Rapid Determination of ^{237} Np and Pu isotopes in Water by Inductively-Coupled Plasma Mass Spectrometry and Alpha Spectrometry

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Abstract

A new method that allows rapid preconcentration and separation of plutonium and neptunium in water samples was developed for the measurement of ^{237}Np and Pu isotopes by inductively-coupled plasma mass spectrometry (ICP-MS) and alpha spectrometry; a hybrid approach. ^{238}U can interfere with ^{239}Pu measurement by ICP- MS as ^{238}UH^{+} mass overlap and ^{237}Np via peak tailing. The method provide enhanced removal of uranium by separating Pu and Np initially on TEVA Resin, then moving Pu to DGA resin for additional removal of uranium. The decontamination factor for uranium from Pu is almost 100,000 and the decontamination factor for U from Np is greater than 10,000. This method uses stacked extraction chromatography cartridges and vacuum box technology to facilitate rapid separations. Preconcentration is performed using a streamlined calcium phosphate precipitation method. Purified solutions are split between ICP-MS and alpha spectrometry so that long and short-lived Pu isotopes can be measured successfully. The method allows for simultaneous extraction of 20 samples (including QC samples) in 4 to 6 hours, and can also be used for emergency response. ^{239} Pu, ^{242}Pu and ^{237} Np were measured by ICP-MS, while

^{236}Pu, ^{238}Pu, and ^{239} Pu were measured by alpha spectrometry.

Introduction

A number of radionuclides are present in the environment as a result of nuclear weapons tests, reactor accidents and reprocessing of nuclear fuels. The measurement of plutonium and neptunium in water is not only important for environmental monitoring but also in response to a radiological emergency event, such as the nuclear accident at Chernobyl or detonation of a radiological dispersal device (RDD) by terrorists [1]. Rapid methods using extraction chromatography and alpha spectrometry have been reported by this laboratory for emergency water and urine samples [2,3]. The advantages and disadvantages of alpha spectrometry and inductively-coupled plasma mass spectrometry (ICP-MS) have been discussed previously [4]. The measurement time for sequential assay by ICP-MS is typically shorter than alpha spectrometry, although alpha spectrometry measurements may be performed simultaneously with large numbers of detectors. ICP-MS is particularly effective for longer-lived actinide isotopes with lower specific activities, where alpha spectrometry works very well for short-lived actinide isotopes. Alpha spectrometry cannot differentiate well between alpha isotopes with overlapping alpha energies. Although alpha spectrometry can measure total ^{239}Pu + ^{240}Pu, for example, it cannot differentiate between ^{239}Pu and ^{240}Pu isotopes. In contrast, ^{239}Pu and ^{240}Pu are easily differentiated by ICP-MS. Actinide determination by ICP-MS, however, can be hampered by isobaric, polyatomic interferences and signal suppression and have limited effectiveness when analyzing relatively short-lived isotopes with very low concentration, for example, ^{238}Pu [5]. Both measurement techniques may require separation of interferences to determine actinide isotopes accurately, depending on the sample matrix and the detection limit required. A variety of online and offline separation techniques have been reported in recent reviews of ICP-MS applications, covering a wide range of matrices (soil, sediment, water, biological and urine samples) [6-8]. This paper will focus more specifically on recent developments and progress with regard to environmental matrices.

Varga *et al* used alpha spectrometry to determine the relatively short-lived isotopes ^{241}Am and ^{238}Pu and inductively-coupled plasma sector field mass spectrometry (ICP-SFMS) for ^{239}Pu, ^{240}Pu and ^{241}Am in small soil samples [9]. UTEVA and TRU Resins were used to separate Am and Pu fractions. The Pu strip solution (0.1M ammonium bioxalate) and the Am strip solution (9M HCl + 4M HCl) from TRU Resin were evaporated to dryness multiple times and wet-ashed with concentrated HNO_3 and H_2O_2 prior to analysis by ICP-SFMS and alpha spectrometry, increasing the sample preparation time.

Ayranov *et al* reported a method which employed TOPO (tri-n-octylphosphine oxide) in cyclohexane liquid-liquid extraction combined with subsequent TRU Resin and TEVA Resin separations [10]. The initial separation using TOPO extraction was reported to be somewhat time-consuming, but more effective for removal of U and Th interferences than using the TRU Resin/TEVA Resin alone. The chemical yields for Pu and Am using this method were good. The Pu recoveries were greater than 90% by high resolution inductively coupled mass spectrometry (HR-ICP-MS), but 79.7% by alpha spectrometry. The Am recoveries were 87% by HR-ICP-MS, 79% by alpha spectrometry.

