

ANALYSIS OF AM, PU AND TH IN LARGE VOLUME WATER SAMPLES IN THE PRESENCE OF HIGH CONCENTRATIONS OF IRON

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1 INTRODUCTION

In far-field studies of actinide behavior, concentrations of analytes approach the detection limits of alpha-spectrometry (within reasonable count times). As actinide concentrations approach zero, larger sample sizes can improve the sensitivity of measurements. In many cases, large water samples do not create a great analytical challenge, as pre-concentration may be achieved by a number of methods¹⁻². However, in cases where the concentration of iron (Fe) is great, such as is the case for sampling of bottom waters in seasonally anoxic basins, it may be necessary to remove Fe from the matrix prior to radiochemical separations. In this paper, a method is presented for the analysis americium (Am), plutonium (Pu), and thorium (Th) in large water samples (20+kg) in the presence of high concentrations of Fe and organic matter (OM). The study site is a seasonally anoxic lake (Pond B), located at the Savannah River Site (a U. S. Department of Energy Facility) in the southeastern United States. Seasonal anoxic conditions in the bottom water of Pond B result in high concentrations of Fe and Mn from early spring (April) through mid-autumn (September) each year. The method presented here was developed as part of a broader study of the association of actinides with the monomictic cycle in Pond B¹. The field procedure is based on a technique for analysis of large seawater samples². The laboratory technique draws from several sources³⁻⁷. The concentrations of actinides in Pond B are quite low (20 µBq to 200 µBq per 50 L sample range) — representative of far-field actinide concentrations and typical concentrations of naturally-occurring thorium isotopes. The method produced excellent chemical

separations — samples were counted for one-week counting periods to quantify the activity of the actinides. In no case was the presence of cross contamination observed for n= 264 counting sources. Chemical recoveries are quite good — average recoveries were 91 +/- 8 % (Am), 84 +/- 6 % (Pu), 67 +/- 14 % (Th) respectively.

2 EXPERIMENTAL

2.1 Field Sampling

Samples were collected via a high-speed electrical pump, using an industrial grade garden hose, with depth demarcations in one-meter increments. The samples were pumped directly to (pre-weighed) new or acid-cleaned 20-L carboys (equipped with spigots for removal of supernatant solution) or 50-L drums. The volumes of solutions presented here presume a 20-L sample size. Samples were acidified immediately (100 mL concentrated HCl, pH 1-2) and weighed. A gas generator was used to supply electrical power to a digital balance to allow weighing of samples in the field. Once acidified, tracer solutions and 15 mL 0.5 M manganous chloride (MnCl_2) were added to the carboys. The carboys were sealed and shaken vigorously and the solutions were allowed to stand for at least one hour. A 15-mL aliquot of freshly-prepared-saturated potassium permanganate (KMnO_4) was then added and the samples were shaken vigorously again to ensure adequate mixing. The bright purple color of the KMnO_4 solution served as a visual clue that mixing was complete (in some cases, the color disappeared quickly as divalent Fe rapidly reduced the Mn). The $\text{MnCl}_2/\text{KMnO}_4$ procedure is designed to complete a redox cycle for Pu^{2+} . Although this may be true for low-Fe content samples, the rapid disappearance of the purple color indicates that large amounts of divalent Fe control the redox state of Pu. Since the presence of Fe^{2+} suggests reducing conditions in the water samples, Pu species present are likely to be the reduced forms (i.e., $\text{Pu}^{3+}/\text{Pu}^{4+}$) that co-precipitate readily with MnO_2 . Thus, Pu co-precipitation via the $\text{MnO}_2/\text{Fe}(\text{OH})_3$ is effective under these conditions, despite the difficulties in cycling redox conditions for samples.

Solutions were allowed to stand one hour. After being allowed to stand, a 150 mL aliquot of concentrated ammonium hydroxide (NH_4OH) was added to adjust the pH of the solutions to about 9. The pH of solutions was verified using pH strips. The carboys were sealed and shaken vigorously and finally let stand (24-36 hours) to allow for settling of the resultant manganese dioxide/iron hydroxide ($\text{MnO}_2/\text{Fe}(\text{OH})_3$) precipitate.

