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Rapid separation and purification of uranium and plutonium from dilute-matrix samples

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ABSTRACT

This work presents a streamlined separation and purification approach for trace uranium and plutonium from dilute (carrier-free) matrices. The method, effective for nanogram quantities of U and femtogram to picogram quantities of Pu, is ideally suited for environmental swipe samples that contain a small amount of collected bulk material. As such, it may be applicable for processing swipe samples such as those collected in IAEA inspection activities as well as swipes that are loaded with unknown analytes, such as those implemented in interlaboratory round-robin or proficiency tests. Additionally, the simplified actinide separation could find use in internal laboratory monitoring of clean room conditions prior to or following more extensive chemical processing.

We describe key modifications to conventional techniques that result in a relatively rapid, cost-effective, and efficient U and Pu separation process. We demonstrate the efficacy of implementing anion exchange chromatography in a single column approach. We also show that hydrobromic acid is an effective substitute in lieu of hydroiodoic acid for eluting Pu. Lastly, we show that nitric acid is an effective digestion agent in lieu of perchloric acid and/or hydrofluoric acid. A step by step procedure of this process is detailed.

Simulated samples were produced by loading appropriate ^{235}U, ^{238}U, ^{239}Pu, and ^{240}Pu onto high purity cotton swipes. Uranium concentration and isotopic composition were measured by Multi-Collector Inductively Coupled Mass Spectrometry (MCICPMS). Corresponding plutonium measurements were conducted with a Three Stage Thermal Ionization Mass Spectrometer (3STIMS). Quantitative U and Pu recoveries were observed with this method. The results of these analyses are described in the context of evaluating this innovative radiochemical processing technique.

Keywords: Uranium, plutonium, environmental samples, safeguards

1. INTRODUCTION

States engaged in declared nuclear-related activities typically allow the International Atomic Energy Agency (IAEA) to access nuclear facilities for inspection. These practices are part of the IAEA safeguards mission to verify that nuclear materials are not diverted or misused to assemble nuclear weapons. At present, 145 states have entered into such agreements with the IAEA; compliance involves submitting nuclear materials, facilities, and activities to the scrutiny of IAEA's safeguards inspectors (IAEA Bulletin, 2001).

Swipe sampling, often referred to as environmental sampling (Cable-Dunlap *et al*., 2013; IAEA Bulletin, 2001), is commonly undertaken by IAEA inspectors to monitor international treaty compliance. Swipes are composed of a variety of materials including cotton and polyester. Typically a swipe is rubbed across flat surfaces, e.g., benchtops, floors, doorknobs, etc., whereupon material is transferred to the swipe. Because a wide variety of surfaces are swiped from one facility to the next, a highly variable amount of bulk material (soil, dust particles, etc.) may be collected. Swipe samples are typically processed through rigorous radiochemical protocols to separate and purify uranium and plutonium constituents for subsequent analysis by mass spectrometry.

Traditional radiochemical separation and extraction processes are typically a "one size fits all" paradigm wherein a wide range of matrices (soils, rocks, vegetation, water, etc.) are separated and purified in a similar manner. For example, although front end processing (ashing, digestion, etc.) varies depending on the sample matrix, subsequent separation and purification steps are relatively consistent from sample to sample. These processes often involve a combination of anion exchange and extraction chromatography steps (Lee *et al*., 2009; Eikenberg *et al*., 2009; Horwitz *et al*., 1995). Although this tried and tested formula is highly effective, it is time consuming and expensive; and it is simply not necessary for all sample types. The motivation for this study is to develop a more streamlined approach specifically of interest to workers in the radioanalytical community engaged in routine swipe sampling, processing, and analysis.

The method described herein applies to cases where very little bulk material is collected on environmental swipes; and it is equally appropriate for swipe samples that have been loaded with

analytes for interlaboratory round-robin or proficiency tests. To validate our streamlined separation technique, the latter sample type was simulated in this study, as described in detail below.

