Rapid Separation Method for ^{237}Np and Pu isotopes in Large Soil Samples

Sherrod L. Maxwell[1], Brian K. Culligan, and Gary W. Noyes

Savannah River Nuclear Solutions, LLC, Building 735-B, Aiken, SC 29808, USA

[1] Author for correspondence (email: sherrod.maxwell@srs.gov)

Keywords: plutonium, neptunium, rapid, soil, lanthanum fluoride, alpha spectrometry

Abstract

A new rapid method for the determination of ^{237}Np and Pu isotopes in soil and sediment samples has been developed at the Savannah River Site Environmental Lab (Aiken, SC, USA) that can be used for large soil samples. The new 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. The large soil matrix is removed easily and rapidly using this two simple precipitations with high chemical recoveries and effective removal of interferences. Vacuum box technology and rapid flow rates are used to reduce analytical time.

Introduction

There are a number of analytical methods reported that use ion exchange/extraction chromatography plus alpha spectrometry to determine actinides in soil. Hou et al. (2009) surveyed a wide range of separation methods for Pu in waters and environmental solid samples. Methods included varied combinations of ion exchange and/or extraction chromatographic techniques. Chemical recoveries for Pu typically varied between 40-85%.

Vajda et al. (2009) reported an interesting method for actinides in soil in which 0.5 g soil samples were fused using lithium metaborate. After preconcentration of actinides using calcium fluoride precipitation, a TRU Resin separation was performed. Tests on IAEA soil standards showed very good results, but tracer recoveries showed some significant variation, as high as 80% for plutonium, but notably as low as 20-30% for uranium. The method could, however, be completed rapidly, but still required ~ 24 hours. The overall results were very good relative to soil reference values, however, two of the IAEA soil samples tested showed relatively low chemical recoveries for Pu and U. The authors concluded that the lower chemical recoveries were caused by the soil matrix. This may have resulted from the use of only 1 ml of TRU Resin to recover all the actinides from the soil sample, even though the soil aliquot was only 0.5 g.

Wang et al. (2004) 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 resin column (Dowex 1x8) was used to collect and separate Pu and Th. The rinse fractions from the anion resin were treated further and processed individually for Am, U and Sr. Several sequential precipitations were carried out. An oxalate precipitation was performed at pH 4.2 on the anion resin rinse solution followed by a Sr Resin separation. A separate oxalate precipitation at pH 1.5 was performed on the supernatant after the first oxalate precipitation to recover Am and separate on TRU Resin. The supernatant from the second oxalate precipitation was passed through a large amount of Chelex 100 resin to collect and purify uranium. Strontium was counted using Čerenkov counting, while all actinide fractions were electrodeposited for counting by alpha spectrometry. The chemical recoveries using this method on NRIP (National Institute of Standards and Technology [NIST] Radiochemistry Intercomparison Program) soil were as follows: plutonium (60-76%), americium (40-59%), uranium (57-76%), and Strontium (63-77%). A large number of sequential steps were required, but the accuracy of the actinide and strontium results versus the NIST reference values was very good.

Eikenberg et al. (2009) compared three different separation methods to determine actinides in soil samples. Samples were leached in 8M nitric acid, filtered and a calcium oxalate precipitation technique that settles overnight was used to preconcentrate actinides. One of the separation methods tested was anion resin (AG-1X2) plus DGA Resin (Eichrom Technologies, Lyle, IL, USA). Am, Cm, and U were collected on DGA Resin, which has a *k*' of approximately 30,000 for Am (Horwitz et al., 2005). The sample was loaded in 3M nitric acid, and uranium was eluted in 0.25M nitric acid, prior to stripping Am and Cm with 0.2M HCL. It was not clear what the uranium tracer recoveries were for these samples, but DGA resin is not typically used to recover and purify uranium because the *k*' in 3M HNO_3 for U on DGA Resin is only about 20. Electrodeposition was used to prepare alpha sources for measurement by alpha spectrometry.

Ageyev et al. (2005) 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 calcium oxalate precipitation, furnace heating of oxalates, redissolution in hydrochloric acid, iron hydroxide precipitation, and a lanthanum precipitation of plutonium, americium and curium. Carbonate, chromate and iron hydroxide precipitations were performed to prepare strontium. 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-iso-butyric acid. Actinides were electrodeposited for alpha counting. Chemical yields were respectable as follows: Pu 60-70%, Am and Cm 50-65%, and Sr 50-70%. The method is, however, relatively complex and would not be considered a rapid method.