After the settling period, the supernatants were decanted and discarded via a spigot. The precipitates were transferred to acid-cleaned 1-L polyethylene reagent bottles and taken to the laboratory for processing.

2.2 Laboratory Procedure

2.2.1 Tracers and Reagents

Tracer solutions were diluted Standard Reference Materials (SRM's) obtained from the United States Department of Commerce National Institute of Standards and Technology (NIST). Dilutions were prepared gravimetrically using a Mettler-Toledo

Model 240 digital balance. The gravimetric dilutions were prepared by diluting to volume in volumetric flasks (and measuring by mass), with a stated uncertainty of $\pm 2\%$ (two sigma). Tracer solutions were prepared at a $100 \mu\text{Bq mL}^{-1}$ nominal concentration (1 mL added per sample by volumetric pipet) to approximate the activity level of 20-50 kg water samples from Pond B. Appropriate measurements ($n = 5$) of diluted SRM's were made to verify the dilution factor of each standard. Tracers were ^{242}Pu , ^{243}Am , and ^{229}Th . Corrections were made for known quantities of ^{241}Am (0.16% correction of ^{243}Am tracer, based on the NIST certificate) and ^{230}Th and ^{232}Th , based on blank measurements ($n = 4$, with one outlier) that indicated a reproducible reagent blank of $0.41\% \pm 0.05\%$ for ^{232}Th and $1.1\% \pm 0.2\%$ for ^{230}Th (uncertainty based on standard deviation of replicates). Reagent blanks did not indicate a significant contribution of $^{239/240}\text{Pu}$ that required a correction for Pu activity calculations.

New labware was purchased for this study. Extensive efforts were made to ensure that no contamination was introduced during sampling and processing. Reagents chosen were American Chemical Society (ACS) Grade, diluted with distilled and de-ionized water.

2.2.2 Laboratory Precipitation Techniques

Precipitates were transferred to acid-cleaned 2-L glass beakers (that were reserved for this low-level project) and acidified with 6 M HCl (to pH <2). Samples were then diluted to 750 mL and heated gently. As heating began, a 25-mL aliquot of $0.1 \text{ g } 10 \text{ mL}^{-1}$ ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) was added to reduce Mn and Fe. This produces a clear to yellowish green solution (depending upon the concentration of Fe). Samples were allowed to heat gently for between 30 minutes and one hour. Next, a 25-mL aliquot of $0.1 \text{ g } 10 \text{ mL}^{-1}$ sodium nitrite (NaNO_2 , freshly prepared) was added to oxidize Fe to the +3 state (while Mn remains divalent). The solutions turn brownish to yellow in color (depending on the concentration of Fe).

Concentrated NH_4OH was added slowly to pH 8 to precipitate amorphous $\text{Fe}(\text{OH})_3$, while Mn^{2+} remains with the supernatant solution. The $\text{Fe}(\text{OH})_3$ precipitation worked best when solutions were boiled vigorously for several minutes as this produced a much denser amorphous solid that settled rapidly with cooling.

The supernatant solutions were decanted and discarded. Samples were then wet-ashed three times using a mixture of concentrated HNO_3 and 30 % H_2O_2 . The precipitates were first acidified with concentrated HNO_3 . Next, a 10-mL aliquot of 30% H_2O_2 was added and the samples were allowed to react at low-heat and taken to dryness (this reaction should be carried out at low heat). This procedure was repeated three times and the samples were then dissolved (and transferred to 50-mL polypropylene centrifuge tubes) with 25 mL 4 M HCl. In some cases, the Fe concentration was sufficiently great to require the use of 250-mL centrifuge bottles. In these cases, the volumes of reagents described here were scaled accordingly.

In the next step, the samples were to be dissolved in HCl and transferred to centrifuge tubes for precipitation with LaF_3 . However, upon dissolution, the presence of a whitish flocculent indicated the presence of amorphous silica gel (Si) in most samples. These were transferred with a minimum amount of 3 M HNO_3 to disposable plastic beakers set-

up in double boiler configurations for gentle heating. To volatilize the Si, 2 mL concentrated hydrofluoric acid (HF) was added and the samples were taken slowly to complete dryness. This procedure was repeated a second time to ensure complete removal of Si. A 5-mL aliquot of 3 M HNO₃ was then added and the samples were taken to complete dryness to remove excess fluoride. This was repeated a second and third time to ensure complete removal of excess fluoride.

