

Reprint copied with permission of
Radioactivity & Radiochemistry

PAPER

MS198

Rapid Actinide-Separation Methods

Sherrod L. Maxwell, III

Westinghouse Savannah River Company

New high-speed actinide-separation methods have been developed by the Savannah River Site Central Laboratory that can be applied to nuclear materials process samples, waste solutions and environmental samples. As part of a reengineering effort to improve efficiencies and reduce operating costs, solvent extraction methods (TTA, Hexone, TBP and TIOA) used for over thirty years in the SRS Central Laboratory were replaced with new rapid extraction column methods able to handle a variety of difficult sample matrices and actinide levels. Significant costs savings were realized and costly mixed-waste controls were avoided by using applied vacuum and 50-100 micron particle-size resins from Eichrom Industries. TEVA Resin[®], UTEVA Resin[®], and TRU Resin[®] columns are used with flow rates of approximately two to three milliliters per minute to minimize sample turnaround times. Single-column, dual-column and sequential-cartridge methods for plutonium, uranium, neptunium, americium and curium were developed that enable rapid, cost-effective separations prior to alpha-particle counting, thermal ionization and inductively coupled plasma mass spectrometry, and laser phosphorescence measurements.

Introduction

Laboratory actinide-separation techniques have historically used solvent extraction and ion-exchange methods to separate and preconcentrate actinides prior to radiochemical analysis. New extraction chromatographic resins from Eichrom Industries, Inc. coated with highly selective extractants have been used to improve actinide-separation techniques for laboratory use.^{1,2}

Recent work at the Westinghouse Savannah River Site Central Laboratory has led to enhanced single-column, dual-column and sequential-column actinide methods that have replaced older solvent extraction techniques and offer greater selectivity than conventional ion-exchange techniques. For the last thirty years, the Central Laboratory has provided analytical support to F-Canyon and H-Canyon nuclear material processing with a variety of instrumental and radiochemical methods. The actinide-separation methods used employed solvents such as Hexone for uranium extractions, thenoyltrifluoroacetone in xylene (TTA) for plutonium extraction, and tri-isooctylamine in xylene (TIOA) for neptunium. To eliminate the use of EPA-listed solvents such as Hexone and xylene

as well as reduce analytical costs, new rapid column-extraction techniques were implemented in the SRS Central Laboratory beginning in July, 1996.

Experimental Reagents

The resins employed in this work are TEVA Resin[®] (Aliquat[™]336), UTEVA Resin[®] (diamylamylphosphonate) and TRU-Resin[®] (tri-n-butylphosphate (TBP) and N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)) available from Eichrom Industries, Inc., Darien, Illinois. Nitric and hydrochloric 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 tests were performed using plutonium standards prepared from stock plutonium and neptunium solutions assayed by controlled potential coulometry. Uranium solution standards were prepared from certified uranium standards obtained from Allied General Nuclear Services.

Procedures

Column preparation

Chromatographic columns were prepared by slurring the appropriate resin in water, then transferring aliquots of the slurry under vacuum to a column body (Whale Scientific, Commerce City, CO) or mini-cartridge (Applied Separations, Inc., Allentown, PA) until the desired bed height was reached. To reduce analysis times and to enhance column performance, small particle size (50-100 micron) was employed, along with a vacuum extraction system (Applied Separations, Inc.). Flow rates of 2-3 mL/min were typically used, much faster than the 0.5 mL/min gravity flow rates observed. Empty Whale Scientific columns were used as reservoirs in the dual-column and multistage column methods when mini-cartridges were employed.

Apparatus

Plutonium measurements were performed by alpha-particle pulse-height measurements using surface barrier silicon detectors or by mass spectrometry using a Finnagin TIMS (Thermal Ionization Mass Spectrometry) system. Uranium measurements were performed using a Model KPA-10 Kinetic Phosphorescence Analyzer (ChemChek Instruments, Richland, WA) or by mass spectrometry using a Finnagin TIMS system.

Results and discussion

Replacement of plutonium-TTA with Pu-TEVA method

Although anion-exchange separations have been used in the SRS Central Laboratory to purify plutonium prior to controlled-potential coulometry assays or to remove pluto-

nium prior to metallic impurity measurements, radiochemical separation of plutonium prior to alpha-particle pulse-height analysis or mass spectrometry has primarily been accomplished using a TTA (thenoyltrifluoroacetone) solvent-extraction technique. TEVA Resin has been typically used to separate technetium-99 or to separate trivalent actinides from lanthanides based on thiocyanate complexing of the actinides.³ A new rapid Pu-TEVA column-extraction method was developed and implemented at SRS (Figure 1) to replace the Pu-TTA method from process control, nuclear safety and waste solution assays for low-level plutonium. This method eliminates the need to perform mixed-waste segregation of the xylene solutions and has resulted in significant cost savings due to shorter analysis times resulting from vacuum-assisted flow rates. The Pu-TEVA method offers extremely high retention for plutonium, optional thorium removal using 6 M hydrochloric acid, and essentially no uranium tailing compared to anion resins such as AGMP-1 (Bio Rad, Richmond, CA). The TEVA resin can be used in relatively low-level nitric acid solutions and therefore valence control of plutonium can be achieved more effectively. The plutonium is adjusted to plutonium (IV) in the column load solution by reducing all plutonium present to plutonium(III) using 0.1 M ferrous sulfate followed by 0.2 M sodium nitrite to oxidize the plutonium to plutonium (IV). Neptunium will track with the plutonium as neptunium (IV), enabling the recovery of both actinides together. When this is desired, ²³⁶Pu can be used as a tracer instead of ²⁴²Pu since the latter tracer interferes with the ²³⁷Np alpha-particle measurement. To remove the neptunium, the load solution is heated to 70 °C for approximately five minutes to oxidize neptunium to unretained Np (V) prior to column loading. Uranium and thorium are removed to greater than 99.9%.

