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New Column Separation Method for Emergency Urine Samples

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Abstract

The Savannah River Site Environmental Bioassay Lab participated in the 2007 NRIP Emergency Response program administered by the National Institute for Standards and Technology (NIST) in May, 2007. A new rapid column separation method was applied directly to the NRIP 2007 emergency urine samples, with only minimal sample preparation to reduce preparation time. Calcium phosphate precipitation, previously used to pre-concentrate actinides and Sr-90 in NRIP 2006 urine and water samples, was not used for the NRIP 2007 urine samples. Instead, the raw urine was acidified and passed directly through the stacked resin columns (TEVA+TRU+SR Resins) to separate the actinides and strontium from the NRIP urine samples more quickly. This improvement reduced sample preparation time for the NRIP 2007 emergency urine analyses significantly. This approach works well for small volume urine samples expected during an emergency response event. Based on initial feedback from NIST, the SRS Environmental Bioassay Lab had the most rapid analysis times for actinides and strontium-90 analyses for NRIP 2007 urine samples.

Introduction

There is an increasing need to develop faster analytical methods for emergency response, including emergency urine samples [1,2]. The Savannah River Site Environmental Bioassay Lab participated in the 2007 NRIP Emergency Response program administered by the National Institute for Standards and Technology (NIST) in May, 2007. A new rapid column separation method was applied directly to the NRIP 2007 emergency urine samples, with only minimal sample preparation to reduce preparation time. Calcium phosphate precipitation, used to pre-concentrate actinides and Sr-90 in NRIP 2006 urine and water samples [3], was not used for the NRIP 2007 urine samples. Instead, the raw urine was acidified and passed directly through the stacked resin columns (TEVA+TRU+SR Resins) to separate the actinides and strontium directly from the NRIP urine samples.

This improvement reduced sample preparation time for the NRIP 2007 emergency urine analyses significantly. This approach works well for the small volume urine samples expected during an emergency response event. Based on initial feedback from NIST, the SRS Environmental Bioassay Lab had the most rapid analysis times for actinides and strontium-90 analyses for NRIP 2007 urine samples. Health Canada/Radiation Protection Bureau (Ottawa, Canada), WIPP (Carlsbad, NM, USA) and Center for Disease Control (Atlanta, GA,USA) also participated in NRIP 2007 for urine samples.

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 [4]. 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.

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.

Sample Preparation. A 20 ml aliquot of each NRIP 2007 urine samples was aliquoted into a 100 ml beaker. Tracers were added and 6 ml of 15.7M HNO3 and 5 ml of 2M $Al(NO_3)_3$ were added to adjust the acidity of each sample and complex anions such as phosphate. The samples were swirled to mix each solution. After acid adjustment, the column load solution was ~3M HNO3 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 UTEVA Resin column was prepared from a water slurry of the resin.

Column separation. The following column separation was performed, as outlined in a previous paper [4]. TEVA, TRU, and SR Resin cartridges were stacked on the vacuum box from top to bottom, in that order. Figure 1 shows the vacuum box apparatus and the stacked TEVA, TRU and Sr Resin cartridges. 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 1.5 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, 20 ml of 9M hydrochloric acid were added.

The plutonium was stripped from TEVA Resin with 20 mls of 0.1M hydrochloric acid-0.05M hydrofluoric acid –0.03M titanium (III) 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 15 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene filters and counted by alpha spectrometry.

The TRU cartridges were placed on a separate vacuum box and processed at the same time as the TEVA Resin cartridges. 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 15 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 15 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.

Actinide filters were counted by alpha spectrometry for approximately one hour. Strontium count times were twenty minutes.