In this work, we describe a technique for measuring U and Pu concentrations and isotopic compositions in unknown samples retained on high purity cotton swipes. This method, involving an effective alternative leaching process, does not require complete dissolution of the swipes. Thus relatively hazardous reagents e.g., hydrofluoric acid and perchloric acid are avoided. In addition, with this approach hydrobromic acid (HBr) is used as a viable eluting agent for Pu in lieu of the more reactive hydroiodoic acid (HI). Lastly our method involves a single column separation technique, employing an anion exchange resin (Dowex AG1X4) without the need for extraction chromatography, e.g. TRU, TEVA, UTEVA resins etc. Thus our method is simpler, time-saving, and less costly than conventional approaches.

Here we detail the complete procedure and provide experimental results supporting the viability of our strategy. The efficacy of this approach was tested by creating simulated samples consisting of cotton swipes loaded with predetermined amounts of ^{235}U, ^{238}U, ^{239}Pu, and ^{240}Pu. These simulated samples were processed and analyzed for U and Pu concentrations and isotopic composition by Multi-Collector Inductively-Coupled Mass Spectrometry (MCICPMS) and Three Stage Thermal Ionization Mass Spectrometry (3STIMS), respectively. We show that this approach, when tailored to nanogram quantities of U and femtogram to pictogram quantities of Pu, offers high U and Pu recoveries, and it is thus a viable alternative to lengthier radiochemical separation processes.

2. EXPERIMENTAL

2.1 Experimental Details

The swipes used in this study were TexWipe® TX 304 (100 % cotton; 100 cm^2). These particular swipes were chosen because of their low impurity and low U content. This material is currently used by IAEA inspectors when collecting samples during actual facility inspections. Although these swipes contain only trace levels of U, appreciably high variability of total U has been observed between individual blank swipes (Cable-Dunlap *et al*., 2013). Thus, to determine the U content in these swipes, six swipes were ashed, leached in 8 M HNO_3, evaporated to dryness and brought up in 0.8 M HNO_3 for total U determination by Kinetic Phosphorescence Analysis (KPA-11: from Chemchek™ Industries). The total U concentration was determined to be 4.77 ± 0.97 ng U. These results were consistent with other studies investigating U in these swipes (Cable-Dunlap et al., 2013).

The simulated samples consisted of duplicate loaded swipes. In addition, a blank swipe, and a reagent blank were analyzed. All sampling processes were conducted by weight on a calibrated semi-micro balance. The samples were loaded with high purity ^{240}Pu (NIST SRM 4338A), ^{235}U and ^{238}U (New Brunswick Laboratory CRM U500). Following initial processing, the samples, sample blanks and reagent blanks were spiked with 0.5 ng of high purity ^{233}U stock solution (1.0311 ng U/g solution from NIST CRM-111-A) and approximately 13 pg of ^{242}Pu stock solution (NIST SRM 4334G). The anion exchange resin used in this study was AG1X4 (Dowex-1, 100-200 mesh, chloride form). See Appendix A for details.

The general scheme for single-column U and Pu separation, purification, and extraction is shown in Fig.1. The step by step procedure is reported in Appendix A. Prior to use, HBr was processed to eliminate coexisting Br_2 (g). This pretreatment procedure is reported in Appendix B. An optimal volume of 9 M HBr was determined experimentally (mainly via initial alpha spectrometry) to elute Pu (see Appendix A for details). Replicate samples were initially electroplated and analyzed by alpha spectrometry to monitor (and experimentally minimize) carryover into respective U and Pu elutions.