The Pu-TEVA alpha-particle spectrometry method has been used to perform nuclear safety analytical measurements when plutonium levels are too low to enable plutonium spectrophotometry to be employed. For trace plutonium isotopic work in the presence of high levels of ²³⁸U, a two-column or three-column pass method is used to enable accurate measurement of the ²³⁸Pu isotope by thermal ionization mass spectrometry.

Figure 2 shows the quality control data for the Pu-TEVA alpha-particle spectrometry method for the first quarter, 1997. The reference standard values are shown in the data table in Figure 2. The plutonium standard values range from 3.05E 6 to 1.049 E7 disintegrations per minute per milliliter (dpm/mL). The average measured results are also shown. The standard deviation of the results (dpm/mL), relative bias (%), relative standard deviation (%) and number of standards analyzed are also shown. Typically, a one-hundred-microliter aliquot of the standard is used for analysis. Tracers are not used for chemical yield correction due to the wide range of plutonium levels in process samples analyzed and the high yield consistently observed (>99%). The relative standard

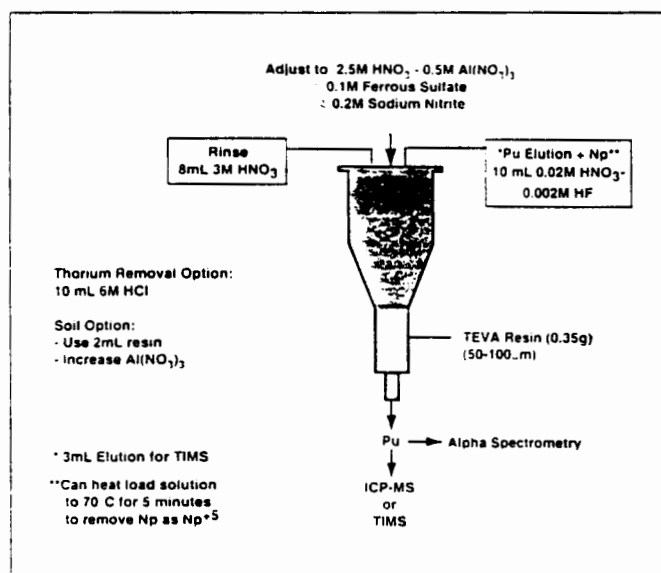


Figure 1 Pu TEVA rapid column method.

