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Determination of ^{237}Np and Pu isotopes in Large Soil Samples by Inductively-Coupled

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Plasma Mass Spectrometry

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Abstract

A new method for the determination of ^{237}Np and Pu isotopes in large soil samples has been developed that provides enhanced uranium removal to facilitate assay by inductively coupled plasma mass spectrometry (ICP-MS). This method allows rapid preconcentration and separation of plutonium and neptunium in large soil samples for the measurement of ^{237}Np and Pu isotopes by ICP-MS. ^{238}U can interfere with ^{239}Pu measurement by ICP-MS as $^{238}\text{UH}^+$ mass overlap and ^{237}Np via ^{238}U peak tailing. The method provides enhanced removal of uranium by separating Pu and Np initially on TEVA Resin, then transferring Pu to DGA resin for additional purification. The decontamination factor for removal of uranium from plutonium for this method is greater than 1×10^6 . Alpha spectrometry can also be applied so that the shorter-lived ^{238}Pu isotope can be measured successfully. ^{239}Pu , ^{242}Pu and ^{237}Np were measured by ICP-MS, while ^{236}Pu and ^{238}Pu were measured by alpha spectrometry.

Introduction

Inductively-coupled plasma mass spectrometry is a powerful tool for the analysis of plutonium isotopes and ^{237}Np in environmental samples. The measurement time for sequential assay by ICP-MS is typically shorter than alpha spectrometry, although the alpha spectrometry measurements may be performed simultaneously with large numbers of detectors. ICP-MS can, however, be hampered by isobaric, polyatomic interferences and signal suppression and have limited effectiveness for relatively short-lived actinide isotopes at low concentrations, for example, ^{238}Pu . [1]

For soil samples in particular, which can contain large amounts of ^{238}U , the measurement of ^{239}Pu can be hampered significantly due to $^{238}\text{UH}^+$ hydride formation and

^{238}U peak tailing. To a lesser extent, ^{238}U can also interfere with ^{237}Np via peak tailing

Both alpha spectrometry and ICP-MS techniques may require separation of sample matrix interferences to determine ^{237}Np and Pu isotopes accurately, depending on the sample matrix and the detection limit required. Kim et al noted that the ^{238}U level in the purified solutions should be less than 100 pg mL^{-1} to minimize spectral interference in the quantitative analysis of ^{239}Pu and ^{237}Np . [2]

There are a number of analytical methods reported that use ion exchange/extraction chromatography to determine actinides in soil. Hou et al. [3] surveyed a wide range of separation methods for Pu in environmental samples. Methods included varied combinations of ion exchange and/or extraction chromatographic techniques. Chemical recoveries for Pu typically varied between 40-85%, often ~60% or less even for smaller sample sizes. When a soil matrix removal/preconcentration step for larger soil samples is not used, lower actinide yields can occur. Mellado et al [4] reported an analytical method for 2 to 5g marine sediment samples using TRU Resin[®] to separate the actinides. While the overall Pu isotope results for IAEA soil standard were very good, the average chemical yield was only about 40%.

Qiao et al [5] described an interesting method for the determination of plutonium isotopes in soil samples using sequential injection chromatography and ICP-MS. Chemical yields were good for 10 g samples ($99.9\% \pm 12.6$ at 1 SD) and 100 g samples ($77\% \pm 12.6$ at 1 SD), with decontamination factors of 6.4×10^4 and 3.8×10^4 for ^{238}U respectively. The method used aqua regia leaching, iron hydroxide precipitation to remove much of the soil matrix, and acid conversion from HCl to HNO_3 . This work reported some difficulty reducing Pu to Pu^{+3} using ascorbic acid, thus the use of potassium disulfite instead. This difficulty may have been the result of adding only 200 mg of ascorbic acid, which may not have been enough reductant to reduce the amount of

Fe^{+3} ions present in large soil samples to Fe^{+2} . In addition, sulfamic acid, often used in concert with ascorbic acid, was not added to scavenge nitrite ions present in nitric acid, which would also have interfered with the reduction step. The potassium disulfite reduction step worked well, but interestingly a more time-consuming ferrous hydroxide precipitation was integrated into this valence adjustment. Though taking additional time, further sample matrix removal likely helped improve chemical yields. A 2M HCl solution containing $\text{NH}_2\text{OH}\cdot\text{HCl}$ reductant was employed to facilitate Pu stripping from TEVA Resin, and the final eluant solution had to be evaporated and redissolved prior to measurement.