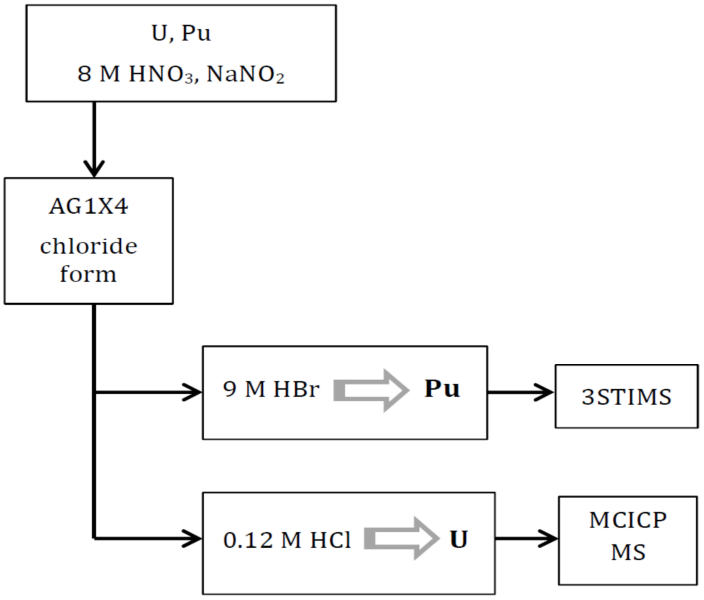

Fig. 1. General scheme for separation and extraction of U and Pu.

2.2 Methodology

To test the viability of this modified radiochemical procedure (Appendix A), blank swipes were initially loaded to produce simulated samples with approximately 11 pg of ^{240}Pu and 27 ng of U500 (containing a 1:1 ^{235}U and ^{238}U mixture). Uranium measurements were conducted with a Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MCICPMS, Nu Plasma HR, Nu Instruments, Wrexham, UK). The instrument is equipped with 12 Faraday cup detectors and 3 secondary electron multiplier (SEM) detectors which allow for high precision isotope ratio measurements by simultaneous detection of all uranium isotopes. Samples are prepared in dilute (~2%) HNO_3 solution and naturally aspirated at ~100 µL/min through a desolvating nebulizer (DSN-100, Nu Instruments) into the plasma source. Plutonium measurements were conducted with a 1960's KAPL (Knolls Atomic Power Laboratory) design Three Stage Thermal Ionization Mass Spectrometer (3STIMS) fabricated in house in the 1970's. The single SEM detector instrument has three 90^0 x 30.5 cm sectors in BBE configuration and routinely analyzes pg mass Pu samples. Purified samples are loaded onto anion exchange resin beads, which are then loaded by hand onto high purity Re filaments and placed in the source region of the mass spectrometer for thermal ionization.

For uranium, isotope ratio measurements were made on purified aliquots of each sample, while isotope dilution mass spectrometry (IDMS) was employed for assay determination. This approach involves spiking a separate aliquot of the sample with a known amount of high purity ^{233}U. The measured spike-to-sample isotopic ratios enable calculation of total U in the samples. Thus MCICPMS analysis required both spiked and unspiked samples: spiked samples for total U determination and unspiked samples for U isotopic determination. For plutonium, a single aliquot of each sample is sufficient and typically spiked with high purity ^{242}Pu. This straightforward approach enables measurement of the major Pu isotopes, while simultaneously making the IDMS measurement for assay determination.

The general scheme for dividing a sample into subsamples for processing and mass spectrometry analysis is shown in Fig. 2.

