

PAPER

Rapid Column Extraction Methods for Urine

Sherrod L. Maxwell, III and David J. Fauth
Westinghouse Savannah River Company

A new, rapid separation method to assay actinides in urine has been developed at the Westinghouse Savannah River Site (SRS). The new method separates plutonium, neptunium, uranium, americium and strontium-90 with high chemical recovery and excellent thorium removal. The method uses calcium phosphate precipitation and a single two-stage column consisting of a TEVA Resin column and a TRU Resin cartridge. Plutonium and neptunium are separated on TEVA Resin, while uranium and americium are simultaneously retained and separated on a TRU Resin cartridge. Plutonium-236 tracer is used to allow simultaneous separation and measurement of plutonium and neptunium using TEVA Resin. Strontium-90 can also be separated on SR Resin by evaporating and redissolving load and rinse solutions collected from the TEVA/TRU column. The method provides high tracer recoveries and excellent ^{228}Th removal.

Introduction

Urine analysis for actinides and strontium is often made difficult by the presence of high levels of phosphate in samples. In addition, very-low levels of detection must be achieved with accuracy and reliability.

Alpha-particle-emitting interferences such as ^{228}Th must be effectively removed to eliminate interference on ^{238}Pu and ^{241}Am alpha-particle peaks and 'false positive' results. New extraction-chromatographic-resin methods from Eichrom Technologies, Inc. coated with highly selective extractants have been used to improve actinide separation techniques for laboratory use. Tandem column extraction methods using TEVA Resin and TRU Resin have been used in previous applications.^{1, 2}

TEVA resin and TRU Resin have typically not been used in a single stacked cartridge where plutonium is oxidized to Pu (IV) because of potential interference from Fe (III) on TRU Resin.

Tandem methods separating Pu on TEVA Resin and Am on TRU Resin have required that the load and rinse solutions from TEVA Resin be collected, evaporated and redissolved.^{3, 4} Ascorbic acid and sulfamic acid can be added to reduce iron to Fe (II) prior to loading the solution onto TRU Resin. Ferrous ions do not interfere with actinide retention on TRU Resin.

A novel method has been developed that uses calcium phosphate precipitation and a single two-stage column

consisting of a TEVA Resin column and a TRU Resin cartridge. The method separates plutonium, neptunium, uranium, americium and strontium-90 with high chemical recovery and excellent thorium removal. Plutonium and neptunium are separated on TEVA Resin, while uranium and americium are simultaneously retained and separated on a TRU Resin cartridge. This unique approach can be used with urine samples because iron is not present at significant levels in urine samples and plutonium reduction is accomplished without adding iron (II) to the sample. The advantages of this approach is that actinides can be loaded onto two separate resins in a single load step that allows the simultaneous extraction and assay of neptunium and plutonium with high chemical recovery and excellent thorium removal.

Experimental

Reagents

The resins employed in this work are TEVA Resin (Aliquat 336) and TRU-Resin (tri-n-butylphosphate (TBP) and N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)) available from Eichrom Technologies, Inc., Darien, Illinois. Nitric, hydrochloric and hydrofluoric acids were prepared from high-purity Optima™ reagents (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 and spikes ^{242}Pu , ^{236}Pu , ^{232}U , ^{243}Am and ^{90}Sr from Amersham that had been diluted to the approximately 0.5 to 1.5 dpm/mL level were employed to enable yield corrections.

Procedures

Column preparation

The TEVA columns were prepared using 2 mL of resin. Chromatographic-TEVA-resin columns were prepared by slurring the appropriate resin in water, then transferring aliquots of the slurry under vacuum to a column body (Image Molding, Commerce City, CO)

until the desired bed height was reached. TRU resin and SR Resin pre-packed cartridges containing 2 mL of resin were obtained from Eichrom Technologies. Small particle size (50-100 micron) was employed, along with a Speedmate 24 vacuum extraction system (Applied Separations, Inc., Allentown, PA.). Flow rates of 1-2 mL/min were typically used, much faster than the 0.25 mL/min gravity flow rates observed.