The samples were then transferred to 50-mL polypropylene centrifuge tubes with 25 mL 4 M HCl. The solutions were diluted with 10 mL 1 g 10 mL⁻¹ NH₂OH•HCl solution (which reduces Fe³⁺ to Fe²⁺ and ensures that Pu is in the +3/+4 states). The actinides were next precipitated (and Fe is removed from the matrix) by the addition of 2 mg La³⁺, followed by 3 mL concentrated hydrofluoric acid (HF) to coprecipitate LaF₃. Samples were centrifuged for five minutes at approximately 2500 rpm and the solution phase was discarded by decanting. This step serves to remove from the matrix not only Fe, but also natural U, which does not co-precipitate with the tri-valent rare earth in the absence of a much stronger reducing agent (such as titanous chloride TiCl₃ or chromous chloride CrCl₃).

The translucent-grayish LaF₃ precipitate was then dissolved in 20 mL 3 M HNO₃-2.5 % boric acid (H₃BO₃) in preparation for column separations.

2.2.3 Column Separations via TEVA/TRU

The method for separation of Am, Pu and Th is similar to that presented by Burnett et al. (1996)² and Schultz (1996)⁸. Best results were obtained using a tandem column arrangement using TEVA and TRU resins (Eichrom Technologies, Darien, IL USA). The methods were refined to minimize the need for redox reagents that are applied frequently to adjust the redox state of Pu. A number of variations of the TEVA/TRU tandem column arrangement have been presented^{5,8}. The arrangement is an attractive alternative to a single column arrangement not only because of time savings during the column separations (elutions are carried out simultaneously), but more importantly, because the method provides for redundant separation steps — this inherently improves elemental separations.

In general, the TEVA/TRU methods that have been presented can be divided into two groups:

- Methods that reduce Pu in the load solution. Pu (and Am) passes through the TEVA column and is retained on the TRU column.
- Methods that do not adjust the oxidation state of Pu in the load solution. Pu (and Th) is retained by the TEVA column, while Am passes through the TEVA and is retained on TRU.

Method 1 is attractive because it provides a redundant separation of Pu and Th, while Method 2 provides this same benefit for the separation of Am and Pu (since Pu is retained on the TEVA column, while Am passes through).

Although each of the above approaches is theoretically sound, experience has shown that trace cross-contamination may occur in each case. In the case of Method 1, Maxwell, et al. (1997)⁵ report that for precise work (such as radiobioassay), trace amounts of Th were found pervasively in Pu spectra. The alternative suggested, for precise work, was to add a second TEVA column to remove trace Th from Pu spectra. On the other hand, when using Method 2, trace amounts of Am tend to be found in Pu spectra as the elution of Am tends to leave trace amounts on the TRU column. Since Pu is eluted in the tri-valent state, using Method 2, any Am that remains on the TRU column is likely to be eluted with Pu. actinide fractions is provided as well, enhancing the purity of the final counting sources. In the alternative method, presented below, the elution volume for Am was increased to 30 mL from 15-20 mL suggested in previous methods. Since Pu is retained on the TEVA column, an increase in the elution volume for Am can be used without regard for Pu leakage into the Am fraction.

2.2.4 *The Alternative Approach to the TEVA/TRU Method*

The method presented here combines characteristics of Method 1 and 2 to produce an approach that proved effective in obtaining excellent chemical recoveries, while providing for outstanding elemental purity and spectral resolution. To summarize, the TEVA and TRU columns are arranged in tandem, so that the load solution (3 M HNO₃) passes through the TEVA column and directly into the TRU reservoir (Fig. 1). Pu is expected to be predominantly in an oxidized form (likely +4) and is retained (with Th⁴⁺) on the TEVA column. Americium (as Am³⁺) passes through the TEVA column and is retained on the TRU column (as are trivalent rare-earth elements). A solution of 3 M HNO₃-0.05 M NaNO₂ is passed over the tandem arrangement to ensure that Pu is maintained in the +4 oxidation state. The addition of NaNO₂ ensures that Am can be removed cleanly from TRU for much the same reason. After rinsing the columns of excess NO₂⁻, the columns are separated (and can be run simultaneously for elution of Am and Th (Fig. 2-3). A 30-mL (3 x 10 mL) elution volume (4 M HCl) removes quantitatively Am from the TRU column, while an equal volume (in 5-mL increments) of 9 M HCl removes virtually all Th from TEVA. However, since trace quantities of Th are known to be retained on TEVA (likely due to adsorption to the resin beads, rather than extraction into the organic phase⁵), a redundant step is needed to ensure that Pu is removed cleanly. This is accomplished by recombining the TEVA and TRU columns in the tandem arrangement (Fig. 4). Pu is eluted using a reductant (hydroquinone in 4 M HCl). The inclusion of the TRU column in the elution of Pu retains any residual Th that is retained on TEVA, thus providing excellent purity for the Pu fraction. Americium is then separated from La by using a second TEVA column (Fig. 5).