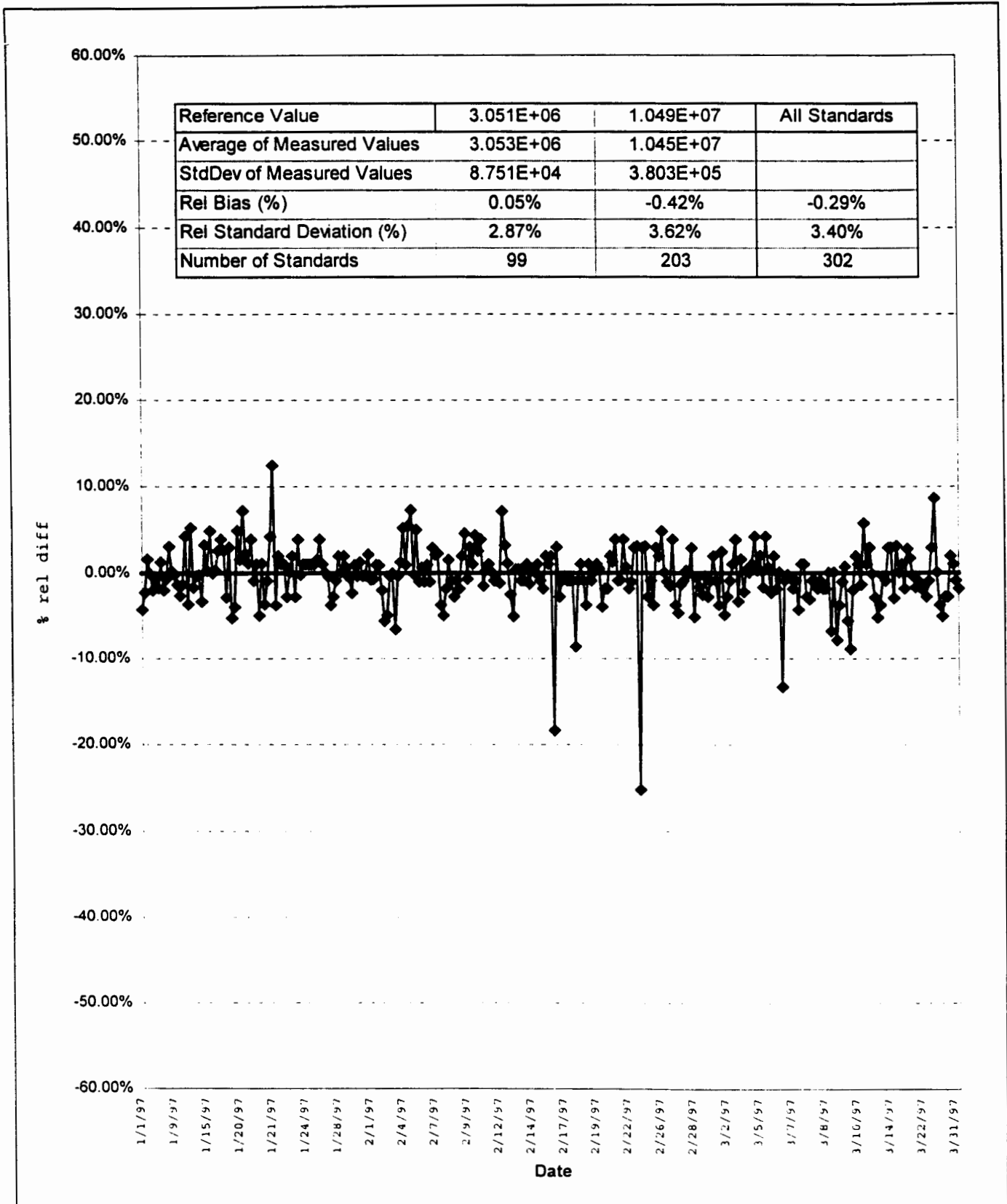


Figure 2 Pu TEVA alpha method quality control data, 1 QTR 97.

deviation was 3.40% and the bias was -0.29% for 302 standards analyzed in the first quarter, 1997. The bias and precision are a significant improvement over the previous TTA solvent-extraction method. The three outliers shown out of 302 standards analyzed by a workforce of approximately 28 technicians are atypical and are likely the result of either poor pipetting, incomplete valence adjustment or overly rapid column-flow rates.

A method to determine % plutonium (IV) versus total plutonium in liquid solution was also implemented based on the fact that plutonium (III) and plutonium (VI) are not retained by TEVA Resin. In this method a load and rinse solution of 1.50 M nitric acid-0.75 M aluminum nitrate-0.25 M sulfamic acid is used for the Pu(IV) alpha-particle separation to avoid inadvertently oxidizing any Pu(III) present to Pu(IV). Standards that are 3.05E6 dpm/mL are routinely analyzed with a bias and relative standard deviation of 5% or less.

For other applications such as soil samples or bioassay samples, a two-milliliter TEVA Resin column instead of a one-milliliter column may be used, with load and strip volumes

increased proportionally. The lower acidity employed allows the use of high levels of aluminum nitrate (up to 0.75 -1.0 M) to complex the soil anion components such as phosphates and oxalates that typically have an adverse effect on plutonium recoveries using standard anion-exchange methods. Plutonium tracer yields of 70% or greater from large soil sample (> 10 g) leachates have been achieved using two-milliliter resin columns due to the high retention of plutonium and the aluminum nitrate present.⁴ These recoveries are comparable or better than what is obtained using much larger anion-resin columns. Plutonium recovery from urine samples can be accomplished using the Pu-TEVA method after calcium phosphate precipitation. At the SRS Central Laboratory, where several orders of plutonium levels are measured and planchet or filament mounting is used, the fluoride level in the strip solution is minimized. For extremely low-level plutonium work using electroplating or cerium fluoride microprecipitation, however, a 0.02 M nitric acid-0.02 M hydrofluoric acid strip solution with increased fluoride should be used to ensure more effective plutonium stripping from the resin.

