Rapid Fusion Method for the Determination of Refractory Thorium and Uranium Isotopes in Soil Samples

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Abstract

Recently, approximately 80% of participating laboratories failed to accurately determine uranium isotopes in soil samples in the U.S Department of Energy Mixed Analyte Performance Evaluation Program (MAPEP) Session 30, due to incomplete dissolution of refractory particles in the samples. Failing laboratories employed acid dissolution methods, including hydrofluoric acid, to recover uranium from the soil matrix. The failures illustrate the importance of rugged soil dissolution methods for the accurate measurement of analytes in the sample matrix. A new rapid fusion method has been developed by the Savannah River National Laboratory (SRNL) to prepare 1-2 g soil sample aliquots very quickly, with total dissolution of refractory particles. Soil samples are fused with sodium hydroxide at 600^{o}C in zirconium crucibles to enable complete dissolution of the sample. Uranium and thorium are separated on stacked TEVA and TRU extraction chromatographic resin cartridges, prior to isotopic measurements by alpha spectrometry on cerium fluoride microprecipitation sources. Plutonium can also be separated and measured using this method. Batches of 12 samples can be prepared for measurement in <5 hours.

Introduction

Uranium is a naturally-occurring element found at low levels in virtually all rock, soil, and water, distributed throughout the environment by wind, rain and geologic processes. Uranium can also be removed and concentrated through mining and refining processes, which generate wastes such as mill tailings. Manufacturing of nuclear fuel and other human activities also release uranium to the environment.

Uranium and thorium mining, milling and processing, tin processing, phosphate rock processing and phosphate fertilizer production, and coal-fired utilities and industrial boilers are the primary anthropogenic sources of thorium release in the air, soil and water [1].

The determination of thorium and uranium isotopes in soil is an important analysis for the environmental analytical laboratory. There are a number of sample preparation methods used to digest soil samples. These include acid leaching with or without hydrofluoric acid, and various fusion techniques. [2] Lee et al. presented a new method for the measurement of uranium isotopes in soil using anion exchange resin and extraction chromatography. [3] The authors note that "A determination of the uranium isotopes in soil and sediment is generally complicated, because chemical recoveries are variable due to interference from major salt ions, the so-called 'matrix effects'. These effects are especially troublesome because there is a strong sample-dependency involving the composition and mineralogy of soil samples." It was also noted that the simplicity of extraction chromatography was advantageous over TBP (tributyl phosphate) and TOPO (trioctylphosphine oxide) liquid solvent extraction methods, stating that "Solvent extraction with toxic TBP is too cumbersome for use with large numbers of samples because it is labor intensive, and creates large volumes of waste, in particular organic extractant waste." It was reported that chemical yields using TBP and TOPO were lower as well. It follows that methods that effectively digest soil samples and collect uranium and thorium with maximum removal of the sample matrix can simplify soil analysis significantly. In addition, newer, simpler extraction chromatographic methods that enhance separation efficiency and reduce acid waste offer significant advantages to the radiochemistry laboratory.

Vajda et al. [4] reported a method for actinides in soil in which 0.5 g soil samples were fused using lithium metaborate in platinum crucibles. After preconcentration of actinides using calcium fluoride precipitation, actinides were separated on TRU extraction chromatographic resin. The use of lithium metaborate fusion ensured that refractory particles were digested. The results agreed well with reference values, however, the method appears to be limited to 0.5g soil aliquots and requires very expensive platinum crucibles.

Wang et al. [5] reported a sequential method to determine actinides and strontium in soil samples. The samples were digested in nitric acid and hydrogen peroxide and redissolved in a large volume of 3M nitric acid. A large anion exchange resin column (Dowex 1x8) was used to collect and separate Pu and Th.

The rinse fractions from the anion exchange resin were treated further and processed individually for Am, U and Sr. Several sequential precipitations were carried out, and the large number of method steps, though sequential, would not be considered very rapid. More importantly, the acid leach used in this method does not effectively digest refractory particles that may be present in the sample.

Jia et al [6] reported a method for determination of thorium isotopes in soil by alpha-spectrometry. After fusion with Na_2CO_3 and Na_2O_2 at 600 ˚C, soil samples were leached with HNO_3 and HCl. Thorium was coprecipitated together with iron (III) as hydroxides and/or carbonates at pH 9, separated from uranium and other alpha-emitters by a Microthene-TOPO (tri-octyl-phosphine oxide) chromatographic column, electrodeposited on a stainless steel disk, and measured by alpha-spectrometry. It was noted in this work that leaching of uranium and thorium from soil sample with only mineral acids (dilute or concentrated), such as HCl, HNO_3, $HClO_4$, HF, etc., may be incomplete. The method also addressed the common problem of resulting silicates, which interfere with subsequent method steps, by evaporation and precipitation of the silicate solids. This method provided total digestion of the soil aliquots by fusion, use of a furnace instead of a burner to allow multiple samples to be processed simultaneously, and a way to address silicates, at least for relatively small sample aliquots. The method also seems to be limited to 0.5 g soil and requires platinum crucibles. The removal of silica required evaporation of a 150 mL leaching solution following the fusion, precipitation and washing of insoluble silicates, and filtration of remaining residue after final dissolution of an iron hydroxide precipitate. The chemical yields reported were very high. However, the alpha spectra showed a bit of overlap between ^{230}Th and ^{229}Th peaks, somewhat surprising since the method used electrodeposition to prepare sources for counting. The paper was thorough, and illustrated quite well the challenges associated with measuring thorium isotopes in soil.

Rugged soil dissolution methods are essential to accurately determine actinide isotopes in soil. Sill et al. have emphasized the need for total sample dissolution and the potential for refractory particles in soil samples. [7] The recent failure by ~80% of participating labs in the U.S Department of Energy Mixed Analyte Performance Evaluation Program (MAPEP) Session 30 was traced to incomplete dissolution of refractory particles in the samples by acid digestion and points to the need for the implementation of robust sample digestion of soil samples. Labs that did not utilize total dissolution methods typically reported ^{234}U and ^{238}U results that were ~60% lower than the soil reference values, even when digesting soils with hydrofluoric acid.

Soil methods were reported from this laboratory that utilized rapid fusion for 1-2 g soil samples using sodium hydroxide fusion in combination with pre-concentration steps to eliminate the soil matrix and remove silicates that adversely impact separation methods. [8] Methods for asphalt, soil and brick have also been reported, tested with soil containing refractory Pu. [9, 10] Recently, our laboratory has begun to focus on optimizing further soil fusion methods for uranium/thorium isotope analysis in soil. As a result, a new rapid fusion method for soil samples that effectively digests refractory thorium and uranium isotopes has been developed in the Savannah River National Laboratory (Aiken, SC, USA). This approach has a sample preparation time for batches of 12 soil samples of <5 hours. The samples were fused with sodium hydroxide at 600^{o}C in relatively inexpensive zirconium crucibles. The fusion can be performed on several samples simultaneously in muffle furnaces, rather than one at a time over burners, and the fusion cake is readily dissolved in warm water.

Sequential precipitation steps with Fe/Ti hydroxide and Ca/La-fluoride separate actinides from the dissolved soil matrix. The Fe/Ti hydroxide removes the alkaline matrix of the fusion, while the Ca/La-fluoride precipitate effectively removes iron and other matrix components that can interfere with the chromatographic separation of the actinides. The fluoride precipitation is particularly effective for the removal of silicates that can precipitate and adversely affect column flow.