Kim et al used ICP-SF-MS coupled with automated sequential injection system to determine Pu isotopes and ^{237}Np in environmental samples [11]. The separation was performed using TEVA Resin, using 5M HNO_3 and 9M HCl rinses, followed by elution using 0.5M HCl. An Aridus (CETAC Technologies, USA) desolvating introduction system was used to try to minimize the ^{238}U interference on ^{239}Pu and ^{237}Np, but the paper emphasized the importance of effective removal of uranium using a separation method to ensure elimination of uranium spectral interference.

A new method has been developed in the Savannah River Site (SRS) Environmental Bioassay Laboratory to allow a flexible, hybrid approach for water samples: the separation of ^{237}Np and Pu isotopes with enhanced uranium removal to allow accurate measurement of ^{237}Np and ^{239}Pu without interference from ^{238}U. As reported previously, a hybrid approach using an offline vacuum box system may be used to assay longer-lived actinide isotopes by ICP-MS and short-lived actinide isotopes by alpha spectrometry [4].

The rapid separation method uses a TEVA cartridge to separate plutonium and neptunium initially, followed by additional decontamination of Pu from U using DGA Resin. ^{239}Pu, ^{242}Pu, ^{237}Np were measured by ICP-MS, while ^{236}Pu, ^{238}Pu, and ^{239} Pu were measured by alpha spectrometry. A rapid calcium phosphate precipitation step was used to preconcentrate Pu and Np from the water samples.

The goal of this work was to provide rapid separation chemistry compatible with both alpha spectrometry and ICP-MS to offer maximum flexibility so that both short-lived and long-lived isotopes can be measured using complementary measurement techniques, with very high decontamination from uranium.

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 ^{239}Pu, ^{242}Pu, ^{237}Np, ^{238}Pu were obtained from Analytics, Inc. (Atlanta, GA, USA) and diluted to the appropriate levels. ^{236}Pu was obtained from the National Physical Laboratory (Teddington, UK). A 1000 mg/l uranium standard was obtained from SpexCertiprep, Inc., Metuchen, NJ, USA.

Procedures

Column preparation. TEVA and DGA-Resin columns were obtained as cartridges containing 2 ml of each resin from Eichrom Technologies, Inc. (Lisle, IL, USA). 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 Co-precipitation. Figure 1 shows a flowchart of the rapid water sample preparation method. After the 200 ml water sample aliquots were dispensed, known amounts of ^{237}Np and Pu isotopes were added to each sample. To test uranium decontamination, 0.1ml 1.00 E6 ng U/ml was also added to each water sample. To perform calcium phosphate coprecipitation, 1 ml 1.25M calcium nitrate (50 mg Ca) and 3 ml 3.2M ammonium hydrogen phosphate were added to each sample. The sample dispensing and the above reagent additions were performed in 225 ml centrifuge tubes to save time. The pH was adjusted to ~pH 9.5 with concentrated ammonium hydroxide using a dark pink phenolphthalein endpoint. The samples were centrifuged at 3500 rpm for ~6 minutes. The precipitate was dissolved in 8 ml 6M HNO_3 and 8 ml 2M $Al(NO_3)_3$ directly in the centrifuge tubes. The final load solution contained 16 ml 3M HNO_3 and 1M $Al(NO_3)_3$. Valence adjustment was performed by adding 0.5 ml 1.5M sulfamic acid, 0.4 ml of 5 mg Fe/ml 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. This column load solution was now ready for column separation.

Column separation. TEVA cartridges were placed on the vacuum box and 50 ml 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 tube 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 enhance 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. To each stacked TEVA+DGA column 15 ml of 3M HNO_3 -0.1M ascorbic acid-0.02M ferrous nitrate (freshly prepared) was added at 1 drop per second to reduce Pu^{4+} to Pu^{3+}. This step transfers unretained Pu^{3+} from TEVA Resin onto DGA Resin, which has very high retention of trivalent and tetravalent actinides in 3M HNO_3 . After this step, the DGA cartridges were rinsed with 5 ml 8M HNO_3 at 1 drop per second to oxidize Pu^{3+} back to Pu^{4+} . 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 Pu^{3+} is still relatively high at low nitric acid concentrations (~50-100 k') on DGA Resin, but the k' for Pu^{4+} is much higher (~1000 at 0.05M HNO_3) [12]. DGA Resin was rinsed with 20 ml 0.1M HNO_3, followed by 10 ml 0.1M HNO_3 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 $Pu^{3+,}$ 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. After elution this volume was adjusted to exactly 12 ml. 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. Since no tracer was used to perform chemical yield adjustment for the ICP-MS measurements, the eluant volume was added in this way with a final volume adjustment to 12 ml after elution.