Apparatus

Plutonium, americium, curium and uranium measurements were performed by alpha-particle pulse-height measurements using Passivated Implanted Planar Silicon (PIPS) detectors. Sr-90 measurements were performed using a Tennelec LB 4100 gas proportional counter. 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 improvement in turnaround times for actinides and Sr-90 in NRIP 2007 urine samples compared to NRIP 2006 turnaround times. The SRS Environmental Bioassay Lab reported Sr-90, Pu-239/240, Pu-238, U-234, U-235, U-238,

and Am-241 in urine well within the 8 hour target time. Sr-90 in NRIP urine samples was reported in only 3.9 hours, instead of the 5.8 hour time in 2006. Actinide isotopes were reported in 4.6 to 5.2 hours, faster than the 7.4 hour times in 2006. The SRS NRIP 2007 report times were faster than the NRIP 2006 samples due to the faster separation method. By eliminating the calcium phosphate precipitation and the ashing step to remove residual organics, the analysis times were reduced. If Sr-89/90 differentiation is needed, there are also Čerenkov counting techniques for more rapid determination of Sr-89 and Sr-90 [5].

Table 2 shows the average difference of the SRS measured values for NRIP-2007 urine samples versus the NIST reference values. The average difference from NIST reference values for 5 samples containing approximately 3 different levels of activity is shown for each analyte. Considering the short count times, the accuracy of the measured values was good, more than adequate for emergency response screening. The same samples were also recounted later to determine the effect of longer count times. Table 2 shows the SRS reported values compared with the NIST reference values for Am-241 for each sample analyzed. The differences, which range from -9.1% to -38%, fall within the reported uncertainty ranges for each reported result at the 95% confidence level. The larger biases correlate with the lower activity samples and the larger reported uncertainties. Table 2 also show the SRS values when the same samples were recounted for 6 hours. The differences from the NIST values range from -3.5% to +7.6%, reducing the biases significantly. The lower level activity samples showed the most reduction in bias. Table 3 shows the SRS reported values compared with the NIST reference values for Pu-239/240 for each sample analyzed. The differences, which range from -36% to +21%, fall within the reported uncertainty ranges for each reported result at the 95% confidence

level. Table 2 also show the SRS values when the same samples were recounted for 6 hours. The differences from the NIST values range from -6.5% to +7.4%. Table 4 shows the SRS reported values compared with the NIST reference values for U-238 for each sample analyzed. The differences, which range from -20% to +1.6%, fall within the reported uncertainty ranges for each reported result at the 95% confidence level. Table 4 also show the SRS values when the same samples were recounted for 6 hours. The differences from the NIST values range from -9.4% to +0.6%. The biases did not change significantly for the 6 hour recount data, presumably due to the higher activity of the U-238 and the lower uncertainties in the I hour count time for the reported values. The data shown for Am-241, Pu-239/240 and U-238 indicate the trend of reduced uncertainty and biases that would be seen for longer count times, depending on the activity level of the samples. The count time that one would use for emergency urine samples can be adjusted depending on the activity levels in the samples and the data quality requirements needed for emergency screening samples.

Figure 3 shows an example of the plutonium spectra for the NRIP 2007 urine samples. The Pu-242 tracer recovery was 96.1% and the Full Width Half Maximum (FWHM) was 73.3 keV, showing acceptable alpha peak resolution. Figure 4 shows an example of the uranium spectra for the NRIP urine samples. The U-232 tracer recovery was 99.1% and the FWHM was 44.1 keV, showing good alpha resolution. Figure 5 shows an example of the americium spectra for the NRIP 2007 urine samples. The Am-243 tracer recovery was 100.4% and the FWHM was 39.7 keV, showing good alpha resolution. 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 [6].

Thorium and curium were not measured in this work. 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. As reported previously, thorium isotopes and curium isotopes can be analyzed together by adding a clean-up step to this sepration method using DGA Resin®, (Diglycolamide Resin, Eichrom Technologies). DGA Resin can be used to remove Ac-225 and allow the separation and analysis of thorium isotopes and curium isotopes using the same sample preparation [7].