Sample Preparation and Actinide Separation

Urine sample were acidified with nitric acid and allowed to stand for two hours. The appropriate tracers (^{236}Pu , ^{232}U , ^{243}Am) were added to 500-mL aliquots of urine sample. Strontium-90 and ^{237}Np spikes were added to a selected number of samples.

Two drops of 1-octanol and 1 mL of 3 M calcium nitrate were added to each sample. Samples were heated on low heat for 1.5 hours and cooled to room temperature. After cooling, 5 mL of 3 M ammonium hydrogen phosphate was added to each sample and the sample was stirred. The samples were adjusted to pH 9 with ammonium hydroxide and the precipitate was allowed to settle for at least one hour. The precipitate and supernate were centrifuged at 3000 rpm for 35 minutes. After decanting the supernate, the precipitate was dissolved in approximately 20 mL of concentrated nitric acid and ashed to dryness on a hot plate at approximately 300-350°F. The samples were ashed with 30-wt% hydrogen peroxide several times and then ashed with a mixture of nitric acid and hydrogen peroxide until the residual salts were white.

The evaporated-resin digest was redissolved in the appropriate acid solution for subsequent-column separations. In this work the residues were redissolved in approximately 6 mL of 6 M nitric acid. The solution was warmed slightly to ensure complete redissolution and 6 mL of 2.5 M aluminum nitrate (scrubbed by passing through UTEVA Resin to remove traces of uranium). The final solution contains approximately 12 mL of 2.5 M nitric acid-1.25 M aluminum nitrate.

A stacked column method using 2 mL TEVA Resin columns and a 2 mL TRU Resin cartridge was employed to isolate the actinides of interest (Figure 1). The TRU cartridge was placed below the TEVA column by luer

connection. Plutonium and Np was retained on TEVA Resin and Am and U on TRU Resin. Ferric ions interfere with americium retention on TRU Resin. Since there are no significant levels of iron in urine, the TRU cartridge can be used in a stacked column with TEVA Resin if the valence adjustment used does not require iron.

The valence of Pu and Np was adjusted to Pu(IV) and Np(IV) by adding 0.5 mL of 1.5 M sulfamic acid and 2 mL of 1.5 M ascorbic acid, waiting 3 minutes, and adding 2 mL of 4 M sodium nitrite. After the valence adjustment, the sample solution was loaded onto the stacked TEVA plus TRU column. The TEVA and TRU column was rinsed with 20 mL of 3 M nitric acid to remove matrix components. After the rinsing with nitric acid, the TRU cartridge was removed. To remove thorium from the TEVA column, 3 mL of 9 M hydrochloric acid and 30 mL 8 M hydrochloric acid were added. The Pu and Np were stripped from TEVA Resin with 30 mL of 0.1 M hydrochloric acid-0.05 M hydrofluoric acid -0.1 M ammonium iodide. Four mL of 0.02 M sulfuric acid and approximately 3 mL of 15.7 M nitric acid was added to each sample and the sample solution was evaporated.

A second-column separation using 1 mL of TEVA Resin was employed to ensure complete removal of all

traces of ^{228}Th (Figure 2). The second column separation is only required when ^{232}U tracer (and its ^{228}Th daughter) are added for uranium assay. Each sample was redissolved in 7.5 mL 3 M nitric acid and 1 mL 2.5 M aluminum nitrate. To adjust the Pu and Np valence, 0.5 mL of 1.5 ferrous sulfate and 1 mL of 1.5 M ascorbic acid was added, followed by 1 mL of 4 M sodium nitrite. To increase the acidity of the load solution to approximately 3 M nitric acid, 1 mL of concentrated nitric acid was added. Rinse and strip volumes used were approximately one half the volumes used for the two mL TEVA column separation. The TEVA column was rinsed with 10 mL of 3 M nitric acid. To remove thorium, 1 mL of 9 M hydrochloric acid and 8 mL of 8 M hydrochloric acid were added to each column. The Pu and Np were stripped with 15 mL of 0.1 M hydrochloric acid-0.05 M hydrofluoric acid -0.1 M ammonium iodide.

