, USA), NAREL Laboratory (EPA Lab, Montgomery, AL, USA), WIPP Lab (Carlsbad, NM, USA), Center for Disease Control (Atlanta, GA, USA) and Health Canada (Radiation Protection Bureau, Canada). The method used in the SRS lab employs stacked TEVA Resin ®, TRU Resin® and Sr-Resin ® cartridges from Eichrom Technologies (Darien, IL, USA) that allow the rapid separation of plutonium, neptunium, uranium, americium, curium and thorium using a single multi-stage column to separate actinide isotopes for alpha spectrometry. To save time, strontium-89/90 is separated at the same time using Sr Resin and measured by gas proportional counting. The new SRS water and urine method rapidly and effectively

separates actinides and strontium-89/90 to meet emergency response needs. The SRS Lab was the only lab to report actinides and Sr-89/90 analyses with the eight hour time period requested.

Experimental

Reagents

The resins employed in this work are TEVA Resin® (Aliquat ™336), TRU-Resin ® (tri-n-butylphosphate (TBP) and N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)), and Sr-Resin ® (4, 4', (5') di-t-butylcyclohexane-18-crown-6), available from Eichrom Technologies, Inc., (Darien, Illinois, USA). Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc.). All water was obtained from a Milli-Q2™ water purification system. All other materials were ACS reagent grade and were used as received. Radiochemical isotope tracers Pu-242, Am-243, and U-232 that were obtained from Analytics, Inc. (Atlanta, GA, USA) and diluted to the approximately 10 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 (7). 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 Cm-244 that were obtained from Analytics, Inc. (Atlanta, GA, USA) and diluted to the approximately 2 pCi/ml level. Sr-90 standard from Analytics, Inc was diluted to approximately 80 pCi/ml for use as an LCS.

Procedures

Column preparation. TEVA, TRU, and SR 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. After water and urine samples were 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 any carbonate present, to reduce heating times previously required to remove carbonate as carbon dioxide. For 100 ml samples, the aliquoting and the above reagent additions were performed in a 225 ml centrifuge tube to save time. The pH was adjusted to pH 10 with concentrated ammonium hydroxide using a phenolphthalein endpoint. 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. For water samples, the precipitate was dissolved in 8 ml of 6M HNO_3 and 8 ml of 2M $Al(NO_3)_3$ directly in the centrifuge tubes. The final load solution contains 16 ml of 3M HNO_3 and 1M $Al(NO_3)_3$. 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. For urine samples, the calcium phosphate precipitate was transferred to a 100 ml glass beaker using

a small volume of concentrated nitric acid. The samples were evaporated to dryness on a hotplate, 3 ml of concentrated nitric acid and 3 ml of 30 wt% of hydrogen peroxide were added. The samples were ashed one time to dryness on the hot plate to help destroy residual organics from the urine.

Column separation. TEVA, TRU, and SR Resin cartridges were stacked on the vacuum box from top to bottom, in that order. Fifty milliliter centrifuge tubes were used to collect rinse or final purified fractions. Column load solutions were loaded at ~1 drop per second, rinse solutions at ~2 drops per second and column strip solutions were added at ~1 drop per second using vacuum.

A valence adjustment was performed by adding 0.5 ml 1.5M sulfamic acid and 1.25 ml 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. Thorium was not measured in this NRIP emergency exercise in the SRS lab, however, if Th analysis were required, the 9M HCl solution can be diluted to a total volume of 45 ml with water to reduce the acidity. Fifty micrograms of cerium as cerium nitrate can be added, along with 5 ml of concentrated hydrofluoric acid (49%). After waiting 20- 30

minutes, the solutions are 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. 50 micrograms of cerium as cerium nitrate was added, along with 1 ml of concentrated hydrofluoric acid (49%). After waiting 20-30 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. 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 20-30 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 20 wt% titanium chloride was added to reduce U to U^{+4} .50 micrograms of cerium as cerium nitrate was added, along with 1 ml of concentrated hydrofluoric acid (49%). After waiting 20-30 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-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. Sr Resin cartridges were handed off to another technician to continue processing on a separate vacuum box.

Both water and urine samples were counted by alpha spectrometry for approximately one hour. Strontium count times were twenty minutes for both water and urine samples.

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.