2.2.5 *Lanthanum/Americium Separation on TEVA*

Following elution from the TEVA/TRU tandem column arrangement, La³⁺ and Am³⁺ were separated via TEVA resin using a solution of ammonium thiocyanate (NH₄SCN) in dilute HCl (Fig. 5). Tri-valent rare earths and tri-valent actinides (trans-plutonium) are known to exhibit remarkably similar behavior and present a unique challenge to ion-exchange and extraction chromatography⁹⁻¹¹. Cation exchange procedures have been used to separate lanthanides and tri-valent actinides. However, due to the similarity in chemistries of these elements, the cation-exchange techniques require large resin beds and generate substantial quantities of acid waste. On the other hand,

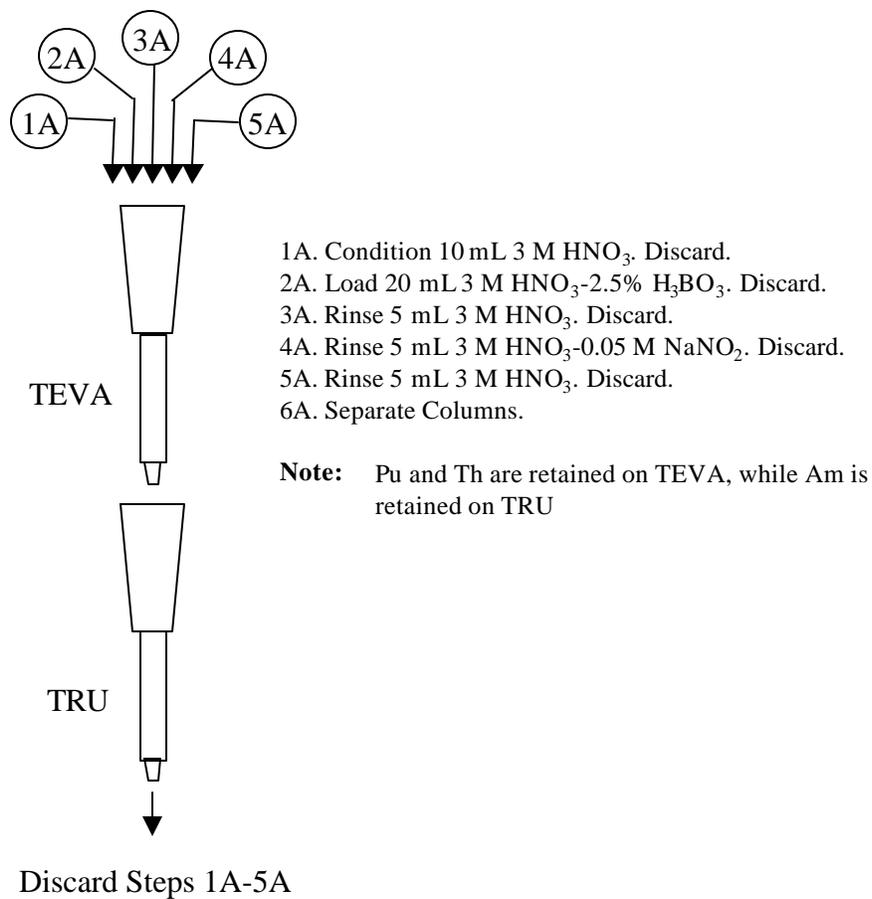


Figure 1 Tandem arrangement of the TEVA and TRU resin columns. Eluents from steps 1A through 5A are discarded.