Röllin et al. [6] reported a method for Pu and Np analyses in soil using ICP-MS. Following a lithium borate fusion of 5 g samples, samples were redissolved in 4.5M HNO_3 and PEG (polyethylene glycol) was used to precipitate the silicates, which were removed by filtering. The method employed large rinse volumes relative to the 2 mL TEVA Resin used, including a 100 mL 3M HNO_3 -0.1mM Fe^{+2} rinse solution. Use of Fe^{2+} reductant in 3M HNO_3 is normally applied only when reduction of Pu to unretained Pu^{3+} is desired so that Np can be separated from Pu. The use of 3M HNO_3 -0.1mM Fe^{2+} rinse solution and Fe^{2+} in the column load solution without subsequent addition of an oxidant is perplexing. The use of such a low concentration of Fe^{2+} in 3M HNO_3 without the presence of ascorbic acid may have accounted for the apparent lack of reduction of Pu to unretained Pu^{3+} . The Pu and Np were eluted using a dilute HNO_3 -HF mixture, which included 0.01mM Fe^{2+} reductant. Chemical yields were 50-80%, with Np yields 75-80% of the Pu yields. This is likely due to the lower retention of Np^{4+} vs. Pu^{4+} on TEVA Resin and the large volume of rinse utilized. Plutonium yields may have also been adversely affected to a slight extent by the use of Fe^{2+} reductant during column load and rinse steps. A decontamination factor of ~20,000 from uranium was achieved.

Tavčar et al reported a method to determine actinides in soil. [7] Soil and sediment samples up to 10g were leached using strong nitric acid, filtration, evaporation, and the residue was redissolved in 1M HNO₃. The valence adjustment was performed using hydroxylamine hydrochloride to reduce Pu to Pu³⁺, followed by sodium nitrite to oxidize Pu to Pu⁴⁺. The acid concentration was increased to 8M HNO₃ 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%. The low Np yields were attributed to poor valence control of Np⁴⁺.

We have previously reported a method in the SRS (Savannah River Site) Environmental Laboratory to determine Pu and Am isotopes in 100-200g soil samples using alpha spectrometry, but a fusion of the soil leachate was used in this process and ²³⁷Np was not investigated in this work. [8]

A new method has been developed that allows the separation of Pu isotopes and ²³⁷Np in large soil samples with very good chemical yields and enhanced removal of uranium to allow accurate measurement by ICP-MS. This Pu and Np in soil method utilizes an acid leaching method, iron/titanium hydroxide precipitation, a lanthanum fluoride soil matrix removal step, and a rapid column separation process with TEVA Resin [9]. Np is also recovered effectively along with Pu due to rigorous valence control of Np as Np⁴⁺ using Ti³⁺ reductant during the iron/titanium hydroxide and lanthanum fluoride precipitations. The rapid separation method uses a TEVA cartridge (2 mL) to separate plutonium and neptunium initially, followed by additional decontamination of Pu from ²³⁸U using DGA Resin. ²³⁹Pu, ²⁴²Pu, ²³⁷Np were measured by ICP-MS, while ²³⁶Pu and ²³⁸Pu were measured by alpha spectrometry. No correction for ²³⁸U interference was necessary because of the high decontamination factors achieved.

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). 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 ²³⁹Pu, ²⁴²Pu, ²³⁷Np, ²³⁸Pu were obtained from Eckert & Ziegler Analytics, Inc. (Atlanta, GA, USA) and diluted to the appropriate levels. ²³⁶Pu was obtained from the National Physical Laboratory (Teddington, UK). A 1000 mg L⁻¹ uranium standard was obtained from SpexCertiprep, Inc., Metuchen, NJ, USA.

Procedures

Column preparation. TEVA Resin was obtained as cartridges containing 2 mL of each resin from Eichrom Technologies, Inc.. Small particle size (50-100 micron) resin was employed, along with a vacuum extraction system (Eichrom Technologies).

Sample Preparation. Soil samples obtained from a location near the Savannah River Site (Aiken, SC, USA) were dried at 110 °C and blended prior to taking sample aliquots. Six 20 g soil samples (soil A), six 50 g samples (soil B) and four 75 g soil sample aliquots (soil B) were analyzed. Samples were aliquoted into large glass beakers.

Known amounts of ²³⁷Np and Pu isotopes were pipetted into each 20 g soil sample to demonstrate performance for both neptunium and plutonium analysis using this method. Uranium removal is particularly important when analyzing for ²³⁹Pu. To

perform additional uranium removal testing with even larger amounts of ^{238}U present, 50g and 75g soil samples were also analyzed, but these samples were spiked only with Pu isotopes. ^{236}Pu (46.2 mBq) and ^{242}Pu (298 mBq) tracers were added to each sample. The uncertainties associated with the known values of ^{237}Np and Pu isotopes added is $\sim 1\%$ at the 95% confidence level.

Figure 1 provides a flow chart of the soil sample preparation method, which was previously been reported for analysis of ^{237}Np and Pu isotopes by alpha spectrometry.[9] This method utilizes iron/titanium hydroxide and lanthanum fluoride precipitations to remove the soil matrix and preconcentrate ^{237}Np and Pu isotopes. Valence adjustment of the column load solution was performed by adding 0.5 mL 1.5M sulfamic acid, 0.4 mL of 5 mg mL^{-1} Fe as ferric nitrate and 1.25 mL 1.5M ascorbic acid with a three minute wait step to reduce plutonium to Pu^{3+} . The iron added, which is converted to Fe^{2+} by ascorbic acid, was added to facilitate rapid ^{237}Np reduction to Np^{4+} . To oxidize plutonium to Pu^{4+} , 1 mL 3.5M sodium nitrite was added to each sample solution. The kinetics of oxidation of Np to Np^{5+} in the presence of sodium nitrite, are negligible at room temperature.

