Rapid Fusion Method for the Determination of Pu, Np, and Am in Large Soil Samples

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Abstract

A new rapid sodium hydroxide fusion method for the preparation of 10- 20 g soil samples has been developed by the Savannah River National Laboratory (SRNL). The method enables lower detection limits for plutonium, neptunium, and americium in environmental soil samples. The method also significantly reduces sample processing time and acid fume generation compared to traditional soil digestion techniques using hydrofluoric acid. Ten gram soil aliquots can be ashed and fused using the new method in 1-2 hours, completely dissolving samples, including refractory particles. Pu, Np and Am are separated using stacked 2 mL cartridges of TEVA and DGA Resin and measured using alpha spectrometry. The method can be adapted for measurement by inductively-coupled plasma mass spectrometry (ICP-MS). Two 10 g soil aliquots of fused soil may be combined prior to chromatographic separations to further improve detection limits. Total sample preparation time, including chromatographic separations and alpha spectrometry source preparation, is less than 8 hours.

Introduction

There are a number of analytical methods reported that use ion exchange/extraction chromatography plus alpha spectrometry to determine actinides in environmental samples. Ageyev et al. [1] reported a method for environmental samples including soil samples. After ashing the samples at 550˚C, the samples were leached with 8M nitric acid, followed by a series of precipitation steps. Plutonium was separated using Dowex 1 anion resin loaded under reduced atmosphere. Am and Cm were precipitated as $LaOH_2$, redissolved in dilute hydrochloric acid, separated on Dowex 50 cation resin loaded under reduced pressure. A gradient elution separation of Am and Cm with rare earths was performed using α-hydroxy-isobutyric acid. Actinides were electrodeposited for alpha counting. Chemical yields were r as follows: Pu 60-70%, Am and Cm 50-65%, and Sr 50-70%. The method seems relatively complex, would not digest refractory particles and would not be considered a rapid method.

Hrnecek et al [2] also reported a method for determination of plutonium in soil by alpha spectrometry and accelerator mass spectrometry. This method also used an acid leaching approach with 8M nitric acid, which would also not fully digest refractory particles. A more traditional ion exchange method was applied.

Tavčar et al. [3] reported a method to determine actinides in soil. Soil and sediment samples up to 10g were leached using strong nitric acid, filtration, evaporation, and the residue was redissolved in 1M HNO_3. Following valence adjustment, the acid concentration was increased to 8M HNO_3 and the samples were loaded onto Dowex 1x8 resin. Pu was eluted using 9M HCl with iodide ion present and Np was eluted with 4M HCl. The chemical yields were ~60% and the Np yields were ~40%. Again, the acid leach used in this method would not effectively digest refractory particles that may be present in the sample.

Soil methods were reported from this laboratory that utilized rapid fusion for 1-2 g soil samples [4, 5] Larger sample aliquots are often needed, however, to achieve lower detection limits for the measurement of Pu, Np and Am isotopes in soil. Acid leach methods have been reported for soil samples up to 200 g from this laboratory; however, refractory particles present will be resistant to acid digestion. [6,7]

Rugged soil dissolution methods are essential to ensure accurate measurement of analytes and chemical equilibrium of yield tracers. The need for rugged sample digestion for actinides is well known. Sill et al have emphasized the need for total sample dissolution and the potential for refractory particles in soil samples. [8] The recent failure by ~80% of participating labs in the U.S Department of Energy Mixed Analyte Performance Evaluation Program (MAPEP) Session 30 points to the need for robust sample digestion of soil samples. The failure of so many labs was traced to incomplete dissolution of insoluble uranium in the MAPEP samples, even using hydrofluoric acid in the acid digestion methods used. The failure of ~40 labs to pass MAPEP 30 testing for uranium isotopes in soil brought the need for total dissolution of soil samples into very clear focus for many radiochemical laboratories.

Applying total dissolution techniques to larger soil aliquots is very challenging. Initial tests using hydrofluoric acid in this laboratory showed that residual undigested soil appeared to act as an ion exchanger and retain Pu isotopes, despite multiple ashing steps with boric acid to remove fluoride. This resulted in lower chemical yields than was desired. The process, which involved multiple soil residue rinsing and evaporation steps, was also very time-consuming. While more effective than nitric acid leaching, hydrofluoric acid still may not totally digest highly insoluble particles, such as in soil containing zircons, as with MAPEP 30 soil samples, or if high-fired Pu oxides are present.

To address these limitations of classical soil digestion techniques, the authors applied rapid sodium hydroxide fusion [4, 5] to 10g aliquots and utilized separation techniques developed for the measurement of actinides in seawater samples [9]. The sample preparation time using this method is less than 8 hours. Ten gram aliquots of soil were prepared using a rapid sodium hydroxide fusion, followed by precipitation steps for matrix removal and chromatographic separation of actinides with TEVA and DGA resin. It was decided to attempt to fuse the 10g soil sample aliquots directly, and utilize some of the lessons learned from processing large seawater samples, which contain large amounts of calcium and other metal ions. For Pu and Np only, only a TEVA Resin cartridge is needed.

Rapid flow rates during chromatographic separations (enabled by vacuum boxes), and stacked resin cartridges using highly selective extractant-coated resins significantly reduce separation times relative to classic gravity flow ion exchange chromatography. Alpha sources are prepared using cerium fluoride microprecipitation for counting by alpha spectrometry. Other measurement techniques, such as inductively-coupled plasma-mass spectrometry (ICP-MS) can also be employed, with slight adaptations to column eluents and enhanced uranium removal. This new method showed high chemical recoveries and effective removal of interferences.

The sodium hydroxide fusion can be performed quickly and simultaneously in a furnace or furnaces at only 600°C in relatively inexpensive zirconium crucibles, unlike other fusion techniques, that are performed one at a time over a burner in platinum crucibles. Additionally, the sodium hydroxide fusion cake is readily dissolved in water with minimal heating, while other fusion cakes, such as lithium metaborate, can be difficult to dissolve. This method can also be applied to other solid samples such as concrete or asphalt samples. [5]

Experimental

Reagents

The extraction chromatography resins employed in this work are TEVA Resin® (Aliquat ™ 336) and DGA Resin ® (N,N,N',N' tetraoctyldiglycolamide), available from Eichrom Technologies, Inc., (Lisle, Illinois, USA) and Triskem International (Bruz, France). Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc., Pittsburgh, PA, USA). All water was obtained from a Milli-Q2™ water purification system. All other materials were ACS reagent grade and were used as received. Radiochemical isotopes ^{242}Pu, ^{243}Am, and ^{237}Np were obtained from Eckert Ziegler/Analytics, Inc. (Atlanta, GA, USA) and diluted to the appropriate levels. ^{236}Pu was obtained from the National Physical Laboratory (Teddington, UK).

Procedures

Column preparation. TEVA and DGA Resin columns were obtained as cartridges containing 2 mL of each resin from Eichrom Technologies, Inc.. Small particle size (50-100 µm) resin was employed, along with a vacuum extraction system (Eichrom Technologies). The small particle size coated support, with enhanced surface area, improves actinide separation efficiencies. Flow rates of ~1-2 mL min^{-1} were typically used for this work, slower on sample loading and final elution steps, faster for the rinses used to remove sample matrix interferences. Column reservoirs and connector tips in the lid can be changed for enhanced removal of interferences.