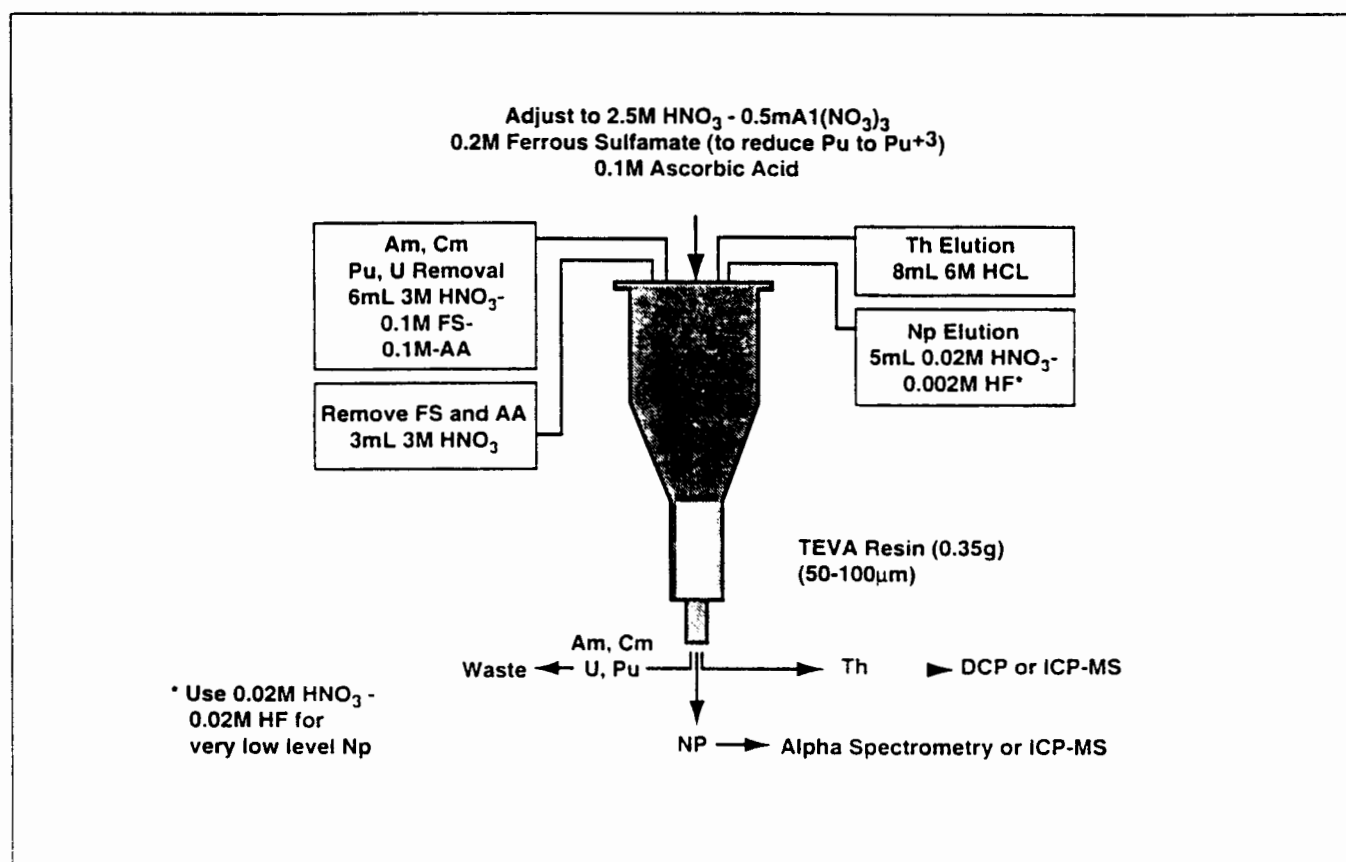


Figure 3 Np TEVA rapid column method.

The Pu-TEVA method has resulted in significant cost savings in the SRS Central Laboratory by eliminating the need for mixed-waste controls and by reducing the analytical separation times by approximately 30-50%.

Replacement of neptunium-TIOA/TTA with Np-TEVA method

Neptunium separations in the SRS Central Laboratory were performed for the last 20-30 years by a TIOA/TTA in xylene solvent extraction method. The Np-TIOA (tri-iso-octylamine) method was replaced by a new rapid Np-TEVA method shown in Figure 3. Neptunium is reduced to neptunium (IV) and plutonium is reduced to the trivalent state using 0.2 M ferrous sulfamate and 0.1 M ascorbic acid in the load solution. Thorium is retained but can be removed if necessary using 6 M hydrochloric acid. An initial rinse solution of 3 M nitric acid-0.10 M ferrous sulfamate -0.10 M ascorbic acid is used to ensure plutonium reduction and ensure maximum plutonium removal. Replacing column tips and reservoirs prior to stripping of the neptunium also enhances plutonium removal. Plutonium (1E6 dpm added) removal of greater than 99.9% is routinely achieved. A two-column method where the neptunium is reloaded onto a second column after re-acidification and addition of additional ferrous sulfamate is used when decontamination from extremely high levels of plutonium is required. The retention of Np-TEVA method is much higher than the older TIOA solvent method, which required multiple extractions to recover the neptunium.

Figure 4 shows quality control data for the Np-TEVA alpha-particle spectrometry method from the first quarter, 1997. The reference standard values are shown in the data table in Figure 4. The neptunium standard values range from 8.06E3 dpm/mL up to 1.00E5 dpm/mL. The average measured results are also shown. The standard deviation of the results (dpm/mL), relative bias (%), relative standard deviation (%) and number of standards analyzed are also shown. Typically, one milliliter of the standard is used for analysis. Tracers are not used for chemical yield correction due to the wide range of neptunium levels in process samples analyzed and the high yield consistently observed (>98%). The relative standard deviation was 4.7% and the bias was -1.55% for 29 standards analyzed in the first quarter, 1997. The bias and precision are a significant improvement over the previous TIOA solvent-extraction method.