Results and Discussion

Table 1 shows the turnaround times for actinides and Sr-90 in the NRIP-06 water and urine for the SRS Environmental Laboratory. The Sr-90 reporting times were less than five hours for water and slightly more than five hours for urine. The Sr-90 in urine result times included time taken to recount the sample due to the relatively low levels measured. The actinides reporting times were less than 8 hours, with report times delayed ~1-1.5 hours of due to slow data processing times involving the Laboratory Information Management System (LIMS) processing times. This problem was traced to an index file problem that slowed data processing time and has since been corrected. Five NRIP urine and water samples plus a blank for each were analyzed.

Table 2 shows a typical timeline for these analyses. The Sr-90 analyses can be performed quickly because Sr-90 is collected at the same time as the actinides by one lab technician and then handed off to a second lab technician to rinse and strip the Sr-90 from the Sr Resin cartridges. If Sr-89/90 differentiation is needed, there are also Čerenkov counting techniques for more rapid determination of Sr-89 and Sr-90 (8).

Tables 3 and 4 show the SRS measured values versus the NRIP reference values for water and urine. Results were reported in a Bequerels per gram of spike added by NIST to each NRIP sample. Considering the short count times, the accuracy of the measured values was good, more than adequate for emergency response screening. The Sr-90 planchets were counted on relatively high background detectors with a large

uncertainty and the accuracy of the Sr-90 measurements was negatively affected. However, the same planchets were counted on different detectors (but not reported) and the accuracy was much better. This demonstrates that the strontium separation method works well. Tables 5 and 6 show results for actinides in water and urine that were recounted for a longer time. The same alpha mounts were recounted for four hours to determine the impact of longer counts on the results. There was a significant improvement in accuracy versus the NRIP reference values. While the one hour count results were adequate to meet emergency response needed, counting four hours improved the accuracy for nearly all the actinide isotopes to less than 10%. The larger bias for the U-235 results was likely due to the much lower activity present for U-235.

Figure 1 shows an example of the plutonium spectra for the NRIP water samples. The Pu-242 tracer recovery was 100.8% and the Full Width Half Maximum (FWHM) was 52.2 keV, showing good alpha peak resolution. Figure 2 shows an example of the plutonium spectra for the NRIP urine samples. The Pu-242 tracer recovery was 100.9% and the FWHM was 52.4 keV, indicating a similar method performance on water and urine. Figure 3 shows an example of the americium spectra for the NRIP urine samples. The Am-243 tracer recovery was 103.3% and the FWHM was 38.0 keV. Figure 4 shows an example of the uranium spectra for the NRIP urine samples. The U-232 tracer recovery was 108.7% and the FWHM was 33.8 keV. The slightly high tracer recovery for U-232 is likely due to a slight difference in alpha calibration efficiency between the sample mounts and the calibration standards. This is not significant, however, as the actinide results are determined by the tracer reference values. This actinide and Sr-90 method can be used for urine samples as well as water samples. This column separation

can be used for routine as well as emergency samples. Larger centrifuge tubes may be used for the analysis of larger sample aliquots. If electrodeposition is desired instead of cerium fluoride microprecipitation for actinide analysis on routine urine samples, 0.04M rongalite (sodium formaldehyde sulfoxylate) can be substituted for titanium chloride reductant in the Pu column strip solution to avoid titanium interference with electroplating (9).

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 emergency analyses of water or urine samples. This method has high tracer recoveries, effectively removes interferences and combines the sample preparation for a large number of actinides and Sr-90 into a single column extraction method. It allows rapid analysis of actinides and Sr-90 to be performed on water and urine samples in the event of a radiological incident in support of emergency response actions. This was demonstrated by the SRS Environmental laboratory performance in the NRIP-06 program.

Acknowledgment

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Table Captions

Figure Captions

Table 1. Turnaround times on NRIP-06 samples

Nuclide	Water	Urine
Pu-238	7.2 hrs.	7.4 hrs.
Pu-239	7.2 hrs.	7.4 hrs.
Am-241	7.2 hrs.	7.4 hrs.
U-234	7.2 hrs.	7.4 hrs.
U-235	7.2 hrs.	7.4 hrs.
U-238	7.2 hrs.	7.4 hrs.
Sr-90	4.6 hrs.	5.8 hrs

Table 2. Time table to analyze NRIP samples

- 7:30 am Pour aliquots/add tracers
- 7:40 am Calcium phosphate precipitation
- 8:30 am Sample loading to columns
- 9:45 am Sr cartridge to 2nd lab technician to rinse/strip/mount
- 11-11:30am Sr to count room (results by ~12 pm)
- 11:30-1:00 pm Actinide fractions to count room
- 12:30-2:00 pm Actinide counts complete