Sample Preparation. Soil samples collected from in and around the Savannah River Site were collected, dried, crushed to a fine powder, and sieved to homogenize the sample as well as possible. Ten gram soil aliquots were placed into 250 mL low form Zr crucibles. A small amount of MAPEP 24 soil reference material was also added to the soil samples to test for ruggedness regarding refractory isotopes. The MAPEP samples were provided by Department of Energy (DOE) – Radiological and Environmental Sciences Laboratory (RESL), Idaho, USA. To spike the samples with plutonium and americium, MAPEP 24 soil standard (350 mg) was added to the spiked replicate sample aliquots. MAPEP 24 soil standard was chosen because the ^{239}Pu present in this soil is refractory. Successful analysis would indicate analytical method ruggedness and applicability when refractory particles are present. For soil aliquots that were also spiked with neptunium, 37 mBq of ^{237}Np was added to each soil aliquot.

Figure 1 shows the rapid furnace heating, fusion and precipitation steps used to remove organics, digest the samples and preconcentrate the actinides from the alkaline fusion matrix. Tracers were added to each crucible and the crucibles were dried briefly on a hotplate. After removing crucibles from the hotplate, the samples were heated to 600˚C for ~2 hours to remove organics present in the soil aliquot. After the furnace heating step, 40 grams of NaOH were added to each crucible. The crucibles were covered with a zirconium lid and placed into a furnace at 600˚C for ~ 20 minutes.

After removing the crucibles from the furnace, they were cooled for about 10 minutes and transferred to a hot plate. Water was added to dissolve the fusion cake and transfer the sample to 500 mL centrifuge tubes. Any residual solid was dissolved from the crucibles by adding water and heating the crucibles on the hot plate as needed. A final rinse of 5 mL 6M HNO_3 heated until very hot on the hot plate was used to ensure complete removal of actinides from the crucible.

The crucible rinses were transferred to the 500 mL centrifuge tube with the sample and 125 mg Fe (added as $Fe(NO_3)_3$) and 10 mg La (as lanthanum nitrate standard) were added to each 500 mL centrifuge tube. If Am measurement is not needed (only Pu or Pu and Np), 12 mg La were added instead of 10 mg La, since La has no impact on TEVA Resin retention. While La has much less retention on DGA Resin than An, large amounts of La could have a slight negative impact on Am retention. The samples were diluted to 450 mL with water and cooled in an ice bath to room temperature.

Two milliliters of 1.25M $Ca(NO_3)_2$ were added to each tube, and tubes were capped and mixed well. The additional calcium has been shown to enhance chemical recoveries for soils with low calcium content. This step would likely not be needed for very high Ca soil and would not be used for concrete samples (which may have ~1g Ca per 10 g sample). Five milliliters of 20% $TiCl_3$ reductant were added to each tube to ensure tracer-analyte valence equilibration and samples were mixed well. The samples were cooled in an ice bath to room temperature. The tubes were centrifuged at 3500 rpm for ~10 minutes, and the supernate was discarded. The iron hydroxide precipitate was rinsed with 150 mL of water (pH of 8.8-8.9). The use of a water rinse (pH 8.8-8.9) facilitates removal of calcium, which can be very high in a 10g aliquot of soil. [9] For soils with very high Ca, or for concrete samples, for example, several water rinses may be warranted.

After centrifuging and pouring off the water rinse, 200 mL 1.5 M HCl was added to each tube to partially dissolve the precipitate. The sample was diluted with 50 mL 0.01M HCl was added to each tube. An additional 2 mg La and 100 mg Ca were added to each sample. To ensure no actinides were in the hexavalent state and facilitate complete precipitation, 3 milliliters of 20% titanium chloride were added to each sample. Forty milliliters of 28M HF were added to each sample. The samples were mixed well, cooled briefly to room temperature and allowed to stand for ~10 minutes and centrifuged for 6 minutes at 3500 rpm. Alhough not tested in this work, it is likely that an equivalent amount of fluoride added as sodium fluoride instead of hydrofluoric acid could be used for laboratories with restrictions on the use of hydrofluoric acid. The CaF_2/LaF_3 precipitation step effectively removes iron from the initial precipitation and any silicates that may have coprecipitated. The effective silicate removal eliminates the need for silicate removal by flocculation with polyethylene glycol.

A small amount of calcium (~100-200 mg) in the CaF_2/LaF_3 step helps to improve the recovery of actinides. The amount of Ca added in the HF precipitation step (100 mg) can be adjusted by waiting to add any additional Ca until the precipitation is performed, and evaluating the volume of CaF_2/LaF_3 present. If the precipitate is very small (<2mL), additional Ca can be added as needed to achieve a precipitate volume of 2-8 mL. If very large CaF_2/LaF_3 precipitates are observed (>8mL), decanting the supernate and washing with 100mL of water is recommended to reduce calcium levels prior to chromatographic separation of the actinides. No additional Ca was added when aliquots of concrete were tested.

The supernate was decanted and the precipitate containing the actinides was dissolved in 10 mL of 3M HNO_3-0.25M H_3BO_3, mixed, and transferred to 50 mL tubes. The 500 mL tubes were rinsed sequentially with 8 mL of 7M HNO_3 and 8 mL of 2 M $Al(NO_3)_3$, The rinses were transferred to the same 50 mL centrifuge tubes as the sample. The samples were vortex mixed and heated 3-5 minutes in a hot block heater at 105°C to ensure complete dissolution. The 50 mL tubes were centrifuged to test for any solid particulates, which were removed if needed.

After cooling the samples to room temperature, a valence adjustment was performed on the load solution by adding 1mg Fe (ferric nitrate standard) and 1.25 mL 1.5M ascorbic acid. Following a three minute wait to ensure reduction of plutonium to Pu(III) and neptunium to Np(IV), 1 mL 3.5M $NaNO_2$ was added to oxidize plutonium to Pu(IV). The nitrate concentration in the sample load solution was increased to reduce Ca retention on DGA Resin [11] by adding 1.5mL of concentrated nitric acid. In previous work, sulfamic acid has been added to scavenge nitrite during the reduction step. However, sulfate produced by the reaction of sulfamic acid and nitrite can cause some precipitation issues if there are borderline solubility problems, sulfamic acid was not used in this method. The ascorbic acid/ Fe^{+2} combination alone offers effective plutonium valence reduction of Pu and Np isotopes.

Actinide separation. Figure 2 shows the chromatographic separation method. TEVA and DGA Resin cartridges were stacked and placed on the vacuum box (TEVA Resin on top) and 50 mL centrifuge tubes were used to collect rinse or final purified fractions. If americium is not measured, the DGA may be omitted. The valence adjusted sample solution was loaded onto the TEVA + DGA Resin stacked cartridges at ~1 drop per second. Plutonium and neptunium are retained on TEVA, and americium (and Cm) are retained on DGA. [11,12] After the sample was loaded, a tube rinse of ~ 5 ml 3M HNO_3 + 50 μL 30wt% H_2O_2 was transferred to the TEVA Resin + DGA Resin column and allowed to pass through the resin at ~1-2 drops per second. Hydrogen peroxide ensures than any U reduced to U(IV) (due to traces of Ti^{+3}

remaining from the precipitation steps) is reoxidized to U(VI) and is not retained on TEVA Resin. A rinse of 10 mL 3M HNO_3 was added to each stacked column at ~2 drops per second. The TEVA Resin and DGA Resin cartridges were separated and processed individually on two different vacuum boxes at the same time.