The Np-TEVA method can also be used on large soil samples using a two-milliliter TEVA Resin column to achieve yields of 70% or better, though retention is less than plutonium. Load, rinse and strip solutions can be scaled up proportionally. Neptunium can also be measured in urine after calcium phosphate precipitation and TEVA Resin separation with high recovery.⁵

Replacement of Hexone and TBP for uranium extraction

UTEVA Resin has been used previously for uranium separations using a gravity flow technique.⁶ A new rapid UTEVA method was implemented July, 1996 to replace the Hexone method for uranium isotopic preparation for mass spectrometry and TBP extraction prior to laser phosphorescence measurements (Figure 5). This method has resulted in significant cost-savings and enabled elimination of mixed-waste controls. Ferrous sulfamate is added to the load solution to reduce plutonium to the trivalent non-absorbed state. An initial rinse of 3 M nitric acid-0.01 M ferrous sulfamate solution is used, followed by 3 M nitric acid. The uranium is stripped from the UTEVA resin using 10% phosphoric acid for phosphorescence measurements, a small volume of 0.02 M nitric acid-0.002 M hydrofluoric acid for thermal ionization mass spectrometry or 0.02 M sulfuric acid for inductively coupled plasma mass spectrometry. Neptunium(IV) tracks with the uranium in this method, as does thorium. If required, thorium can be removed using 6 M hydrochloric acid. Neptunium can be eluted quantitatively for analysis using 1.75 M nitric acid-0.125 M oxalic acid, while uranium is retained on the column (Figure 7). This single-column method for uranium and neptunium has been used for selected samples in the Central laboratory since March, 1997.

Figure 6 shows the QC data for the uranium laser phosphorescence measurements in the first quarter, 1997. The reference standard values are shown in the data table in Figure 6. The uranium standard values range from 0.00504 to 0.0211 (g/L). The average measured results are also shown. The standard deviation of the results (g/L), relative bias (%) and relative standard deviation (%) and number of standards analyzed are also shown. A two-hundred-microliter aliquot of the standard is used for analysis. Tracers are typically used in the laser phosphorescence method for chemical yield correction due to the wide range of uranium levels in process samples analyzed and the high yield observed (>98%). Uranium-233 tracers are used when uranium concentration assays are performed by thermal ionization mass spectrometry measurements. The relative standard deviation was 6.1% and the bias was -1.1% for 265 standards analyzed in the first quarter, 1997. The five outliers shown out of 265 standards analyzed by a workforce of approximately 28 technicians are atypical and are likely the result of either pipetting errors or overly rapid column flow rates. The regression line shown indicates a slight bias trend during the quarter, however, this trend is too small to be significant relative to customers needs. It was likely caused due to a change in laser phosphorescence calibration standards or a slight bias in the pipetters used.