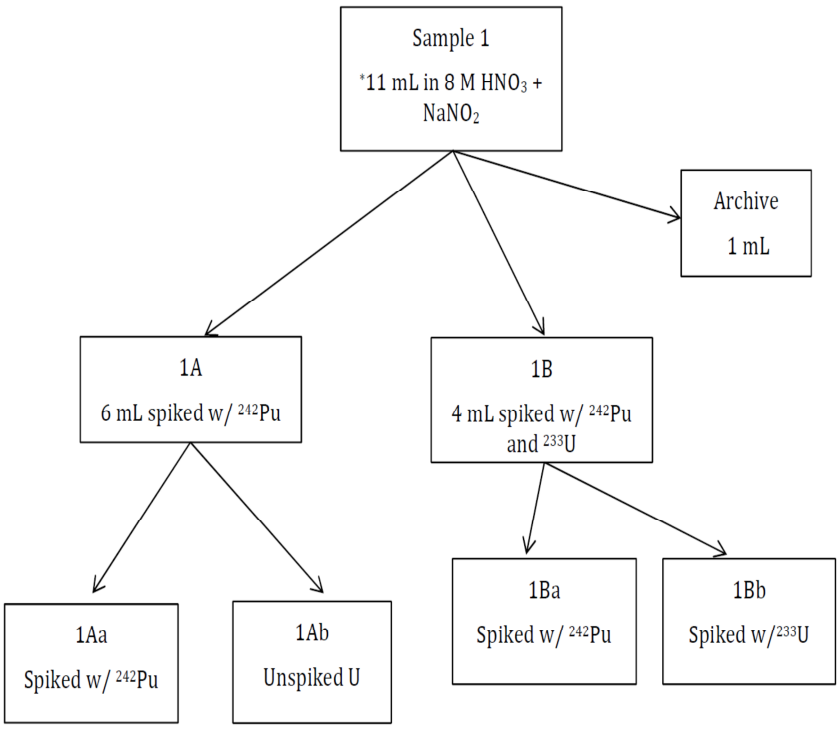

Fig. 2. Sample division scheme for U (MCICPMS) and Pu (3STIMS) analysis. *minus the 1 % screen.

After the ashing and leaching steps were completed, the sample volumes were approximately 11 mL in an 8 M HNO_3 matrix (see Appendix A for complete sample treatment details).

Approximately 1 % of each sample was extracted and screened by MCICPMS for approximate U and Pu content and isotopics, thus offering guidance in choosing appropriate spike concentrations. The samples were divided into fractions as follows. Note this approach also resulted in two separate aliquots for TIMS which afforded more flexibility in the event of sample loss (e.g., resin bead dislodging from filament etc.) during analysis. Each sample solution was thus divided into three fractions: 6 mL ('A' fraction), 4 mL ('B' fraction), and 1 mL (archived fraction). The 'A' fraction was spiked with ^{242}Pu while the 'B' fraction was spiked with both ^{242}Pu and ^{233}U. The 'A' fraction was passed through the column and the spiked Pu and unspiked U aliquots were eluted with 9 M HBr and 0.12 M HCl respectively ('Aa' and 'Ab' respectively). Similarly, the 'B' fraction was passed through a column; however in this case both spiked Pu and U aliquots were eluted ('Ba' and 'Bb' respectively).

3. RESULTS AND DISCUSSION

The uranium and plutonium concentrations and isotopic compositions were measured by MCICPMS and 3STIMS respectively.

3.1 Uranium Results

The actual and measured U concentrations and isotopic compositions measured by MCICPMS are reported in Table 1. Note: the swipes are treated as part of the sample, thus the U content inherent in the swipes are included (~ 5 ng of uranium with an isotopic composition assumed to be natural) in the total U determination. Very good agreement between the loaded (actual) quantities and the measured values was observed. For total U, quantitative recovery was observed within 2-sigma uncertainty.

Table 1. Summary of MCICPMS results for uranium with 2-sigma uncertainty.

Sample	Total U actual (ng)	Total U measured (ng)
1	32.13 ± 0.98	32.80 ± 1.90
2	32.95 ± 0.98	33.00 ± 1.90
	^{234}U/^{238}U actual	**^{234}U/^{238}U measured**
1	0.00793 ± 0.00043	0.00788 ± 0.00008
2	0.00799 ± 0.00043	0.00790 ± 0.00003
	^{235}U/^{238}U actual	**^{235}U/^{238}U measured**
1	0.73475 ± 0.04006	0.75533 ± 0.00180
2	0.74062 ± 0.03950	0.75698 ± 0.00089
	^{236}U/^{238}U actual	**^{236}U/^{238}U measured**
1	0.00114 ± 0.00006	0.00115 ± 0.00002
2	0.00115 ± 0.00006	0.00115 ± 0.00001