Column separation. After the valence adjustment, the sample solution was loaded onto the TEVA column at approximately ~ 1 drop per second. After the sample was loaded, a beaker rinse of ~ 3 mL 3M HNO_3 was transferred to the TEVA column and allowed to pass through the resin at ~ 2 drops per second. The column reservoirs were changed at this point to remove any residual uranium still on the reservoir walls was eliminated. This allows subsequent column rinses to be free of uranium when they contact the TEVA Resin itself for maximum uranium removal. A rinse of 15 mL 3M HNO_3 was added directly to the TEVA column at ~ 2 drops per second. To maximize uranium removal on TEVA Resin, the TEVA cartridge was rinsed again with 15 mL 3M

nitric acid at ~2 drops per second. To elute thorium from TEVA Resin, 15 mL 9M hydrochloric acid was added at ~1-2 drops per second.

DGA Resin cartridges were placed below each TEVA cartridge. This was done only after the sample had been loaded and rinsed on TEVA Resin to minimize the amount of uranium that contacted DGA Resin. To each stacked TEVA+DGA column 15 mL of 3M HNO₃-0.1M ascorbic acid-0.02M ferrous nitrate (freshly prepared) was added at 1 drop per second to reduce Pu⁴⁺ to Pu³⁺. This step transfers unretained Pu³⁺ from TEVA Resin onto DGA Resin, which has very high retention of trivalent and tetravalent actinides in 3M HNO₃. After this step, the DGA cartridges were disconnected from the TEVA Resin cartridges and rinsed slowly with 5 mL 8M HNO₃ (1 drop per second or less) to oxidize Pu³⁺ back to Pu⁴⁺. This oxidation enhances retention of Pu on DGA Resin during very low nitric acid rinses which were used to optimize uranium removal. The retention of trivalent actinides such as Pu³⁺ is still relatively high at low nitric acid concentrations (~50-100 k') on DGA Resin, but the k' for Pu⁴⁺ is much higher (~1000 at 0.05M HNO₃). [10] DGA Resin was rinsed with 20 mL 0.1M HNO₃, followed by 10 mL 0.05M HNO₃ to remove residual uranium.

The plutonium was eluted from the DGA Resin cartridges with 11 mL 0.02M HCL-0.005M HF-0.0001M titanium (III) chloride strip solution. Ti(III) reductant was used to reduce Pu to Pu³⁺, which can be eluted easily in dilute HCL. Trace level Ti(III) effectively strips Pu from DGA Resin and is compatible with ICP-MS analysis. Typically, when a tracer is used in this laboratory, no volume adjustment is made and 12 mL would be added directly to the column and collected. The final volume was adjusted to exactly 12 mL after elution so that exactly 1/3 of the eluant volume could be taken for alpha spectrometry.

The purified solutions were analyzed by alpha spectrometry and ICP-MS. Four milliliters of each plutonium eluant solution was transferred to a separate 50 mL tube, and diluted to 10 mL with 0.25M HCL. Fifty micrograms of cerium as cerium nitrate were added to the tubes, along with 1 mL concentrated hydrofluoric acid (49%). After waiting 15 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene filters (Resolve[®] filter-Eichrom Technologies) and counted by alpha spectrometry. The remaining solution was transferred to the ICP-MS for measurement of Pu isotopes.

The TEVA cartridges were placed on a separate vacuum box and processed at the same time as the DGA Resin cartridges to minimize sample processing time. Five milliliters of 3M HNO₃ were added to each TEVA column to remove residual ferrous ions. at ~2 drops per second. This step was included to minimize the residual iron introduced into the ICP-MS. The ²³⁷Np was eluted from the TEVA Resin cartridges with 14 mL of 0.25M HCL-0.005M HF-0.001M titanium (III) chloride strip solution. The elution of ²³⁷Np seemed to be enhanced with Ti(III) present, presumably displacing Np(IV) on TEVA Resin to some extent as an anionic titanium complex. After elution this volume was adjusted to exactly 15 mL so that an accurate volume could be obtained since no tracer was used for ICP-MS analysis of ²³⁷Np. To minimize uranium contamination, the vacuum box lids were kept very clean and connector tips through the box lid were replaced just prior to final elution.

Apparatus

Plutonium analyses were also performed by alpha-particle pulse-height measurements using Passivated Implanted Planar Silicon (PIPS) detectors (16 hour count

time). The PIPS detectors have an active surface area of 450 mm². 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.

An Agilent Quadrupole ICP-MS with octopole collision cell was used to perform the ICP-MS measurements. The octopole was operated in the “no gas” mode; instrument operating conditions are shown in Table 1.