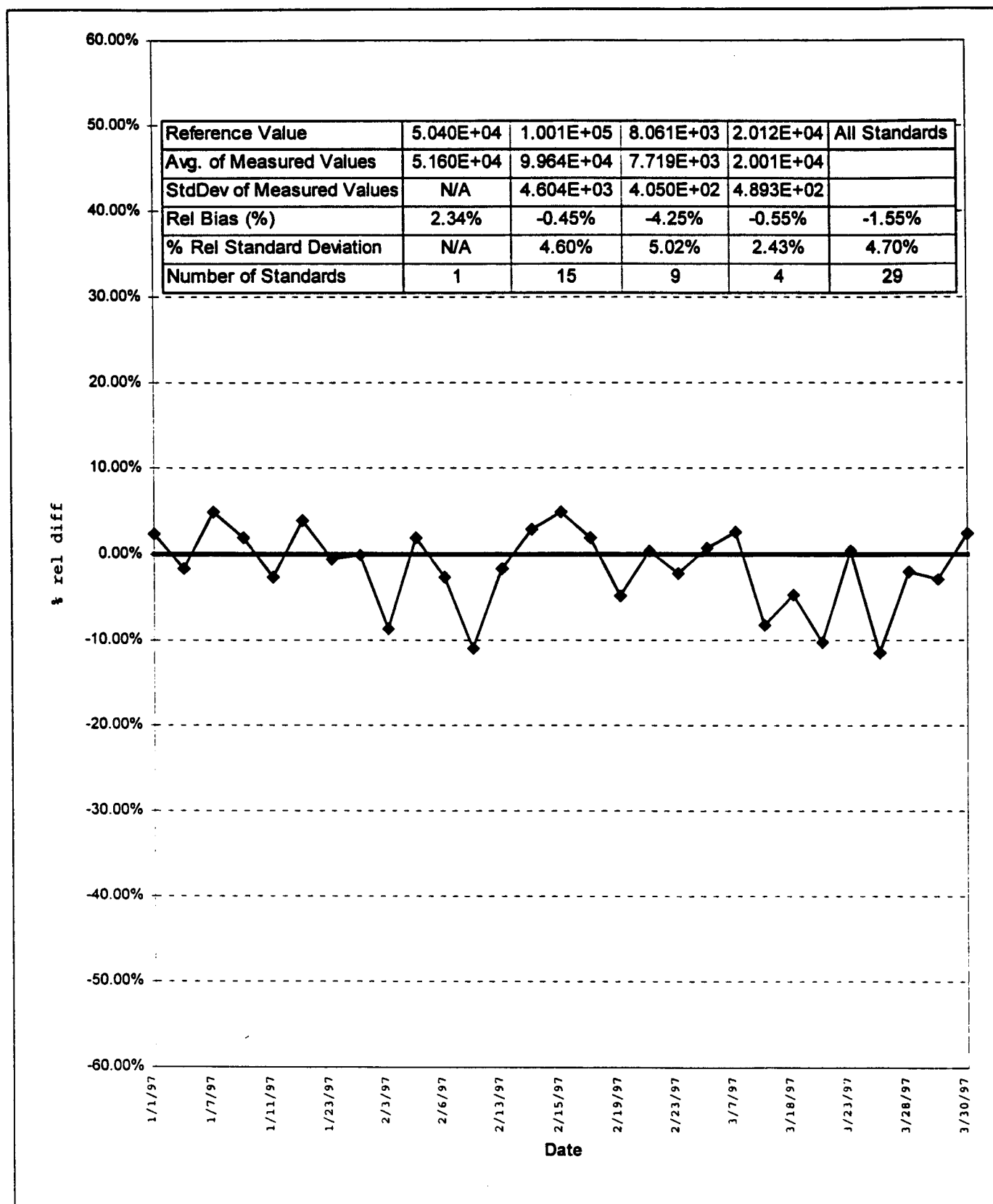


Figure 4 Np TEVA alpha quality control data, 1 QTR 97.

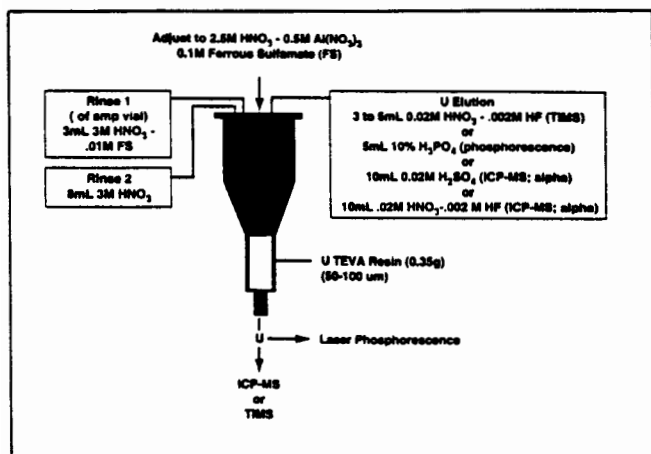


Figure 5 UTEVA rapid column method.

Dual column and sequential separation schemes

To achieve further cost savings, a new dual column method combining the Pu-TEVA method and UTEVA methods was implemented in September, 1996 for samples where the same aliquot size could be used (Figure 8). A UTEVA Resin cartridge is attached to the bottom luer tip of a TEVA Resin column to enable separate retention of the uranium, that passes quantitatively through the TEVA resin. After rinsing with 3 M nitric acid, the TEVA column and UTEVA cartridge are detached from each other and stripped separately using the appropriate strip solution to recover the plutonium (with or without neptunium), thorium and uranium separately. If any plutonium, neptunium and/or thorium passes through the TEVA resin and is retained on the UTEVA column, a 1.75 M nitric acid-0.125 M oxalic acid rinse step can be employed to remove the plutonium, neptunium and thorium prior to uranium removal from the column. Plutonium Quality control data using the Pu/U dual-column method is folded in with the PuTEVA and UTEVA QC data shown in Figure 2 and Figure 6 respectively.

As a variation to this scheme to recover americium and/or curium, the load and rinsings from the dual column may be re-acidified (or evaporated if the volume is too large and redissolved in 2.5-3 M nitric acid), ascorbic acid may be added to reduce interfering ferric ions to ferrous ions and the resulting solution may be loaded to TRU resin to recover americium and curium (Figure 9). The americium/curium can be stripped effectively with 0.01 M nitric acid, which does not remove extractant from the resin as sometimes occurs with the typical strip step using 4 M hydrochloric acid. In tests performed using this method while spiking in 3E5 dpm Pu, no Pu was found in the Am/Cm fraction. When 1E3 dpm/mL ^{241}Am standard was added to test Am recovery, the ^{241}Am recovery was found to be 103%, based on four

replicates. If a small amount of plutonium had made it through the TEVA Resin, this plutonium would likely not be stripped along with the Am/Cm due to the high retention of Pu on TRU Resin. Pu removal is therefore greater using this sequential method than with the typical TRU Resin Pu/Am separation. Larger two-milliliter columns and cartridges may be used for soil and bioassay matrices.