The purified solutions were analyzed by alpha spectrometry and ICP-MS. Four milliliters of each plutonium/neptunium 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 save time. Five milliliters of 3M HNO_3 were added to each TEVA column to remove residual ferrous ions. at ~2 drops per second. The ^{237}Np 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 ^{237}Np 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.

The purified solutions were analyzed by alpha spectrometry and ICP-MS. Five milliliters of each neptunium eluant solution was transferred to a separate 50 ml tube, diluted to 10 ml with 0.25M HCL. Cerium fluoride microprecipitation was performed as described previously to prepare alpha sources for counting by alpha spectrometry. The remaining solution was transferred to the ICP-MS for ^{237}Np measurement. 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.

Plutonium alpha source filters were counted by alpha spectrometry for approximately 16 hours, but shorter count times (<1 hour) can also be performed for emergency response samples using higher level tracers, depending on the detection limit needed.

Apparatus

Plutonium and neptunium were performed by alpha-particle pulse-height measurements using Passivated Implanted Planar Silicon (PIPS) detectors. The PIPS detectors have an active surface area 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.

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" [13]. The calibration is mass bias adjusted using ^{232}Th and ^{238}U standards. At each standard concentration, the slope of the line defined by ^{232}Th and ^{238}U 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

The rapid separation method was performed on six 200 ml drinking water samples that were spiked with ^{237}Np, Pu isotopes and uranium. Calcium phosphate precipitation, as described above, was applied to all six samples. Samples were analyzed for ^{238}Pu, ^{239}Pu and ^{236}Pu isotopes by alpha spectrometry and ^{237}Np, ^{239}Pu and ^{242} Pu isotopes were analyzed by ICP-MS.

The results for the determination of ^{237}Np, ^{239}Pu and ^{242}Pu by ICP-MS are shown in Table 2. The average ^{237}Np result was 0.0723 ng/ml, with a -1.0% bias and 1SD (standard deviation) of 0.005. The reference and measured values represent the final concentration of ^{237}Np in the purified solution at the ICP-MS.

^{238}U was also measured by ICP-MS to determine uranium decontamination in the purified ^{237}Np fraction. The ^{238}U added to each sample (0.1ml of 1E6 ng/ml) is equivalent to 6.66E3 ng ^{238}U /ml in the final eluant solution (15ml) at the ICP-MS. The average ^{238}U found in the purified Np eluant solutions was 0.46 ng ^{238}U /ml ±0.11 at 1SD. This is equivalent to an average decontamination factor of 1.44E4 of ^{238}U from ^{237}Np.

The average ^{239}Pu result by ICP-MS was 0.0290 ng/ml, with a -4.0% bias and 1SD of 0.0048. The Pu results by ICP-MS were not corrected for ^{242} Pu yield, but could have been corrected if needed. Since the yields were so close to 100%, no yield correction was necessary. The average result for ^{242}Pu was 0.167 ng/ml, with a -2.3% bias and 1SD of 0.0062, indicating excellent recovery of ^{242}Pu as well.

The ^{238}U added to each sample (0.1ml of 1E6 ng/ml) is equivalent to 8.33E3 ng ^{238}U /ml in the final Pu eluant solution (12ml) at the ICP-MS. The average ^{238}U found in the purified Pu eluant solutions was 0.0.089 ng ^{238}U /ml ±0.013 at 1SD. This is equivalent to an average decontamination factor of 9.3E4, nearly a factor of 100,000 for removal of ^{238}U from ^{239}Pu.

Table 3 shows the ^{239} Pu and ^{238} Pu results by alpha spectrometry. The average ^{236}Pu tracer yield was 94.6% (± 8.1SD). The average ^{238} Pu result was 0.063 Bq, with a negative bias of –1.6% and 1SD of 0.0030. The reference value was 0.0644 Bq ^{238} Pu per 200 ml sample (0.322 Bq/l). The average ^{239} Pu result was 0.80 Bq, with a negative bias of -4.1% and 1SD of 0.060. The reference value was 0.833 Bq ^{239} Pu per 200 ml sample (4.16 Bq/l).

Figure 1 shows an example of the plutonium spectra for the water sample. The ^{236}Pu tracer recovery was 94% and the Full Width Half Maximum (FWHM) was 26 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.

