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Actinide Recovery Method for Large Soil Samples

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Actinide Recovery Method for Large Soil Samples

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Abstract

A new Actinide Recovery Method has been developed by the Savannah River Site Central Laboratory to preconcentrate actinides in very large soil samples. Diphonix Resin® is used eliminate soil matrix interferences and preconcentrate actinides after soil leaching or soil fusion. A rapid microwave digestion technique is used to remove the actinides from the Diphonix Resin®. After the resin digestion, the actinides are recovered in a small volume of nitric acid which can be easily loaded onto small extraction-chromatography columns, such as TEVA Resin ®, U-TEVA Resin® or TRU Resin® (Eichrom Industries). This method enables the application of small, selective extraction-columns to recover actinides from very large soil samples with high selectivity, consistent tracer recoveries and minimal liquid waste.

Diphonix Resin®, a resin with geminally-substituted-diphosphonic acid groups chemically bonded to a styrene-divinylbenzene matrix, was developed by Argonne National Laboratory and the University of Tennessee. (1, 2, 3) Diphonix Resin® exhibits a high affinity for actinide ions in the tri-, tetra and hexavalent oxidation states. Diphonix Resin® has previously been used in a method to preconcentrate actinides in five gram soil samples.(4) This method is somewhat tedious, however, requiring elution of the actinides from the Diphonix Resin® using a HEDPA extractant. The HEDPA stripping agent must be destroyed using a time-consuming hot-plate digestion prior to calcium phosphate precipitation of the actinides.

Other preconcentration approaches have been attempted. Dipex® Resin (Eichrom Industries), a resin coated with diphosphonic acid extractant, was applied to five-gram samples (5). This method uses isopropanol to remove the extractant from the resin, oxidation of the Dipex® using a sodium hydroxide fusion, and calcium phosphate precipitation to scavenge the actinides. Thorium tracer losses were encountered, presumably due to thorium precipitation on the resin support during the isopropanol removal step. Yields for plutonium and americium for five-gram samples were in the 25 to 50% range.

In the SRS method, tracer yields greater than 80% were achieved for Pu, U and Am for 10 gram EML QAP samples. For samples that were leached, a microwave method was employed that uses a nitric acid (13 mL) - hydrochloric acid (4mL) mixture heated to 180C for 20 minutes. The leachate is filtered and evaporated to dryness. A sodium hydroxide fusion method that utilizes a predigest step with hydrofluoric acid to remove silica developed by Robert Henderson of the SRS Environmental Lab was employed to fuse the samples. The resulting hydroxide precipitate is acidified using 6M HCl and evaporated to dryness. The soil residue is redissolved and adjusted to 0.5M HCL containing 0.5M to 1M HF. Solid ascorbic acid is added to adjust the digest to 0.075M to

0.15M ascorbic acid. The ascorbic acid is added to reduce Fe^{+3} to Fe^{+2}, since Fe^{+3} is strongly retained on Diphonix Resin® and will interfere with actinide recoveries. A sequential multistage column method using TEVA Resin®and UTEVA Resin® in tandem with TRU ® Resin was employed to isolate actinides after the soil-matrix-elimination (6,7). An additional separation on TEVA Resin® to optimize Am removal from interfering rare earth elements was employed that utilizes higher ammonium thiocyanate levels than has been previously reported (8).

A predigest step is used to digest the 2.8 mL of resin in 15.7M nitric acid at 190C for 20 minutes. This step allows a larger volume of resin to be used, since the vessel pressure is released between the predigest and the primary digestion step. After cooling and releasing the pressure to the microwave vessels, the resin is digested at 220C for 35 minutes. After cooling the vessels, 3.5 mL of 30 wt% hydrogen peroxide is added to each vessel and the resin is digested at 210C for 15 minutes. After cooling the digested resin solution is transferred to a small glass beaker, 3 mL of 30 wt % hydrogen peroxide is added and each solution is evaporated to dryness. The residue is wet ashed with 3 mL of 30 wt% hydrogen peroxide two more times, followed by 2 mL of 15.7M nitric and 1 mL of 30 wt% hydrogen peroxide.

The evaporated resin digest is redissolved in the appropriate acid solution for subsequent extraction column separations. In this work the residues were redissolved in approximately 6 mL of 5M nitric acid. The solution was warmed slightly to ensure complete redissolution and 4 mL of 2M aluminum nitrate and 2 mL of 0.1M nitric acid was added to rinse the residue container in preparation for subsequent column separations. The final solution contains 12 mLs of 2.5M nitric acid-0.67M aluminum nitrate. A three-column separations method was used instead of a two-column method (such as UTEVA Resin plus TRU Resin) because the large amounts of thorium present in 10 grams of soil was found to adversely affect uranium retention on U-TEVA Resin.

Table 1 shows results on EML QAP soil samples that were leached. Pu-242 and and Am-243 tracer recoveries are typically greater than 80%. The Pu results show good agreement with the EML values. Table 2 shows EML QAP results for plutonium, uranium and americium. Pu and Am tracer recoveries averaged greater than 80%. The Pu, U, and Am results agree well with the EML reference values. Uranium shows higher retention on Diphonix Resin than plutonium and americium. U-232 and total uranium spike recoveries have been shown to be approximately 95% for leached samples for sample sizes up to 50 grams. Since Rongalite (sodium formaldehyde sulfoxylate) was not available in this initial work to reduce uranium from U^{+6} to U^{+4} to ensure complete hydroxide precipitation, the lower U-232 recoveries are likely due to incomplete precipitation of hexavalent uranium. Future fusion work will include rongalite to improve uranium recoveries.

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Table 1 Plutonium Results on Leached EML QAP Samples

Smp. Wt.	Pu-242 Tracer Recovery	Pu-238 (dpm/g)	Pu-239 (dpm/g)
9509 EML Value	--------	1.05	0.310
10.121g	82%	1.10	0.320
10.090g	75%	1.07	0.308
10.390g	72%	1.01	0.310
Avg.	76%	1.06 (+1%)	0.313 (+1%)
9403 EML Value	--------	0.672	0.216
9.957g	90%	0.664	0.200
10.100g	80%	0.663	0.223
14.980g	97%	0.632	0.211
Avg.	89%	0.653 (-2.8%)	0.211 (-2.4%)

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Table 2 Pu, Am and U Results on Fused EML QAP Samples

Smp. Wt.	Pu-242 Tracer Recovery	Pu-238 (dpm/g)	Pu-239 (dpm/g)
9609 EML Value	--------	0.068	1.31
10.00g	73%	0.080	1.47
10.00g	82%	0.047	1.43
10.00g	85%	0.053	1.41
10.00g	80%	0.063	1.39
Avg.	80%	0.061 (-10%)	1.42 (+11%)

Smp. Wt.	Am-243 Tracer Recovery	Am-241 (dpm/g)
9609 EML Value	--------	0.81
10.00g	84%	0.94
10.00g	87%	0.83
10.00g	73%	0.95
Avg.	80%	0.90 (+11%)

Smp. Wt.	U-232 Tracer Recovery	U-234 (dpm/g)	U-238 (dpm/g)
9609 EML Value	--------	2.35	2.50
10.00g	37%	2.23	2.42
10.00g	30%	2.29	2.42
10.00g	24%	2.58	2.75
Avg.	30% *	2.37 (+11%)	2.53 (+1%)

*Low U-232 recoveries since Rongalite was not used to reduce U^{+6} to U^{+4} in fusion method.

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