Fifteen milliliters of 3M HNO_3 was added to each TEVA Resin column at ~2 drops per second, followed by Th removal with 20 ml 9M HCl rinse at 1-2 drops per second. It should be noted that additional Th removal can be achieved by increasing the 9M HCl rinse on TEVA Resin as needed. Plutonium and neptunium are recovered from TEVA with 20 mL of 0.1M HCl-0.05M HF-0.01M $TiCl_3$.

The DGA Resin is rinsed with 10 mL of 3M HCl at ~2 drops per second to ensure complete Ca removal. Lanthanum and uranium are removed with rinses of 3mL 1M HNO_3 and 15 mL 0.1M HNO_3 at ~1-2 drops per second. Removal of any thorium that may have bled through TEVA, is achieved with 25 mL of 3M HNO_3-0.25M HF. Five milliliters of 4M HCl removes any residual fluoride ions, and Am isotopes are eluted with 12 mL 0.25M HCl at ~ 1 drop per second.

The Am eluent solutions were transferred to 100 mL glass beakers using ~3 mL of concentrated nitric acid with 0.05mL of 1.8M sulfuric acid. The Am eluent solutions were evaporated to dryness on a hotplate and ashed with 2 mL concentrated nitric acid and 2 mL 30 wt% hydrogen peroxide to destroy any residual extractant that may have bled off the resin. The samples were redissolved in 5 mL of 4M ammonium thiocyanate-0.1M formic acid, warming gently as needed. These solutions were loaded onto a TEVA cartridge to remove any native rare earths present in the soil sample which can degrade alpha spectrometry peak resolution. The TEVA cartridges were rinsed with 10-12 mL of 1.5M ammonium thiocyanate-0.1M formic acid. The original load solution beaker was rinsed with 5 mL of warm 1M HCl to ensure all the americium was removed from this beaker. The beaker rinse solution, followed by an additional 15 mL of 1M HCl also used to rinse the beaker, was passed through the TEVA Resin to recover the americium.

Cerium fluoride microprecipitation was used to prepare the purified samples for alpha spectrometry counting. Fifty micrograms of Ce (as Ce(III) nitrate standard), 0.5 mL 30wt% H_2O_2 and 1 mL 28 M HF were added to each Pu-Np and Am fraction. The hydrogen peroxide ensures additional removal of any uranium ions present, by oxidizing U(IV) to U(VI). After waiting 15 minutes, the solution was filtered using a 25 mm polypropylene filter (0.1 µm pore size disposable Resolve™ filter funnel). Each sample tube was rinsed with ~5 mL deionized water, adding the rinse to the filter. After the entire sample was filtered, 3mL of ethanol was added to each filter to facilitate drying. The filters were heated briefly under a heat lamp to ensure dryness. Samples were counted for 24 hours to ensure sufficient counts were obtained and reduce counting uncertainty to effectively evaluate performance on the spiked samples. Blank soil aliquots were analyzed to determine actinide content in the unspiked soil and corrections were applied if the levels were found to be significant versus the spike levels added.

While alpha spectrometry is used in this work to demonstrate the effectiveness of the new method, this method can be adapted for ICP-MS. The sample can be counted for ^{238}Pu by alpha spectrometry and then redissolved from the sample test source filter using warm 3M HNO_3-0.25M boric acid. The dissolved Pu isotopes processed quickly through TEVA Resin, eluted and measured by ICP-MS to determine the ^{239}Pu / ^{240}Pu ratio . The CeF_3 microprecipitation step with hydrogen peroxide present can remove an additional 1000 x ^{238}U, so this approach, in combination with another TEVA Resin separation, can result in extremely high ^{238}U decontamination factors. If the redissolved sample is reprocessed through TEVA Resin, a Pu eluent solution of 0.05M HCl-0.025M HF-0.02M hydroxlyamine hydrochloride may be used to allow ICP-MS assay.

For enhanced ^{238}U removal to facilitate the measurement of ^{239}Pu and ^{240}Pu by ICP-MS, Pu can be eluted directly from TEVA Resin as Pu^{+3} (with 3M HNO3-0.1M ascorbic acid-0.02M Fe^{+2}) through a coupled UTEVA Resin cartridge (1mL) onto a stacked DGA Resin cartridge to achieve very high uranium decontamination factors (~$1x10^7$). This eliminates eluting and reloading Pu to TEVA Resin multiple times. After a single elution and rapid clean-up on DGA Resin, Pu isotopes can be eluted from DGA Resin with a 5mL volume of 0.02M HCl-0.005M HF (or also with -0.01M hydroxylamine hydrochloride) and assayed by ICP-MS. [10]

The DGA Resin separation for Am is described below. Ten milliliters of 3M HCl were added to each DGA Resin cartridge at ~2 drops per second to ensure complete Ca removal. Three milliliters of 1M HNO_3 were added to each column to remove chloride ions. To remove much of the La present, 15 mL 0.1M HNO_3 was added to each DGA resin cartridge at ~1-2 drops per second. To remove any thorium present, 25 mL 3M HNO_3-0.25M HF was added at ~1-2 drops per second. Next, 5 mL 4M HCl was added to remove any residual fluoride ions. Am isotopes were eluted with 12 mL 0.25M HCl at ~ 1 drop per second.

These Am eluent solutions were transferred to 100 mL glass beakers using ~3 mL of concentrated nitric acid and 0.05mL of 1.8M sulfuric acid was added to enhance destruction of any extractant in this solution. The Am eluent solutions were evaporated to dryness on a hotplate. These fractions were ashed once using 2 mL concentrated nitric acid and 2 mL 30 wt% hydrogen peroxide to remove any residual extractant that may have bled off the resin. The samples were redissolved in 5 mL of 4M ammonium thiocyanate-0.1M formic acid, warming gently as needed. These solutions were loaded onto a TEVA cartridge to remove rare earths present, which interfere with alpha spectrometry peak resolution. The TEVA cartridges were rinsed with 10-12 mL of 1.5M ammonium thiocyanate-0.1M formic acid to remove rare earths, and the americium was eluted using 20 mL of 1M HCl. The original load solution beaker was rinsed with 5 mL of warm 1M HCl to ensure all the americium was removed from this beaker. This solution, followed by 15 mL of 1M HCl also used to rinse the beaker, was passed through the TEVA Resin to remove the americium. Fifty micrograms of cerium as cerium nitrate was added, along with 2 mL of concentrated hydrofluoric acid (49%). After waiting 15 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene (0.1 µm pore size disposable Resolve™ filter funnel) and counted by alpha spectrometry. Samples were counted for 24 hours because only 0.35g of MAPEP soil standard was added to ensure sufficient counts were obtained and reduce counting uncertainty to effectively evaluate performance on the spiked samples. Blank soil aliquots were analyzed to determine actinide content in the unspiked soil and corrections were applied if the levels were found to be significant versus the spike levels added.