Uranium and thorium are separated quickly and efficiently on stacked TEVA and TRU Resin cartridges. For thorium isotopes alone, only a TEVA Resin cartridge is needed. Rapid flow rates achieved using vacuum box technology, and stacked resin cartridges with highly selective extraction chromatographic resins significantly reduce separation times and waste volumes. Alpha spectrometry sources were prepared by cerium fluoride microprecipitation, however, electrodeposition can also be used. Other measurement techniques such as inductively-coupled plasma mass spectrometry (ICP-MS) can also be employed. This method can also be applied to other solid samples such as concrete or asphalt samples.

Experimental

Reagents

The extraction chromatography resins employed in this work are TEVA Resin® (Aliquat ™ 336) and TRU-Resin® (tri-n-butylphosphate (TBP) and octyl (phenyl) N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)), 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 tracers ^{242}Pu, ^{233}U, ^{232}U, and ^{229}Th were obtained from Eckert Ziegler/Analytics, Inc. (Atlanta, GA, USA) and diluted to the appropriate levels. Th-227 was separated from ^{227}Ac (Oak Ridge National Laboratory) as previously described. [11]

Procedures

Column preparation. TEVA and TRU Resins were obtained as 2 mL cartridges. Small particle size (50-100 micron) 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. To facilitate enhanced removal of interferences, column reservoirs and connector tips in the lid were changed after sample loading and prior to final elution of analytes.

Sample Preparation. One gram aliquots of MAPEP 30 soil were placed into 250 mL low form zirconium crucibles. The MAPEP samples were provided by Department of Energy (DOE) – Radiological and Environmental Sciences Laboratory (RESL), Idaho, USA. MAPEP 30 soil standard was chosen because the soil contains refractory zircons in the soil. Successful analysis would indicate analytical method ruggedness and applicability when refractory particles are present.

Figure 1 shows the rapid furnace heating, fusion and precipitation steps used to remove organics, digest the samples and preconcentrate the uranium and thorium from the alkaline fusion matrix. Tracers (^{229}Th and ^{232}U) were added to each crucible, and the crucibles were dried briefly on a hotplate. The self-cleaning ^{232}U tracer [12] was mixed using a vortex stirrer and centrifuged immediately before use to more effectively remove the ^{228}Th daughter .

After removing crucibles from the hotplate, the samples were heated to 600˚C for ~0.5 hour to remove organics present in the soil aliquot. Some soils may not even require this heating step depending on the organic content. After the furnace heating step, 15 grams of NaOH pellets were added to each crucible. The crucibles were covered with a zirconium lid and placed into a furnace at 600˚C for ~ 15-20 minutes. The crucibles were removed from the furnace, cooled for about 10 minutes, and transferred to a hot plate. Water was added to dissolve the fusion cake and transfer the sample to 225 mL centrifuge tubes. Residual solids were removed from the crucibles by adding water and heating the crucibles on the hot plate as needed. A final rinse of 10 mL 3M HNO_3 (or alternately 5 mL 6M HNO_3) was added to the crucibles, which were then heated until very hot on the hot plate to ensure complete removal of uranium and thorium from the crucible. Thorium, in particular, will cling to the crucible if a warm acid rinse is not employed, so it is very important to use the warm nitric acid rinse to achieve high chemical yields for Th. This is particularly important for blank samples (no soil), where up to 65% (Table 1) of the Th can remain in the crucible following the dissolution of the fusion cake with water, likely due to adsorption of highly insoluble thorium hydroxides to the zirconium surface. The behavior of uranium is nearly identical with and without soil present, presumably due to the higher solubility of uranyl hydroxides.

One hundred and twenty-five milligrams of Fe (added as Fe $(NO_3)_3$) and 5 mg of La (as lanthanum nitrate standard) were added to each 225 mL centrifuge tube prior to transferring the alkaline solution and solids from the crucibles into the tubes. The samples were diluted to 180 mL with water and cooled in an ice bath to room temperature.

Two milliliters of 1.25M $Ca(NO_3)_2$ and 4 mL 3.2M ammonium hydrogen phosphate were added to each tube, and each tube was capped and mixed well. The calcium and phosphate ions were added to enhance chemical recovery of uranium. Five milliliters of 20% $TiCl_3$ were added to each tube to reduce U(VI) to U(IV) to improve uranium recovery during the precipitation steps. The samples were mixed and cooled in an ice bath to room temperature. The tubes were centrifuged at 3500 rpm for ~5 minutes and the supernatant was discarded. The precipitates were partially dissolved by adding 1.5 M HCl to a total volume of 80 mL in each tube and diluting to 170mL with 0.01M HCl, mixing well with each addition. After dilution, 1 mg of La (as lanthanum nitrate standard) and 25 mg Ca was added to each sample. To ensure no actinides were in the hexavalent state and facilitate complete precipitation, 3 mL 20% titanium chloride were added to each sample. Twenty-five milliliters of 28M HF were added to each tube. The samples were mixed well, dissolving any remaining Fe-Ti hydroxide solids and forming a La-Ca-fluoride precipitate. The tubes were cooled briefly in an ice bath for ~5 minutes, removed and allowed to stand for ~5 minutes. and centrifuged for 5 minutes at 3500 rpm. The LaF_3 removal step effectively removes almost all of the Fe and Ti, as well as silicates that can affect column flow.

The supernate was discarded 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 225 mL tubes were rinsed with 6 mL of 7M HNO_3 and 8.5 mL of 2 M $Al(NO_3)_3$, respectively, transferring the rinses to the 50 mL centrifuge tubes. The samples were mixed using a vortex stirrer and heated 2-5 minutes in a hot block heater at

105°C. The 50 mL tubes were centrifuged to test for any traces of solid particulates, which were removed if needed.

Typically, the sample load solutions are very clear. If gel-like solids are observed in the sample load solutions or flow problems are encountered for more difficult soil types, that particular soil may require slightly less titanium chloride or Ca added to facilitate dissolution. The 20% $TiCl_3$ may be reduced from 5 mL to 3-4 mL if needed to reduce Ti carryover into the load solution. Ca may be reduced as well, for example, from 2 mL to 1 mL 1.25M calcium nitrate during the initial preconcentration step.

Since Th(IV) forms strong fluoride complexes, higher levels of boric acid (10ml 3M HNO_3-0.25M H_3BO_3) and aluminum ions (8.5 ml of 2 M $Al(NO_3)_3$) are used to complex fluoride ions more effectively and mitigate any adverse effects of fluoride ions on Th retention on TEVA Resin. For samples with a higher than usual La-Ca-fluoride precipitate (>5 mL), more 2 M $Al(NO_3)_3$ may be needed to complex the Th to achieve good chemical yields. It should be noted that if only U or Pu/U isotopes are desired, a load solution consisting of 7 mL 3M HNO_3-0.25M H_3BO_3, 6 mL of 7M HNO_3 and 7 mL of 2 M $Al(NO_3)_3$ may be used instead.

A valence adjustment was performed on the load solution by adding 1mg Fe (as iron nitrate) and 1.25 mL 1.5M ascorbic acid with a three minute wait step to reduce plutonium to Pu(III). It is convenient to allow the Fe to be reduced to Fe(II) by ascorbic acid in the load solution, rather than add Fe(II) ions directly, since these solutions have short shelf lives (~1 week) due to air oxidation. Following the reduction step, 1 mL 3.5M $NaNO_2$ was added to oxidize plutonium to Pu(IV). This ensures any Pu present is retained on TEVA Resin as Pu(IV). In previous work, sulfamic acid was added to facilitate the reduction step, particularly when no Fe(II) is added. Because the reaction of sulfamic acid and nitrite results in sulfate formation, and sulfate 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, however, offers effective plutonium valence reduction of Pu isotopes to Pu(III) and thus enable effective adjustment of plutonium to Pu(IV) upon the addition of $NaNO_2$.