Conclusions

The new urine method developed in the SRS Environmental Laboratory is a rapid method for the analysis of urine samples that is well-suited for the small volumes of urine expected during a radiological emergency response event. This method has high tracer recoveries, effectively removes interferences and combines the sample preparation for actinides and Sr-90 into a single column extraction method. The improved report times in the NRIP-2007 program by the SRS Environmental laboratory demonstrate the speed and effectiveness of this new method.

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References

1. Inn, K.G.W., et al., Proceedings of the 50th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry, Cincinnati, OH, 11/3/04, 113
2. Stricklin, D.L., et al., 2002, J. Radioanal. Nucl. Chem 251, No.1, (2002) 69
3. Maxwell, S.L, J. Radioanal. Nucl. Chem., 275, No.3 (2008)
4. Sill, C. , Analytical Chemistry, Vol. 46, No. 11, (1974) 1426
5. Martin, J.P. and Odell, K.J., Radioactivity and Radiochemistry, Vol. 9, No 3, (1998), 49
6. Maxwell, S. L. and Fauth, D. J. , Radioactivity and Radiochemistry, Vol. 11, No 3., (2000), 28
7. S. L. Maxwell, J. Radioanal. Nucl. Chem, Vol. 267, No.3 (2006), 537

Table Captions

Figure Captions

Table 1. Improved turnaround times on NRIP-07 urine samples

Nuclide	NRIP 2006	NRIP 2007
Am-241	7.4 hrs	4.6 hrs
Pu-238, 239	7.4 hrs	4.8 hrs
U-234, 235, 238	7.4 hrs	5.2 hrs
Strontium-90	5.8 hrs	3.9 hrs

Table 2. NRIP-2007 Urine Analysis Average Results

Nuclide	Avg. Difference Reported vs NIST	Avg. Difference Longer Recounts
Pu-238	8.4 %	4.8%
Pu-239	-2.7 %	1.8%
Am-241	-22 %	1.7%
U-238	-7.7 %	-6.0%
U-234	12 %	-5.2%
Sr-90	-7.4 %	-11.6%

Actinides: 1 hour count time / Recounts: 6 hour count time

Sr-90: 20 minute count time/Recounts: 1 hour count time

Table 3. NRIP-2007 Urine Analysis Results for Am-241

Sample ID	NIST Value (Bq/Smp)	SRS Reported Value (Bq/Smp ± %, k=2)	Difference (±%)
721	0.1999	0.125 ±46%	-38
725	0.1999	0.134 ±47%	-33
733	0.3360	0.257 ±36%	-24
738	0.6124	0.548 ±26%	-11
741	0.5943	0.540 ±27%	-9.1

Sample ID	NIST Value (Bq/Smp)	SRS 6 hr Count (Bq/Smp ± %, k=2)	Difference (±%)
721	0.1999	0.215 ±19%	+7.6
725	0.1999	0.192 ±19%	- 3.5
733	0.3360	0.343 ±17%	+2.1
738	0.6124	0.609 ±16%	-0.6
741	0.5943	0.613 ±15%	-3.2

Table 4. NRIP-2007 Urine Analysis Results for Pu-239/240

Sample ID	NIST Value (Bq/Smp)	SRS Reported Value (Bq/Smp ± %, k=2)	Difference (±%)
721	0.0848	0.077 ±56%	-9.2
725	0.0845	0.054 ±73%	-36
733	0.1426	0.150 ±44%	+5.2
738	0.2599	0.273 ±32%	+5.0
741	0.2522	0.306 ±31%	+21

Sample ID	NIST Value (Bq/Smp)	SRS 6 hr Count (Bq/Smp ± %, k=2)	Difference (±%)
721	0.0848	0.085 ±25%	-0.4
725	0.0845	0.079 ±27%	- 6.5
733	0.1426	0.156 ±21%	+9.4
738	0.2599	0.253 ±21%	-2.6
741	0.2522	0.271 ±21%	+7.3