Table 3 Analysis results-NRIP water samples

Nuclide	Reference (Bq/g)	Measured (Bq/g)	Difference (%)
Pu-238	1.712	2.040	19.2 %
Pu-239	1.632	2.090	28.1 %
Am-241	1.560	1.700	9.0 %
U-238	4.027	4.470	11.0 %
U-234	3.879	4.090	5.4 %
U-235	0.185	0.156	-15.7 %
Sr-90*	3.749	6.820	81.9 %
Sr-90**	3.749	4.330	15.5 %

* Counted on high background gas proportional counters-reported

**Counted on low background counters <8 hrs. but not reported

Table 4 Analysis results-NRIP urine samples

Nuclide	Reference (Bq/g)	Measured (Bq/g)	Difference (%)
Pu-238	2.008	2.138	6.5 %
Pu-239	1.914	1.888	-1.4 %
Am-241	1.830	1.458	-20.3 %
U-238	4.723	4.342	-8.1 %
U-234	4.549	4.632	1.8 %
U-235	0.217	0.164	-24.4 %
Sr-90*	4.397	8.128	84.8 %
Sr-90**	4.397	4.590	4.4 %

* Counted on high background gas proportional counters-reported

**Same mounts counted on low background counters later- not reported

Table 5 Analysis results-NRIP water samples (longer counts)

Nuclide	Reference (Bq/g)	Measured (Bq/g)	Difference (%)
Pu-238	1.712	1.810	5.7 %
Pu-239	1.632	1.787	9.5 %
Am-241	1.560	1.572	0.77 %
U-238	4.027	4.386	8.9 %
U-234	3.879	4.207	8.5 %
U-235	0.185	0.237	28.1 %

4 hour counts instead of 1 hour

Table 6 Analysis results-NRIP urine samples (longer counts)

Nuclide	Reference (Bq/g)	Measured (Bq/g)	Difference
Pu-238	2.008	1.874	-6.7 %
Pu-239	1.914	1.852	-3.2 %
Am-241	1.830	1.614	-11.8 %
U-238	4.723	4.681	-0.89 %
U-234	4.549	4.789	5.3 %
U-235	0.217	0.288	32.7 %

