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New Method for Determination of Actinides and Strontium in Animal Tissue

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Abstract

The analysis of actinides in animal tissue samples is very important for environmental monitoring. There is a need to measure actinide isotopes with very low detection limits in animal tissue samples, including fish, deer, hogs, beef and shellfish. A new, rapid actinide separation method has been developed and implemented that allows the measurement of plutonium, neptunium, uranium, americium, curium and strontium isotopes in large animal tissue samples (100-200 g) with high chemical recoveries and effective removal of matrix interferences. This method uses stacked TEVA Resin®, TRU Resin® and DGA-Resin® cartridges from Eichrom Technologies (Darien, IL, USA) that allows the rapid separation of plutonium (Pu), neptunium (Np), uranium (U), americium (Am), and curium (Cm) using a single multi-stage column combined with alpha spectrometry. Sr-90 is collected on Sr Resin® from Eichrom Technologies (Darien, IL, USA). After acid digestion and furnace heating of the animal tissue samples, the actinides and Sr-89/90 are separated using column extraction chromatography. This method has been shown to be effective over a wide range of animal tissue matrices. By using vacuum box cartridge technology with rapid flow rates, sample preparation time is minimized.

Introduction

The analysis of plutonium, neptunium, uranium, americium, curium and strontium-89/90 at extremely low levels requires the analysis of large animal tissue samples. A. Erikson used a series of coprecipitation steps after sample ashing to separate and measure actinides and strontium in animal tissue samples. [1] J. Mellado described a new method to determine actinides and strontium in fish samples using UTEVA Resin, TRU Resin and Sr-Resin.[2] Samples up to 40 grams were analyzed with tracer recoveries typically at 40% or less. Am recoveries varied from 2% to 80%, depending on sample size. S. Lee reported high chemical recoveries for marine environmental samples using a combination or anion exchange and column extraction chromatography, however, the anion exchange work required the use of relatively large volumes of acids with evaporation steps as well as an additional calcium oxalate precipitation step to preconcentrate americium. [3]

As part of a food surveillance program at the Savannah River Site (Aiken, SC, USA), freshwater and saltwater fish, shellfish, deer and hogs are routinely analyzed for radionuclide content. A new animal tissue method was developed in the SRS Environmental Laboratory that is simple, effective and allows the use of small resin cartridges to separate actinides and strontium isotopes from 200 gram tissue samples with high tracer recoveries and effective removal of interferences. This method was tested over a wide range of animal tissue matrices. This new method uses stacked TEVA Resin®, TRU Resin® and DGA-Resin® 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 (using 2 ml resin volumes) to separate actinide isotopes for alpha spectrometry. DGA-Resin®, which has very strong retention for americium and curium, is used to enhance chemical recoveries of those analytes from this difficult matrix. The DGA Resin has a capacity (k') factor of approximately 30,000 in 3M nitric acid, much higher than americium retention on TRU Resin (~100). [4]

Strontium was collected from the evaporated column load and rinse solutions, redissolved and separated using Sr Resin. Three milliliters of Sr Resin was used to ensure very high recoveries of strontium, but two milliliters of resin probably could have been used to minimize costs with a moderate decrease in strontium yields.

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)), DGA Resin (N,N,N',N' tetraoctyldiglycolamide), 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-236, U-232 and Am-243 were obtained from Analytics, Inc. (Atlanta, GA, USA) and diluted to the approximately 1-2 pCi/ml (0.074 Bq/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. Laboratory Control Standards (LCS) were analyzed using Pu-238, Am-241, U-235, Np-237 and Cm-244 standards that were obtained from Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 2 pCi/ml (0.074 Bq/ml).