Column separation. Figure 2 shows the column separation method used. TEVA Resin cartridges and TRU 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. To assay thorium isotopes alone only TEVA Resin is needed.

After the valence adjustment as described above, the sample solution was loaded onto the stacked TEVA and TRU Resin cartridges at ~1 drop per second. After the sample was loaded, a tube rinse of ~ 5 mL 6M HNO_3 + 50 µL 30wt% H_2O_2 was transferred to the TEVA and TRU resin cartridges and allowed to pass through the resin at ~1-2 drops per second. Hydrogen peroxide ensures than any uranium that may have been reduced to U(IV) (possibly due to traces of Ti(III) remaining from the precipitation steps) is reoxidized to U(VI) and not retained on TEVA Resin. Tracer yields for U increased when hydrogen peroxide was added. In past work reported by this laboratory [8], adding concentrated nitric acid at this step likely facilitated higher U yields by oxidizing some of the U(IV) that may have formed. Increasing nitrate levels with larger amounts of Al ions present, however, can cause solubility problems. The hydrogen peroxide addition is simple and more effective.

The column reservoir was replaced to ensure maximum removal of interferences and the cartridges were rinsed with 10 mL of 3M HNO_3 at ~2 drops per second. The TEVA Resin and TRU Resin cartridges were separated and processed separately on two different vacuum boxes simultaneously to minimize processing time.

Each TEVA Resin column was rinsed with 10mL of 3M HNO_3 at ~2 drops per second, followed by Th elution into to new labeled 50 mL tubes with 15 mL 9M HCl at 1-1.5 drops per second. It should be noted that Pu can also be determined also using this method by eluting Pu from TEVA resin following the Th elution. After the elution of Th from TEVA Resin, column rinses of 5 mL 9M HCl at 1-2 drops per second followed by 5mL 3M HNO_3 at ~2 drops per second are used to remove any traces of Th and reduce any extractant bleed-off. Pu is eluted at ~1 drop per second with 20 mL of 0.1M HCl-0.05M HF-0.01M $TiCl_3$ for measurement by alpha spectrometry. For electrodeposition of purified eluents, sodium formaldehyde sulfoxylate (rongalite) reductant should be used instead of $TiCl_3$.

The TRU Resin cartridge is rinsed with 5mL 8M HNO_3 at ~1-2 drops per second. Twenty milliliters of 4M HCl-0.2M HF-0.002M $TiCl_3$ was added at 1-2 drops per second to TRU Resin to remove any Th, Am, Cm, Pu, Np, and Po present, followed by 10 mL 8M HNO_3 to ensure complete Po removal. After changing the column reservoirs and connector tips, U was eluted with 15 mL of 0.1M ammonium bioxalate at ~1 drop per second.

Cerium fluoride microprecipitation was used to prepare the purified samples for alpha spectrometry counting. For uranium samples, 100 µg Ce, 0.3-0.5 mL 20%$TiCl_3$ and 1 mL 28 M HF were added. For Th samples, the 15 mL 9M HCl volumes were diluted to 40 mL with water, 40 µg Ce and 5 mL 28 M HF were added. After mixing well by vortex mixing and waiting 15-20 minutes, the solution was filtered using a 25 mm polypropylene filter (0.1 µm pore size disposable Resolve™ filter funnel, Eichrom Technologies, Inc.). Each sample tube was rinsed with ~5 mL deionized water and added to the filters. The filters were then rinsed with 2-3mL of ethanol to facilitate drying and affixed to adhesive disks (Environmental Express, Mount Pleasant, SC, USA). Alternately, filters can be affixed to stainless steel planchets using a glue stick. The filters were heated briefly under a heat lamp to ensure dryness.

Apparatus

Plutonium, uranium and thorium 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 28-30%. The distance between the sample and detector surface is ~3 mm.

Recovery of ^{227}Th and ^{233}U tracers from the NaOH fusion cakes in zirconium crucibles was determined by measuring ^{227}Th by gamma spectrometry (ORTEC GEM series HpGe coaxial detector with DSPC LF digital signal processor) and ^{233}U by liquid scintillation counting (Packard Tricarb model 2550 TR/AB scintillation counter and Ultima Gold scintillation cocktail).

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 2 shows the individual results for the determination of ^{238}U in twelve 1 g MAPEP 30 soil samples using this rapid separation method and alpha spectrometry. The results were corrected for ^{232}U tracer yield. The average ^{238}U result was 85.8 mBq g^{-1}, with a 3.3% bias and SD (standard deviation) of 2.3 mBq g^{-1}. The average tracer recovery for ^{232}U was 86.6% ± 8.1% (SD). The high ^{232}U tracer recoveries and excellent results for the analyte versus known values indicate the ruggedness of the sample preparation and measurement steps, even for refractory U isotopes. The uncertainties for the individual ^{238}U results were typically ± 7-8% (1 SD), with a 16 hour count time. Table 3 shows the individual results for the determination of ^{234}U in twelve 1 g MAPEP 30 soil samples this rapid separation method and alpha spectrometry. The average ^{234}U result was 80.2 mBq g^{-1}, with a -1.0% bias and SD (standard deviation) of 1.9 mBq g^{-1}. These results are in stark contrast to results that were reported for uranium isotopic results reported on MAPEP 30 soil samples by labs using acid digestion (even with hydrofluoric acid). Those results were 50-60% low, even though samples appeared to be dissolved.

Table 4 shows the individual results for the determination of ^{228}Th in the same twelve 1 g MAPEP 30 soil aliquots. The results were corrected for ^{229}Th tracer yield. The average ^{228}Th result was 50.2 mBq g^{-1}, with a 1.7% bias and SD (standard deviation) of 1.9 mBq g^{-1}. The average tracer recovery for ^{229}Th was 91.0% ± 6.1% (SD). The tracer recoveries were not only very high, indicating method ruggedness, but also very consistent. The uncertainties for the individual ^{228}Th results were typically ± 7-8% (1 SD), with a 16 hour count time.

Table 5 shows the individual results for the determination of ^{230}Th in the same twelve 1 g MAPEP 30 soil aliquots. The results were corrected for ^{229}Th tracer yield. The average ^{230}Th result was 98.4 mBq g^{-1}, with a 2.3% bias and SD (standard deviation) of 5.9 mBq g^{-1}. The average tracer recovery for ^{229}Th was 91.0% ± 6.1% (SD). The use of 40 μg of cerium in the final microprecipitation step to prepare the Th sources for alpha spectrometry provided enhanced resolution of the ^{230}Th alpha peak, which can be somewhat challenging to resolve from the ^{229}Th alpha peak. The uncertainties for the individual ^{230}Th results were typically ± 6-7% (1 SD), with a 16 hour count time.

Table 6 shows the individual results for the determination of ^{232}Th in the same twelve 1 g MAPEP 30 soil aliquots. The results were corrected for ^{229}Th tracer yield. The average ^{232}Th result was 49.9 mBq g^{-1}, with a 2.2% bias and a SD (standard deviation) of 3.3 mBq g^{-1}. The average tracer recovery for ^{229}Th was 91.0% ± 6.1% (SD). The overall bias not only was very small, but the individual results were very consistent for the set of twelve measurements. The uncertainties for the individual ^{232}Th results were typically ± 7-8% (1 SD), with a 16 hour count time.