4 hour counts instead of 1 hour

Figure 1 Vacuum box system with stacked cartridges

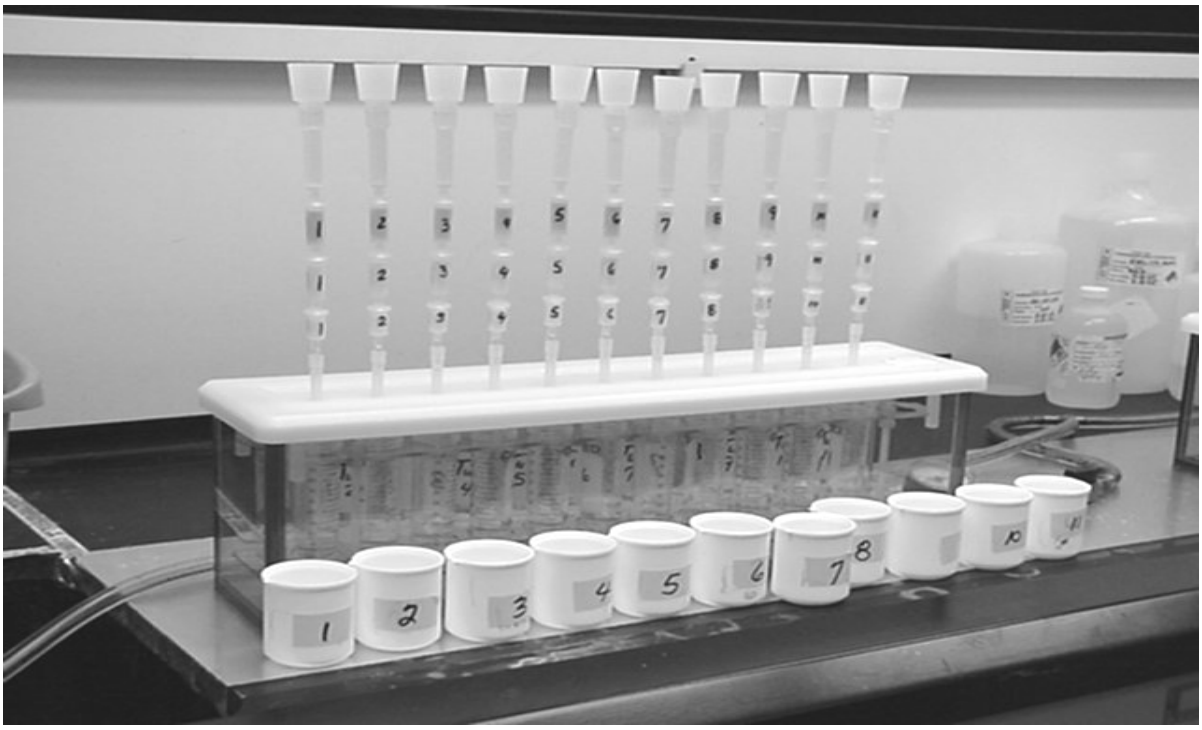


Fig. 2 Alpha spectra showing Pu Isotopes in NRIP water

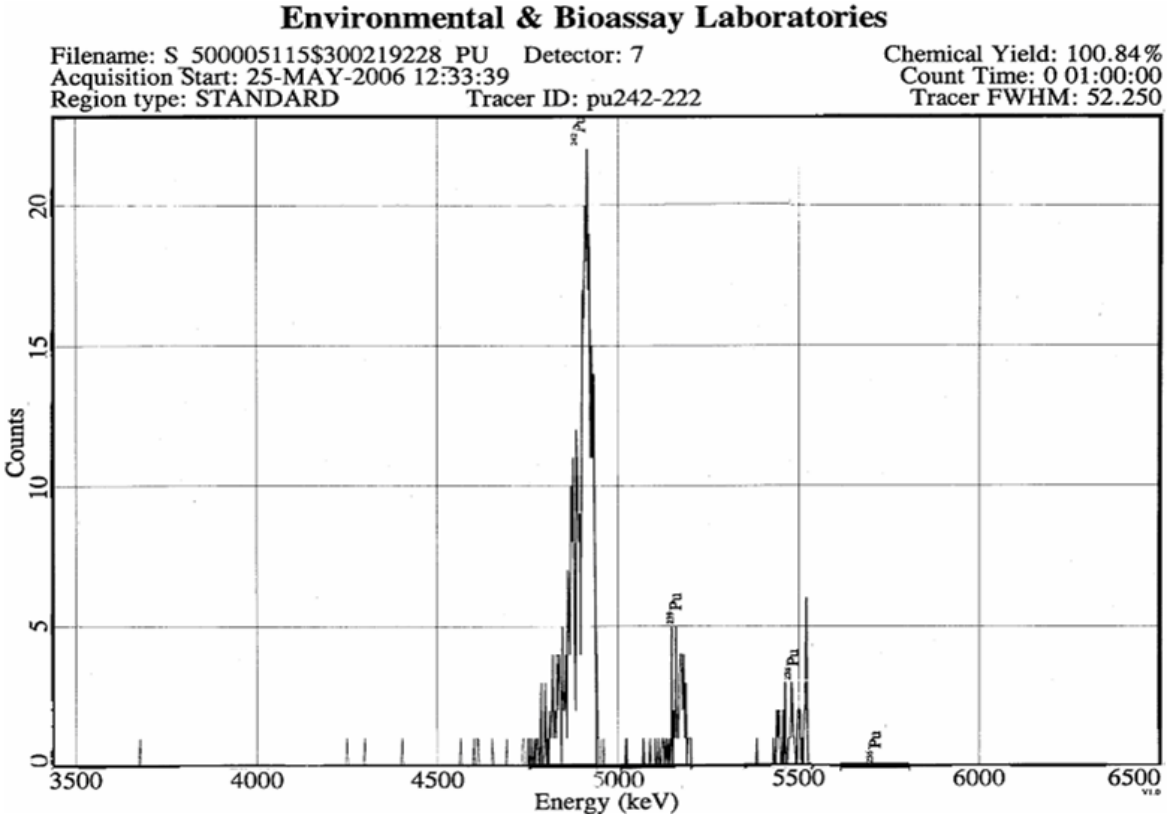