Procedures

Column preparation. TEVA, TRU, DGA 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, Inc.). 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. The animal tissue samples were digested on a hot plate using a mixture of 400 ml of aqua regia (4 parts concentrated nitric acid plus 1 part concentrated hydrochloric acid), followed by the addition of 100 ml of 30 wt% hydrogen peroxide after the volume was reduced to ~100 ml. Figure 1 shows acid-digested fish samples. The sample solutions were evaporated to dryness and placed in a furnace at 550˚C for ~16 hours. After removing the samples from the furnace the samples were wet-ashed using

concentrated nitric acid and 30 wt% hydrogen peroxide several times until the samples were white or nearly white. Additional heating of the samples at 550˚C was usually necessary to turn the residual solids completely white. Figure 2 shows the fish samples after they have been ashed to a white color. The ashed samples were dissolved in 12 ml 6M nitric acid and 12 ml 2M aluminum nitrate, adding additional 3M nitric acid as needed to dissolve the solids completely. 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 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 0.75 ml of 1.5M sulfamic acid and 3 ml of 1.5M ascorbic acid. When Np-237 separation is desired, 0.5 ml of 5 mg/ml Fe as ferric nitrate is also added to facilitate Np-237 reduction to Np^{4+}. The ferric ions are reduced to ferrous ions by the ascorbic acid, which reduces Np effectively to Np^{4+}. After a three-minute wait step, 2.5 ml of 3.5M sodium nitrite (freshly prepared) was added to each sample to adjust plutonium to Pu^{4+}. After the valence adjustment, the sample solution was loaded onto the stacked column at approximately 1 drop per second. The column load and rinse solution were collected to recover strontium which passes through the resins. After the sample was loaded, a beaker rinse of 5 ml of 6M HNO3 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. Eight milliliters of 0.1M nitric acid were added to each DGA column to remove any residual strontium that may have been retained on the DGA cartridges. This rinse was added to the initial column load and rinse solutions and were evaporated to dryness on a hot plate. 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 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^{6+}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 micron 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 rinsed with 3 ml 1M nitric acid, followed by 10 ml of 0.1M nitric acid to remove interferences. The rinse was discarded to waste. The DGA Resin was stripped with 10 ml of 0.25M HCl to elute 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 micron 25 mm polypropylene 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+}. 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 evaporated load and rinse solutions were redissolved in 15-20 ml 3M nitric acid, warming on a hot plate as needed. These solutions were loaded to 3 ml Sr resin cartridges (stacked 2 ml plus 1 ml Sr Resin cartridges). The SR Resin cartridges were rinsed with 10 mL of 8M HNO3, 5 ml 3M HNO3-0.05M oxalic acid, and 5 ml 8M HNO3. The Sr-89/90 was stripped from the Sr Resin using 13 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.

Fig. 3 shows the vacuum box apparatus and the stacked TEVA, TRU and DGA Resin cartridges. A second vacuum box 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. Figure 4 shows the Sr Resin cartridges stacked on a vacuum box.

Apparatus

Plutonium, neptunium, uranium, americium, and curium 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. Vacuum boxes were obtained from Eichrom Technologies (Darien, IL, USA).

Results and Discussion

Table 1 shows the performance of the method on 200 g fish samples. The average Pu-236 tracer recovery was 99.8%. Matrix spikes were also added. The Pu-238 matrix spike recovery was 100.0%, while the Np-237 recovery was 90.0%. The use of Pu-236 tracer allows the measurement of Np-237 and Pu isotopes in the same purified fraction. Figure 5 shows an example of the plutonium and neptunium isotopes spectra. The Pu-236 tracer recovery was 107.65% and the Full Width Half Maximum (FWHM) was 42.99 keV, showing very good alpha peak resolution. The average Am-243 tracer recovery was 109%, while the Am-241 matrix spike recovery was 94.3% and the Cm-244 matrix spike recovery was 94.1%. Figure 6 shows an example of the americium isotopes spectra. The Am-243 tracer recovery was 102.63% and the Full Width Half Maximum (FWHM) was 49.1 keV, showing good alpha peak resolution. The average U-232 tracer recovery was 97.1%, while the U-235 matrix spike recovery was 91.1%. Figure 7 shows an example of

the uranium isotopes spectra. The U-232 tracer recovery was 103.85% and the Full Width Half Maximum (FWHM) was 46.1 keV, showing good alpha peak resolution. The average Sr carrier recovery was 84.9% and the average Sr-90 matrix spike recovery was 97.7%, showing excellent results. If individual Sr-89 and Sr-90 results are required, a second count measured after 7-14 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. [6]

