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Rapid Column Extraction Methods for Urine

Sherrod L. Maxwell, III and David J. Fauth
Westinghouse Savannah River Company
Aiken, SC 29808

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Abstract

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 thorium-228 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-emitting interferences such as thorium-228 must be effectively removed to eliminate interference on Pu-238 and Am-241 alpha 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 Pu-242, Pu-236, U-232, Am-243 and Sr-90 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 slurrying 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 (Pu-236, U-232, Am-243) were added to 500 mL aliquots of urine sample. Sr-90 and Np-237 spikes were added to a selected number of samples.

Two drops of 1-octanol and 1 ml of 3M 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 ammonium hydrogen phosphate was added to each sample and 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 300-350F. The samples were ashed with 30 wt% hydrogen peroxide several times and then ashed 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 6M nitric acid. The solution was warmed slightly to ensure complete redissolution and 6 mL of 2.5M aluminum nitrate. The final solution contains approximately 12 mLs of 2.5M nitric acid-1.25M 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. Pu 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 1.5M sulfamic acid and 2 mLs of 1.5M 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 mls of 3M 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 mLs of 9M hydrochloric acid and 30 mLs 8M hydrochloric acid were added. The Pu and Np were stripped from TEVA Resin with 30 mLs of 0.1M hydrochloric acid-0.05M hydrofluoric acid –0.1M ammonium iodide. Four mLs of 0.02M sulfuric acid and approximately 3 mls of 15.7M 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 Th-228 (Figure 2). Each sample was redissolved in 7.5 mLs 3 M nitric acid and 1 mL 2.5M 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 4M sodium nitrite. 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 mls of 3M nitric acid. To remove thorium, 1 mL of 9M hydrochloric acid and 8 mLs of 8M hydrochloric acid were added to each column. The Pu and Np were stripped with 15 mLs of 0.1M hydrochloric acid-0.05M hydrofluoric acid –0.1M ammonium iodide.

The americium was stripped from each TRU cartridge using 12 mLs of 4M hydrochloric acid. The uranium was stripped using 20 mL of ammonium bioxalate. To prepare for electrodeposition, solutions were evaporated, wet-ashed using 15.7M 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 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 evaporated 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 mLs of 8M nitric acid and stripped with 10 mL of 0.05M nitric acid. The strip solutions were evaporated on planchets that had been annealed in a muffle furnace at 1600°F for 3-1/2 hours in a stainless steel pan. The planchets were cooled and counted for 20 minutes using a gas proportional

counter. Sr-90 spikes (205 dpm) were added to blank urine samples to perform Sr-90 yield corrections.

Apparatus

Plutonium, americium and uranium measurements were performed by alpha-particle pulse-height measurements using surface barrier silicon detectors. Sr-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

Figure 3 shows tracer recoveries using TEVA Resin to analyze 500 mL urine samples with Pu-242 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 Pu-242 tracer recovery when cerium fluoride precipitation is used is 102%. When 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 mLs of 0.02M sulfuric acid to enhance fluoride volatilization.

Figure 4 shows tracer recoveries using TEVA Resin to analyze 500 mL urine samples with Pu-236 tracer (0.425 dpm) added to all samples and Np-237 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 Pu-236 tracer recovery was found to be 98.4% and the average Np-237 spike recovery was found to be 94.8%. The agreement between Pu-236 tracer recovery and Np-237 spike recovery of approximately 3.7% illustrates that Np-237 can be adequately traced using Pu-236. In addition, tests were performed on twenty-four urine control standards containing Np-237 (1.12 dpm/L) and Pu-236 tracer (0.425 dpm/L). Two Np control standards were analyzed with each of twelve sample batches containing approximately sixteen samples each. An average Np-237 value of 1.104 dpm/L was obtained using the Pu-236 tracer recoveries. The bias was found to be -1.49% and the standard deviation was 14.6%. This shows excellent agreement and confirms that the Pu-236 can be used to assay Np-237.

Figure 5 shows tracer recoveries using TRU Resin to analyze 500 mL urine samples with Am-243 tracer (1.55 dpm) and U-232 tracer (0.554 dpm) added. The average tracer Am-243 recovery was 96.9% and the average U-232 recovery was 84.7% when samples were electroplated.

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

The average bias for Pu-238 and Pu-239 was –14.7% and +12.4% respectively. The average bias for Am-241 measurements was -3.4%. For uranium, the average bias for U-234 and U-238 was +7.8% and +1.5% respectively. The Sr-90 recoveries used to perform yield corrections averaged 90.2%. The Sr-90 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 Pu-236 confirm that Pu and Np can be separated together on TEVA Resin when Pu-236 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.

Acknowledgment

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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**, **No 4**, 36, (1997)
3. Maxwell, S. L., "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.