Fig. 3 Alpha spectra showing Pu Isotopes in NRIP urine

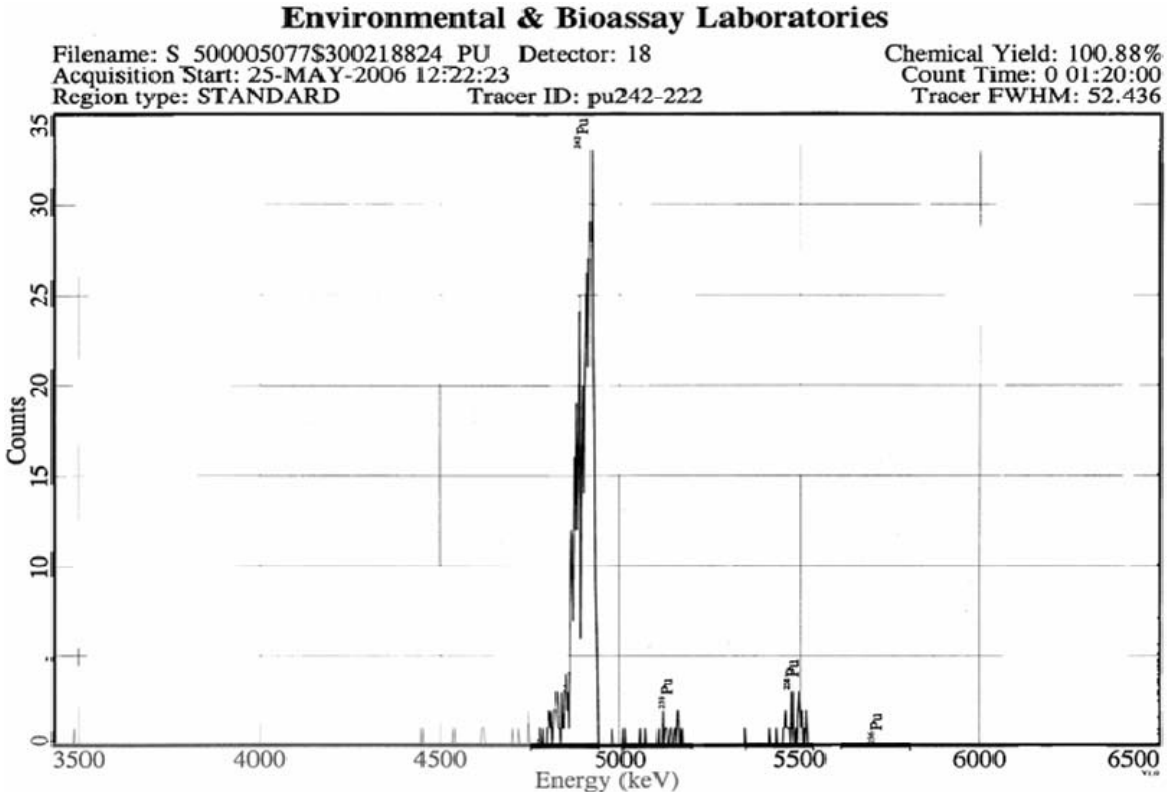


Figure 4 Alpha Spectra showing U Isotopes in NRIP urine

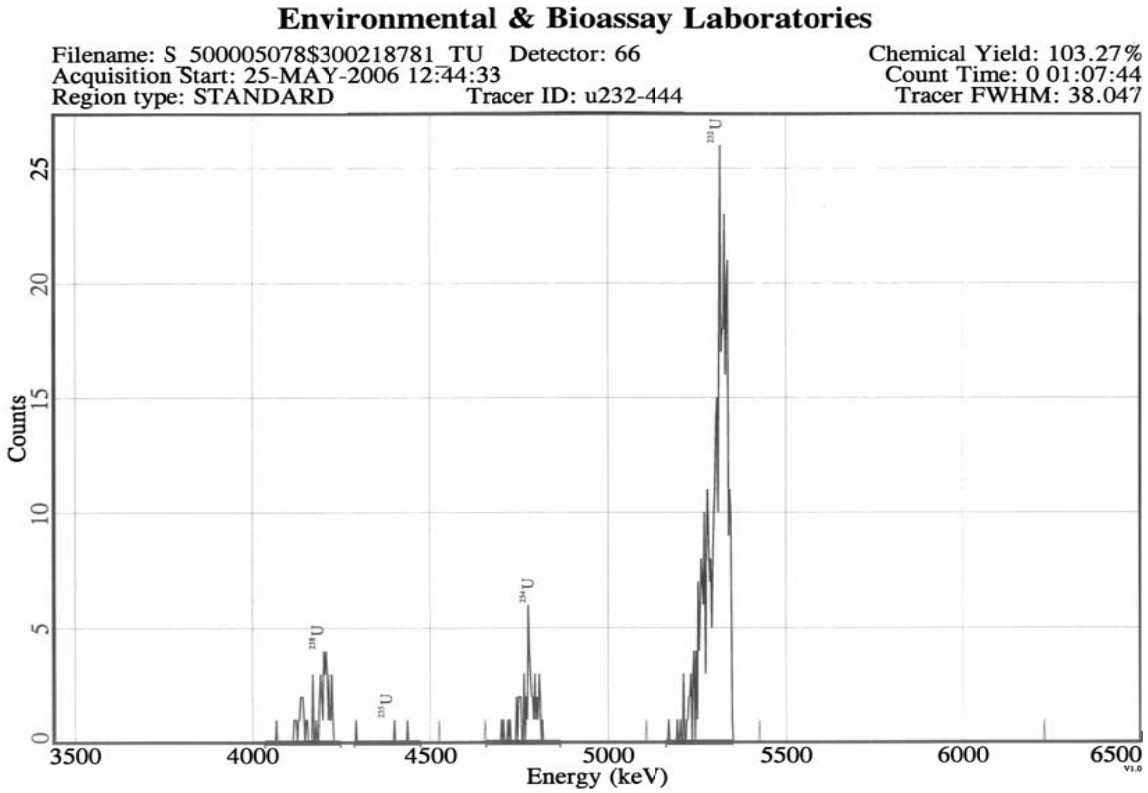