Tavčar et al. (2005) 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. The valence adjustment was performed using hydroxylamine hydrochloride to reduce Pu to Pu^{+3}, followed by sodium nitrite to oxidize Pu to Pu^{+4}. 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%. The low Np yields were attributed to poor valence control of Np^{+4}.

We have previously used TEVA Resin plus TRU Resin plus DGA Resin in the SRS (Savannah River Site) Environmental Laboratory to determine Pu and Am isotopes in 5-10g soil samples. TRU Resin was used in tandem with DGA Resin to effectively recover uranium and provide very high chemical recoveries for Am and Cm. The method first uses nitric acid –hydrofluoric acid to digest samples and remove silica, then uses an alkaline fusion to digest the samples, an iron hydroxide precipitation, followed by a cerium fluoride preconcentration step to remove the sample matrix and preconcentrate the actinides (Maxwell and Culligan, 2006). A version of this method to determine Pu and Am in 200 gram soil samples using acid leaching only was also reported (Maxwell and Culligan, 2008)., but a fusion of the soil leachate was still used in this process.

A new method has been developed in the SRS Environmental Lab (Aiken, SC, USA) that allows the separation of Pu isotopes and ^{237}Np in large soil samples with high yields and effective separation. The 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. This series of rapid precipitations enables high yields and effective removal of interferences. The final precipitate, due to the selectivity of lanthanum fluoride, is very small and easily dissolved in s small column load solution. This work is simpler and more rapid than previously published work from this laboratory with large soil samples because no fusion step is required. In addition, Np, which was not included in the previous work, is also recovered effectively along with Pu due to rigorous valence control of Np as Np^{+4} using Ti(III) reductant during the iron/titanium hydroxide and lanthanum fluoride precipitations.

Experimental

Reagents

TEVA Resin® (Aliquat ™336), available from Eichrom Technologies, Inc., (Lisle, Illinois, USA). Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc.). All water was obtained from a Milli-Q2™ water purification system. All other materials were ACS reagent grade. Radiochemical isotope tracer ^{236}Pu was obtained from the National Physical Laboratory (Teddington, UK) to enable yield corrections. ^{239}Pu, ^{238} Pu and ^{237} Np standards were obtained from Eckert and Ziegler Analytics, Inc. (Atlanta, GA, USA). MAPEP 20 and MAPEP 21 soil standards (Mixed Analyte Performance Evaluation Program) were obtained from Department of

Energy (DOE) – Radiological and Environmental Sciences Laboratory (RESL), Idaho Falls, ID, 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). Flow rates of 1-2 ml min^{-1} were typically used for this work.

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. Eight 20 g soil samples, six 30 g samples and three 50 g soil sample aliquots were analyzed. Samples were aliquoted into large glass beakers. To all but two of the 20 g soil samples, 1g MAPEP 21 soil standard was added. ^{237}Np (37 mBq) was added to each sample since MAPEP standards do not contain ^{237}Np.

Figure 1 provides a flow chart of the sample preparation method. ^{236}Pu tracer (46.2 mBq) was added to each sample. The first two 20 g soil samples were analyzed without MAPEP 21 soil standard to determine the Pu content of the soil. The assumption was made that the ^{237}Np activity in this soil was negligible compared to the 37 mBq ^{237}Np added.

Acid leach volumes were adjusted slightly for sample size. For 20 g soil samples, 30 ml concentrated nitric acid and 10 ml concentrated hydrochloric acid were added to each beaker and samples were heated to dryness on a hot plate. For 30 g and 50 g soil samples, the nitric acid and hydrochloric acid volumes were increased proportionally. For 20 g and 30 g soil samples, 30 ml of concentrated nitric acid were added to each sample

(50 ml for 50 g samples). The beakers were warmed on a hot plate and the leachate and some of the solids were transferred to a 225 ml centrifuge tube.

The residual solids were rinsed two more times. Fifteen to twenty-five milliliters of concentrated nitric acid were added to each beaker, warmed on a hot plate and the leachate plus additional solids were transferred to the centrifuge tube. The centrifuge tubes were centrifuged at 3500 rpm for 10 minutes. The leachate was transferred to a 600 ml beaker, heated on a hot plate to evaporate the leachate to dryness. Fifteen to twenty-five milliliters of concentrated nitric acid was added to each beaker with residual solids to rinse the solids. This rinse solution plus additional solids was transferred to the centrifuge tube. The centrifuge tubes were centrifuged at 3500 rpm for 10 minutes and the rinse solution was transferred to the evaporating leachate. The leachate solutions were evaporated to dryness on a hot plate on low to medium heat as needed to prevent splattering.