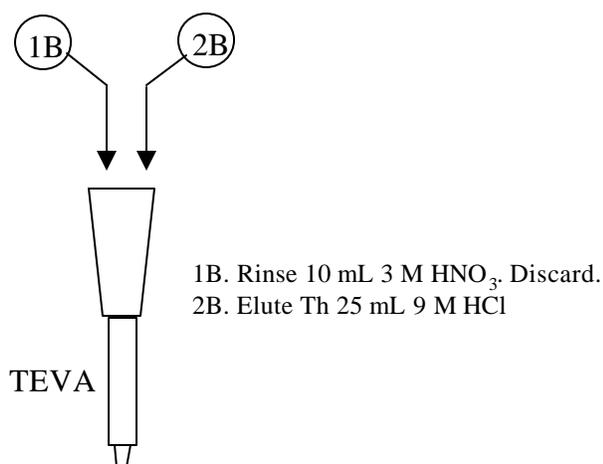


Figure 2 Elution of Th from the TEVA column after the columns are split.

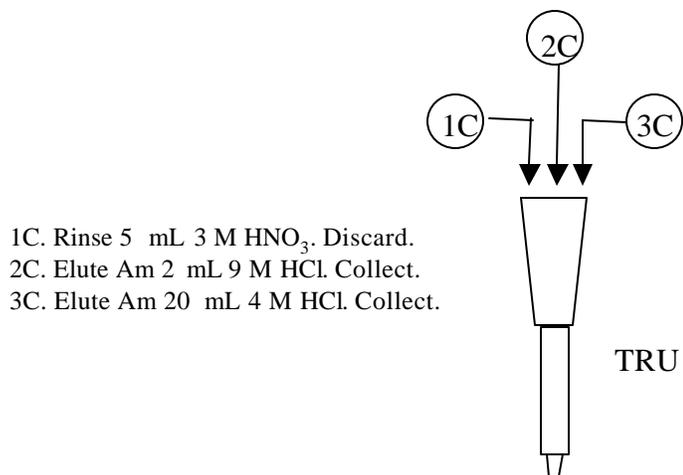


Figure 3 Elution of Am (and La) from the TRU column. Pu is retained on the TRU column during this step.

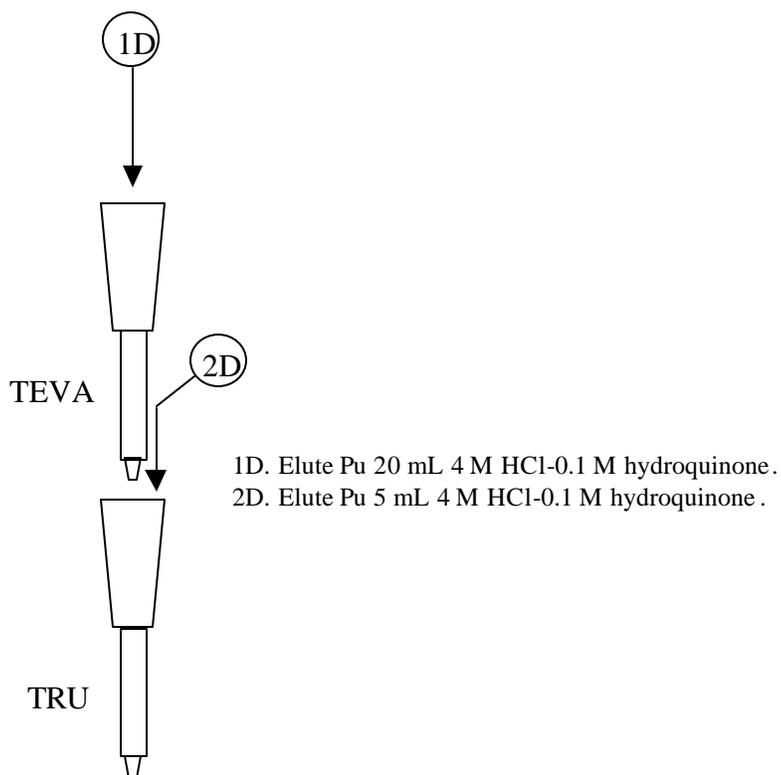


Figure 4 TEVA and TRU columns are restacked for elution of Pu with hydrochloric acid and hydroquinone.