Figure 1. TEVA and TRU Column Separation

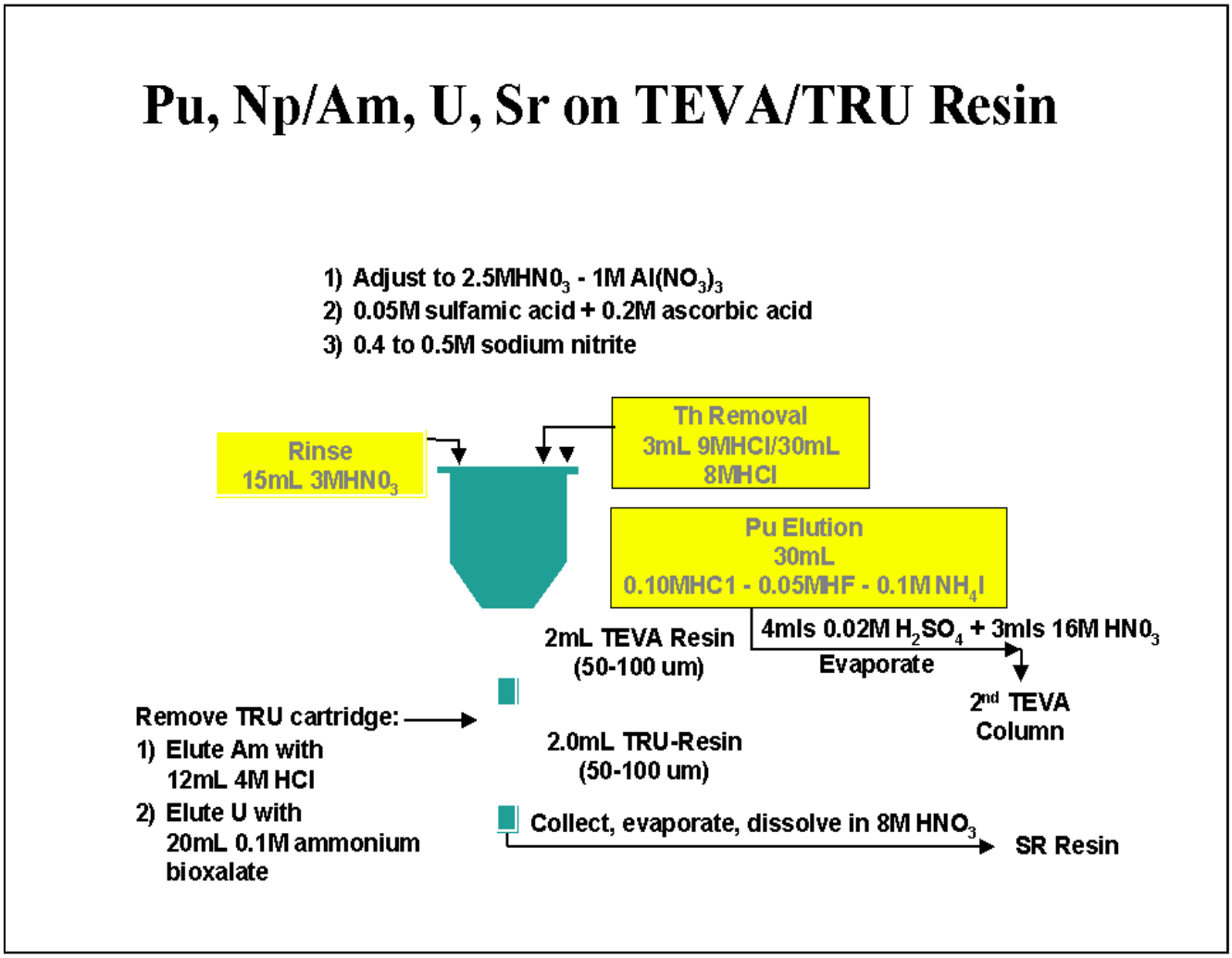

Figure 2. Second TEVA Column Separation

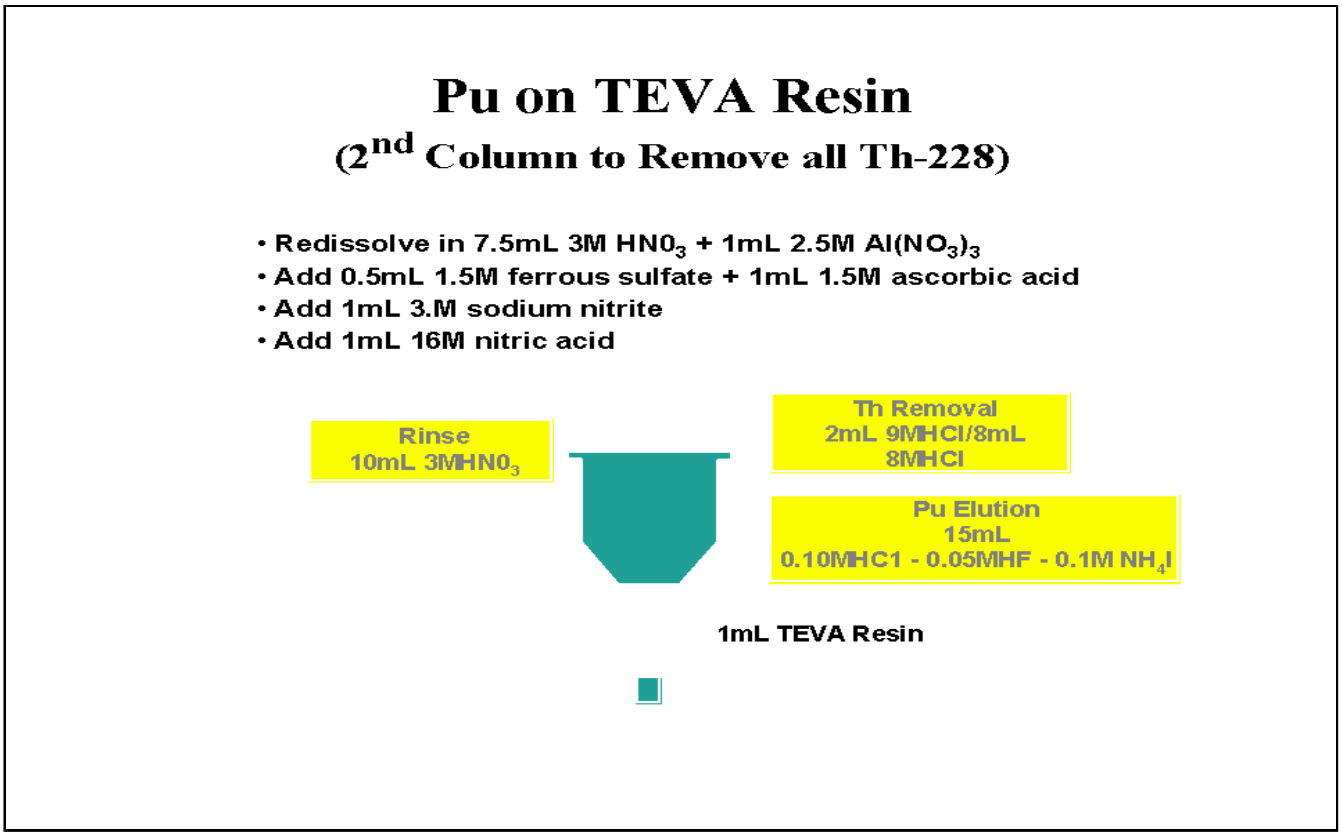

Figure 3. Pu Tracer Recoveries on TEVA Resin

% Pu-242 Recovery (CeF_3 microprecipitation)		% Pu-242 Recovery (Electroplating)	
1)	110	1)	84.4
2)	93.3	2)	72.4
3)	92.6	3)	69.3
4)	95.2	4)	69.6
5)	101.5	5)	79.8
6)	99.3	6)	84.5
7)	97.7	7)	79.1
8)	115.4	8)	85.5
9)	107.9	9)	84.8
10)	106.8	10)	77.0
11)	101.6	11)	82.5
12)	102.6	-	-
Avg. =102.0%		Avg. =79.0%	

Figure 4. Pu and Np Tracer Recoveries on TEVA Resin

-	% Pu-236 Recovery	% Np-237 Recovery
1)	94.0	***
2)	92.5	***
3)	101	***
4)	100	***
5)	111	***
6)	91.0	88.1
7)	91.9	86.7
8)	105	102.9
9)	109	102.0
10)	88.9	94.2
-	Avg. = 98.4%	Avg. = 94.8%

Figure 5. Am and U-232 Tracer Recoveries on TRU Resin

% Am-243 Recovery (Electroplating*)		% U-232 Recovery (Electroplating*)	
1)	93.2	1)	97.9
2)	92.1	2)	74.1
3)	107.4	3)	85.6
4)	70.3	4)	102.9
5)	102.4	5)	90.6
6)	103.0	6)	83.1
7)	100.2	7)	57.7
8)	103.3	8)	81.0
9)	102.6	9)	80.4
10)	94.7_	10)	93.3
Avg. = 96.9%		Avg. = 84.7%	

Figure 6. Accuracy on Spiked Urine Samples

	Pu-238	Pu-239	Am-241	Sr-90
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
Average 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)
-	-	-	-	-
-	**U-234**	**U-238**	**U-235**	**-**
Levels	0.197-2.04 dpm/L	0.147-3.02 dpm/L	**** dpm/L	-
No. Samples	N=4	N=4	****	-
Average Bias	+7.8%	+1.5%	****	-
Blanks	0.008 (N=12)	0.012 (N=10)	-0.001 (N=12)	-
-	-	-	-	-
DOELAP criteria (Bias: -25% to +50%)				

Biography

The author, 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 B. S. Degree in Biology at Southwestern At Memphis (now Rhodes College) in 1978 and an M. S. in Analytical Chemistry at the University of South Carolina in1983. 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.

The author, David J. Fauth, III is a Fellow Scientist at the Westinghouse Savannah River Site, specializing in bioassay radiochemistry techniques and quality assurance. He obtained a B. S. Degree in Chemistry at Thiel College in 1973 He was a 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.