To each evaporated leachate, 15 to 20 ml 1M hydrochloric acid were added and warmed on a hot plate to easily dissolve the residue. This solution was transferred to 225 centrifuge tube and 5 mg La as lanthanum nitrate was added to each tube. To each 20 g sample, 125 mg Fe was added as ferric nitrate. For the 30g and 50g samples, the 125 mg Fe were not added since large amounts of Fe were already present in the soil. Twenty-five milliliters of concentrated ammonium hydroxide was added to each tube and the solution was diluted to 180 ml with water.

Ten milliliters of 20% titanium (III) chloride were added to each tube (15 ml 20% $TiCl_3$ for the 30g and 50g samples) to ensure reduction of Np to Np^{+4} and to enhance precipitation via titanium hydroxide precipitation. The red to orange color changed to a beige or brown color, indicating reduction of Fe to Fe^{+2}, important to ensure effective reduction of Np to Np^{+4}. After mixing well, 1 ml 10% barium nitrate was added to each sample to complex any carbonate present. The tubes were centrifuged at 3500 rpm for 6 minutes and the supernatant was discarded. The remaining precipitate was dissolved as much as possible in a total volume of 1.5M HCl as follows: ~60 ml total volume for 20 g samples, ~70 ml total volume for 30g samples, and ~90 ml total volume for 50 g samples). This solution was diluted to ~170 ml with 0.01M HCL. Three milligrams of lanthanum as lanthanum nitrate were added to each sample. Ten milliliters of 20% titanium chloride were added to each sample to ensure Np is Np^{+4}. Twenty-two milliliters of 28M HF were added to each sample. More of the undissolved precipitate resulting from the iron hydroxide/titanium hydroxide precipitate will redissolve at this point and a new, much smaller lanthanum fluoride precipitate will form. The samples were placed on ice for ~10 minutes to reduce solubility and centrifuged for 10 minutes at 3500 rpm. The LaF_3 precipitate is very small and can be dissolved easily in a small volume column load solution.

The supernatant was removed and the residual solids were dissolved in 6 ml of warm 3M HNO_3-0.25M boric acid, 7 ml of 7M HNO_3, 9 ml of 2 M aluminum nitrate and 3 ml 3M HNO_3. The solids were transferred to 100 ml teflon beakers during this step and warmed to redissolve the solids. If any residual solids remained, the solutions were centrifuges at 3500 rpm for 5 minutes to remove any trace of solids to ensure good column flow.

Valence adjustment 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. From our experience in this laboratory, the kinetics of oxidation of Np to Np^{+5} in the presence of sodium nitrite, are negligible at room temperature. This column load solution was now ready for column separation.

Column separation. TEVA Resin cartridges were placed on the vacuum box. Fifty milliliter centrifuge tubes were used to collect rinse or final purified fractions. (Figure 2)

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 ~5 ml 3M HNO_3 was transferred to the TEVA column and a rinse of 15 ml 3M HNO_3 was added directly to the stacked column to remove sample matrix components. To elute thorium from TEVA Resin, 20 ml 9M hydrochloric acid were added and discarded. A 5 ml volume of 3M HNO3 was added to TEVA Resin (and discarded) to ensure complete removal of sample matrix components and to minimize organic extractant bleed-off that sometimes occurs when strong HCL is passed through TEVA Resin..

The plutonium was stripped from TEVA Resin with 20 ml 0.1M hydrochloric acid-0.05M hydrofluoric acid –0.01M titanium (III) chloride (freshly prepared). Fifty micrograms of cerium as cerium nitrate were added to the tubes, along with 1 ml of concentrated hydrofluoric acid (49%), prior to elution of the plutonium to reduce microprecipitation wait times. A 0.5 ml volume of 30 wt% hydrogen peroxide was added after the plutonium was eluted to oxidize any residual uranium to U^{6+} as a precaution. After waiting 15 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene filters and counted by alpha spectrometry. Cerium is customarily used in our laboratory to prepare alpha sources for alpha spectrometry but other rare earth elements such as lanthanum, neodymium, etc could have been used.