Apparatus

Plutonium, americium, and neptunium isotopic measurements were performed by alpha-particle pulse-height measurements using Passivated Implanted Planar Silicon (PIPS) detectors. The PIPS detectors have an active surface of 450 mm^2. The nominal counting efficiency for these detectors is 0.30. The distance between the sample and detector surface is ~3mm.

Polycarbonate vacuum boxes with 24 positions and a rack to hold 50 mL plastic tubes were used. Two boxes were connected to a single vacuum source by using a T-connector and individual valves on the tubing to each box.

Results and Discussion

Table 1 shows the individual results for the determination of ^{239}Pu [actually $^{239+240}$Pu] in ten 10 g soil samples spiked with MAPEP 24 soil using this rapid separation method and alpha spectrometry. The results were corrected for ^{242}Pu tracer yield. The average ^{239}Pu result was 3.41 mBq g^{-1} sample, with a -0.7% bias and SD (standard deviation) of 0.19 mBq g^{-1}. The average tracer recovery for ^{242}Pu was 84.5% ± 9.1% (SD). The high ^{242}Pu tracer recoveries and excellent results for the analyte versus known values indicate the ruggedness of the sample preparation and measurement steps even for refractory Pu. Samples 1-6 and 7-10 were aliquots from two different soil samples. A small correction for samples 1-6 was applied for the $^{239/240}$Pu content found in the blank soil, while no correction was needed for samples 7-10.

Table 2 shows the results for the determination of ^{237}Np in spiked soil samples using alpha spectrometry. The average ^{237}Np result was 4.19 mBq g^{-1}, with a 5.0% bias and SD of 0.16 mBq g^{-1}. The average tracer recovery for ^{236}Pu was 82.3% ± 3.9% (SD). The ^{236}Pu tracer corrections were applied to the ^{237}Np sample results. This illustrates that under these conditions that ^{236}Pu works very well as a yield monitor for ^{237}Np. The effective removal of interferences facilitates the use of ^{236}Pu tracer to determine chemical yield for ^{237}Np.

Table 3 shows the results for the determination of ^{241}Am for spiked soil samples. The ^{241}Am isotope results by alpha spectrometry were corrected for ^{243}Am tracer yield. The average ^{241}Am result was 2.07 mBq g^{-1} (SD of 0.16 mBq g^{-1}). The average ^{243}Am tracer yield was 89.2% ± 6.5% (SD). The high chemical yields demonstrate the ruggedness of the sample preparation method and the powerful retention of Am on DGA Resin.

Table 4 shows the individual results for the determination of ^{239}Pu in replicate 10 g concrete samples spiked with MAPEP 24 soil using this rapid separation method and alpha spectrometry. The results were corrected for ^{242}Pu tracer yield. The average ^{239}Pu result was 3.40 mBq g^{-1} sample, with a -0.76% bias and SD (standard deviation) of 0.21 mBq g^{-1}. The average tracer recovery for ^{242}Pu was 86.2% ± 7.6% (SD) for all the replicates analyzed, including unspiked concrete and asphalt sample aliquots. While the data set is limited, the preliminary indications are this method can be applied to asphalt and concrete samples as well. For concrete samples, the additional Ca removal steps were essential.

The MDA (Minimum Detectable Activity) for Pu, Np and Am isotopes using this method with measurement by alpha spectrometry was calculated according to equations prescribed by Currie: [13]

$$\mathrm{MDA} = [2.71+4.65\sqrt{B}\,]/\,(CT*R*V*Eff*\mathbf{A}*0.060)$$

where B = Total Background counts, = BKG (rate) * sample count time ; CT = sample count time (min)

R = Chemical Recovery; V = Sample aliquot **(**g) ; EFF = Detector Efficiency ; A = Isotopic abundance (in most cases this will be ~1) ; 0.060 = conversion from dpm to mBq.

The MDA (minimum detectable activity) for the alpha spectrometry results can be adjusted as needed, depending on the sample aliquot and count time. For a 10g soil aliquot, the method MDA for the actinide isotopes with a 24 hour count time is ~35 uBq g^{-1}. Figure 3 shows the MDA plotted vs. sample aliquot size using 28% efficient alpha spectrometry detectors and a 90% yield, with an assumption of 1 background count per 960 minutes and an isotopic abundance of 1.

Figure 4 shows an example of the spectra of Pu isotopes in a 10g sample. The ^{236}Pu tracer recovery was 84.5% and the Full Width Half Maximum (FWHM) was 50.4 keV, showing acceptable alpha peak resolution and good tracer recovery. The ^{239}Pu peak labeled on the spectra represents ^{239}Pu plus ^{240}Pu, since these isotopes have overlapping alpha energies.

Figure 5 shows an example of the spectra of Am in a 10g soil sample. The ^{243}Am tracer recovery was 92.1% and the Full Width Half Maximum (FWHM) was 38.6 keV, showing acceptable alpha peak resolution and good tracer recovery. The resolution of the ^{243}Am tracer and ^{241}Am peak was very good, allowing reliable quantification of the ^{241}Am in the soil sample. This indicates that the rare earth removal step was effective. While the removal of La can be done fairly easily using DGA Resin alone, the removal of other heavier rare earth elements in the 10g soil aliquot which have greater affinity for DGA Resin is more problematic, thus the use of the TEVA Resin-thiocyanate option.

The furnace heating and rapid fusion method plus precipitation steps takes about 4 hours for a batch of 10 samples, followed by Pu, Np and Am separation steps that take about 2.5 to 4 hours to complete (depending on flow rates used and whether Am is also needed). Samples may be counted by alpha spectrometry as needed for routine analyses using appropriate level tracers for the desired count time to minimize counting uncertainty.

20g soil option

To further lower detection limit capability while still ensuring the total dissolution of refractory particles, two 10g soil aliquots were fused separately and combined during the sample preparation steps after the fusion. The ^{242}Pu tracer was split between each of 2 separate soil aliquots and 0.25g of refractory MAPEP 24 soil was added to each as well. Following the fusion steps, the Fe/Ti precipitate for each 10g aliquot was rinsed twice with water (pH 8.8-9.0) to remove Ca. The Fe/Ti precipitate for one 10g aliquot was dissolved in 100 mL 1.5M HCl and moved to the other 500 mL tube containing the other Fe/Ti precipitate, the second half of the 20g sample. The initial tube was rinsed with three 50 mL volumes of 1.5M HCl and this rinse was transferred to the second centrifuge tube. To this tube, 100 g Ca, 2 mg La and 4 mL 20% TiCl3 were added. Forty milliliters of 28M HF were added to each sample. The samples were mixed well, cooled briefly to room temperature and allowed to stand for ~10 minutes and centrifuged for 6 minutes at 3500 rpm. The supernatant was removed and the LaF_3/CaF_2 precipitate containing Pu was redisssolved and separated on TEVA Resin as described earlier.

Table 5 shows the results, with an average tracer yield of 76.2% and an average bias of -4.6%. The MDA for measurement of Pu isotopes using alpha spectrometry (16 hour count) is ~20 uBq g^{-1}. The analysis of 20 g of soil with total dissolution of refractory particles, with the ability to apply either alpha spectrometry or ICP-MS measurement techniques seems like a significant step forward for the radiochemical analysis of soil. Additional work with concrete samples, which is more difficult to extend to 20g aliquot size due to high Ca levels, is warranted. The defensibility of data for regulatory reasons is very important, as well as maintaining the public trust with high quality measurements. This new method increases the range for fused soil sample aliquots to 10-20g. Having this capability adds a level of quality and assurance that may be of significant benefit to the environmental laboratory.