The actual and measured isotopic ratios for ^{234}U/^{238}U, ^{235}U/^{238}U, and ^{236}U/^{238}U were generally consistent. As mentioned previously, the high purity cotton swipes used in this study contain a variable amount of total U from swipe to swipe. Batches vary from 2 – 5 ng U (Cable-Dunlap *et al.*, 2013). This variability leads to the high uncertainty observed in the actual values reported in Table 1; and this is perhaps most evident in the actual ^{235}U/^{238}U ratio. This uncertainty could be reduced with a more rigorous blank swipe quantitative analysis, but that is beyond the scope of this investigation.

3.2 Plutonium Results

The simulated samples were processed and analyzed for plutonium via 3STIMS. A comparison of the actual and measured values is reported in Table 2. Very good agreement between the expected and measured results is observed. The Pu recovery in all samples is quantifiable within 2 – sigma uncertainty.

Table 2. Summary of 3STIMS results for plutonium with 2-sigma uncertainty.

Sample	Total Pu pg (^{239}Pu + ^{240}Pu) actual	Total Pu pg (^{239}Pu + ^{240}Pu) measured
1 Aa	6.07 ± 0.24	5.55 ± 0.57
2 Aa	6.07 ± 0.24	5.47 ± 0.57
1 Ba	4.04 ± 0.16	3.87 ± 0.40
2 Ba	4.04 ± 0.16	3.67 ± 0.38

The isotopic mass results (in femtograms) for ^{240}Pu and very minor ^{239}Pu are reported in Table 3. Very good agreement is observed between the duplicate 'A' and 'B' samples. No measurable ^{239}Pu, ^{240}Pu, or ^{241}Pu was observed in neither the reagent blank nor the swipe blank. The results from the simulated samples are in line with expected values based upon the ^{240}Pu loading (high purity ~ 99.99 % ^{240}Pu). There may be a slight ^{239}Pu contribution from the swipes themselves, i.e., ~ 1 fg, but it is too low to be quantified. No quantifiable ^{241}Pu was detected in any of the samples.

Table 3. Summary of mass spectrometry results (3STIMS) for plutonium with 2-sigma uncertainty.

1Aa	Mass Isotope (fg)	±2 sigma
Pu-239	1.31738	0.21018
Pu-240	5549.78875	574.32458
2Aa		
Pu-239	1.11283	0.18557
Pu-240	5467.32487	565.76929
1Ba		
Pu-239	2.08122	0.27814
Pu-240	3872.77392	400.76307
2Ba		
Pu-239	2.28241	0.34988
Pu-240	3671.32149	380.01739

3.3. Comparison with other single column techniques

With our single column anion exchange approach, sodium nitrite is added to the sample (with gentle heating) to adjust the Pu valence prior to loading the column. The ion exchange column is initially conditioned with 8 M HNO_3 and the sample is loaded. Several column volumes of 9 M HCl are then passed through the column and the U and Pu are retained to the chloride anion exchange resin while any thorium present in the sample washes out. Plutonium is initially eluted from the column via valence reduction with 9 M HBr. Uranium is subsequently eluted from the column using dilute (0.12 M) HCl.

As shown in Tables 2 and 3, our single column ion exchange approach is effective for purifying and separating femtogram to picogram quantities of Pu as quantitative recoveries are observed. Previous efforts involving single column U and Pu separation employ extraction chromatography e.g., using a UTEVA resin (Lee et al., 2011; Morgenstern *et al*., 2002) rather than employing only an anion exchange resin. The Morgenstern *et al*. study reported good Pu and U recoveries (93 % and 91 % respectively) with larger quantities of material (0.18 µg ^{238}Pu and 1.3 mg ^{235}U). The Lee *et al*. study reported good recoveries for Pu and U (94 % and 95 % respectively) and employed Pu and U quantities (40 pg ^{242}Pu and 5 ng ^{235}U) more similar to those used in this study.