Table 5. NRIP-2007 Urine Analysis Results for U-238

Sample ID	NIST Value (Bq/Smp)	SRS Reported Value (Bq/Smp ± %, k=2)	Difference (±%)
721	0.2254	0.207 ±35%	-8.2
725	0.2244	0.179 ±37%	-20
733	0.3789	0.373 ±28%	-1.6
738	0.6905	0.660 ±23%	-4.4
741	0.6700	0.643 ±24%	-4.0

Sample ID	NIST Value (Bq/Smp)	SRS 6 hr Count (Bq/Smp ± %, k=2)	Difference (±%)
721	0.2254	0.204 ±18%	-9.5
725	0.2244	0.206 ±18%	-8.2
733	0.3789	0.381 ±15%	+0.6
738	0.6905	0.253 ±15%	-3.4
741	0.6700	0.271 ±15%	-9.6

Figure 1 Vacuum box system with stacked cartridges

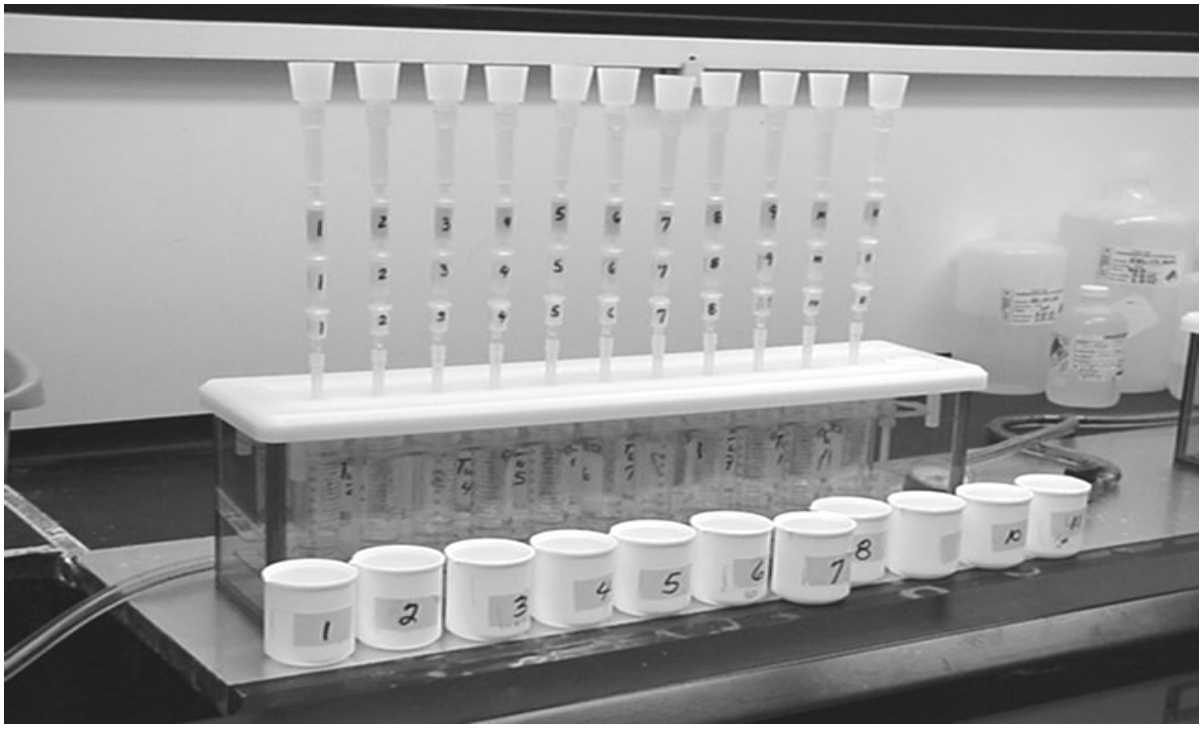

Figure 2 Emergency Column Extraction Method for Raw Urine