Conclusions

A new rapid method to determine Pu, Np, and Am isotopes in 10-20 g soil samples has been developed that allows the separation of these isotopes with high chemical yields and effective removal of interferences. The fusion technique is fast and rugged, demonstrating very good recoveries of MAPEP standards added which contain refractory $^{239+240}$Pu. The TEVA Resin + DGA Resin stacked approach was shown to be a viable separation option, and can be applied successfully. The method can be extended to 20 g aliquots for soil by fusing two 10 g aliquots, combining and purifying plutonium using a single 2 mL TEVA cartridge.

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Figure 1 Rapid Sample Preparation Method for 10g Soil Aliquots

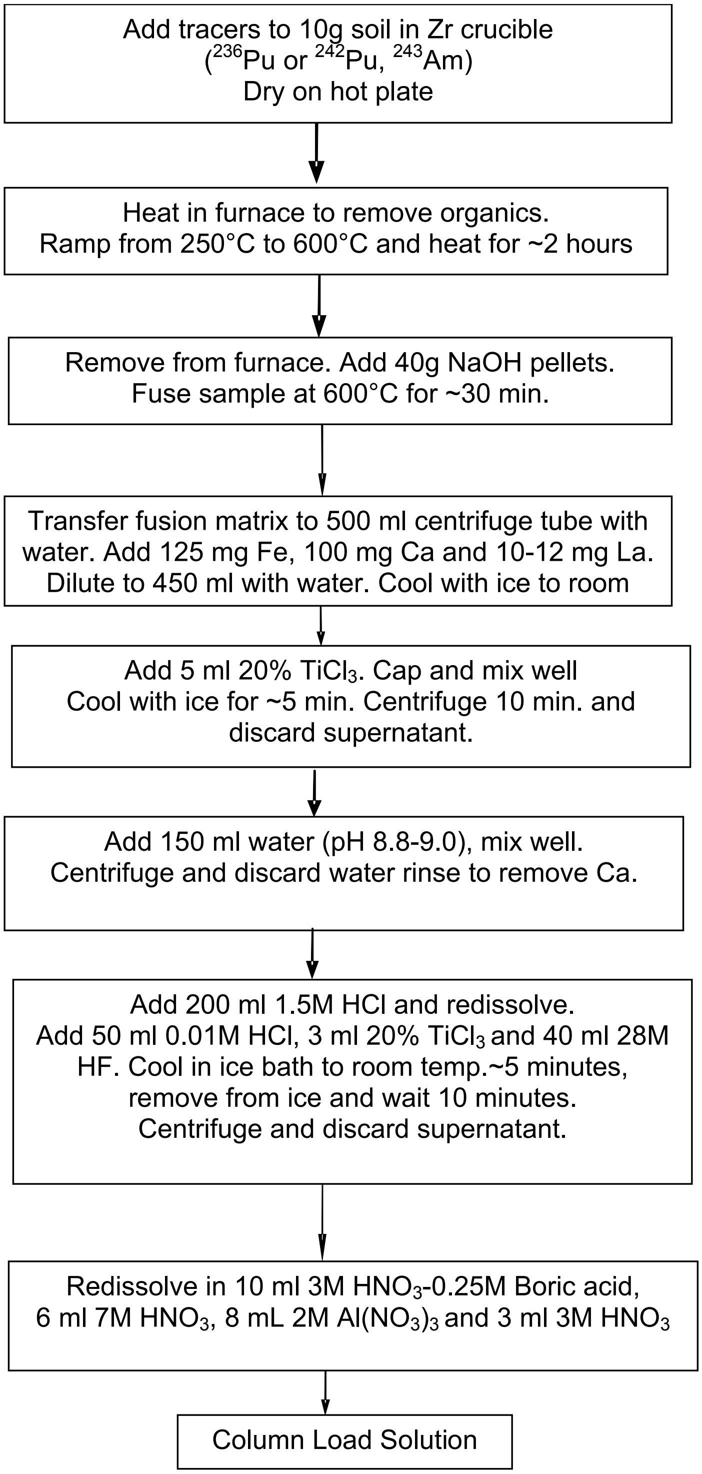


Figure 2 Rapid TEVA+DGA Resin Separation Method for 10g Soil Aliquots

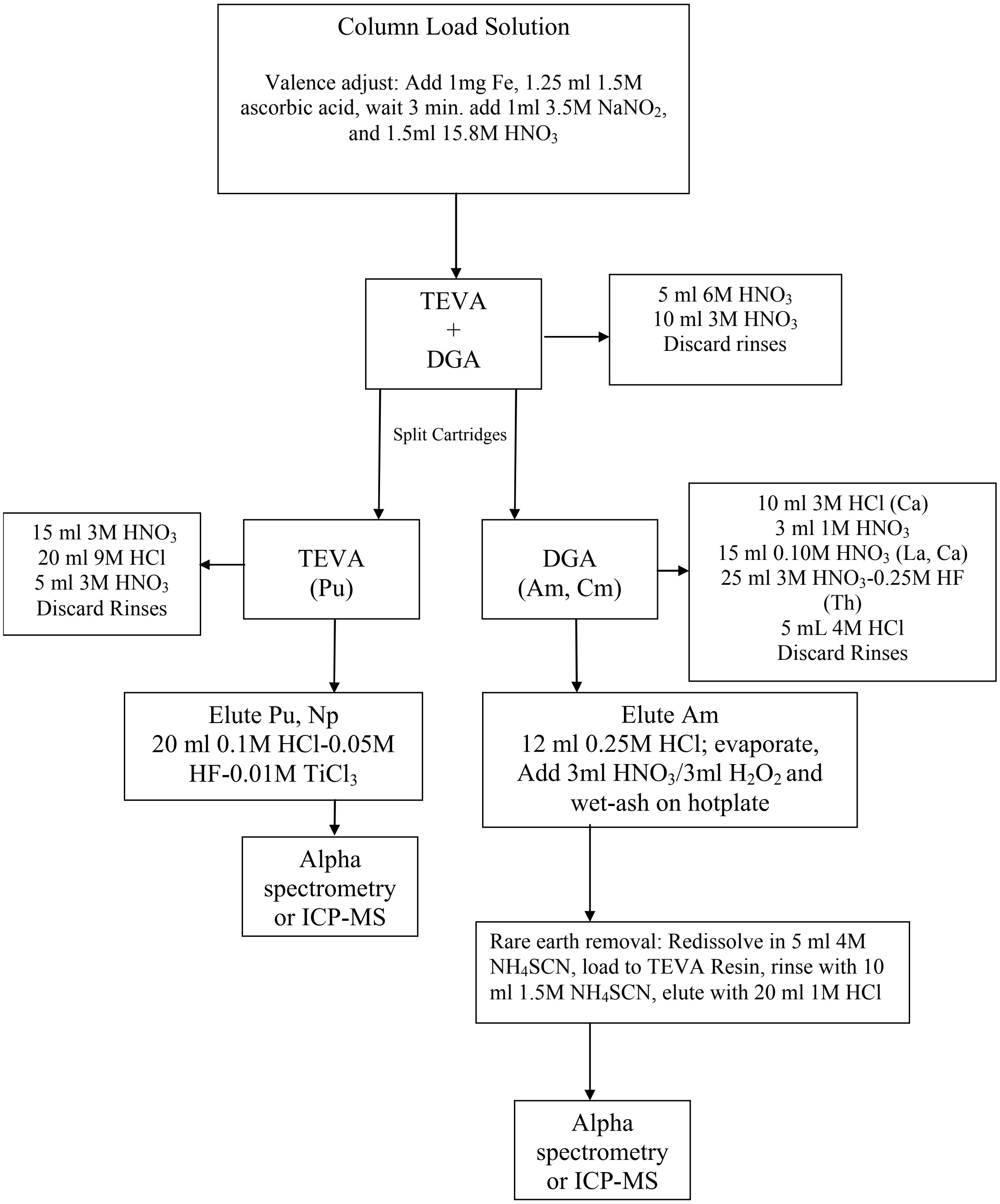


Figure 3 MDA for 24 Hour Count Time vs. Sample Aliquot (g)