Apparatus

Plutonium, americium, and uranium 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 results for the determination of ^{237}Np, ^{239}Pu and ^{238}Pu using this method for eight 20 g soil samples. Samples 1 and 2 were analyzed to determine Pu content while samples 2 through 8 were spiked with 1g MAPEP 21 soil standard. ^{237}Np (37.0 mBq) was added to all 8 soil samples since MAPEP standards do not contain added ^{237}Np. The Pu isotopes and ^{237}Np were corrected for tracer yield. The average tracer recovery for ^{236}Pu was 87.8% ± 5.0% at 1SD (standard deviation).

Based on the results from the two unspiked samples, the average total ^{239}Pu content in 20 g of this soil was 1.685 mBq and the average total ^{238}Pu activity was 0.265 mBq. After correction for the Pu content in the unspiked soil, the average ^{239}Pu activity found was 118.4 mBq ± 6.7mBq at 1 SD. The average bias for the ^{239}Pu measurements was 1.8%. After correction for the Pu content in the unspiked soil, the average ^{238}Pu activity found was 67.1 mBq ± 4.2 mBq at 1 SD. The average bias for the ^{238}Pu measurements was 6.2%. The average ^{237}Np result was 39.0 mBq ± 3.7 mBq at 1 SD. ^{237}Np activity is the soil was assumed to be neglible relative to the ^{237}Np spike activity added and no correction for unspiked activity was made. The average bias for the ^{237}Np measurements was 5.5%.

The DOE-RESL Laboratory MAPEP acceptance limits are typically ±20% of the reference value so the biases observed are well within acceptance limits.. Uncertainties on reference values in the MAPEP samples were not provided to our laboratory but are assumed to be 1-2% for all the measured actinide isotopes at the 95% confidence level, significantly less than the measurement uncertainty for the analyses.

Table 2 shows the results for the determination of ^{237}Np, ^{239}Pu and ^{238}Pu using this method for six 20g soil samples spiked with 1g MAPEP 20 soil and ^{237}Np (37.0 mBq). The average tracer recovery for ^{236}Pu was 95.8% ± 6.6% at 1 SD. Correction for ^{239}Pu and ^{238}Pu activity were applied as noted previously. After correction for the Pu content in the unspiked soil, the average ^{238}Pu activity found was 24.6 mBq ± 1.6mBq at 1 SD. The average bias for the ^{238}Pu measurements was -2.6%. The MAPEP 20 soil standard did not contain significant levels of ^{239}Pu activity and the results met false positive test acceptance limits. The average ^{237}Np result was 34.6 mBq ± 2.1 mBq at 1 SD. The average bias for the ^{237}Np measurements was -6.5%.

Table 3 shows the results for the determination of ^{237}Np, ^{239}Pu and ^{238}Pu using this method for six 30g soil samples spiked with 1g MAPEP 21 standard and ^{237}Np (37.0 mBq). The average tracer recovery for ^{236}Pu was 82.1% ± 6.0% at 1 SD. Based on the results from the two unspiked samples, the average total ^{239}Pu content in 30 g of this soil was 2.53 mBq and the average total ^{238}Pu activity was 0.398 mBq. After correction for the Pu content in the unspiked soil, the average ^{239}Pu activity found was 116.34 mBq (± 5.3mBq at 1 SD). The average bias for the ^{239}Pu measurements was 4.4%. After correction for the Pu content in the unspiked soil, the average ^{238}Pu activity found was 68.3 mBq ± 4.6 mBq at 1 SD. The average bias for the ^{238}Pu measurements was 8.1%, slightly higher but still well within acceptance limits. The average ^{237}Np result was 34.5 mBq (± 3.6 mBq at 1 SD). The average bias for the ^{237}Np measurements was -6.8%.

Table 4 shows the results for the determination of ^{237}Np, ^{239}Pu and ^{238}Pu using this method for six 50 g soil samples spiked with 1g MAPEP 21 standard and ^{237}Np (37.0 mBq). The average tracer recovery for ^{236}Pu was 87.8% ± 6.0% at 1 SD. Based on the results from the two unspiked samples, the average total ^{239}Pu content in 50 g of this soil was 4.22 mBq and the average total ^{238}Pu activity was 0.663 mBq. After correction for the Pu content in the unspiked soil, the average ^{239}Pu activity found was 113.9 mBq ± 3.8 mBq at 1 SD. The average bias for the ^{239}Pu measurements was -2.0%. After correction for the Pu content in the unspiked soil, the average ^{238}Pu activity found was 63.7 mBq (± 2.2 mBq at 1 SD. The average bias for the ^{238}Pu measurements was 0.8%. The average ^{237}Np result was 20.8 mBq ± 10.9 mBq at 1 SD with an average bias for the ^{237}Np measurements of -43.8%. The negative bias for ^{237}Np is likely due to sample matrix interferences on TEVA Resin.