Table 2 shows the tracer recoveries and Sr carrier recovery for a wide range of animal tissue samples analyzed using this new method. Composite samples were prepared. The sample size for the edible fish samples was 200 grams, except for bream which was 100 grams. The sample size for deer, beef, hog and shellfish was 100 grams. The data also includes results from nonedible fish samples (25 gram samples). The average tracer recoveries were typically 95-100% for Pu-236 and Am-243 tracer across a wide range of sample matrices. One of the reasons the Am tracer recoveries were so high is the strong retention of Am on DGA Resin. DGA Resin, which has been applied to large soil to improve americium recoveries, clearly makes high, consistent recoveries of americium possible. [7] This is a significant improvement over methods which use only TRU Resin, and show lower, less consistent chemical recoveries for americium. U-232 and Sr carrier recoveries were closer to 90%, but still very good. The relative standard deviation of the tracer/carrier recoveries in most cases was less than 10%, indicating very good consistency for the method. In a few cases, the relative standard deviation was larger for a few of the small batches which had 1 or 2 results that had lower recoveries than the rest of the measurements. The wet-ashing and furnace heating of the animal tissue samples takes several days, but the column extraction chromatography takes only about 1 day.

Samples were typically counted 16 hours for actinide measurements. The minimum detectable concentration for Pu, Np, U, Am and Cm is approximately 4E-5 pCi/g (0.0015 Bq/kg) for a 200g sample counted for 16 hours. The minimum detectable activity for Sr-90 in a 200 gram samples is approximately 3E-3 pCi/g (0.11Bq/kg) counted 30 minutes. There is a need to measure actinides in human tissue samples as well. [8] This method was developed for animal tissue but it is assumed that it could be adapted for use on human tissue samples as well.

Conclusions

The new animal tissue method developed in the SRS Environmental Laboratory is a new method for plutonium, neptunium, uranium, americium, curium and strontium isotopes that provides very low detection limits with good chemical recoveries for a wide range of animal tissue matrices. The minimum detectable concentration for Pu, U, Am and Cm is approximately 4E-5 pCi/g (0.0015 Bq/kg) and 3E-3 pCi/g (0.11 Bq/kg) for Sr-90. This method has high tracer recoveries, effectively removes interferences and combines the sample preparation for plutonium, neptunium, uranium, americium, curium and strontium into a single multi-stage column extraction method. The new method utilizes the new resin, DGA Resin, which has very strong retention for americium and curium. As a result, americium and curium chemical recoveries are extremely high, typically 95-100%.

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Table Captions

Figure Captions

Table 1. Performance on 200 g Fish Samples

Tracer/carrier	Avg. Tracer Recovery	Matrix Spike Recovery
Pu-236	99.8%	100% (Pu-238)
		90.0% (Np-237)
Am-243	109%	94.1% (Am-241)
		94.3% (Cm-244)
U-232	97.1%	91.1% (U-235)
Sr carrier	84.9%	97.7% (Sr-90)

N=6

Tracers levels =2.0 pCi

Matrix Spike levels =1.0 pCi, except Sr-90 (80 pCi)

Table 2. Typical Actinide Tracers and Sr Carrier Recoveries for Animal Tissue Matrices