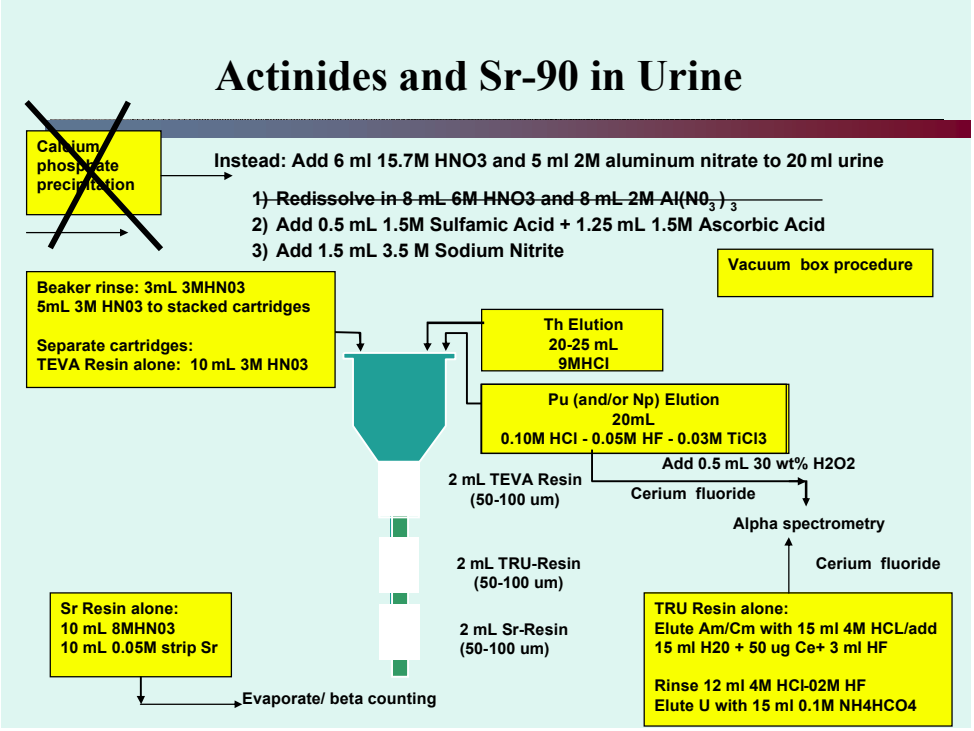

Fig. 3 Alpha spectra showing Pu Isotopes in NRIP 2007 urine

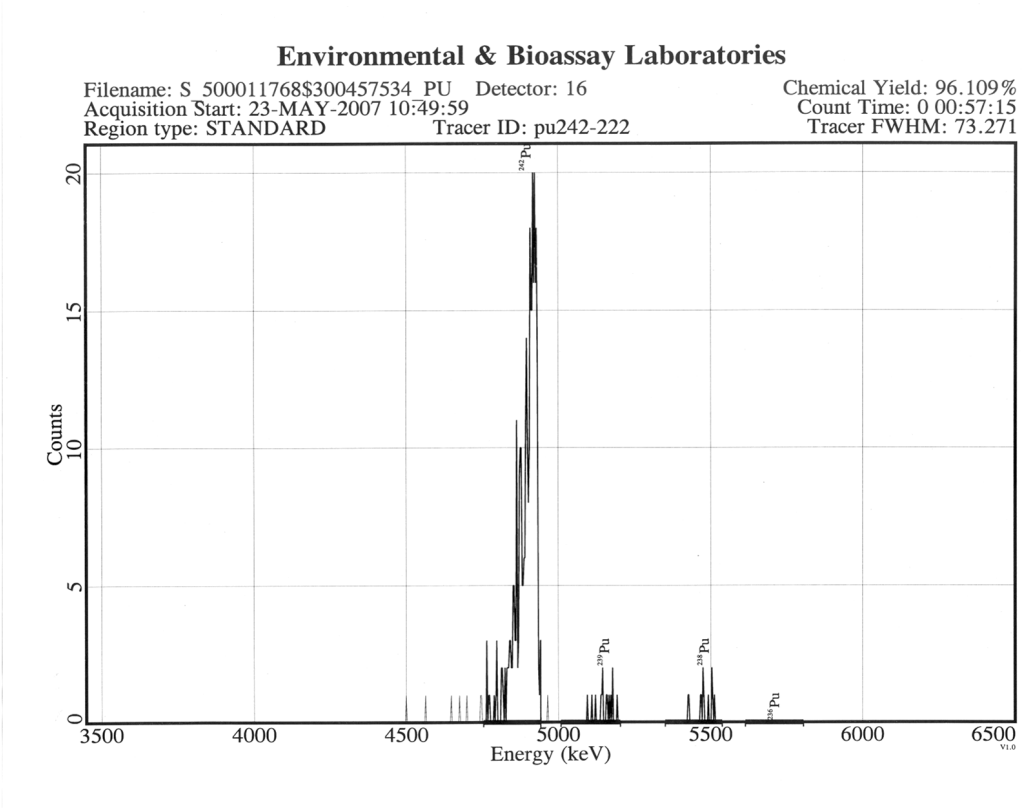

Figure 4 Alpha Spectra showing U Isotopes in NRIP 2007 urine

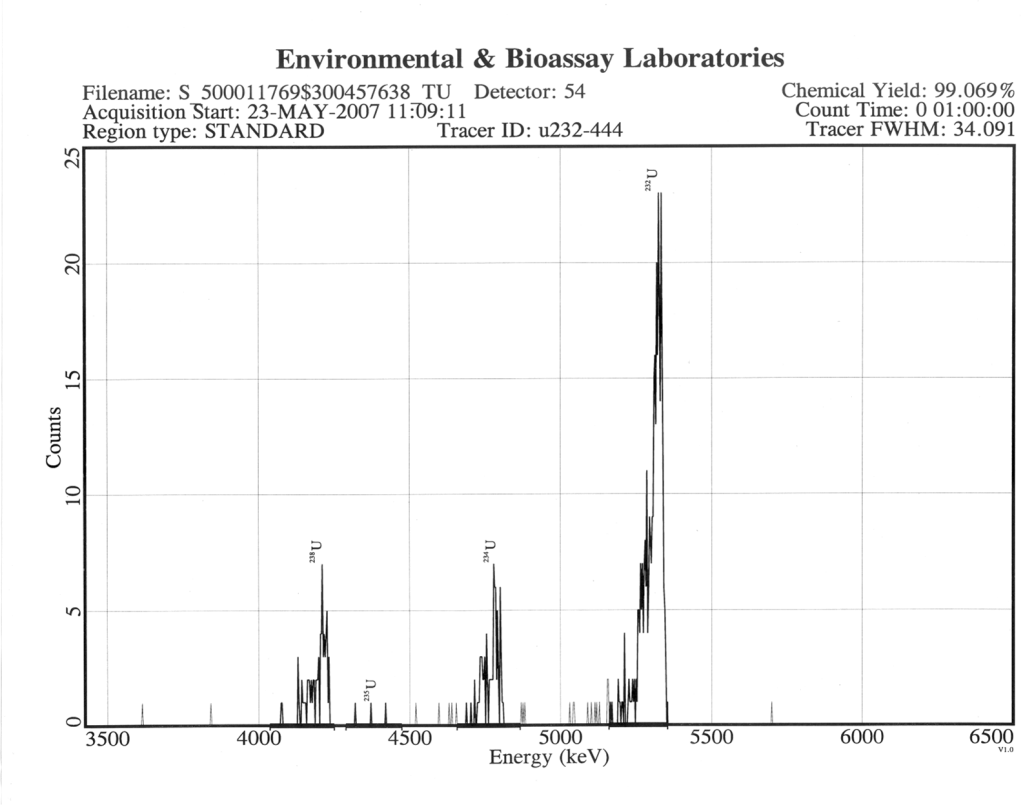

Figure 5 Alpha spectra showing Am isotopes in NRIP 2007 urine