The americium was stripped from each TRU cartridge using 12 mL of 4 M hydrochloric acid. The uranium was stripped using 20 mL of ammonium bioxalate. To prepare for electrodeposition, solutions were evaporated, wet-ashed using 15.7 M nitric acid and 30 wt.% hydrogen peroxide, redissolved in a sodium bisulfate matrix and electroplated for 2.5 hours using 0.5 amp current. Additional testing using cerium fluoride

Pu, Np/Am, U, Sr on TEVA/TRU Resin

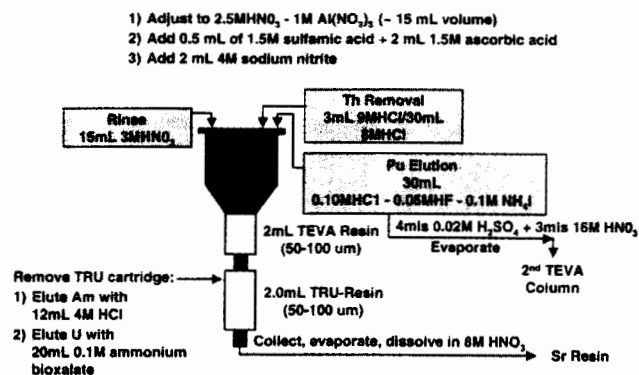


Figure 1 TEVA and TRU column separation.

Pu, Np on TEVA Resin (2nd Column to Remove all Th-228)

- Redissolve in 7.5 mL 3M HNO₃ + 1 mL 2.5M Al(NO₃)₃
- Add 0.5 mL 1.5M ferrous sulfate + 1 mL 1.5M ascorbic acid
- Add 1 mL 4 M sodium nitrite
- Add 1 mL 16M nitric acid

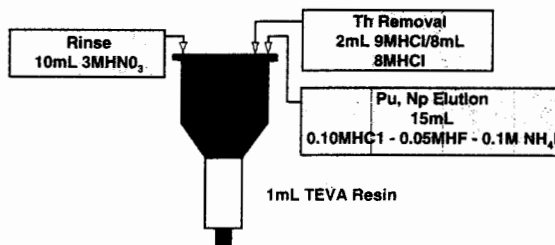


Figure 2 Second TEVA column separation.

microprecipitation was performed using 50 micrograms of cerium in the presence of hydrofluoric acid and filtration and mounting on Gelman 25-mm filters. Solutions prepared for cerium fluoride precipitation did not have to evaporate prior to filtration.

Load and rinse solutions were collected from the TEVA –TRU Resin stacked column, evaporated on a hot plate, and redissolved in 10 mL of 8M nitric acid. Each solution was loaded on to a 2-mL Sr Resin cartridge. The column was rinsed with 15 mL of 8 M nitric acid and stripped with 10 mL of 0.05 M nitric acid. The strip solutions were evaporated on planchets that had been annealed in a muffle furnace at 1600 EF for 3 ½ hours in a stainless steel pan. The planchets were cooled and counted for 20 minutes using a gas proportional counter. Strontium-90 spikes (205 dpm) were added to blank urine samples to perform ⁹⁰Sr yield corrections.

Apparatus

Plutonium, americium and uranium measurements were performed by alpha-particle pulse-height measurements using surface barrier silicon detectors. Strontium-90 measurements were performed using an Oxford 4100 gas proportional counter.

Electroplating was performed using a ten position constant current system with BIO RAD Power Pac 200 power supply and 2-cm stainless steel disks. A Fisher Scientific filtration apparatus and Gelman polysulfone funnels were used for cerium microprecipitation.

Results and Discussion

Table 1 shows tracer recoveries using TEVA Resin to analyze 500-mL urine samples with ²⁴²Pu tracer (1.25 dpm) added. In this initial test performed using TEVA Resin only, ferrous sulfate and ascorbic acid were used to adjust the Pu valence to Pu (III) and sodium nitrite was used to adjust the Pu valence to Pu (IV). The average ²⁴²Pu-tracer recovery when cerium fluoride precipitation is used is 102%. The tracer recovery greater than 100% is likely due to alpha-particle counting uncertainty or uncertainty in the tracer value. When