Matrix	Pu-236	Am-243	U-232	Sr Carrier
Beef (N=6)	98.7% ±5.7%	97.1% ± 8.4%	93.4% ±4.7%	96.3% ±0.5%
Deer (N=59)	99.3% ±12%	93.4% ±10%	90.4% ±8.0%	83.4%±3.5%
Fish-Bass (N=72)	96.2% ±14%	101.8%±13%	95.1% ±8.1%	89.0% ±16%
Fish-Bream (N=57)	96.6% ±12%	98.4% ±7.7%	91.1% ±6.3%	91.7% ±10%
Fish-Catfish (N=69)	98.3% ±12%	103.7% ±7.6%	89.4% ±12%	89.4% ±17%
Fish-Mullet (N=6)	96.2% ±6.8%	100.4% ±8.9%	91.0% ±8.1%	85.6% ±17%
Fish-Red Fish (N=6)	99.5% ±11%	105.2% ±8.6%	95.7% ±3.2%	77.7% ±21%
Fish-Sea Trout (N=6)	100.5% ±5.0%	102.2% ±7.6%	83.5% ±20%	74.4% ±25%
Hog (N=17)	93.0% ±20%	96.4% ±9.7%	86.4% ±15%	86.0% ±7.1%
Shellfish (N=5)	101.3 ±2.2%	97.4% ±7.1%	81.7 ±3.2%	97.5% ±0.89%

Composite tissue samples

100 gram-deer, hog, bream, shellfish
200 gram-catfish, bass, red drum, mullet, sea trout
25 gram- nonedible fish samples including bones

Fig. 1 Acid Digestion of Fish samples

Fig. 2 Ashed Fish Samples

Fig. 3 Vacuum box with stacked cartridges (TEVA+TRU+DGA Resin)