The ICP-MS methodology is described in American Society for Testing and Materials (ASTM) Vol. 12.01, C1590-04 (2009) "Standard Practice for Alternate Actinide Calibration for Inductively Coupled Plasma-Mass Spectrometry". [11] The calibration is mass bias adjusted using ²³²Th and ²³⁸U standards. At each standard concentration, the slope of the line defined by ²³²Th and ²³⁸U is used to derive linear calibration curves for each mass of interest (amu 232-244) using interference equations. The mass bias corrected calibration curves, although generated from interference equations, are specific to the instrument operating parameters and tuning in effect at the time of data acquisition. One of the benefits of this standard practice is the ability to calibrate for the analysis of highly radioactive actinides using calibration standards at much lower specific activities.

Results and Discussion

Table 2 shows the individual results for the determination of ²³⁹Pu in six 20 g soil samples (soil A). The ²³⁹Pu results were corrected for ²⁴²Pu tracer yield. The individual results are given to show very good repeatability. The average ²³⁹Pu result was 0.030 ng

mL⁻¹, with a -0.25% bias and 1SD (standard deviation) of 0.0004. The average tracer recovery for ²⁴²Pu was 87.2% ± 3.9% at 1SD. The reference and measured values represent the final concentration of ²³⁹Pu in the purified solution at the ICP-MS.

Table 3 shows the results for the determination of ²³⁸Pu for the same 20 g soil samples using alpha spectrometry. The average ²³⁸Pu result was 0.064 Bq per 20g sample, with a -1.2% bias and 1SD of 0.0004. The average tracer recovery for ²³⁶Pu was 84.3% ± 3.0% at 1SD. The ²³⁶Pu tracer corrections were applied to the ²³⁹Pu results sample results. While ²⁴²Pu tracer could also have been applied, ²³⁶Pu tracer was added to in this work to include an additional Pu isotope. It should be noted that 0.0644 Bq ²³⁸Pu in final 12 mL volume is equivalent to 8.5 x10⁻⁶ ng mL⁻¹, illustrating why alpha spectrometry was used to determine ²³⁸Pu instead of ICP-MS.

Table 4 shows the results for the determination of ²³⁷Np for the six 20 g soil samples using ICP-MS. The ²³⁷Np results were not corrected for tracer yield. The average ²³⁷Np result was 0.062 ng mL⁻¹, with a -14.8% average difference and 1SD of 0.004. The Np yield (~85%) is comparable to the Pu tracer yield in Table 2. A yield correction for ²³⁷Np could easily have been made using ²³⁹Np, eliminating the negative bias.

The following results illustrate that Pu yields and uranium removal is adequate even for larger soil samples. The 50g and 75 g soil aliquots were taken from a different soil sample (soil B). Table 5 shows the results for the determination of ²³⁹Pu for six 50 g soil sample aliquots. The average ²³⁹Pu result was 0.030 ng mL⁻¹, with a 0.75% bias and 1SD of 0.0005. The average tracer recovery for ²⁴²Pu was 74.9% ± 5.8% at 1SD. The ²⁴²Pu tracer corrections were applied to the sample results.

Table 6 shows the results for the determination of ²³⁹Pu for the four 75 g soil samples. The average ²³⁹Pu result was 0.030 ng mL⁻¹, with a 0.75% bias and 1SD of 0.0003. The

average tracer recovery for ^{242}Pu was $70.2\% \pm 3.3\%$ at 1SD. The ^{242}Pu tracer corrections were applied to the sample results.

Table 7 shows ^{238}U decontamination factors achieved using this method on the 20 g, 50 g and 75 g aliquot analyses. ^{238}U was measured by ICP-MS to determine uranium decontamination in the purified fractions for the 20 g, 50 g, and 75 g sample aliquots. The total ^{238}U in 20 g aliquot of soil A was determined by routine analysis method [12] to be 0.39 ± 0.06 Bq (3.13×10^4 ng). The total ^{238}U for the 50 g and 75 g aliquots of soil B was 0.83 ± 0.13 Bq (6.68×10^4 ng) and 1.25 ± 0.20 Bq (1.00×10^5 ng) respectively. The equivalent ^{238}U sample values for each sample aliquot were calculated for the final ^{239}Pu eluant solutions (12mL) and ^{237}Np eluant solutions (15 ml) at the ICP-MS. The average decontamination factors for the overall method were determined based on ICP-MS measurements shown for ^{238}U in those solutions. The average ^{238}U found in the purified ^{237}Np eluant solutions was $0.0265 \text{ ng mL}^{-1} \pm 0.0005$ at 1SD. The average decontamination factor for the 20 g ^{237}Np eluant solutions was 7.9×10^4 .