Table 7 shows the results for the determination of ^{239}Pu and ^{238}Pu for the MAPEP 30 soil samples. Pu-239 represents ^{239}Pu plus ^{240}Pu, since these isotopes have overlapping alpha energies. As described earlier, the Pu isotopes are eluted after Th is removed from TEVA Resin, and measured by alpha spectrometry. The ^{239}Pu isotope results by alpha spectrometry were corrected for ^{242}Pu tracer yield. The average ^{239}Pu result was 79.3 mBq g^{-1} (SD of 3.1 mBq g^{-1}), with an average bias of 3.3%. The average ^{242}Pu tracer yield was 91.9% ± 3.8% (SD). The high chemical yields demonstrate the ruggedness of the sample preparation method. The uncertainties for the individual ^{239}Pu results were typically ± 7-8% (1 SD), with a 16 hour count time.

The MDA (Minimum Detectable Activity) for Pu, U and Th 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 1g soil aliquot, the method MDA for the actinide isotopes with a 16 hour count time is ~500 uBq g^{-1}.

Figure 3 shows an example of the spectra of U isotopes for a 1 g MAPEP 30 sample. The ^{232}U tracer recovery was 89.9% and the Full Width Half Maximum (FWHM) was 37.8 keV, showing acceptable alpha peak resolution and good tracer recovery. Figure 4 shows an example of the spectra of Th istopes in a 1 g MAPEP soil sample. The ^{229}Th tracer recovery was 94.2% and the Full Width Half Maximum (FWHM) was 69.1 keV, also showing acceptable alpha peak resolution and good tracer recovery. The resolution of the ^{229}Th tracer and ^{230}Th peak was acceptable, allowing reliable quantification of the ^{230}Th in the soil sample. Daughter isotopes of ^{228}Th are also shown in the spectra at energies higher than 5500 keV.

The furnace heating and rapid fusion method plus precipitation steps takes <2.5 hours for a batch of 10 samples, followed by separation steps that take about 2-3 hours to complete (depending on flow rates used). The method may be used for emergency soil samples following a radiological incident or for routine sample analyses. 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. Rapid sodium hydroxide fusion offers advantages over acid dissolution, as well as other fusion techniques. The preconcentration techniques effectively at eliminating soil matrix interferences, and result in high chemical yields. Total dissolution is very important for soil analysis, and this new method provides total digestion of refractory particles in soil.

Conclusions

A new rapid fusion method to determine Pu, U, and Th isotopes in 1 g -2 g soil samples has been developed that allows the separation of these isotopes with high chemical yields and effective removal of interferences. It has been validated using MAPEP 30 soil standards containing refractory isotopes. The sodium hydroxide fusion technique is fast and rugged. The TEVA Resin + TRU Resin stacked cartridge approach is rapid, effective and has been optimized for chemical yields and removal of interferences.

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Figure 1 Rapid Fusion Method for U, Th Isotopes in Soil

