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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 Bioassay 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 the requested 8 hour turnaround time. A new, 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. By using vacuum box cartridge technology and stacked cartridges with rapid flow rates, sample preparation time was minimized. 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.

Key Words

Water

Urine

Actinide analysis

Emergency preparedness

Extraction chromatography

Separations

Resin

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 Laboratory for several years for a variety of sample matrices (3, 4, 5). A new method was recently reported by this laboratory for rapid analysis of actinides and Sr-89/90 in water (6). This method has also been applied 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 Bioassay Laboratory (Aiken, SC, USA), Fluor Daniel (Hanford Site, Richland, WA), NAREL Laboratory (EPA Lab, Huntsville, AL), 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 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. To save time, strontium 89/90 is separated at the same time as the actinides using stacked Sr Resin cartridges 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 that participated in NRIP-06 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). 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. Four milligrams of stable strontium were added to each sample. 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 Analytcs, Inc. (Atlanta, GA, USA) and diluted to the approximately 2 pCi/mL level. Sr-90 standard from Analytcs, 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 were 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 100 mL samples, the aliquoting and the above reagent additions were performed in a 225mL 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 HNO₃ and 8 mL of 2M Al(NO₃)₃ directly in the centrifuge tubes. The final column 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. For urine samples, the calcium phosphate precipitate was transferred to a 100 ml glass beaker using a small volume of concentrated nitric acid. The sample was evaporated to dryness on a hotplate, 3 ml of concentrated nitric acid and 3 ml of 30 wt% of hydrogen peroxide were added and 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. 50 mL centrifuge tubes were used to collect rinse or final purified fractions.

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 ~ 1 drop per second. The column load solution and column strip solution flow rates were ~1 drop per second, while column flow rates were passed through the columns ~2 drops per second. Because of the relatively small particle size and tight packing, there is no channeling when cartridges go dry during the separations. 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. Fifty 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-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. 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 Bioassay 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 their 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. 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 as part of this exercise. Table 2 shows a typical timeline for these analyses. The actinides reported included plutonium,

uranium and americium isotopes. Table 3 shows the measured SRS values for the water samples compared to the NIST reference values. The accuracy for the actinide isotopes was very good, considering the short count times, and more than adequate to meet emergency response needs. The Sr-90 results were biased high due to counting on relatively high background detectors and the relatively low level of Sr-90 in the samples. The same Sr planchets were counted on different, low background counters within the 8 hour time frame and the bias was only 15.5%, more than adequate for emergency response needs. Table 4 shows the measured SRS values for the urine samples compared to the NIST reference values. Like the water results, the accuracy was more than adequate to meet emergency response needs. As with the water, the Sr-90 results were biased high due to counting on relatively high background detectors and the relatively low level of Sr-90 in the samples. The same Sr planchets were counted later on different, low background counters and the bias was only 4.4%, demonstrating very good accuracy for the method. Tables 5 and 6 show results for the same alpha mounts counted for 4 hours and compared to the NIST reference values. Most of the actinide isotopes were within 10% of the NIST reference values for both water and urine samples, more than adequate to meet emergency response needs. The U-235 results had a more significant bias, but this is likely due to the very low levels of U-235 present in the samples and relatively short count times. Figure 1 shows an example of the plutonium spectra for NRIP water samples. The Pu-242 tracer recovery was 100.8% and the Full Width Half Maximum (FWHM) was 52.2, showing very good alpha peak resolution. Figure 2 shows an example of the plutonium spectra for NRIP urine samples. The Pu-242 tracer recovery was 100.9% and the Full Width Half Maximum (FWHM) was 52.4. The Pu recoveries and FWHM were very similar for water

and urine. Figure 4 shows an example of the uranium spectra for urine samples. The U-232 tracer recovery was 103.3% and the Full Width Half Maximum (FWHM) was 38.0. Figure 5 shows an example of the americium spectra for urine samples. The Am-243 tracer recovery was 108.7% and the Full Width Half Maximum (FWHM) was 33.8. The Sr-90 analyses can be performed quickly because Sr-90 was 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. It should be noted that the rapid column separation method can also be applied to air filters, vegetation and foods after the appropriate sample preparation steps, such as acid digestion and /or furnace heating of the samples. This is routinely performed in the SRS Environmental Bioassay lab.

Conclusions

The new stacked cartridge method developed in the SRS Environmental Bioassay 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-89/90 into a single column extraction method. It allows rapid analysis of actinides and Sr-89/90 to be performed on both water and urine samples in the event of a radiological incident in support of emergency response actions. This was demonstrated by the SRS Environmental Bioassay Laboratory performance in the NRIP-06 program.