Since no detectable ^{238}U was detected in the 20g ^{239}Pu eluant solutions, it was difficult to calculate the exact decontamination factor. But if the ^{238}U value is assumed to be $<0.0012 \text{ ng mL}^{-1}$ ($-0.0008 \text{ ng mL}^{-1} + 5\text{SD}$), the average decontamination factor can still be estimated to be $>2.2 \times 10^6$ for ^{238}U from ^{239}Pu . The average ^{238}U found in the purified ^{239}Pu eluant solutions for the 50g sample aliquots was $0.0055 \text{ ng mL}^{-1} \pm 0.0002$ at 1SD. This is equivalent to an average decontamination factor of 1.0×10^6 of ^{238}U from ^{239}Pu for the overall method.

The average ^{238}U found in the purified ^{239}Pu eluant solutions for the 75g sample aliquots was $0.0057 \text{ ng mL}^{-1} \pm 0.0006$ at 1SD. This is equivalent to an average decontamination factor of 1.5×10^6 of ^{238}U from ^{239}Pu . It is estimated from experience in this laboratory that only about 50% of the uranium in the soil is removed using acid

leaching. Even accounting for this initial reduction in ^{238}U , the decontamination factors using this two step column process are very good and are less than the recommended maximum amount of $0.100 \text{ ng } ^{238}\text{U mL}^{-1}$ in the purified solutions [2].

Table 8 shows method LLD (lower limit of detection) and LLQ (lower limit of quantitation) values for the different isotopes by ICP-MS using the 20 g, 50 g and 75 g sample aliquots. The LLD and LLQ results were calculated using the equations as prescribed by Taylor. [13] The method concentration factors for a 20 g soil aliquot were 1.33 and 1.67 for ^{237}Np and ^{239}Pu respectively. The method concentration factors for ^{239}Pu using 50 g and 75 g soil aliquots were 4.17 and 6.25 respectively. The LLD values for ^{239}Pu using 50 g and 75 g soil aliquots were 1.2 pg g^{-1} and 0.7 pg g^{-1} . It should be noted that the eluant solutions were not evaporated to reduce volume. The volumes could have been evaporated and redissolved in very small volume and introduced with a microinjection system to further decrease the LLD. The purpose of this work was to demonstrate enhanced uranium removal with good chemical yields on large soil samples. This method can be adapted, however, for use with other ICP-MS units (ex. double focusing sector field ICP-MS) with enhanced sample introduction techniques as needed to lower the LLD.

The MDA (Minimum Detectable Activity) for the actinide isotopes by alpha spectrometry were calculated according to equations prescribed by Currie: [14]

$$\text{MDA} = [3 + 4.65\sqrt{B}] / (\text{CT} * \text{R} * \text{V} * \text{Eff} * 0.060)$$

Where B = Total Background counts, = BKG (rate) * BKG Count time

CT = sample count time (min)

R = Chemical Recovery

V = Sample aliquot (g)

EFF = Detector Efficiency

0.060 = conversion from dpm to mBq

In low-level counting, where a zero background count is quite common, the constant 3 is used to prevent an excessively high false positive rate.

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 50 g sample aliquot, the method MDA for ^{238}Pu with a 16 hour count time is 0.007 mBq g^{-1} .

Depending on the MDA required, the sample aliquot and count time may be adjusted accordingly.

Figure 3 shows an example of the spectra for a large soil sample. The ^{236}Pu tracer recovery was 80.1% and the Full Width Half Maximum (FWHM) was 35.2 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.

Conclusions

A new method to determine ^{237}Np and Pu isotopes has been developed that allows the separation of ^{237}Np and Pu isotopes in large soil samples with high chemical yields and enhanced decontamination from uranium. Purified solutions are split between ICP-MS and alpha spectrometry so that longer-lived Pu isotopes as well as ^{238}Pu can be measured successfully. The method offers good chemical recoveries and excellent removal of interferences, particularly ^{238}U . A decontamination factor for uranium of greater than 1×10^6 can be achieved using a simple, two step column separation process to eliminate or minimize the $^{238}\text{UH}^+$ interference on ^{239}Pu .

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Table Captions

Table 1 Operating Conditions for Agilent 7500 ICP-MS

Table 2	^{239}Pu results for 20 g samples by ICP-MS
Table 3	^{238}Pu results for 20 g samples by alpha spectrometry
Table 4	^{237}Np results for 20 g samples by ICP-MS
Table 5	^{239}Pu results for 50 g samples by ICP-MS
Table 6	^{239}Pu results for 75 g samples by ICP-MS
Table 7	^{238}U Decontamination Factor Results
Table 8	LLD and LLQ ICP-MS Results Using Different Soil Aliquots

Table 1 Operating Conditions for Agilent 7500 ICP-MS

Plasma Conditions

RF Power	1300 W
RF Matching	1.7 V
Torch Depth	6 mm
Plasma Gas	15 L min ⁻¹
Carrier Gas	1 L min ⁻¹

Sample Pump 0.1 rps

Ion Lenses

Extract 1	-195 V
Extract 2	-100 V
Einzel 1, 3	-100 V
Einzel 2	18 V
Omega Bias	-33 V
Omega (+)	11 V
Omega (-)	8 V
QP Focus	12 V
Plate Bias	-36 V