²⁴² Pu recovery % (CeF ₃ microprecipitation)	²⁴² Pu recovery % (electroplating)
110.0	84.4
93.3	72.4
92.6	69.3
95.2	69.6
101.5	79.8
99.3	84.5
97.7	79.1
115.4	85.5
107.9	84.8
106.8	77.0
101.6	82.5
102.6	
Avg = 102.0% (± 7.0 @ 1s)	Avg = 79.0% (± 6.2% @ 1s)

Table 1 Plutonium tracer recoveries on TEVA resin.

samples were electroplated, a average tracer recovery of 79% was obtained. The lower efficiency of electroplating for these samples may be explained by traces of fluoride that were not completely removed despite multiple ashing steps with nitric acid and hydrogen peroxide and the addition of 4 mL of 0.02 M sulfuric acid to enhance fluoride volatilization.

Table 2 shows tracer recoveries using TEVA Resin to analyze 500-mL urine samples with ²³⁶Pu tracer (0.425 dpm) added to all samples and ²³⁷Np spike (1.40 dpm) added to half the samples. In this test using the stacked TEVA column plus TRU cartridge, sulfamic acid and ascorbic acid were used to adjust the Pu valence to Pu (III) and sodium nitrite was used to adjust the Pu valence to Pu (IV). Alpha mounts were prepared using cerium fluoride precipitation. The average ²³⁶Pu tracer

^{236}Pu % recovery	^{237}Np % recovery
94.0	
92.5	
101.0	
100.0	
111.0	
91.0	88.1
91.9	86.7
105.0	102.9
109.0	102.0
88.9	94.2
Avg = 98.4% (± 7.9 @ 1s)	Avg = 94.8% (± 7.6 @ 1s)

Table 2 Plutonium and neptunium tracer recoveries on TEVA resin.

^{243}Am % recovery	^{232}U % recovery
93.2	97.9
92.1	74.1
107.4	85.6
70.3	102.9
102.4	90.6
103.0	83.1
100.2	57.7
103.3	81.0
102.6	80.4
94.7	93.3
Avg = 96.9% (± 10.6 @ 1s)	Avg = 84.7% (± 12.9 @ 1s)

Table 3 Americium and uranium tracer recoveries on TRU resin.

recovery was found to be 98.4% and the average ^{237}Np -spike recovery was found to be 94.8%. The agreement between ^{236}Pu -tracer recovery and ^{237}Np -spike recovery of approximately 3.7% illustrates that ^{237}Np could possibly be traced adequately using ^{236}Pu .

In addition, tests were performed on 24 urine control standards containing ^{237}Np (1.12 dpm/L) and ^{236}Pu tracer (0.425 dpm/L). Two Np control standards were analyzed with each of 12 sample batches containing approximately 16 samples each. An average ^{237}Np value of 1.104 dpm/L was obtained using the ^{236}Pu tracer recoveries. The bias estimate was found to be $-1.49 \pm 6.17\%$ (-7.66 to +4.86%) at the 95% confidence interval and the estimated standard deviation was 14.6%. The bias appears to be small relative to the overall method uncertainty and the standard deviation is similar to what has been achieved using ^{237}Np spikes to perform yield

corrections. This indicates that an adequate correlation exists between ^{236}Pu and ^{237}Np such that ^{236}Pu tracer can be used to assay ^{237}Np and meet the DOELAP bias criteria of -25 to +50%.

Table 3 shows tracer recoveries using TRU Resin to analyze 500-mL urine samples with ^{243}Am tracer (1.55 dpm) and ^{232}U tracer (0.554 dpm) added. The average tracer ^{243}Am recovery was 96.9% and the average ^{232}U recovery was 84.7% when samples were electroplated.

Table 4 shows the accuracy achieved on spiked urine samples. The urine samples contained ^{238}Pu in the range 0.145 to 4.95 dpm/L (N=12), ^{239}Pu in the range 0.022 to 3.62 dpm/L (N=12), ^{241}Am in the range 0.55 to 3.5 dpm/L (N=7), ^{234}U in the range 0.197 to 2.04 dpm/L (N=4), ^{238}U in the range 0.147 to 3.07 dpm/L (N=4) and ^{90}Sr in the range 4.4 to 188 pCi/L (N=6).