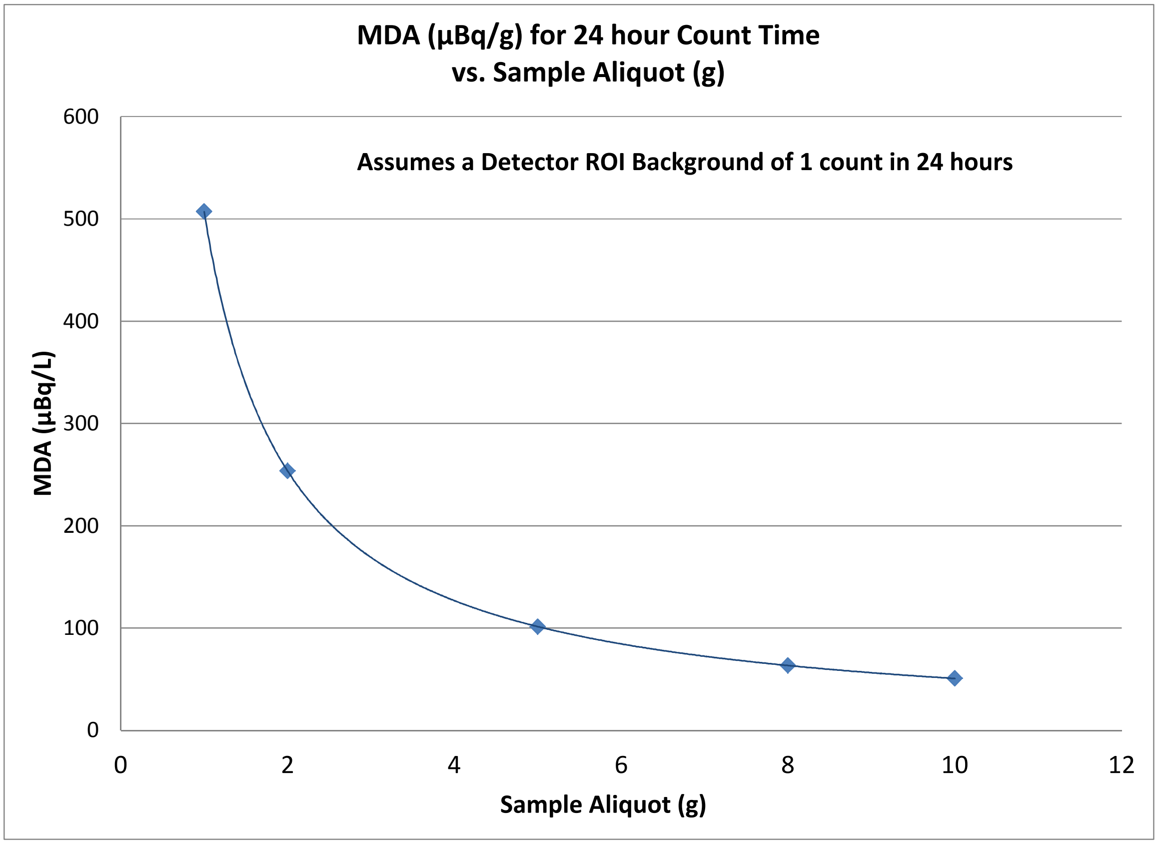


Figure 4 Pu isotopes and ^{237}Np Alpha Spectra for 10g Soil

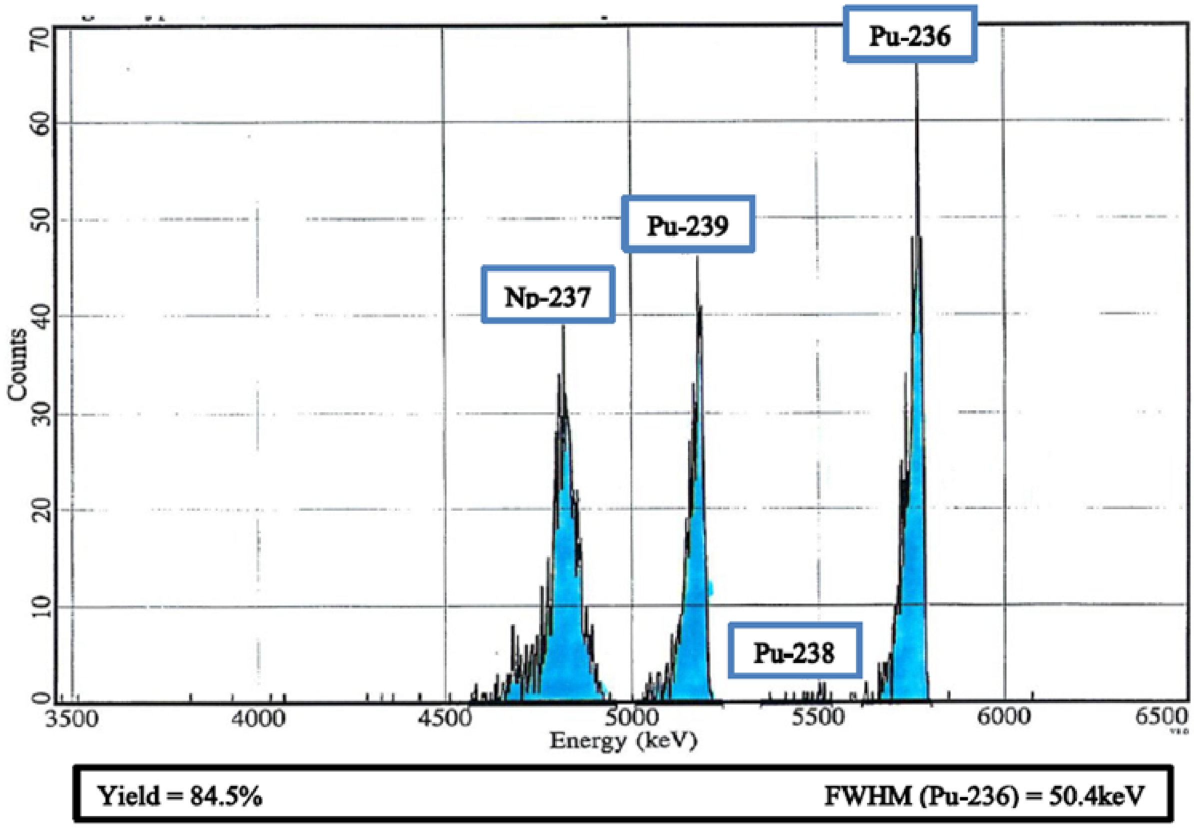
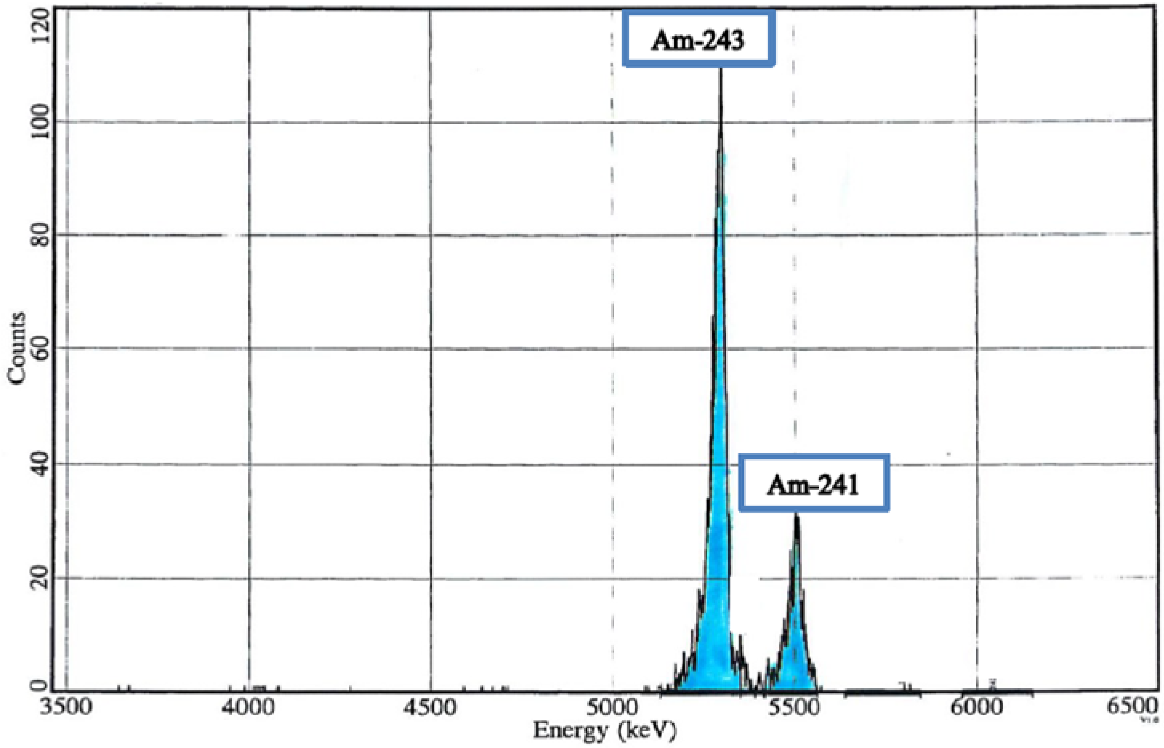


Figure 5 Am Isotopes Alpha Spectra for 10g Soil

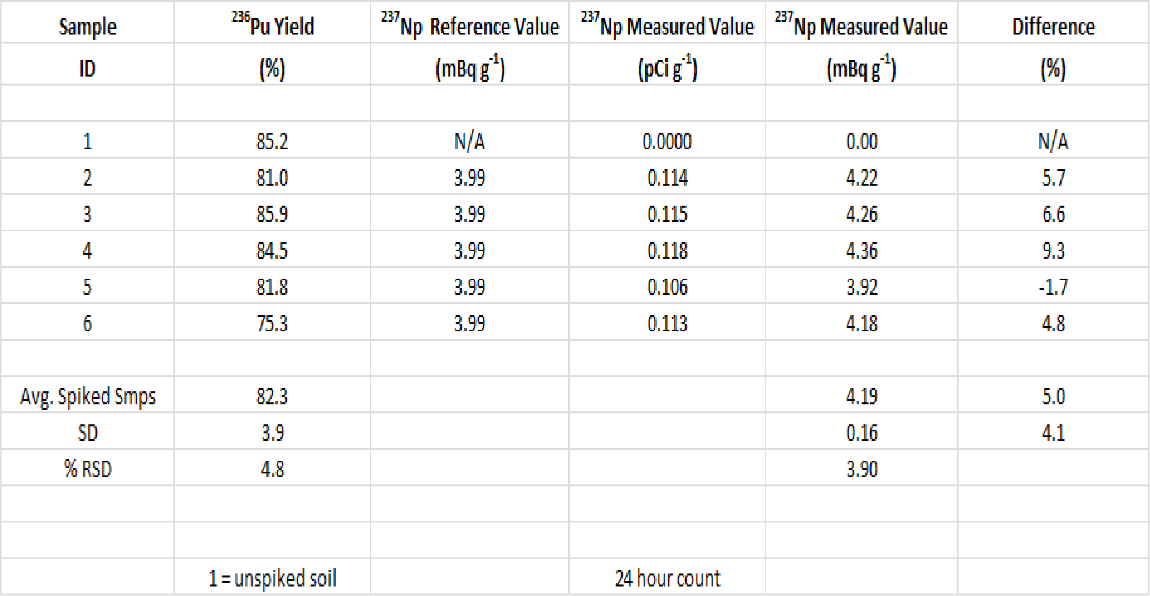


Yield = 92.1% **FWHM (Am-243) = 38.6keV**

Table 1 ^{239} Pu results for 10g soil samples spiked with MAPEP 24 standard

Sample	**^{236}Pu /^{242}Pu Yield**	**^{239}Pu Reference Value**	**^{239}Pu Measured Value**	**^{239}Pu Measured Value**	**^{239}Pu Corrected Value**	**Difference**
ID	**(%)**	**(mBq g^{-1})**	**(pCi g^{-1})**	**(mBq g^{-1})**	**(mBq g^{-1})**	**(%)**
1	91.1	3.43	0.094	3.46	3.46	1.0
2	80.9	3.43	0.087	3.23	3.23	-5.8
3	89.8	3.43	0.093	3.44	3.44	0.4
4	76.6	3.43	0.085	3.15	3.15	-8.2
5	83.9	3.43	0.093	3.43	3.43	0.0
6	84.0	3.43	0.099	3.64	3.64	6.3
7	99.3	3.43	0.091	3.35	3.35	-2.3
8	84.7	3.43	0.097	3.57	3.57	4.2
9	71.8	3.43	0.103	3.80	3.80	10.7
10	82.5	3.43	0.091	3.36	3.36	-2.1
Avg. Spiked Smps	84.5				3.44	0.4
SD	7.7				0.19	5.6
% RSD	9.1				5.6	
			24 hour count			
		1-6 corrected for blank assay Pu-239/240 (0.074 mBq g^{-1})				