Q-Pole

AMU Gain	122
AMU Offset	124
Axis Gain	0.999
Axis Offset	0.04
QP Bias	0 V

Detector

Discriminator	8.7 V
Analog HV	1820 V
Pulse HV	1230 V

Typical Tune

Counts	>100,000 cps Tl-205 at 10 ug L ⁻¹
RSD%	< 5%
Oxide 156/140	< 1%
Background	< 10 cps at Tl-205
Resolution	0.65 - 0.80 amu at 10% peak height

Data Acquisition

Integration	0.33 sec pt ⁻¹ , 3 pt amu ⁻¹ , 0.99 sec amu ⁻¹
Replicates	6

Table 2 ^{239}Pu results for 20g samples by ICP-MS

Sample ID	^{242}Pu Tracer Recovery (%)	^{239}Pu Reference Value (ng ml $^{-1}$)	^{239}Pu Measured Value (ng ml $^{-1}$)	Difference (%)
1	86.2	0.0302	0.0302 ± 0.003	-0.15
2	89.9	0.0302	0.0300 ± 0.003	-0.77
3	91.2	0.0302	0.0298 ± 0.003	-1.34
4	87.5	0.0302	0.0308 ± 0.003	2.03
5	88.7	0.0302	0.0299 ± 0.003	-0.96
6	80.1	0.0302	0.0301 ± 0.003	-0.30
Avg.	87.2		0.030	-0.25
SD	3.9		0.0004	
% RSD	4.5		1.2	

Concentration (ng mL $^{-1}$) in final solution at ICP-MS

Table 3 ^{238}Pu results for 20g samples by alpha spectrometry

Sample ID	^{236}Pu Yield (%)	^{238}Pu Reference Value (Bq)	^{238}Pu Measured Value (Bq)	Difference (%)
1	77.9	0.0644	0.061 ± 0.009	-4.6
2	84.3	0.0644	0.062 ± 0.009	-4.0
3	85.4	0.0644	0.067 ± 0.010	4.0
4	86.3	0.0644	0.063 ± 0.009	-2.3
5	87.1	0.0644	0.063 ± 0.009	-1.7
6	84.9	0.0644	0.065 ± 0.010	1.1
Avg.	84.3		0.064	-1.2
SD	3.0		0.002	
%RSD	3.5		3.0	

0.0644 Bq ^{238}Pu in 12 mL final volume = 8.5 x 10 $^{-6}$ ng mL $^{-1}$

Table 4 ^{237}Np results for 20g samples by ICP-MS

Sample ID	^{237}Np Reference Value (ng mL ⁻¹)	^{237}Np Measured Value (ng mL ⁻¹)	Difference (%)
1	0.0730	0.0607 ± 0.006	-16.8
2	0.0730	0.0656 ± 0.006	-10.1
3	0.0730	0.0666 ± 0.006	-8.8
4	0.0730	0.0631 ± 0.006	-13.6
5	0.0730	0.0592 ± 0.006	-18.9
6	0.0730	0.0581 ± 0.006	-20.4
Avg.		0.062	-14.8
SD		0.003	
% RSD		5.6	

Concentration (ng mL⁻¹) in final solution at ICP-MS

No tracer correction

Table 5 ^{239}Pu results for 50g samples by ICP-MS

Sample ID	^{242}Pu Tracer Recovery (%)	^{239}Pu Reference Value (ng mL ⁻¹)	^{239}Pu Measured Value (ng mL ⁻¹)	Difference (%)
1	71.4	0.0302	0.0314 ± 0.003	3.84
2	78.2	0.0302	0.0301 ± 0.003	-0.21
3	72.7	0.0302	0.0301 ± 0.003	-0.24
4	75.1	0.0302	0.0303 ± 0.003	0.18
5	67.7	0.0302	0.0306 ± 0.003	1.38
6	84.4	0.0302	0.0301 ± 0.003	-0.44
Avg.	74.9		0.030	0.75
SD	5.8		0.0005	
% RSD	7.8		1.6	

Concentration (ng mL⁻¹) in final solution at ICP-MS

Table 6 ²³⁹Pu results for 75g samples by ICP-MS

Sample ID	²⁴² Pu Tracer Recovery (%)	²³⁹ Pu Reference Value (ng mL ⁻¹)	²³⁹ Pu Measured Value (ng mL ⁻¹)	Difference (%)
1	65.3	0.0302	0.0302 ± 0.003	-0.13
2	72.7	0.0302	0.0306 ± 0.003	1.21
3	71.4	0.0302	0.0301 ± 0.003	-0.45
4	71.4	0.0302	0.0298 ± 0.003	-1.43
Avg.	70.2		0.030	-0.20
SD	3.3		0.0003	
% RSD	4.8		1.1	