The average bias for ^{238}Pu and ^{239}Pu was -14.7% and +12.4% respectively. The average bias for ^{241}Am

	²³⁸ Pu	²³⁹ Pu	²⁴¹ Am	⁹⁰ Sr
Levels	0.145-4.95 dpm/L	0.022-3.62 dpm/L	0.55-3.5 dpm/L	5.4-188 picoCi/L
No. samples	N=12	N=12	N=7	N=6
Avg bias	-14.7%	+12.4%	-3.4%	-4.8%
Blanks	0.016 (N=8)	0.012 (N=8)	0.007 (N=23)	-0.05 (N=4)
	²³⁴ U	²³⁸ U	²³⁵ U	
Levels	0.197-2.04 dpm/L	0.147-3.02 dpm/L	****	
No. samples	N=4	N=4	****	
Avg bias	+7.8%	+1.5%	****	
Blanks	0.008 (n=12)	0.012 (N=10)	-0.001 (N=12)	
DOELAP criteria (Bias: -25% to +50%)				

Table 4 Accuracy on spiked urine samples.

measurements was -3.4%. For uranium, the average bias for ²³⁴U and ²³⁸U was +7.8% and +1.5% respectively. The ⁹⁰Sr recoveries used to perform yield corrections averaged 90.2%. The ⁹⁰Sr bias averaged -4.8% for the spiked samples.

The average bias results are well within the DOELAP bias criteria of -25 to +50%. The average blank values for each radionuclide shown were sufficiently low to be acceptable for SRS bioassay needs.

Conclusions

A new two-stage column consisting of a TEVA Resin column and a TRU Resin cartridge developed at SRS separates plutonium, neptunium, uranium, americium and strontium-90 with high chemical recovery and excellent thorium removal. Tests using ²³⁶Pu confirm that plutonium and neptunium can be separated together

on TEVA Resin when ²³⁶Pu tracer is used. Accuracy on spiked urine samples was demonstrated. The new method allows actinides can be loaded onto two separate resins in a single load step with high chemical recovery and excellent thorium removal. This method will enable faster analysis times, significant labor cost savings, minimize acid versus anion-exchange methods and reduce rework.

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References

1. E. Philip Horwitz et al., "Separation and Preconcentration of Actinides by Extraction Chromatography Using a Supported Liquid Anion Exchanger: Application to the Characterization of High-Level Nuclear Waste," *Analytica Chimica Acta*, **310**, 63, (1995).
2. S.L. Maxwell III, "Rapid Actinide-Separation Methods", *Radioactivity and Radiochemistry*, **8**, (4), 36, (1997).
3. S.L. Maxwell, "Rapid Separation Methods for the 21st Century", presented at National ACS Meeting, San Francisco, CA, March 27, 2000.
4. S.L. Maxwell III and D.J. Fauth, "New Fecal Method for Plutonium and Americium at SRS", Eichrom Annual Users Workshop at BAER'99 Conference, Gaithersburg, MD, October 20, 1999.

Biographies

Sherrod L. Maxwell III

is a Fellow Scientist at the Westinghouse Savannah River Site, specializing in ion exchange and extraction chromatography separations. He obtained a BS Degree in Biology at Southwestern At Memphis (now Rhodes College) in 1978 and an MS in Analytical Chemistry at the University of South Carolina in 1983. He began working as a chemist for E.I. du Pont De Nemours and Company at the Savannah River Site in 1984. He has been awarded the George Westinghouse Signature Award for Technical Excellence seven times.

David J. Fauth

is a Fellow Scientist at the Westinghouse Savannah River Site, specializing in bioassay -

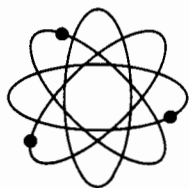
radiochemistry techniques, quality assurance, and industrial hygiene. He obtained a B. S. Degree in Chemistry at Thiel College in 1973. He was awarded a Ph.D. in Chemistry from the University of South Carolina in 1978. He began working as a chemist for E.I. du Pont De Nemours and Company at the Savannah River Site in 1978. He has been awarded the George Westinghouse Signature Award for Technical Excellence two times.

Westinghouse Savannah River Company
Building 704-17F
Aiken, SC 29808, USA
Phone: 803-952-4530
Fax: 803-952-3550
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