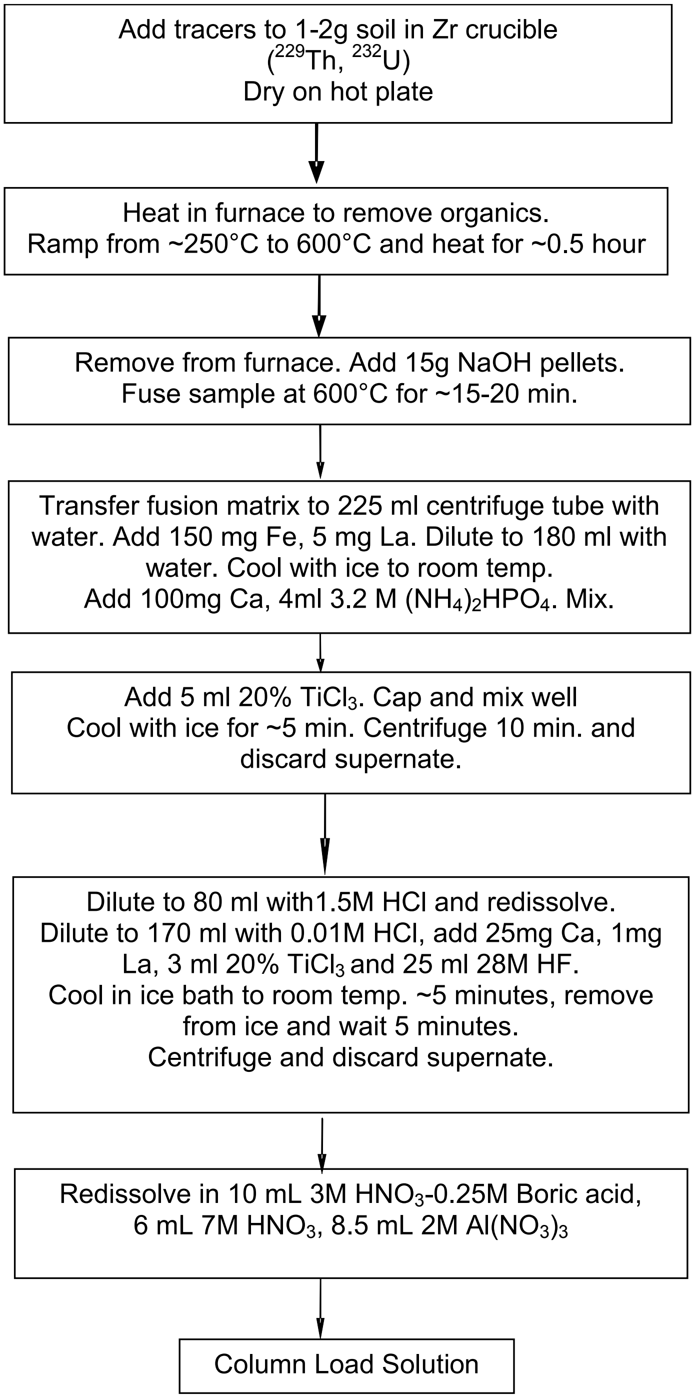


Figure 2 Rapid Column Separation Method for U, Th Isotopes in Soil

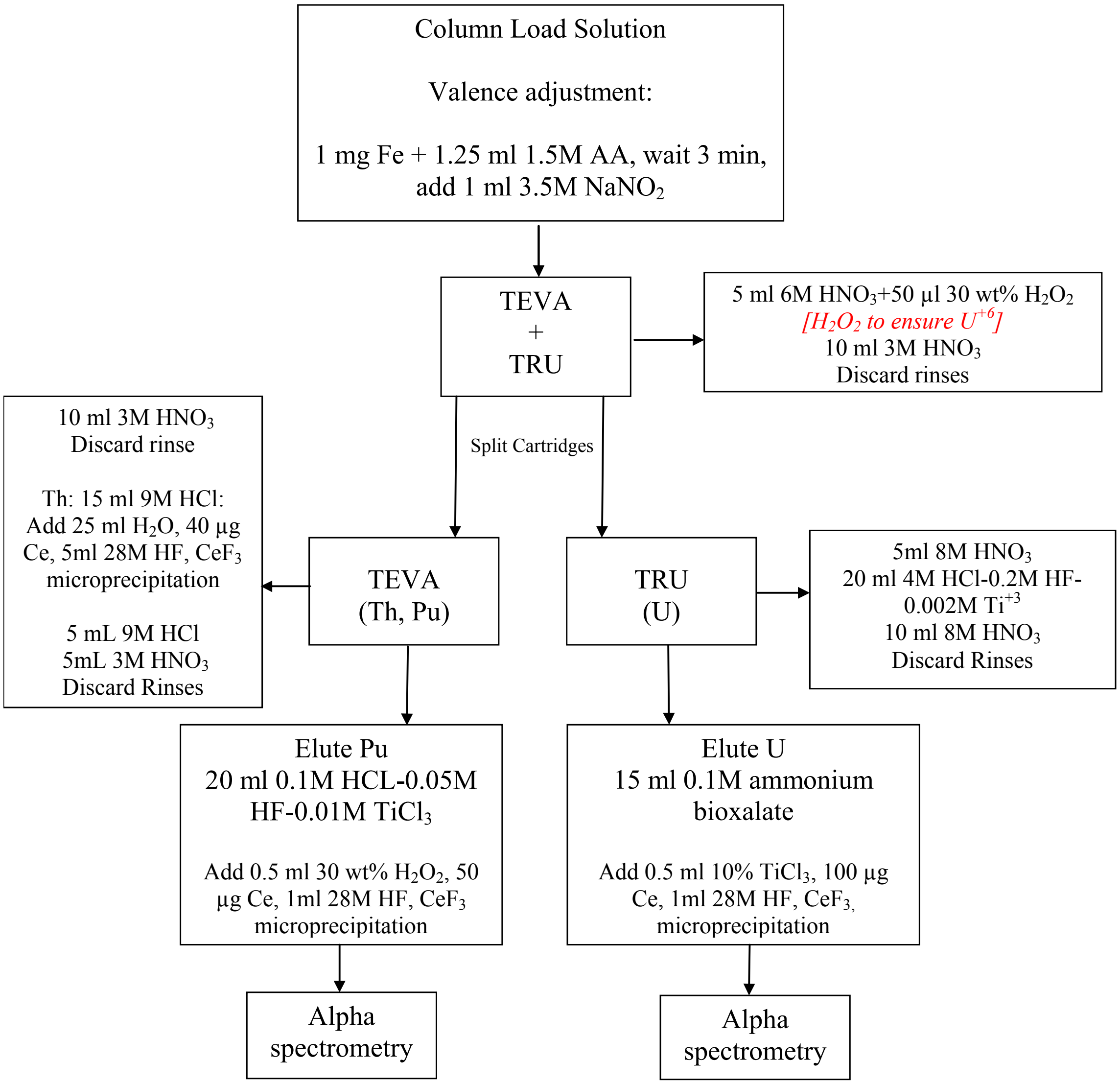
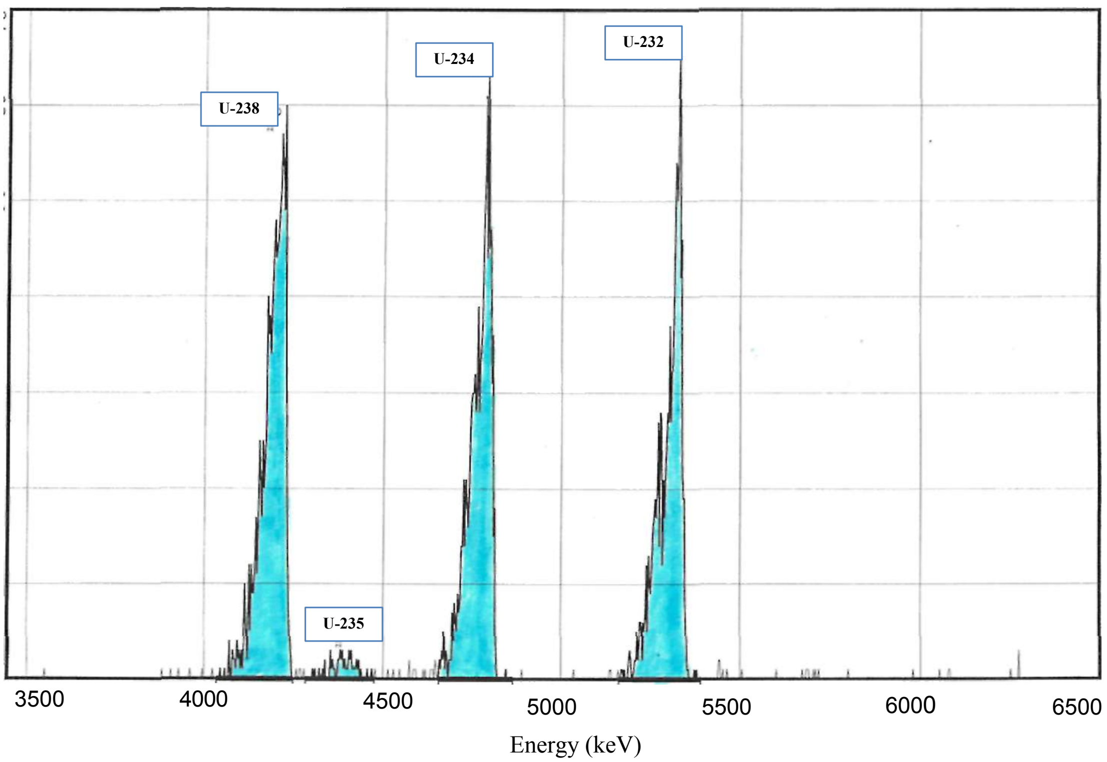
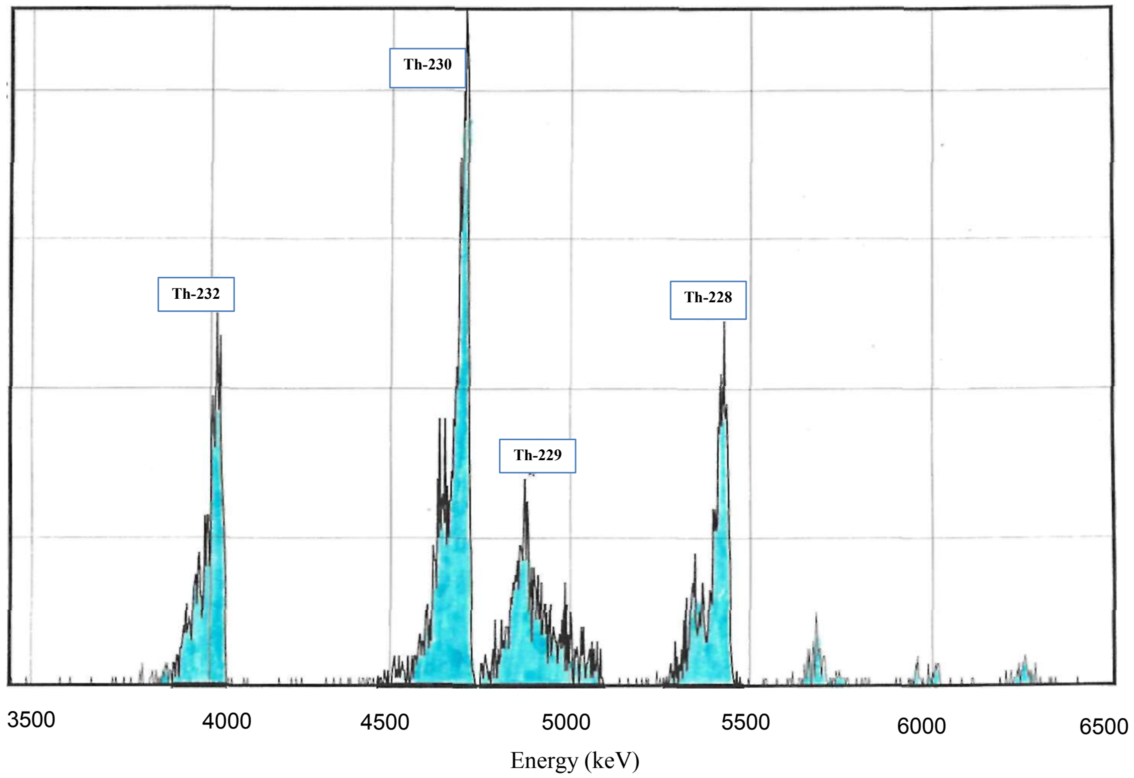