Since the k' for Np^{+4} (~5,000) is significantly less than the k' for Pu^{+4} (~30,000) in 3M HNO_3 on TEVA Resin (Horwitz et al., 1995), Np is more likely to have losses due to sample matrix interferences. The Pu yields are very good even for 50 gram samples. It may be possible to improve Np yields with 50 gram samples by increasing the amount of TEVA Resin used. A separate Np tracer such as ^{239}Np may also be used instead of using ^{236}Pu tracer for Np.

Figure 3 shows an example of the spectra for a large soil sample. The ^{236}Pu tracer recovery was 97.9% and the Full Width Half Maximum (FWHM) was 37.1 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 essentially the same alpha energy.

The method appears to work very well for Pu and Np in large soil samples. For samples up to 30 g, Pu and Np yields were good. Pu results were good for 50 g soil samples. It is likely, based on previous experience in this laboratory, that Pu yields with 75g to100 g samples will likely still be high, due to the high K' for Pu on TEVA resin.

A subsequent test with 75g soil samples showed an average ^{236}Pu yield of 78.1% ± 1.5% (1SD, N=4), confirming that Pu yields are still high with larger soil samples, even with only 2ml of TEVA Resin. To compensate for lower Np yields with larger soil samples, ^{239}Np tracer may be used instead of ^{236}Pu.

If separation of Pu from Np is desired (for example so that ^{242}Pu can also be determined), the Pu can likely be eluted from TEVA Resin prior to Np using 9M HCl-0.2M NH_4I. It should be noted that Np and Pu can also be measured by ICP-MS using this same method by utilizing an ICP-MS compatible strip solution for TEVA Resin, 0.25M HCl-0.005M HF-0.0001M TiCl3. (Maxwell and Jones, 2009)

Conclusions

A new method to determine ^{237}Np and Pu isotopes has been developed in the SRS Environmental Lab (Aiken, SC, USA) that allows the separation of ^{237}Np and Pu isotopes in large soil samples with high yields and effective separation of interferences. The new method was tested using 20g, 30g, and 50g soil samples spiked with MAPEP soil standards with very good results. The yields for Pu and Np were very good for 20 and 30 gram soil samples. For 50 gram soil samples, Pu yields were good but Np showed lower, more inconsistent yields. The final precipitate, due to the selectivity of lanthanum fluoride, is very small and easily dissolved in a small column load solution and separated using only a 2ml TEVA resin cartridge. The combination of iron hydroxide precipitation (enhanced with titanium(III) reductant) with a lanthanum fluoride matrix removal step is a simple, powerful sample preparation tool for analysis of ^{237}Np and Pu isotopes in large soil samples.

Acknowledgment

This work was performed under the auspices of the Department of Energy, DOE Contract No. DE-AC09-96SR18500. The authors wish to acknowledge Shermette Upson, Jack Herrington and Becky Chavous for their assistance with this work.

References

1. Ageyev, V.A., Odintsov, O.O. and Sajeniouk, A.D., 2005. Routine radiochemical method for the determination of ^{90}Sr, ^{238}Pu, $^{239+240}$Pu, ^{241}Am and ^{244}Cm in environmental samples, J. Radioanal. Nucl.Chem. 264 (2), 337
2. Eikenberg J., Jäggi, M, Beer,H., Rüthi,M., and Zumsteg, I., 2009. Separation techniques for low-level determination of actinides in soil samples, Applied Radiation and Isotopes**,** 67**,** 776
3. Horwitz, P., McAlister, D. Bond, A., and Barrans Jr, A. B., 2005. Novel extraction chromatographic resins based on tetraalkyldiglycolamides: characterization and potential applications, Solvent Extr. Ion Exch. 23, (3**),** 319
4. Horwitz, E. P., Dietz, M., Chiarizia, R. Diamond, H., Maxwell, S., and Nelson, M., 1995. Separation and preconcentration of actinides by extraction chromatography using a supported liquid anion exchanger: application to the characterization of high-level nuclear waste solutions, Analytica Chimica Acta, 310, (No.1), 63