Fig. 4 Samples Loading onto Sr Resin

Fig. 5 Alpha -spectra showing Pu-Np isotopes

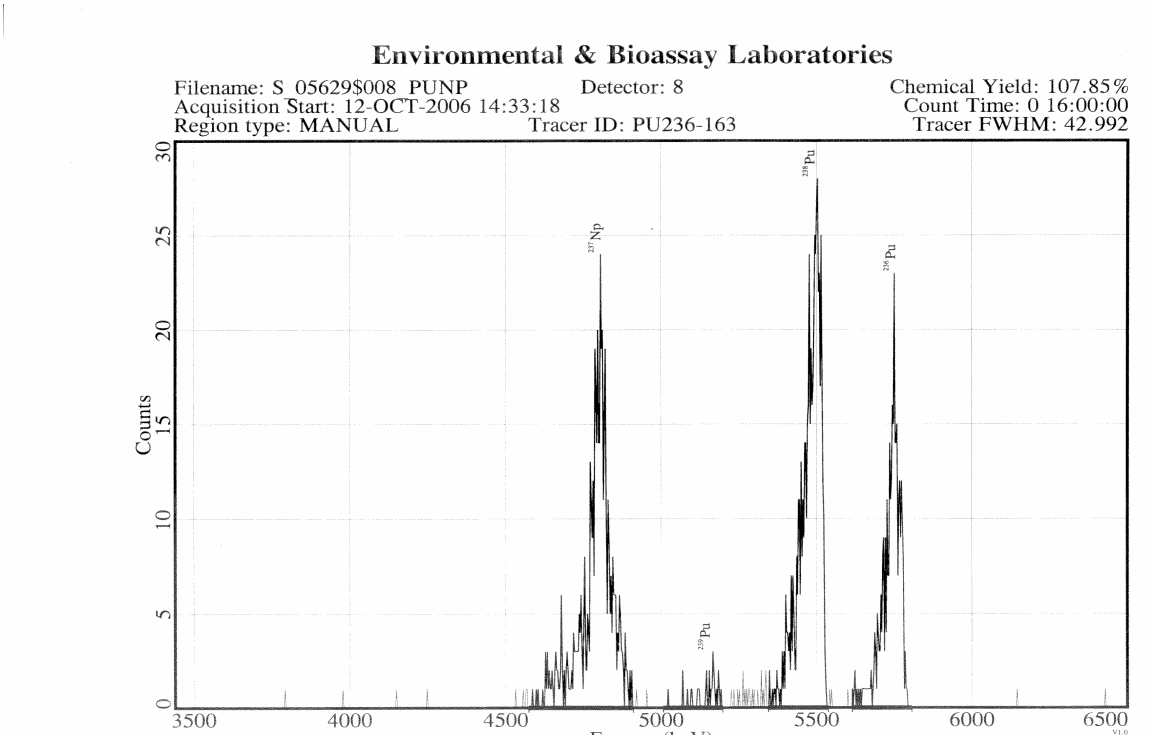

Fig. 6 Alpha -spectra showing Am isotopes

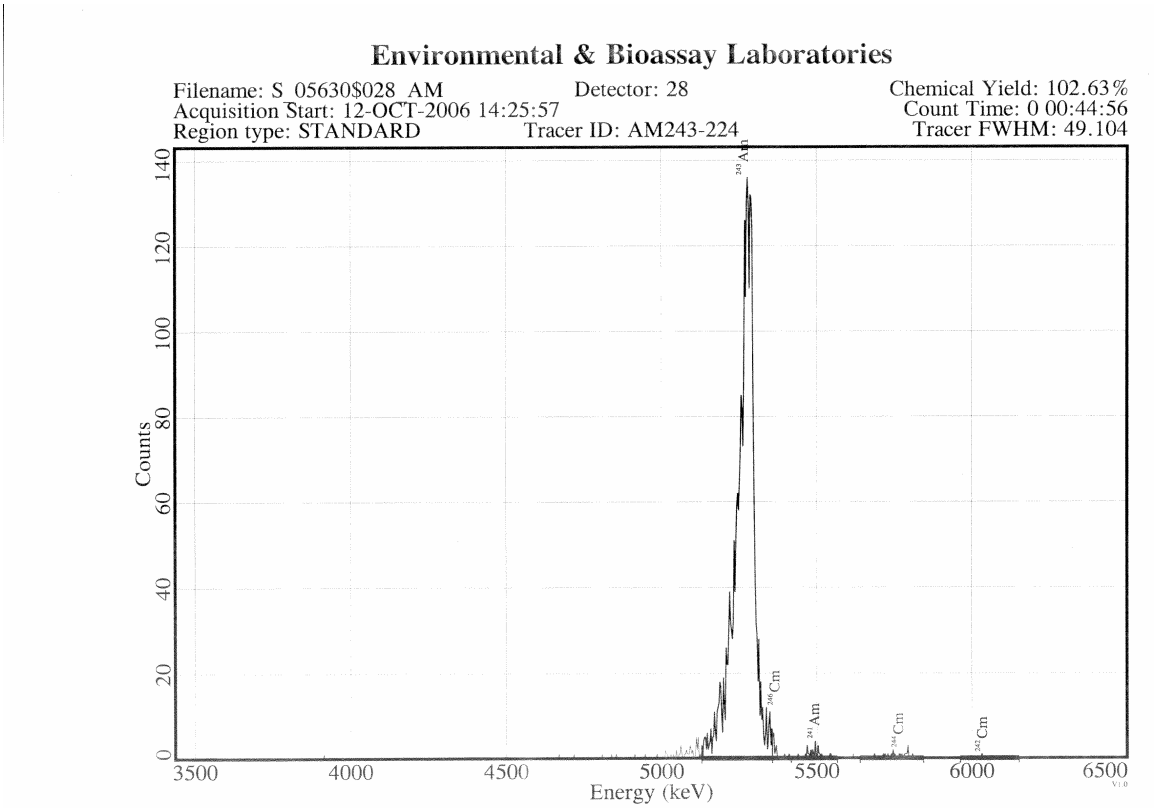

Fig. 7 Alpha -spectra showing U isotopes