Figure 3 Uranium Isotope Alpha Spectra for MAPEP 30 Soil



Yield = 89.9%	**FWHM (U-232) = 37.8 keV**

Figure 4 Thorium Isotope Alpha Spectra for MAPEP 30 Soil



Yield 94.2% **FWHM (Th-229) = 69.1keV**

Table 1. Percent Recovery of Tracers from NaOH Fusion in Zr Crucible

			warm	
		water	**3M HNO_3**	**total**
Tracer	**Sample**	**dissolution**[a]	**Rinse**[b]	**% recovery**
^{227}Th	Blank	37 ± 2	56 ± 6	94 ± 6
^{227}Th	1g Soil	95 ± 2	3.5 ± 0.5	99 ± 2
^{233}U	Blank	75 ± 10	31 ± 9	106 ± 4
^{233}U	1g Soil	80 ± 3	21 ± 4	101 ± 2

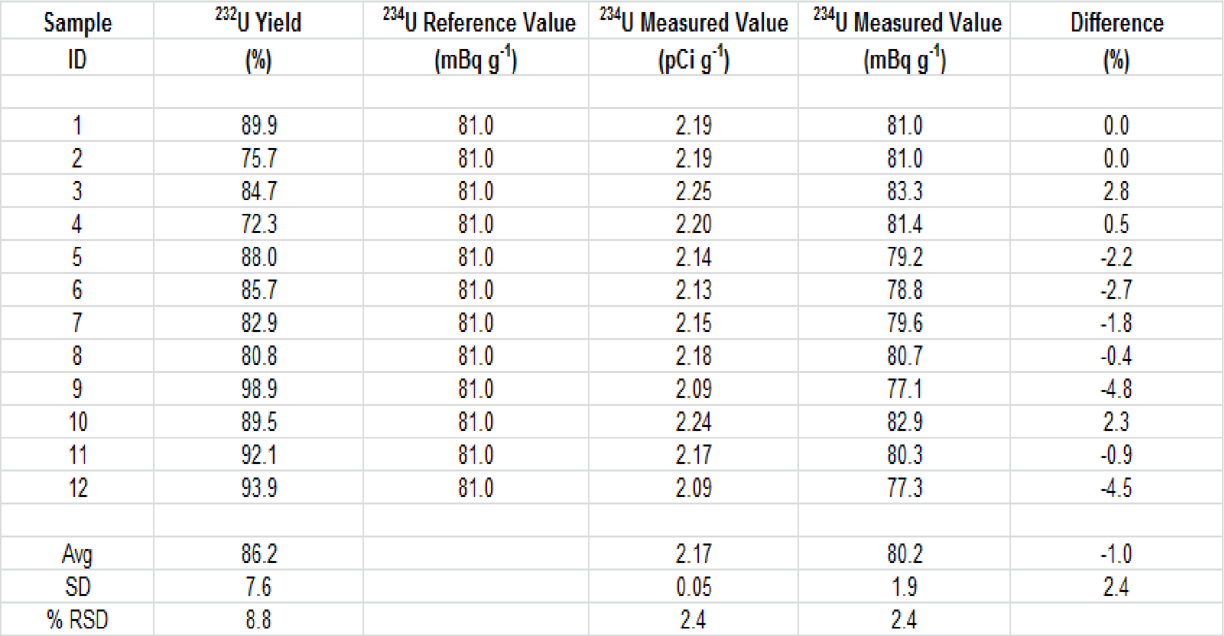
[a] 50mL warm DI water (30mL to dissolve cake, 2 x 10mL crucible rinse)

[b] 10mL 3M HNO_3 (heat at 150-200°C, rinse crucible with 2 x 10mL DI water)

Table 2 Results for U-238 in MAPEP 30 Soil

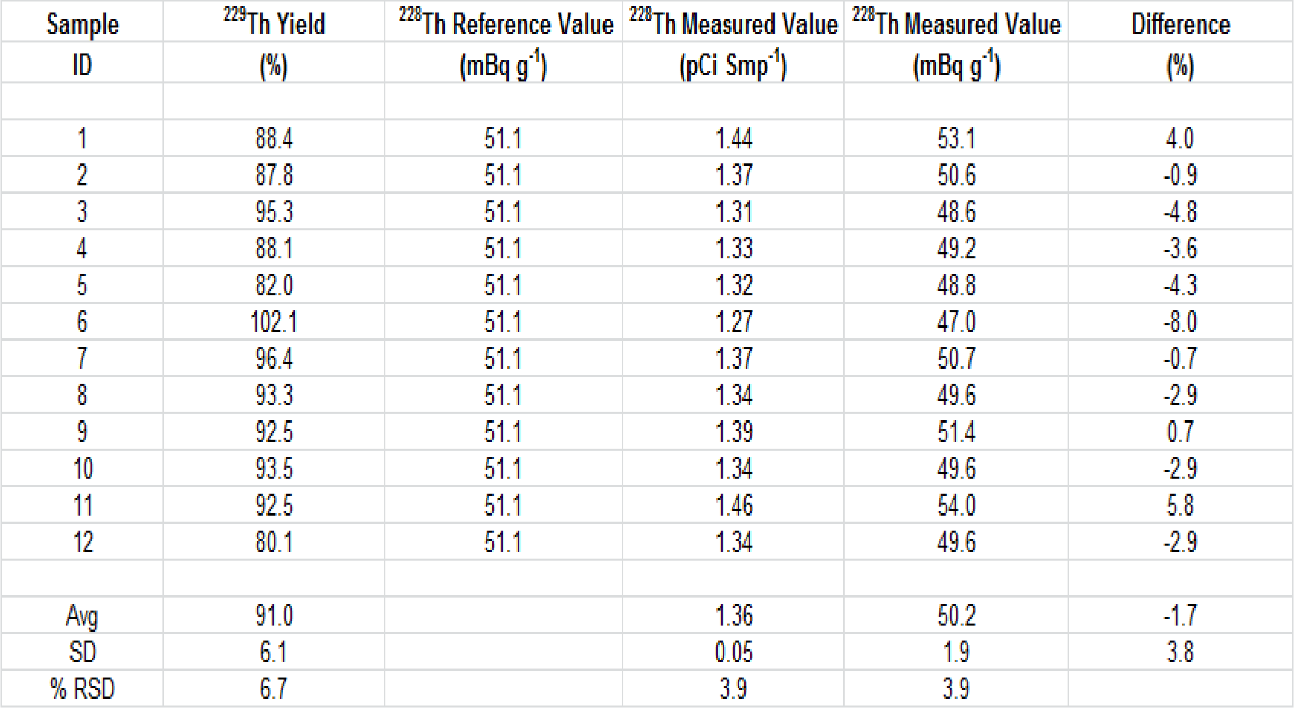
Sample ID	^{232}U Yield (%)	^{238}U Reference Value (mBq g^{-1})	^{238}U Measured Value (pCi g^{-1})	^{238}U Measured Value (mBq g^{-1})	Difference (%)
1	89.9	83.0	2.32	85.7	3.3
2	75.7	83.0	2.36	87.3	5.1
3	84.7	83.0	2.27	84.1	1.4
4	72.3	83.0	2.25	83.3	0.4
5	88.0	83.0	2.27	84.1	1.4
6	85.7	83.0	2.22	82.3	-0.8
7	82.9	83.0	2.33	86.1	3.7
8	80.8	83.0	2.42	89.6	8.0
9	98.9	83.0	2.30	84.9	2.3
10	89.5	83.0	2.42	89.6	8.0
11	92.1	83.0	2.36	87.3	5.1
12	98.8	83.0	2.30	84.9	2.3
Avg	86.6		2.32	85.78	3.35
SD	8.1		0.06	2.32	2.79
% RSD	9.4		2.7	2.7	