5. Hou, X., Qiao, J., Miro, M. and Roos, P., 2009. Determination of plutonium isotopes in waters and environmental solids: A review, Analytical Chimica Acta, in press, doi:10.1016/j.aca.2009.03.010
6. Maxwell, S. and Culligan, B., 2006. Rapid column extraction method for actinides in soil, J. Radioanal. Nucl. Chem, 270 (No.3), 699
7. Maxwell, S. and Culligan, B., 2008. Rapid method for determination of plutonium, americium and curium in large soil samples, J. Radioanal. Nucl. Chem, 275 (No.2), 395
8. Maxwell III, S.L. and Jones, V.D., 2009. Rapid determination of actinides in urine by inductively coupled plasma mass spectrometry and alpha spectrometry: A hybrid approach: Talanta, 80 (No.1), 143
9. Tavčar, P., Jakopič, R. and Benedik, L., 2005. Sequential Determination of ^{241}Am, ^{237}Np, Pu Radioisotopes and ^{90}Sr in Soil and Sediment Samples, Acta. Chim.Slov, 52, 60
10. Vajda, N., Törv´enyi, A., Kis-Benedek, G., Kim, C. K. , Bene, B. and M´acsik, Zs., 2009. Rapid method for the determination of actinides in soil and sediment samples by alpha spectrometry, Radiochimica Acta, 97, 395
11. Wang, J., Chen, I, and Chiu, J., 2004. Sequential isotopic determination of plutonium, thorium, americium, strontium and uranium in environmental and bioassay samples, Applied Radiation and Isotopes, 61, 299

Table Captions

Table 1	Pu and Np results for 20g samples spiked with MAPEP 21 standard
Table 2	Pu and Np results for 20g samples spiked with MAPEP 20 standard
Table 3	Pu and Np results for 30g samples spiked with MAPEP 21 standard
Table 4	Pu and Np results for 50g samples spiked with MAPEP 21 standard

Table 1 Pu and Np results for 20g samples spiked with MAPEP 21 standard

Sample ID	^{236}Pu Yield (%)	^{238}Pu Measured mBq	^{239}Pu Measured mBq	^{237}Np Measured mBq
1	91.3	0.25	1.68	35.5
2	82.0	0.28	1.69	45.9
3	100.8	60.3	112.1	34.5
4	89.0	68.8	125.4	38.5
5	85.8	71.8	126.9	38.9
6	93.8	65.9	120.6	36.6
7	85.4	71.0	124.0	41.4
8	87.1	66.6	111.7	41.1
Avg.	89.4	67.4	120.1	39.0
^{A}Corr. Avg.		67.1	118.4	39.0
1SD	5.9	4.2	6.7	3.7
%RSD	6.6	6.2	5.6	9.5
Reference		63.2	116.3	37.0
% Difference		6.2	1.8	5.5

avg ^{238}Pu in unspiked 20g sample = 0.265 mBq
avg ^{239}Pu in unspiked sample = 1.685 mBq

^{A} average spiked sample result corrected for unspiked content

Table 2 Pu and Np results for 20g samples spiked with MAPEP 20 standard

Sample ID	^{236}Pu Yield (%)	^{238}Pu Measured mBq	^{239}Pu Measured mBq	^{237}Np Measured mBq
1	101.3	25.5	1.67	33.3
2	90.4	24.8	2.07	35.9
3	105.1	22.9	1.63	31.1
4	96.4	24.4	2.22	34.8
5	94.7	24.1	2.85	36.6
6	87.2	27.8	2.33	35.9
Avg.	95.8	24.9	2.13	34.6
^{A}Corr. Avg.		24.6	0.44	34.6
1SD	6.6	1.6	0.5	2.1
%RSD	6.9	6.6	21.4	6.0
Reference		25.3	^{B} N/A	37.0
% Difference		-2.6	^{B} N/A	-6.5

avg ^{238}Pu in unspiked 20g sample = 0.265 mBq
avg ^{239}Pu in unspiked sample = 1.685 mBq

[A] average spiked sample result corrected for unspiked content
[B] acceptable result-false positive/sensitivity test