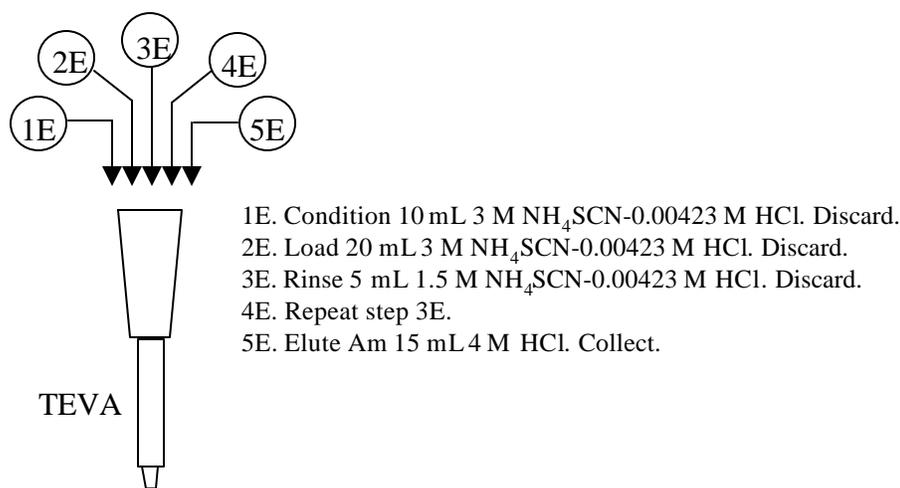


Figure 5 Separation of Am and La (rare earth carrier) using TEVA resin in a dilute hydrochloric acid/ammonium thiocyanate medium.

extraction chromatographic techniques can be performed using standard 2-mL resin beds and relatively smaller quantities of acid waste are generated.

The method of choice has been the use of a thiocyanate/formic acid solution to effect the separation⁹. These authors studied the potential for separation of europium (Eu) and Am, using a number of quaternary ammonium salts, including Aliquot-336 (general formula R₃CH₃NCl, where R is a mixture of C₈ and C₁₀ carbon chains, with C₈ predominating¹⁰). Aliquot-336 thiocyanate/formic acid was found to effect, by far, the best separation. The reason for the improved separation using the thiocyanate media is found to be the tendency of the thiocyanate ligand to form inner sphere complexes more readily with actinides than with lanthanides (in weakly acidic solutions) and in the tendency of ions with 5f electrons (actinides) to bond to soft donor ligands¹¹.

The original method utilized a liquid/liquid extraction approach employing Aliquot-336 as the organic phase and the thiocyanate/formic acid solution as the acid phase⁹. Since the extractant impregnated on the TEVA resin is Aliquot-336, the approach was easily adapted to the use of this extraction chromatography resin. However, for practical environmental radiochemistry applications, following a TRU-resin separation from other actinides, the formic acid medium does not dissolve quantitatively residues that are obtained as the elution volume is taken to dryness. It seemed reasonable that another acid, with better solvation properties, at the correct concentration, should produce the same effect as the formic acid. Hydrochloric acid was chosen because of its common usage in laboratories and its qualities as a solvent for many substances. The appropriate concentration (pH) was calculated by using the acid constant K_a for HCOOH (1.8 E-08), which translates to a pH of 2.37 and a concentration of HCl of 4.23 E-03 M. In initial tests, the approach proved to be effective in achieving high chemical recoveries and excellent resolution for Am spectra (Average Chemical Recovery 86%, standard deviation 12%, n=3). Variability was reduced by preparing precisely the HCl/NH₄SCN solutions to ensure that the pH of the load and rinse solutions was correct (Average Chemical Recovery 96%, standard deviation 2%, n=5). Results were excellent also for complete analyses for the work presented in this paper — for Am in large water samples in the

presence of large amounts of Fe, where the use of the LaF_3 co-precipitation was effective in removing Fe from the matrix, but necessitated a quantitative separation of La and Am.