4. CONCLUSIONS

In this work, a detailed description of a rapid and cost effective radiochemical separation technique for the separation and purification of U and Pu was detailed. This approach is ideally suited for dilute-matrix samples, e.g., environmental swipe samples that contain a small amount of collected bulk material. This single-column method, resulting in quantitative U and Pu recoveries, is highly effective for separation and purification of nanogram quantities of U and femtogram to picogram quantities of Pu in dilute-matrix samples.

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Appendix A

Procedure for separation and purification of U and Pu isotopes from dilute-matrix (carrier-free) samples

1.0 PURPOSE

The purpose of this work instruction is to detail a methodology for the separation and purification of uranium and plutonium from dilute-matrix samples (swipes).

2.0 SCOPE AND APPLICATION

This work instruction describes the separation and purification of uranium and plutonium from bulk solid samples, specifically swipe samples. Because these swipe samples are loaded (i.e., spiked) with actinide containing material for a round robin style analysis, the sample matrices are low in dissolved ions (i.e., dilute-matrix or carrier-free samples); thus this work instruction is narrowly tailored to suit these types of matrices, and therefore does not apply to typical environmental samples (rocks, soils, vegetation, etc).

This work instruction will concentrate and purify U and Pu for analysis of their isotopic composition by multi collector inductively coupled plasma mass spectrometry (MCICPMS) and thermal ionization mass spectrometry (TIMS) respectively.

3.0 APPARATUS AND MATERIALS

3.1 Acid leached pyrex beakers
3.2 Muffle furnace capable of attaining 600 ^{o}C
3.3 Acid leached conical Teflon vials with screw tops
3.4 Ion exchange columns (acid leached) with 2 mL bed capacity (e.g., BioRad, Poly-Prep)
3.5 Column racks and/or stands
3.6 Hot plate
3.7 Spatulas
3.8 Automated pipets and pipet tips
3.9 Fume hood
3.10 Sharpie Marker
3.11 UniPAINT pen

4.0 STANDARDS AND REAGENTS

4.1 Use high purity reagents when available
4.2 High purity water is used: Type I (resistivity: 18 MΩ-cm)
4.3 Hydrochloric Acid (HCl): 9 M HCl, 0.12 M HCl
4.4 Nitric Acid (HNO_3): 8 M HNO_3, 0.5 M HNO_3

4.5 Hydrobromic acid (HBr): 9 M HBr
4.6 Ion exchange resin: AG1X4, 100-200 mesh, chloride form
4.7 Calibrated uranium (U-233) tracer solution
4.8 Calibrated plutonium (Pu-242) tracer solution
4.9 Sodium Nitrite ($NaNO_2$), solid

5.0 PROCEDURE

5.1 SAMPLE PREPARATION – ASHING AND LEACHING

5.1.1 Assign laboratory IDs to the client sample IDs and record in the logbook. Label a leached 100 mL pyrex beaker with both a sharpie marker and a "uniPAINT" pen. Record the weight of each 100 mL pyrex beaker.

5.1.2 Transfer the sample into the beaker using separate gloves for each sample. Remove each sample from its respective bag by folding the swipe. If the treated surface is visible, fold that surface inward. Fold the swipe again and place it into the 100 mL leached beaker. Change gloves. Record the weight of each 100 mL beaker with sample. Cover the beaker with a small piece of aluminum foil and, with a leached spatula, pierce a small hole in the top middle of the foil.

5.1.3 Place the beaker with sample in the muffle furnace. Note the location of each beaker in the furnace in the logbook. Dry ash using the following furnace program:

1. Ramp to 150 ^{o}C, soak for 2 hours.
2. Ramp to 250 ^{o}C, soak for 2 hours.
3. Ramp to 350 ^{o}C, soak for 3 hours.
4. Ramp to 425 ^{o}C and soak overnight (or 8 hours minimum).
5. Ramp furnace down to 105 ^{o}C.
6. Remove samples from the furnace. Allow samples to cool. Remove aluminum foil from the beakers. Place beakers into the furnace in their initial positions.
7. Ramp to 550 ^{o}C for 4 hours.
8. Ramp furnace down to 30 ^{o}C.