Table 3 Results for U-234 in MAPEP 30 Soil



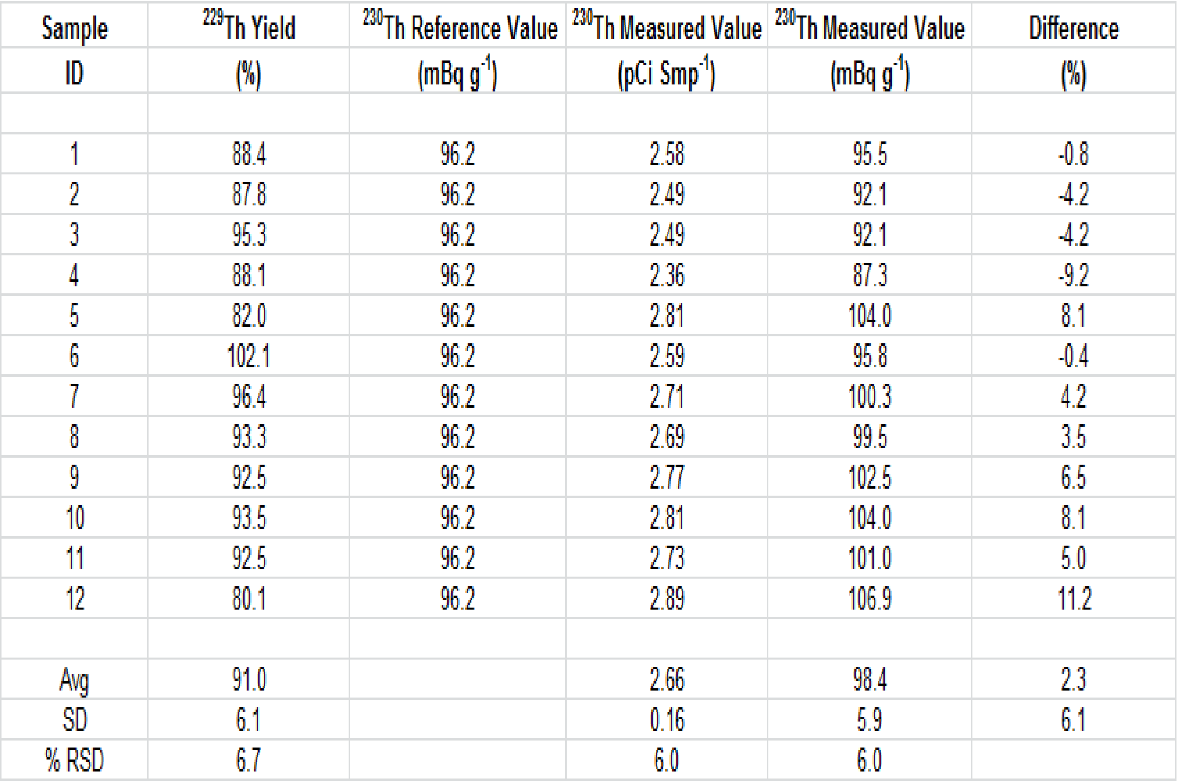
Sample ID	^{232}U Yield (%)	^{234}U Reference Value (mBq g^{-1})	^{234}U Measured Value (pCi g^{-1})	^{234}U Measured Value (mBq g^{-1})	Difference (%)
1	89.9	81.0	2.19	81.0	0.0
2	75.7	81.0	2.19	81.0	0.0
3	84.7	81.0	2.25	83.3	2.8
4	72.3	81.0	2.20	81.4	0.5
5	88.0	81.0	2.14	79.2	-2.2
6	85.7	81.0	2.13	78.8	-2.7
7	82.9	81.0	2.15	79.6	-1.8
8	80.8	81.0	2.18	80.7	-0.4
9	98.9	81.0	2.09	77.1	-4.8
10	89.5	81.0	2.24	82.9	2.3
11	92.1	81.0	2.17	80.3	-0.9
12	93.9	81.0	2.09	77.3	-4.5
Avg	86.2		2.17	80.2	-1.0
SD	7.6		0.05	1.9	2.4
% RSD	8.8		2.4	2.4	

Table 4 Results for Th-228 in MAPEP 30 Soil



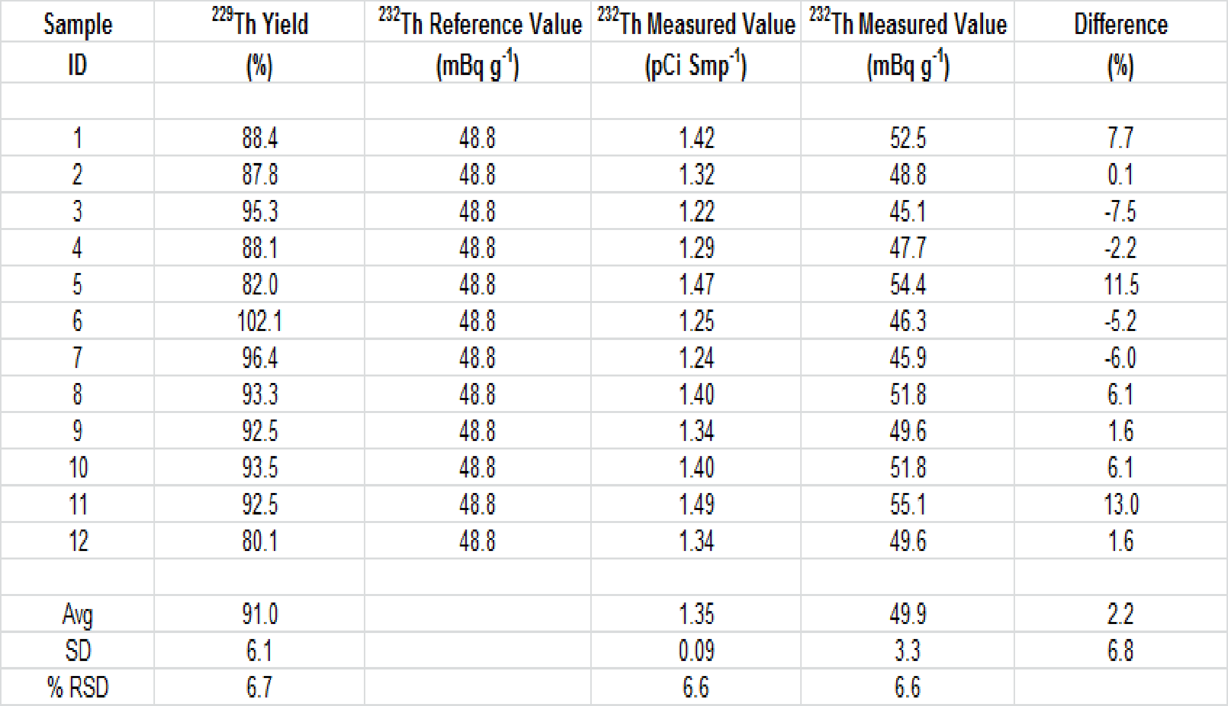
Sample ID	^{229}Th Yield (%)	^{228}Th Reference Value (mBq g^{-1})	^{228}Th Measured Value (pCi Smp^{-1})	^{228}Th Measured Value (mBq g^{-1})	Difference (%)
1	88.4	51.1	1.44	53.1	4.0
2	87.8	51.1	1.37	50.6	-0.9
3	95.3	51.1	1.31	48.6	-4.8
4	88.1	51.1	1.33	49.2	-3.6
5	82.0	51.1	1.32	48.8	-4.3
6	102.1	51.1	1.27	47.0	-8.0
7	96.4	51.1	1.37	50.7	-0.7
8	93.3	51.1	1.34	49.6	-2.9
9	92.5	51.1	1.39	51.4	0.7
10	93.5	51.1	1.34	49.6	-2.9
11	92.5	51.1	1.46	54.0	5.8
12	80.1	51.1	1.34	49.6	-2.9
Avg	91.0		1.36	50.2	-1.7
SD	6.1		0.05	1.9	3.8
% RSD	6.7		3.9	3.9	