Table 3 Pu and Np results for 30g samples spiked with MAPEP 21 standard

Sample ID	^{236}Pu Yield (%)	^{238}Pu Measured mBq	^{239}Pu Measured mBq	^{237}Np Measured mBq
1	87.6	66.2	118.0	32.9
2	78.8	62.5	117.7	32.9
3	75.2	74.4	131.0	41.1
4	90.6	63.3	118.8	35.9
5	82.1	67.7	124.7	32.6
6	78.1	69.6	121.4	31.5
Avg.	82.1	68.7	124.0	34.5
^{A}Corr. Avg.		68.3	121.4	34.5
1SD	6.0	4.6	5.3	3.6
%RSD	7.3	6.7	4.3	10.3
Reference		63.2	116.3	37.0
% Difference		8.1	4.4	-6.8

avg ^{238}Pu in unspiked 30g sample = 0.398 mBq
avg ^{239}Pu in unspiked sample = 2.53 mBq

^{A} average spiked sample result corrected for unspiked content

Table 4 Pu and Np results for 50g samples spiked with MAPEP 21 standard

Sample ID	^{236}Pu Yield (%)	^{238}Pu Measured mBq	^{239}Pu Measured mBq	^{237}Np Measured mBq
1	87.2	67.7	124.3	19.6
2	89.5	65.1	117.7	23.7
3	79.9	65.5	118.0	8.9
4	97.9	62.2	112.5	23.3
5	84.7	64.0	118.4	12.6
6	87.5	61.8	118.0	36.6
Avg.	87.8	64.4	118.2	20.8
[A]Corr. Avg.		63.7	113.9	20.8
1SD	6.0	2.2	3.8	9.8
%RSD	6.8	3.4	3.2	47.0
Reference		63.2	116.3	37.0
% Difference		0.8	-2.0	-43.8

avg ^{238}Pu in unspiked 50g sample = 0.663 mBq
avg ^{239}Pu in unspiked sample = 4.22 mBq