5.1.4 Remove samples from the furnace and allow beakers to cool to room temperature. Record the weight of the 100 mL beakers containing the ashed samples.

5.1.5 Add 5 mL of 8 M HNO_3 to each beaker and rinse the inner walls of the beakers. Gently heat samples (do not reach a boil) on a hotplate in the fume hood and evaporate solutions to incipient dryness.

5.1.6 While gently rinsing the inner walls of the beakers, add 10 mL of 8 M HNO_3 to each beaker.

5.1.7 Gently heat the samples for 1 or more hours. Allow samples to cool. Record the weight of the beaker and solution.

5.1.8 Label acid leached, conical Teflon vials with the sample IDs.

5.1.9 Pipet ~ 1 % of volume (~ 0.1 mL) from each beaker into the corresponding Teflon vials. Record the weight of the beaker and solution (minus the pipetted volume).

5.1.10 Pipet 425 µL of Q water into each Teflon vial (to obtain a final volume of ~ 0.5 mL). Cap the Teflon vials and gently mix the solutions.

5.1.11 Submit the samples in the Teflon vials for MCICPMS analysis for a preliminary screening of uranium and plutonium concentrations.

5.2 U/PU SPIKE ADDITION

At this point, the samples need to be divided into separate fractions, 'A', and 'B'. 'A' fractions: spiked with appropriate Pu-242; and 'B' fractions spiked with appropriate Pu-242, and U-233.

5.2.1 For each individual sample, label separate leached 100 mL pyrex beakers A, and B, with the corresponding IDs. Record the weight of the empty beakers.

5.2.2 Pipet approximately half of the sample and solution from beakers in Step 6.1.9 into each 'A' and 'B' beaker. Record the weights.

5.2.3 Tare the beakers and spike all 'A' samples with appropriate U-232 standards, and 'B' samples with appropriate U-232 and Pu-242 standards. Record the weight of each spike addition.

5.2.4 Evaporate all samples to incipient dryness.

5.2.5 Dissolve the spiked samples with 10 mL of 8 M HNO_3.

5.2.6 Gently warm spiked samples on a hotplate and allow to cool.

5.3 COLUMN SEPARATION OF U AND PU

5.3.1 Add about 10 mg of NaNO2 to each beaker. Gently warm on the hotplate for about 5 minutes to dissolve any residue (do not evaporate solution). Allow the beakers to cool to room temperature.

5.3.2 Prepare ten 2.0 mL anion exchange (AG1X4) resin columns and allow columns to drain completely into collection beakers.

5.3.3 Add 2 mL of 9 M HCl to the top of each column and allow the columns to drain completely into the collection beaker.

5.3.4 Add 2 mL of 0.12 M HCl to the top of the columns and allow the columns to drain completely.

5.3.5 Repeat previous step, two more times.

5.3.6 Add 2 mL of 8 M HNO_3 to the top of the columns and allow the columns to drain completely into the collection beakers.

5.3.7 Repeat previous step, two more times.

5.3.8 Sample loading: Add the samples from the beakers in step 5.3.1 to the tops of the corresponding columns. Allow the columns to drain completely.

5.3.9 Rinse the sample beakers with another 3 mL of 8 M HNO_3 and add it to the columns. Allow the columns to drain completely.

5.3.10 Add 2 mL of 8 M HNO_3 to the tops of the columns and allow the columns to drain completely into the collection beakers.