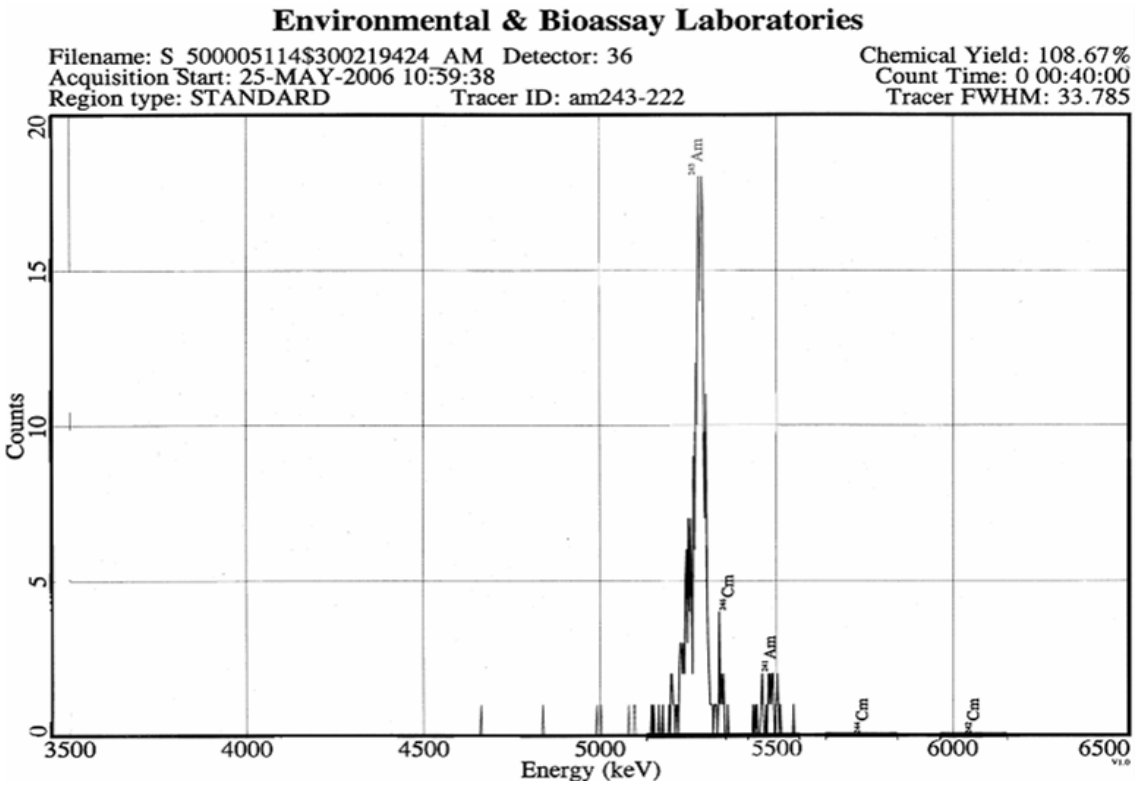


Figure 5 Alpha spectra showing Am isotopes in NRIP urine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Energy (keV)
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244Cm
241Am
240Cm
242Cm