[A] average spiked sample result corrected for unspiked content

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

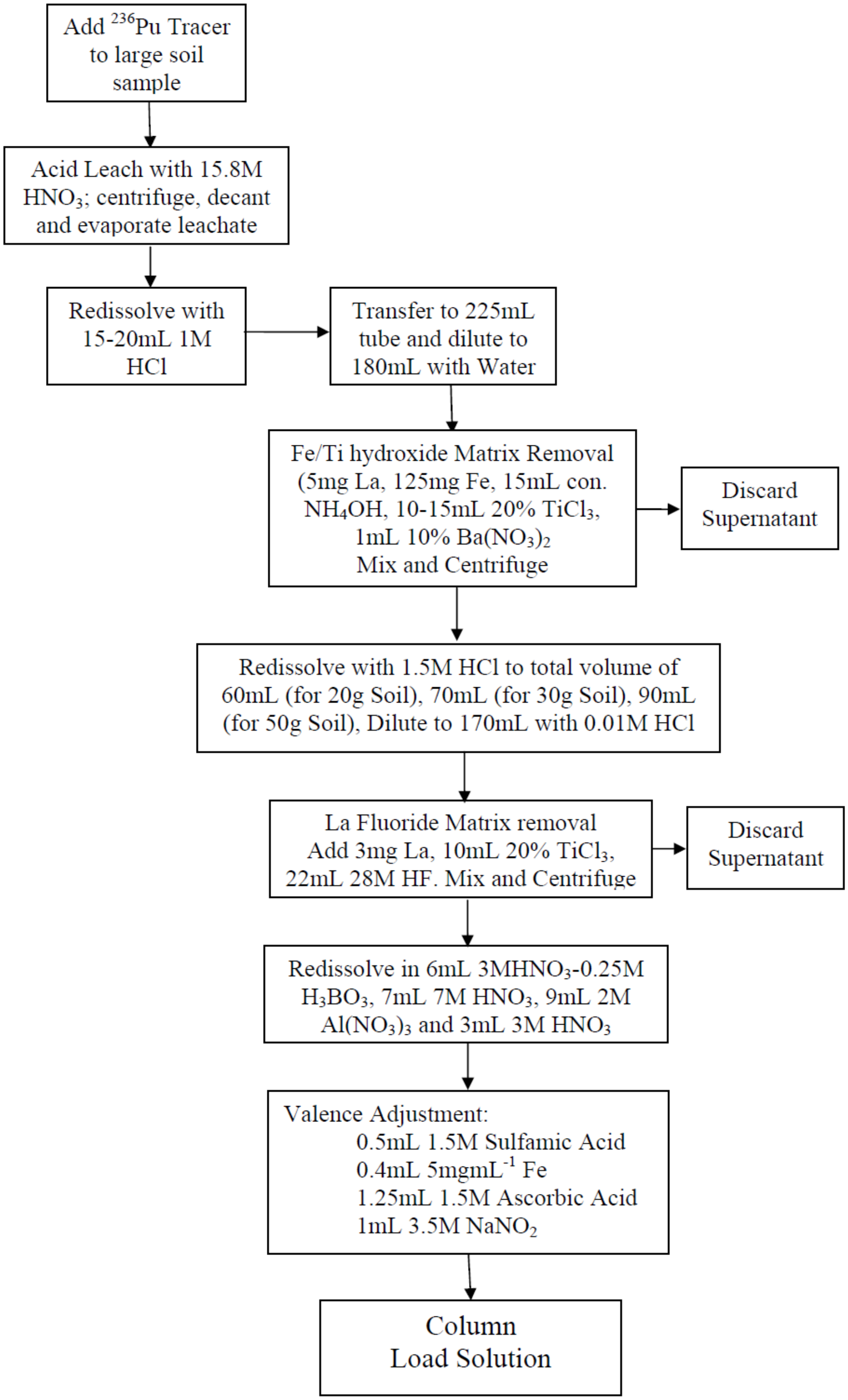

Figure 2 Rapid Column Separation for Large Soil Samples

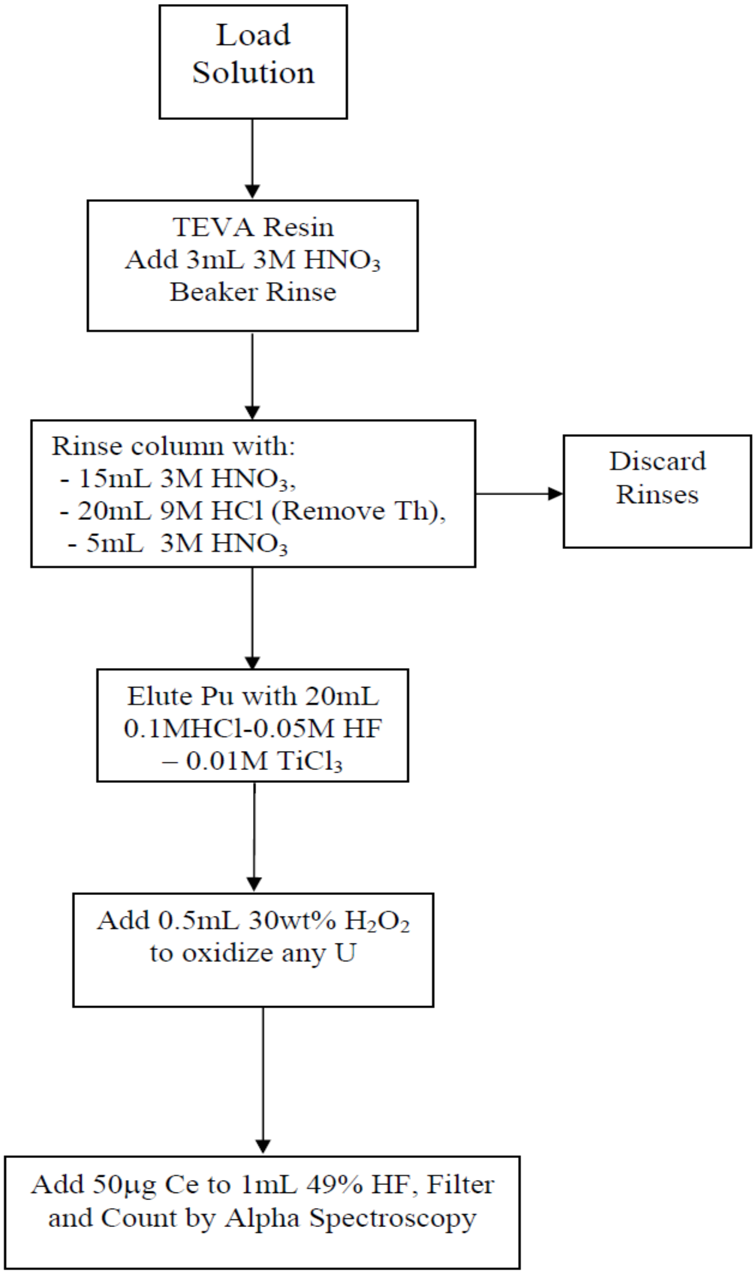

Figure 3 Alpha spectra for ^{237}Np and Pu Isotopes in Large Soil Sample