Conclusions

New rapid column-extraction techniques have been implemented at the SRS Central Laboratory which provide faster, more precise and accurate radiochemical measurements on nuclear process and waste solutions. Larger batches can be handled in a more rapid manner than the older solvent extraction techniques, and no hazardous listed solvents are employed. Significant cost savings have been realized due to reduced analysis times. Dual-column and sequential-column techniques using cartridge technology have been implemented where applicable to further improve efficiencies. These techniques can also be applied to environmental and bioassay samples, by using 2-mL resin volumes instead of 1-mL columns. The Pu-TEVA column technique is very effective at retaining plutonium and removing interferences. Uranium, in particular, shows less tailing on TEVA resin than conventional anion resins, particularly important when cleaning up plutonium isotopic samples for mass spectrometry and when the minimization of liquid waste is desired. Valence adjustment at the relatively dilute nitric acid used is extremely effective. This avoids one of the primary pitfalls in obtaining consistent plutonium recoveries in environmental analyses, i.e. attempting plutonium valence reduction in 8 M nitric acid. Vacuum-assisted flow rates provide flow rates approximately five times faster than gravity-flow column methods and the dual column and sequential columns provide additional time savings.

Acknowledgment

This work was performed under the auspices of the Department of Energy, DOE Contract No. DE-AC09-96SR18500. The author wished to acknowledge Vernon D. Jones of the SRS Central Laboratory for providing timely inductively coupled plasma mass spectrometry analysis in support of the rapid actinide methods development.

References

1. E. Philip Horwitz et al., "Separation and Preconcentration of Actinides from Acidic Media By Extraction Chromatography", *Analytica Chimica Acta*, 281, 361, (1993).

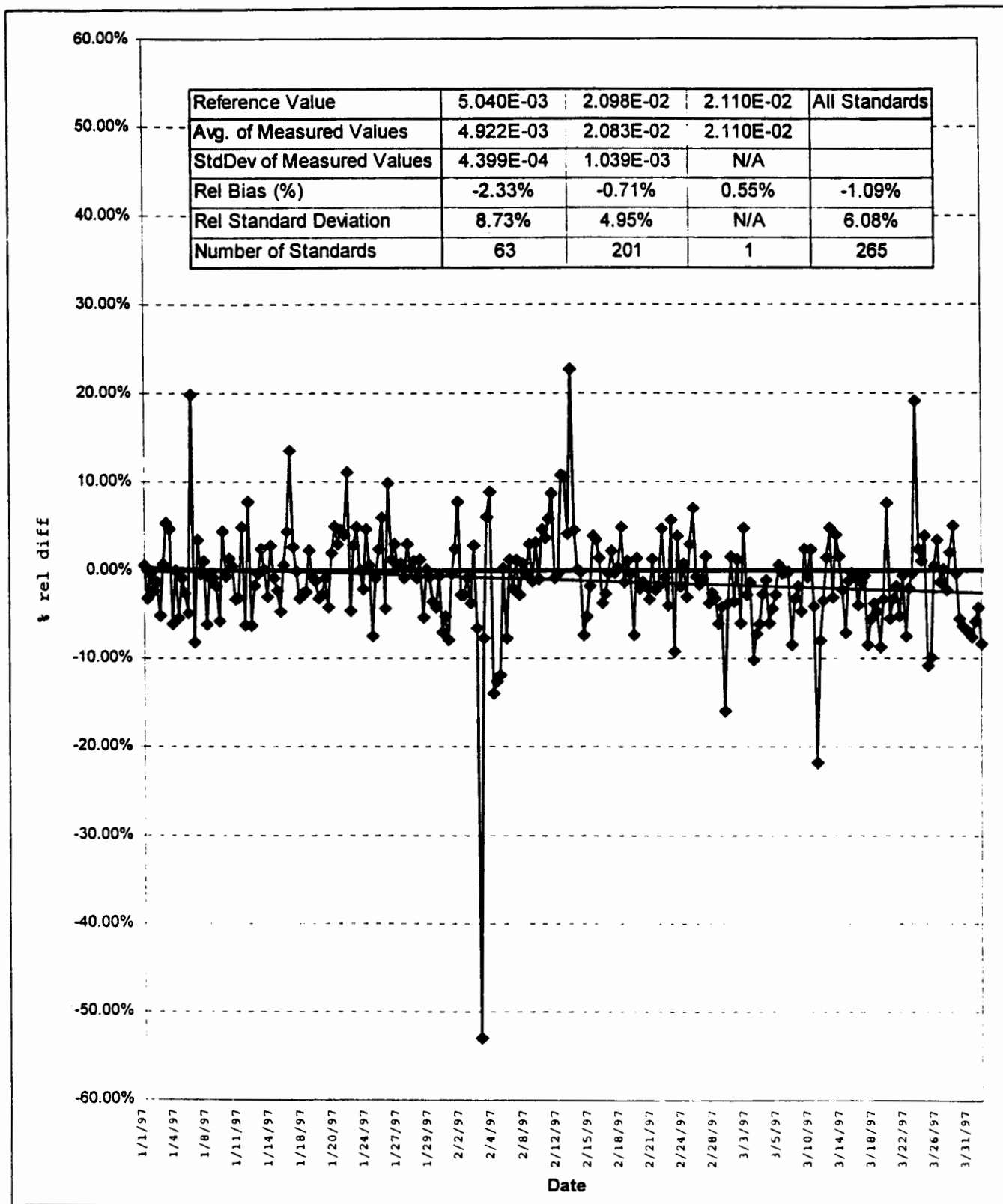


Figure 6 UTEVA laser phosphorescence quality control data, 1 QTR 97.