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Table Captions

Table 1. Turnaround Times on NRIP-06 Samples

Table 2. Time Table to Analyze NRIP Samples

Table 3 Analysis Results-NRIP Water Samples

Table 4 Analysis Results-NRIP Urine Samples

Table 5 Analysis Results-NRIP Water Samples (Longer counts)

Table 6 Analysis Results-NRIP Urine Samples (Longer counts)

Figure Captions

Figure 1. Vacuum Box System with Stacked Cartridges

Figure 2. Alpha Spectrometry Spectra showing Pu Isotopes in NRIP-06 Water Samples

Figure 3. Alpha Spectrometry Spectra showing Pu Isotopes in NRIP-06 Urine Samples

Figure 4. Alpha Spectrometry Spectra showing U Isotopes in NRIP-06 Urine Samples

Figure 5. Alpha Spectrometry Spectra showing Am Isotopes in NRIP-06 Urine Samples

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

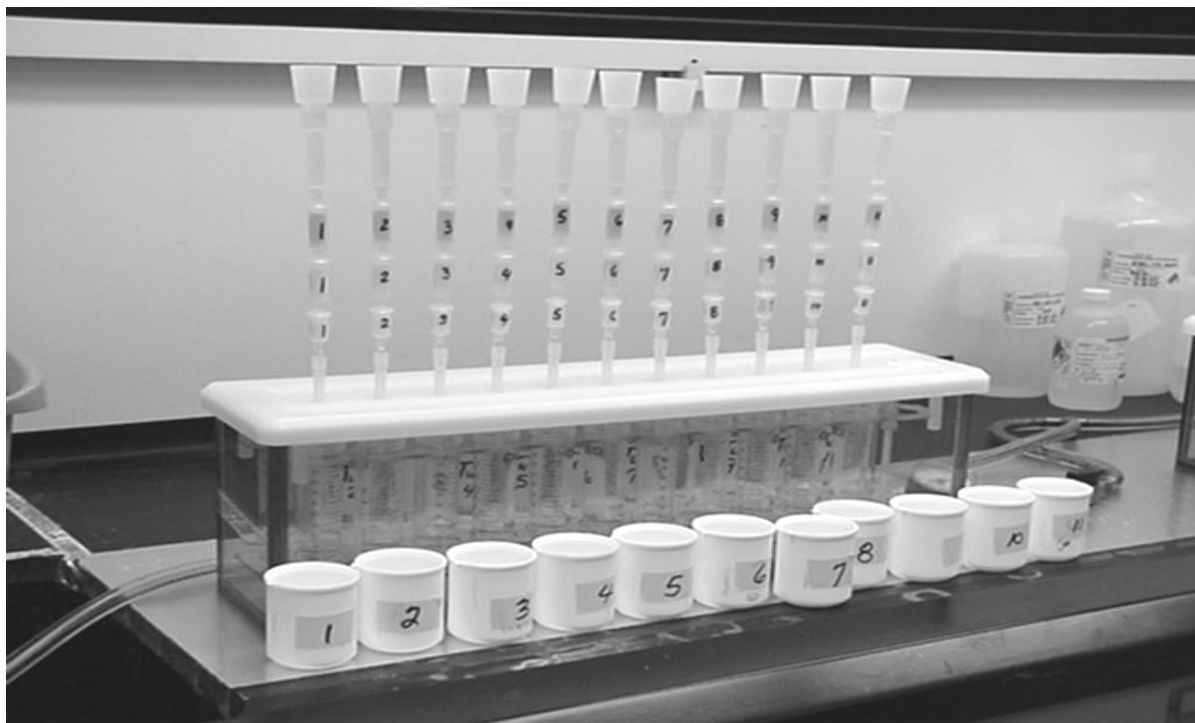


Figure 2 Alpha Spectra showing Pu Isotopes in NRIP Water

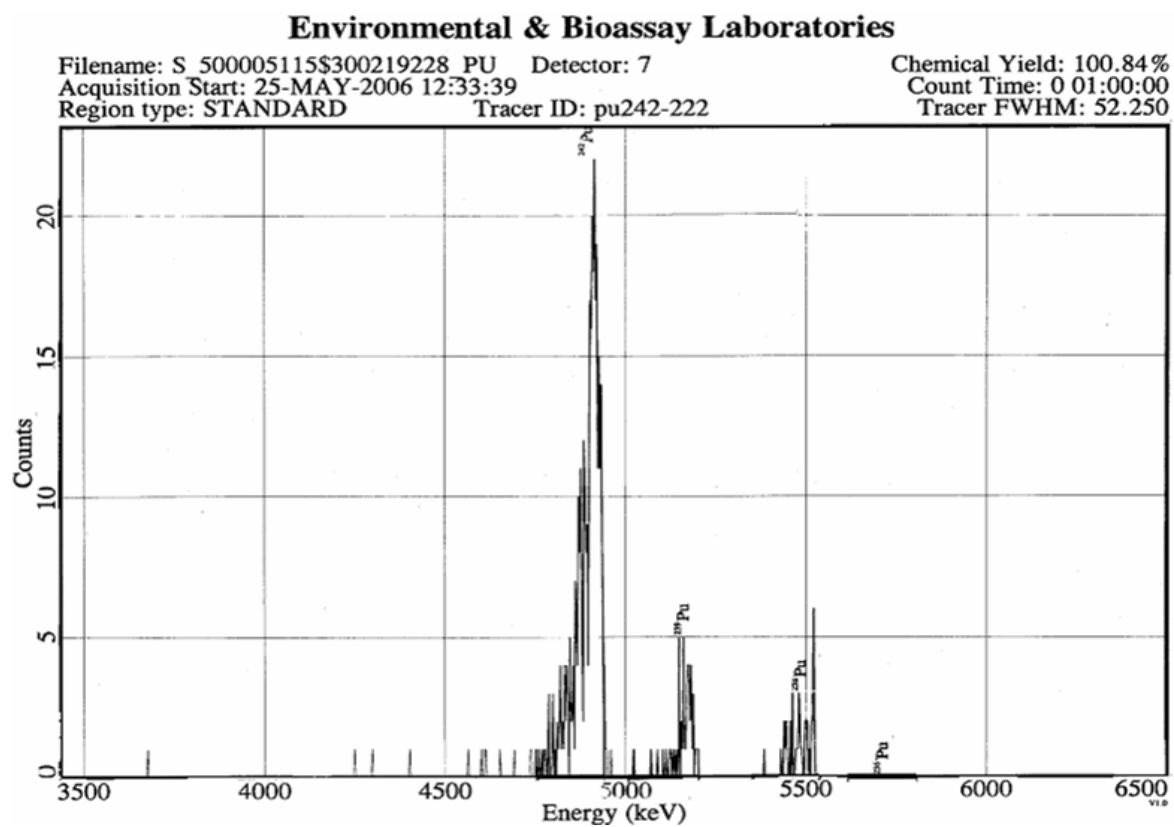


Figure 3 Alpha Spectra showing Pu Isotopes in NRIP Urine

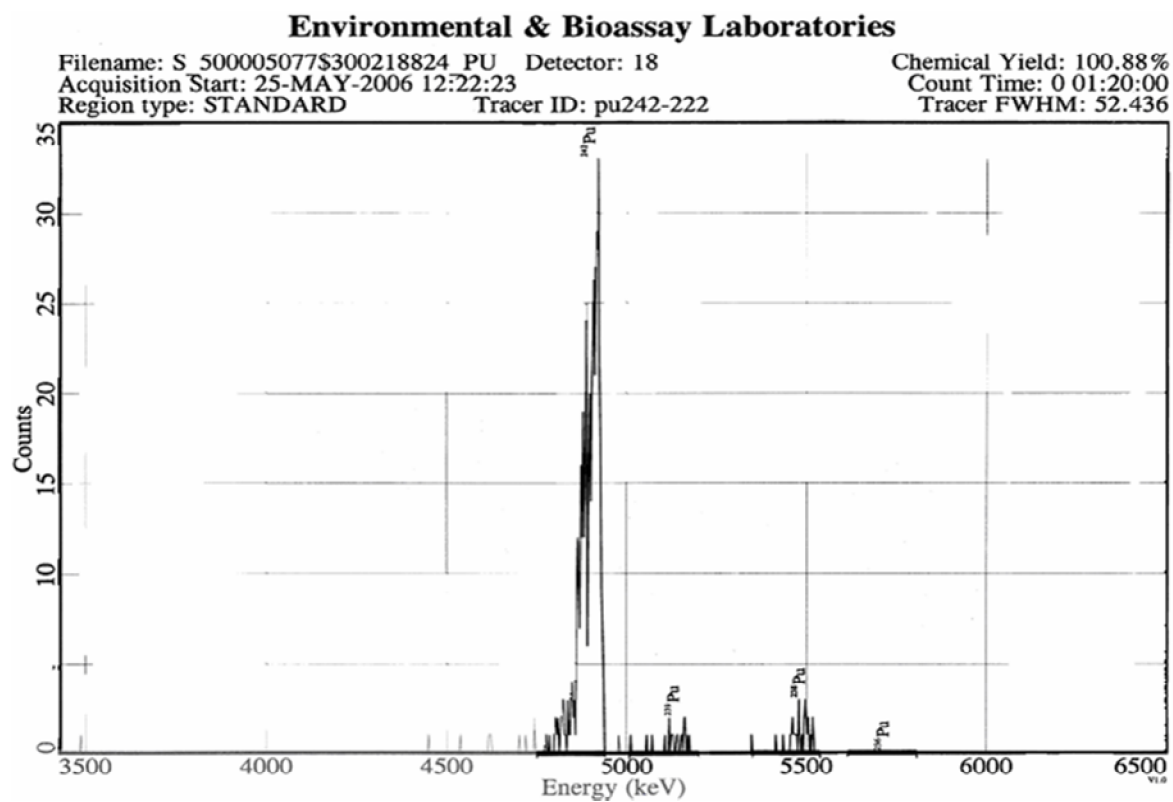


Figure 4 Alpha Spectra showing U Isotopes in NRIP Urine