Table 2 ^{237}Np results for 10g soil samples spiked with MAPEP 24 standard

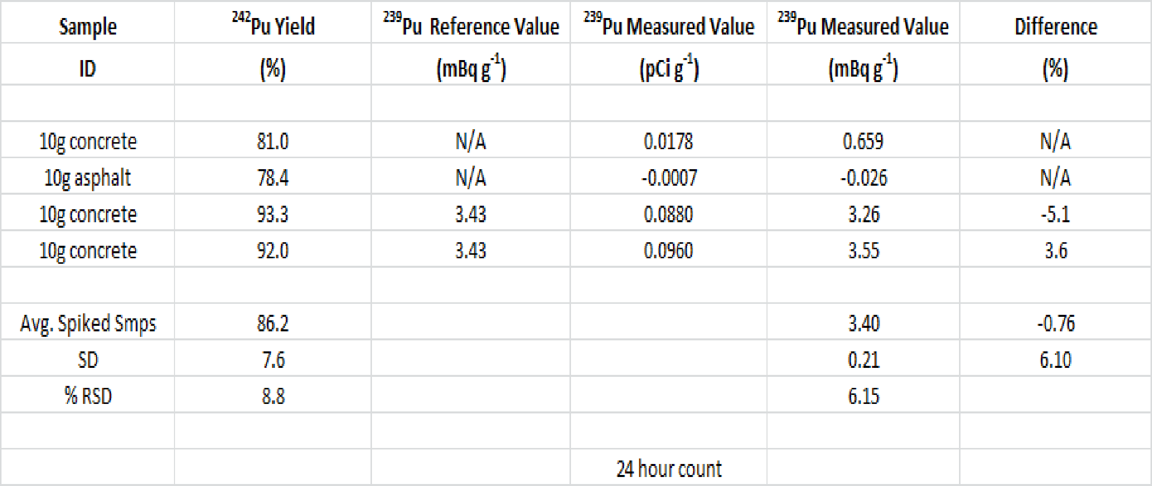


Sample ID	^{236}Pu Yield (%)	^{237}Np Reference Value (mBq g^{-1})	^{237}Np Measured Value (pCi g^{-1})	^{237}Np Measured Value (mBq g^{-1})	Difference (%)
1	85.2	N/A	0.0000	0.00	N/A
2	81.0	3.99	0.114	4.22	5.7
3	85.9	3.99	0.115	4.26	6.6
4	84.5	3.99	0.118	4.36	9.3
5	81.8	3.99	0.106	3.92	-1.7
6	75.3	3.99	0.113	4.18	4.8
Avg. Spiked Smps	82.3			4.19	5.0
SD	3.9			0.16	4.1
% RSD	4.8			3.90	
	1 = unspiked soil		24 hour count		

Table 3 ^{241}Am results for 10g soil samples spiked with MAPEP 24 standard

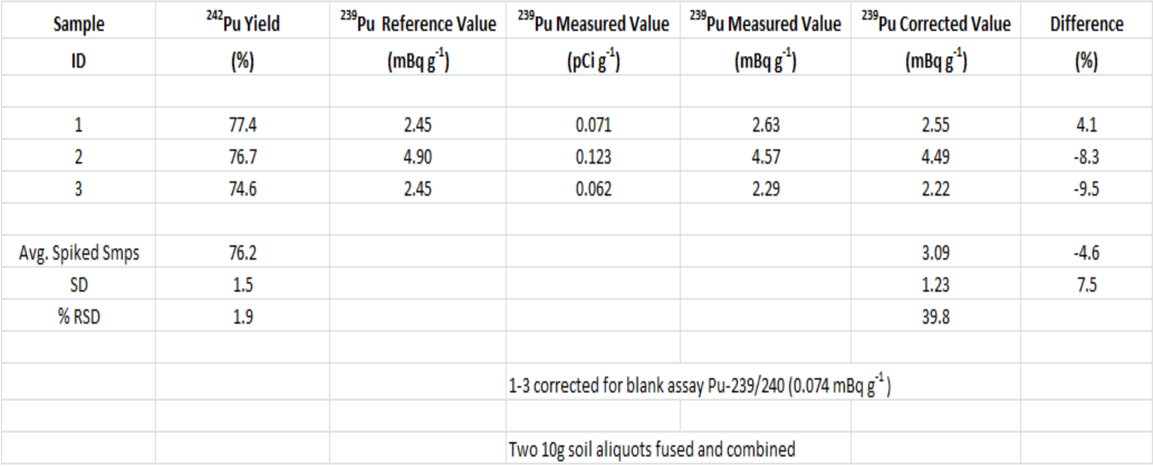
Sample	^{243}Am Yield	^{241}Am Reference Value	^{241}Am Measured Value	^{241}Am Measured Value	Difference
ID	(%)	(mBq g^{-1})	(pCi g^{-1})	(mBq g^{-1})	(%)
1	83.5	N/A	0.0012	0.04	N/A
2	81.0	2.14	0.0581	2.15	0.5
3	92.2	2.14	0.0601	2.22	3.9
4	83.5	2.14	0.0521	1.93	-9.9
5	82.3	2.14	0.0586	2.17	1.3
6	87.9	2.14	0.0591	2.19	2.2
7	91.3	2.14	0.0504	1.86	-12.9
8	96.4	2.14	0.0598	2.21	3.4
9	97.7	2.14	0.0537	1.99	-7.2
10	86.6	2.14	0.0588	2.18	1.7
11	99.1	2.14	0.0490	1.81	-15.3
Avg. Spiked Smps	89.2			2.07	-1.6
SD	6.5			0.16	6.8
% RSD	7.3			7.55	
			24 hour count		

Table 4 Pu Results for 10g Concrete Samples Spiked with MAPEP 24 standard



Sample ID	^{242}Pu Yield (%)	^{239}Pu Reference Value (mBq g^{-1})	^{239}Pu Measured Value (pCi g^{-1})	^{239}Pu Measured Value (mBq g^{-1})	Difference (%)
10g concrete	81.0	N/A	0.0178	0.659	N/A
10g asphalt	78.4	N/A	-0.0007	-0.026	N/A
10g concrete	93.3	3.43	0.0880	3.26	-5.1
10g concrete	92.0	3.43	0.0960	3.55	3.6
Avg. Spiked Smps	86.2			3.40	-0.76
SD	7.6			0.21	6.10
% RSD	8.8			6.15	
			24 hour count		

Table 5 ^{239} Pu results for 20g soil samples spiked with MAPEP 24 standard



Sample ID	^{242}Pu Yield (%)	^{239}Pu Reference Value (mBq g^{-1})	^{239}Pu Measured Value (pCi g^{-1})	^{239}Pu Measured Value (mBq g^{-1})	^{239}Pu Corrected Value (mBq g^{-1})	Difference (%)
1	77.4	2.45	0.071	2.63	2.55	4.1
2	76.7	4.90	0.123	4.57	4.49	-8.3
3	74.6	2.45	0.062	2.29	2.22	-9.5
Avg. Spiked Smps	76.2				3.09	-4.6
SD	1.5				1.23	7.5
% RSD	1.9				39.8	
			1-3 corrected for blank assay Pu-239/240 (0.074 mBq g^{-1})			
			Two 10g soil aliquots fused and combined			