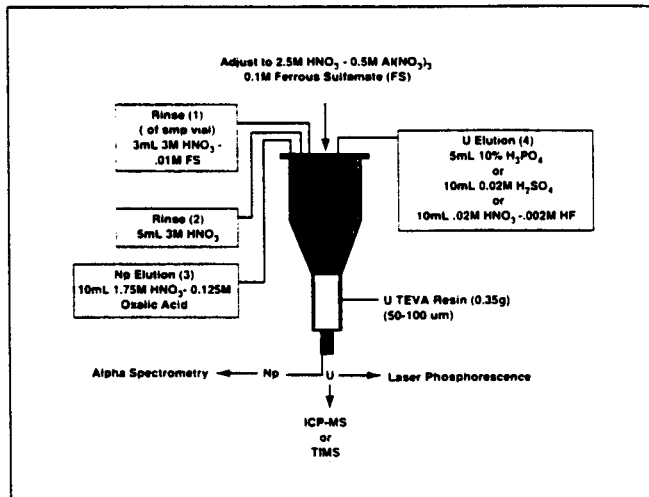


Figure 7 U/Np UTEVA single-column method.

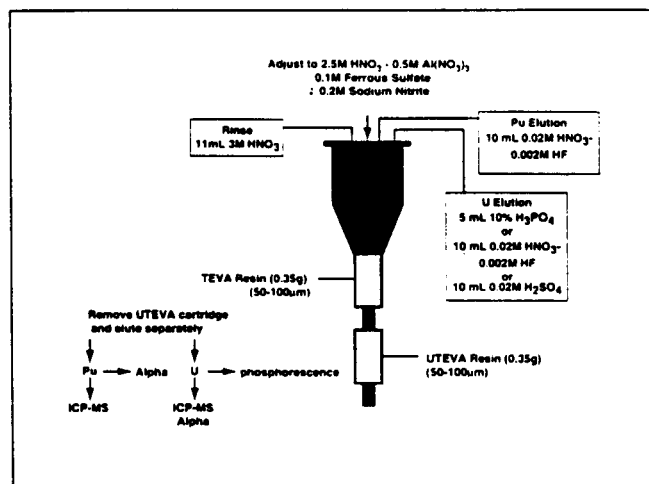


Figure 8 Pu/U dual-column method.

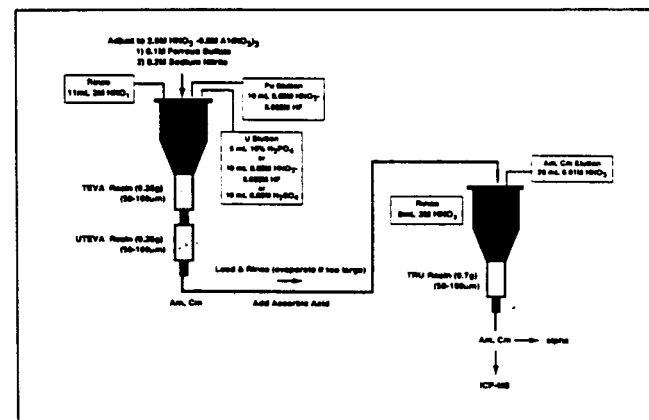


Figure 9 Pu/U Dual Column method plus Am/Cm separation.

2. S.L. Maxwell, III and M. R. Nelson, "Measurement of Actinides and Strontium-90 in High Activity Waste", Proceedings of 35th Annual Meeting for the Institute for Nuclear Materials Management. Naples, FL, July, 1994.
3. 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).
4. Personal correspondence, Timothy C. Kenna, Woods Hole Oceanographic Institute, Wood Hole, Massachusetts.
5. Anil Thakkar, "An Improved Procedure for the Determination of Neptunium in Urine Samples, Eichrom Industries Eastern User's Seminar, Oak Ridge, Tennessee, May 20, 1997.
6. E. Philip Horwitz et al., "Separation and Preconcentration of Uranium from Acidic Media By Extraction Chromatography", *Analytica Chimica Acta*, 266, 25, (1992).

Biography

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 in 1983. He began working as a chemist for E.I. du Pont De Nemours and Company at the Savannah River Site in 1984. The rapid column separation work described in this paper was nominated as a corporate finalist in the George Westinghouse Signature Award for Technical Excellence competition within the Westinghouse Corporation. He has been awarded the George Westinghouse Signature Award for Technical Excellence four times.

Sherrod L. Maxwell III
 Westinghouse Savannah River Company
 Building 772-F
 Aiken, SC 29808, USA
 Phone: 803-952-4139; Fax: 803-952-3550
 Email: sherrod.maxwell@srs.gov