5.3.11 Add 2 mL of 9 M HCl to the tops of the columns and allow the columns to drain completely.

5.3.12 Add 6 mL of 9 M HCl to the tops of the columns and allow the columns to drain completely.

5.3.13 Cover the "waste" beakers with parafilm and set aside for storage.

5.3.14 Label ten clean, leached 50 mL pyrex beakers (for Pu separation).
5.3.15 Place the labeled 50 mL pyrex beakers beneath the corresponding columns.
5.3.16 Elute the columns (Pu): Add 2 mL of cleaned 9 M HBr to the top of each column and allow it to drain completely through the column.
5.3.17 Add 5 mL of cleaned 9 M HBr to the top of each column and allow it to drain completely.
5.3.18 Repeat previous step two more times.
5.3.19 Cover the Pu beakers with parafilm and set aside for short term storage.
5.3.20 Label ten clean, leached 50 mL pyrex beakers (for U separation).
5.3.21 Place the labeled 50 mL pyrex beakers beneath the corresponding columns.
5.3.22 Elute the columns (U): Add 2 mL of 0.12 M HCl to the top of each column and allow the column to drain completely.
5.3.23 Repeat previous step, three more times.
5.3.24 Cover the U beakers with parafilm and set aside for short term storage.

6.4 PREPARATION FOR MASS SPECTROMETRY

6.4.0 U fraction:

6.4.1 Evaporate the U samples to incipient dryness on a hotplate.
6.4.2 Add 5 mL of 0.5 M HNO_3 to U samples and evaporate to incipient dryness.
6.4.3 Repeat previous step.
6.4.4 Label acid leached, conical Teflon vials with the sample ID.
6.4.5 To the dry U beakers, pipet 1 mL of 0.5 M HNO_3.
6.4.6 Gently warm the beakers on a hotplate (to facilitate dissolution of residue). Gently swirl the solutions, and then transfer the solutions to the conical Teflon vials with a transfer pipet.
6.4.7 To the U beakers, pipet 1 mL of 0.5 M HNO_3, gently swirl the solutions, and then transfer the solutions to the conical Teflon vials with a transfer pipet.
6.4.9 Repeat previous step (3 mL total solution in the conical Teflon vials).

6.4.10 Pu fraction:

6.4.11 Evaporate the Pu samples to incipient dryness on a hotplate.
6.4.12 Add 5 mL of 8 M HNO_3 to the Pu samples and evaporate to incipient dryness.
6.4.13 Repeat previous step.
6.4.14 Label acid leached, conical Teflon vials with the sample ID.
6.4.15 To the dry Pu beakers, pipet 1 mL of 8 M HNO_3.
6.4.16 Gently warm the beakers on a hotplate (to facilitate dissolution of residue). Gently swirl the solutions, and then transfer the solutions to the conical Teflon vials with a transfer pipet.
6.4.17 To the Pu beakers, pipet 1 mL of 8 M HNO_3, gently swirl the solutions, and then transfer the solutions to the conical Teflon vials with a transfer pipet.
6.4.18 Repeat previous step (3 mL total solution in the conical Teflon vials).

Appendix B

Concentrated HBr treatment to remove Br_2 (g)

1. Prepare a 3 mL anion resin column in a disposable column by adding 3 mL of Biorad AG 1-X4 resin slurry and allowing the column to drain completely into a collection beaker.

2. Add 3 mL of 9 M HCl to the top of the column and allow the column to drain completely into the collection beaker.

3. Repeat step 2, two more times.

4. Add 3 mL of 0.12 M HCl to the top of the column and allow the column to drain completely.

5. Repeat step 4, two more times.

6. Add 3 mL of 9 M HCl to the top of the column and allow the column to drain completely into the collection beaker.

7. Repeat step 6, two more times.

8. Add 3 mL of concentrated HBr to the top of the column and allow it to drain completely.

9. Repeat step 8, two more times.

10. Remove the collection beaker and put it on the hotplate to evaporate to dryness.

11. Carefully rinse a 125 mL Teflon bottle with 10 mL of 9 M HCl and discard the acid.

12. Place the bottle under the column and carefully add concentrated HBr to the column to drain through until the bottle is full. Cap and mark as pretreated HBr. Store pretreated HBr in the dark.