To separate Am and La, the eluted solutions from the TRU column were taken to near complete dryness. A single wet-ashing step was used to oxidize organic material, which is dissolved from the TRU resin bed. Five mL of concentrated HNO_3 was added to the cooled samples in 50-mL glass beakers. To this solution was added a 2-mL aliquot of 30% H_2O_2 and the solution was heated gently (covered) to complete dryness (but not baked). Once dry, a 5-mL aliquot of 9 M HCl was added to remove the remaining HNO_3 and the solution was heated to complete dryness (uncovered). Next, a 2-mL 1 M HCl was added to ensure that all remaining HNO_3 was removed and the samples were taken slowly to very near complete dryness (uncovered). Once the HNO_3 was removed, the samples were dissolved in 10 mL of 0.00846 M HCl (covered, with gentle heating to achieve complete dissolution). To the cooled samples was added 10 mL 6 M NH_4SCN and the samples were swirled and allowed to stand for several minutes to ensure complete mixing (the NH_4SCN solution is quite viscous) and complete dissolution. Trace amounts of Fe were evidenced (in some samples) by the presence of a reddish color — Fe forms a blood-red complex with thiocyanate in solution. The separation was then carried out by washing the column with two 5-mL washes with 3 M NH_4SCN -0.00423 M HCl to remove La. Finally, Am was eluted with a 15 mL rinse with 4 M HCl. Four drops of 10 mg mL^{-1} Fe^{3+} solution were added (to inhibit adsorption to the glass beaker) and the eluted Am solutions were taken to complete dryness by gentle heating (uncovered) in preparation for source preparation by NdF_3 micro-precipitation.

2.2.6 Source Preparation using NdF_3 microprecipitation

Alpha-counting sources for this work were prepared by neodymium fluoride microprecipitation. Solutions eluted from columns were taken to complete dryness and treated in the same manner as described above for Am. Following the addition and drying step, residues were dissolved in 5 mL 2 M HCl and heated gently. The solutions were transferred to 50-mL polypropylene centrifuge tubes with 5 mL DIW. To the solutions was added 50 μg Nd^{3+} solution and the solutions were swirled and allowed to stand several minutes. Plutonium samples were reduced by dropwise addition of ascorbic acid (noted by a color change of the solutions from yellow to clear, as Fe is reduced). The presence of reduced Fe ensures that Pu exists in solution as $\text{Pu}^{3+}/\text{Pu}^{4+}$ — the oxidation states that are coprecipitated with the rare earth fluoride. Next, a 2-mL aliquot of concentrated HF was added and the solutions were let stand 30 minutes to allow complete precipitation of NdF_3 . Sources were then prepared by filtration, using 25-mm diameter (0.1 μm mesh) polypropylene Gelman™ filters, pre-rinsed with 80% ethanol (EtOH). The centrifuge tubes were rinsed with ~5 mL EtOH solution (transferred over the filters to rinse out excess F^-). The filters were dried, at 50°C for about 20 minutes and mounted to self-adhesive 2-inch metal planchets for counting.

3. METHOD SUMMARY AND EVALUATION

In this paper, a method is presented for the analysis of actinides Am, Pu and Th in large water samples (20+ kg) — in presence of high concentrations of Fe. Initial pre-concentration of actinides, from the bulk water samples, can be accomplished by an

alkaline $\text{MnO}_2/\text{Fe}(\text{OH})_3$ precipitation step. Manganese is then removed by selective precipitation of Fe as a hydroxide. Actinides are then separated from Fe using a LaF_3 co-precipitation technique. The rare-earth fluoride is dissolved in a mixture of nitric and boric acids and the actinides are separated by use of extraction chromatography resins TEVA and TRU. Finally, La and Am are separated using TEVA resins (by use of NH_4SCN in dilute HCl). Precise preparation of the $\text{NH}_4\text{SCN}/\text{HCl}$ solution at pH 2.37 is produces best results. Counting sources are prepared by micro-precipitation with NdF_3 . The method produced excellent chemical separations — samples were counted for one-week counting periods to quantify the activity of the actinides. In no case was the presence of cross contamination observed for $n=264$ counting sources. Chemical recoveries are quite good — average recoveries were 91 +/- 8 % (Am), 84 +/- 6 % (Pu), 67 +/- 14 % (Th) respectively.

4. ACKNOWLEDGEMENTS

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