Concentration (ng mL⁻¹) in final solution at ICP-MS

Table 7 ^{238}U Decontamination Factor Results

Sample	Isotope	^{238}U in sample ng mL ⁻¹	^{238}U measured ng mL ⁻¹	Decontamination Factor
Soil A - 20g	^{237}Np eluant	2.09×10^3	0.0265 ± 0.0050	7.9×10^4
Soil A - 20g	^{239}Pu eluant	2.61×10^3	* -0.0008 ± 0.0004	$>2.2 \times 10^6$
Soil B - 50g	^{239}Pu eluant	5.56×10^3	0.0055 ± 0.0020	1.0×10^6
Soil B - 75g	^{239}Pu eluant	8.34×10^3	0.0057 ± 0.0006	1.5×10^6

20g, 50g - N=6, \pm values 1SD

75g - N=4, \pm values 1SD

Concentration (ng mL⁻¹) in final solution at ICP-MS

^{237}Np eluant volume = 15 ml

^{239}Pu eluant volume = 12 ml

* assume less than $0.0012 \text{ ng mL}^{-1}$ ($-0.0008 + 5 \times \text{SD}$)

Table 8 LLD and LLQ ICP-MS Results Using Different Soil Aliquots

	²³⁷ Np (pg g ⁻¹)	²³⁹ Pu (pg g ⁻¹)	²³⁹ Pu (pg g ⁻¹)	²³⁹ Pu (pg g ⁻¹)
Sample aliquot (g)	20	20	50	75
Final eluent volume (ml)	15	12	12	12
Method concentration factor (g ml ⁻¹)	1.33	1.67	4.17	6.25
Overall method LLD (pg g ⁻¹)	8.7	2.2	1.2	0.7
Overall method LLQ (pg g ⁻¹)	29.2	7.3	4.0	2.4