Table 5 Results for Th-230 in MAPEP 30 Soil



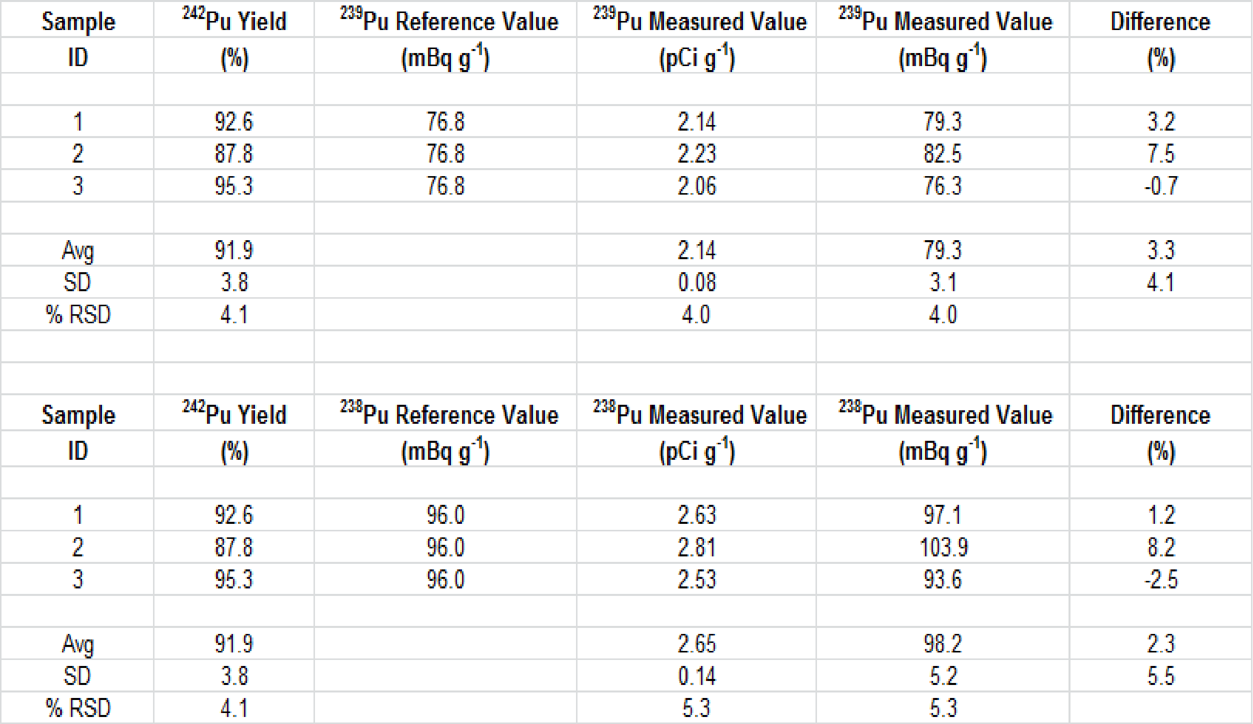
Sample ID	^{229}Th Yield (%)	^{230}Th Reference Value (mBq g^{-1})	^{230}Th Measured Value (pCi Smp^{-1})	^{230}Th Measured Value (mBq g^{-1})	Difference (%)
1	88.4	96.2	2.58	95.5	-0.8
2	87.8	96.2	2.49	92.1	-4.2
3	95.3	96.2	2.49	92.1	-4.2
4	88.1	96.2	2.36	87.3	-9.2
5	82.0	96.2	2.81	104.0	8.1
6	102.1	96.2	2.59	95.8	-0.4
7	96.4	96.2	2.71	100.3	4.2
8	93.3	96.2	2.69	99.5	3.5
9	92.5	96.2	2.77	102.5	6.5
10	93.5	96.2	2.81	104.0	8.1
11	92.5	96.2	2.73	101.0	5.0
12	80.1	96.2	2.89	106.9	11.2
Avg	91.0		2.66	98.4	2.3
SD	6.1		0.16	5.9	6.1
% RSD	6.7		6.0	6.0	

Table 6 Results for Th-232 in MAPEP 30 Soil



Sample ID	^{229}Th Yield (%)	^{232}Th Reference Value (mBq g^{-1})	^{232}Th Measured Value (pCi Smp^{-1})	^{232}Th Measured Value (mBq g^{-1})	Difference (%)
1	88.4	48.8	1.42	52.5	7.7
2	87.8	48.8	1.32	48.8	0.1
3	95.3	48.8	1.22	45.1	-7.5
4	88.1	48.8	1.29	47.7	-2.2
5	82.0	48.8	1.47	54.4	11.5
6	102.1	48.8	1.25	46.3	-5.2
7	96.4	48.8	1.24	45.9	-6.0
8	93.3	48.8	1.40	51.8	6.1
9	92.5	48.8	1.34	49.6	1.6
10	93.5	48.8	1.40	51.8	6.1
11	92.5	48.8	1.49	55.1	13.0
12	80.1	48.8	1.34	49.6	1.6
Avg	91.0		1.35	49.9	2.2
SD	6.1		0.09	3.3	6.8
% RSD	6.7		6.6	6.6	

Table 7 Results for Pu Isotopes in MAPEP 30 Soil



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 (%)
1	92.6	76.8	2.14	79.3	3.2
2	87.8	76.8	2.23	82.5	7.5
3	95.3	76.8	2.06	76.3	-0.7
Avg	91.9		2.14	79.3	3.3
SD	3.8		0.08	3.1	4.1
% RSD	4.1		4.0	4.0	
Sample ID	**^{242}Pu Yield (%)**	**^{238}Pu Reference Value (mBq g^{-1})**	**^{238}Pu Measured Value (pCi g^{-1})**	**^{238}Pu Measured Value (mBq g^{-1})**	**Difference (%)**
1	92.6	96.0	2.63	97.1	1.2
2	87.8	96.0	2.81	103.9	8.2
3	95.3	96.0	2.53	93.6	-2.5
Avg	91.9		2.65	98.2	2.3
SD	3.8		0.14	5.2	5.5
% RSD	4.1		5.3	5.3	