Figure Captions

Fig. 1 Rapid Sample Preparation for Large Soil Samples

Fig. 2 Rapid Column Separation for Large Soil Samples

Fig. 3 Alpha spectra for ^{237}Np and Pu Isotopes in Large Soil Sample

Figure 1 Rapid Soil Sample Preparation for Large Soil Samples

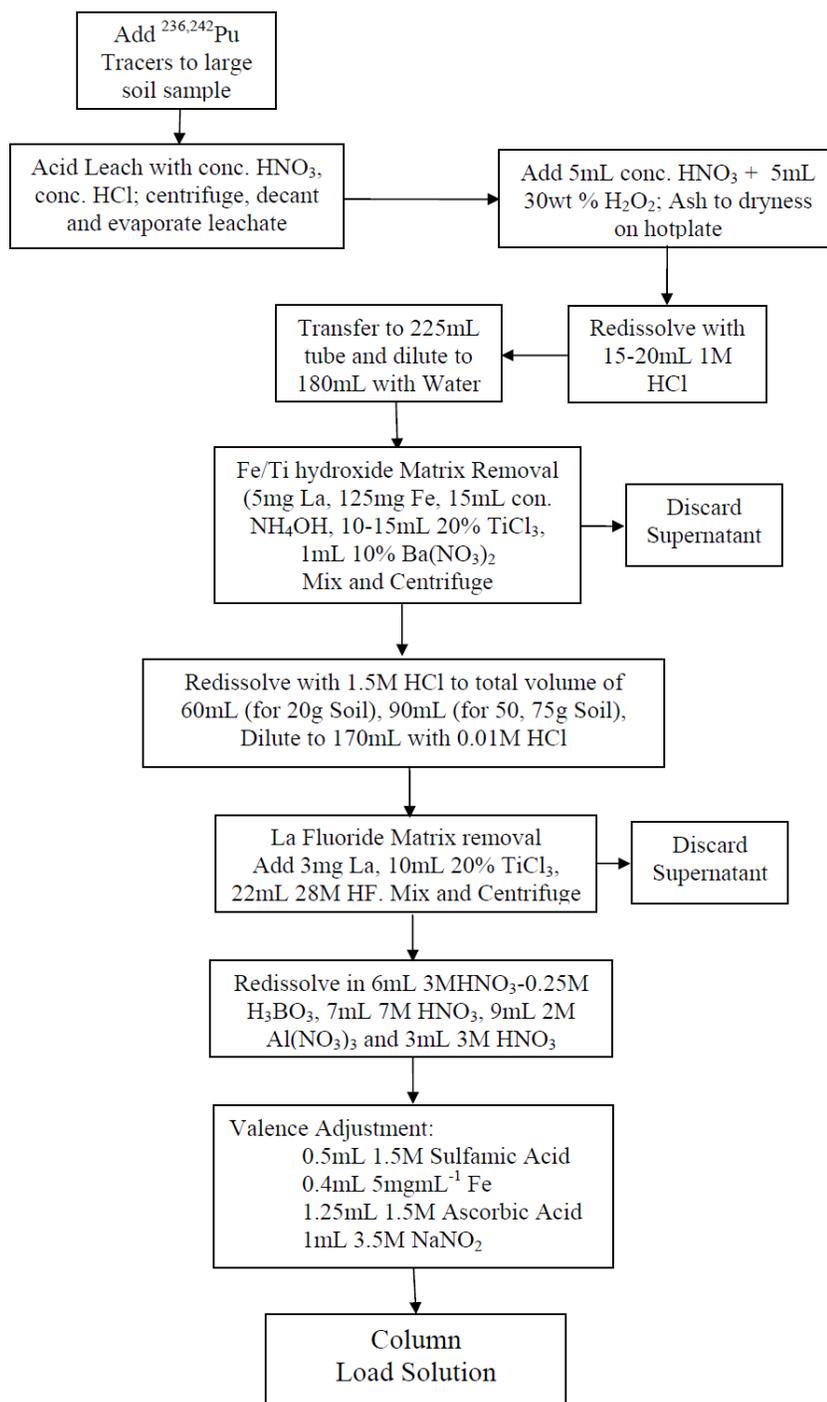


Figure 2 Rapid Column Separation for Large Soil Samples

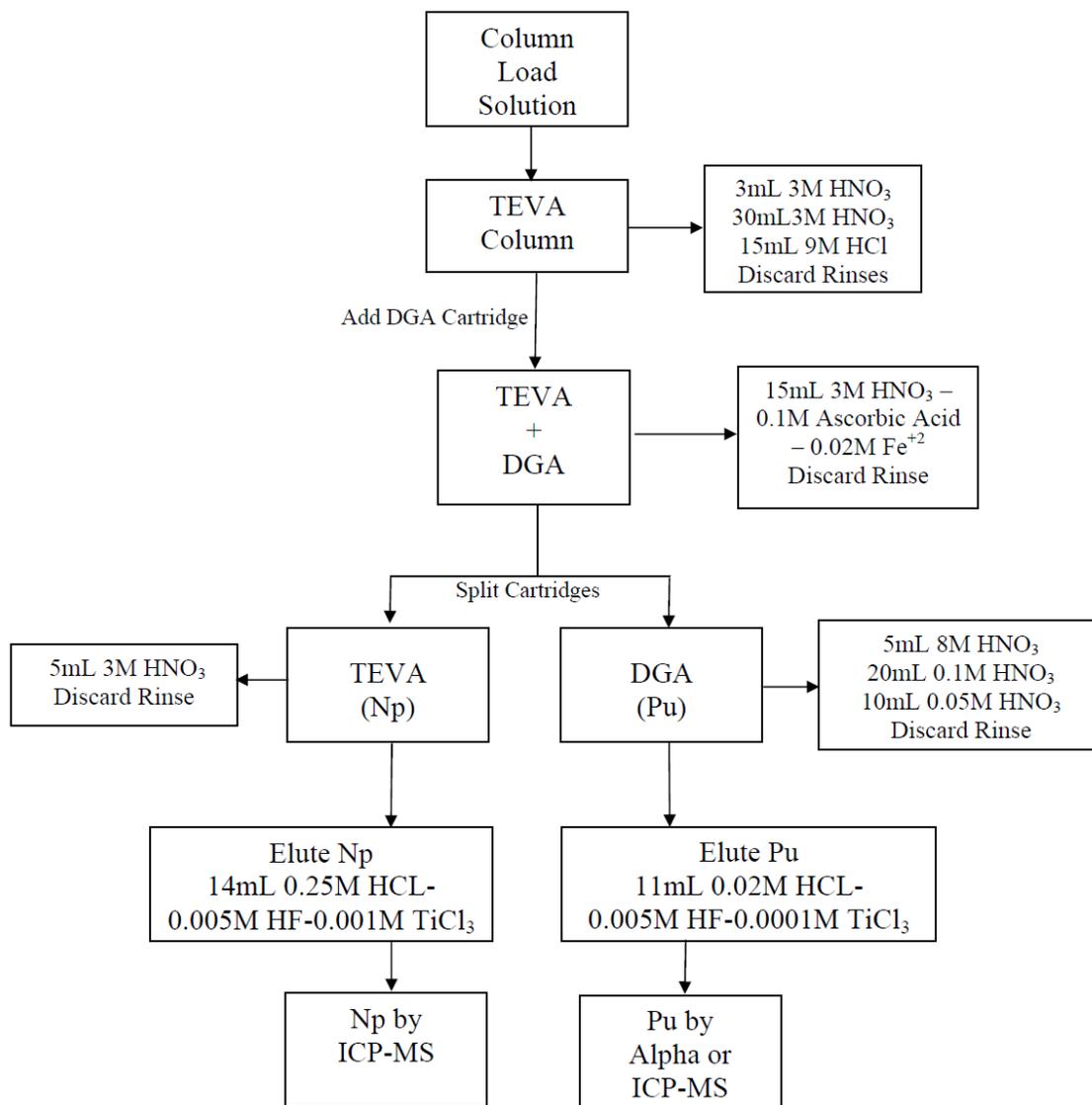


Figure 3 Alpha spectra for Pu Isotopes in Large Soil Sample