Table 4 shows method LLD (lower limit of detection) and LLQ (lower limit of quantitation) values for the different isotopes by ICP-MS using a 200 ml sample aliquot. The LLD and LLQ results were calculated using the equations as prescribed by Taylor [14]. These method LLD and LLQ results include a preconcentration factor of 16.7 for all the Pu isotopes except the ^{237}Np results, which include a preconcentration factor of 13.3. The LLD and LLQ results can be lowered by increasing the sample aliquots as needed, adjusting ICP-MS parameters (integration time, replicates, etc.) or sample introduction equipment. Epov et al noted significant improvements in LLD with ELAN-5000 and ELAN DRC II quadrupole instruments (Perkin Elmer SCIEX, Concord, Canada), and a double focusing sector field Element II ICP-MS (Thermo Finnigan MAT GmBH, Breman, Germany) by using Aridus (CETAC Technologies, USA) and Apex (Element Scientific, Omaha, NE, USA) desolvating units [15].It should also be noted that this column separation method with enhanced uranium removal could likely be adapted to an automated flow injection method similar to what has been reported for urine and air filters by Larivière et al [16-17] . The strip solutions containing titanium should be stable long enough to allow an automated version since the dilute HCL-HF acid mixtures are non-oxidative.

The MDA (Minimum Detectable Activity) for the actinide isotopes by alpha spectrometry were calculated according to equations prescribed by Currie [18]:

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

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

CT = sample count time (min)

R = Chemical Recovery

V = Sample Volume (Liters)

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 200 ml sample aliquot, the MDA for a 2 hour count time is 8.15 mBq L^{-1}. For a 200 ml sample aliquot, the MDA for a 22 hour count time is 0.75 mBq L^{-1}. Depending on the MDA required, the sample aliquot and count time may be adjusted accordingly.

The rapid column separation is compatible with ICP-MS or alpha spectrometry. The chemical yields were very good and the accuracy and precision of the measurements on the actinide isotopes spiked into the water samples standards were excellent. The trace level titanium chloride (0.0001M) used in the plutonium stripping solution effectively reduces Pu to Pu^{3+} for effective elution of Pu from DGA Resin without adversely affecting the ICP-MS assay.

The vacuum box column separation system is a low budget alternative to flow injection separation techniques. This stacked cartridge approach provides rapid flow rates and effective removal of spectral and other sample matrix interferences for a large number of samples prepared simultaneously. Multiple vacuum box locations can be used to prepare a large number of samples in an emergency that can be analyzed by alpha spectrometry and/or ICP-MS. Tracer corrections were not applied to the ICP-MS results to highlight the high chemical yields and minimal sample matrix impacts observed, but tracer corrections may be easily applied as needed.

Conclusions

A new rapid separation method that allows separation and preconcentration of ^{237}Np and Pu isotopes in emergency or routine water samples was developed for the determination of longer-lived Pu and Np isotopes by inductively-coupled plasma mass spectrometry (ICP-MS) and short-lived Pu isotopes by alpha spectrometry. Purified solutions are split between ICP-MS and alpha spectrometry so that long and short-lived isotopes can be measured successfully. The method is rapid, flexible, offers high chemical recoveries, excellent removal of interferences such as ^{238}U and can be used to provide high sample throughput in a radiological emergency. A uranium decontamination factor of almost 100,000 can be achieved for uranium removal from Pu to remove the ^{238}UH^{+} interference on ^{239}Pu.

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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
Carrier Gas	1 L/min
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
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., 3 pt/amu, 0.99 sec/amu
Replicates	6

Table 2 ICP-MS Results for ^{237}Np and Pu Isotopes

Isotope	Reference ng/ml	Measured ng/ml	Difference %
^{237}Np	0.0730	0.0723 ± 0.0050	-1.0
^{239}Pu	0.0302	0.0290 ± 0.0048	-4.0
^{242}Pu	0.1708	0.167 ± 0.0062	-2.3

N=6, ± values 1SD

Concentration (ng/ml) in final solution at ICP-MS

Table 3 Pu Isotope Results by Alpha Spectrometry

^{236}Pu Yield	Isotope	Reference Bq	Measured Bq	Difference %
94.6 ± 8.1	^{238}Pu	0.0644	0.063 ± 0.0030	-1.6
	^{239}Pu	0.833	0.80 ± 0.060	-4.1

N=6, ± values 1SD
Bq added to 200 ml sample

Table 4 LLD and LLQ ICP-MS Results Using 200 ml Sample Aliquots

	^{237}Np ng/ml	^{239}Pu ng/ml
Column Concentration Factor	13.3*	16.7*
Overall Method LLD	1.2.E-03	2.9.E-04
Overall Method LLQ	4.0.E-03	9.8.E-04

*200 ml reduced to 15ml (^{237}Np) and 12ml (^{239}Pu)

Figure 1 Figure 1 Rapid Water Sample Preparation

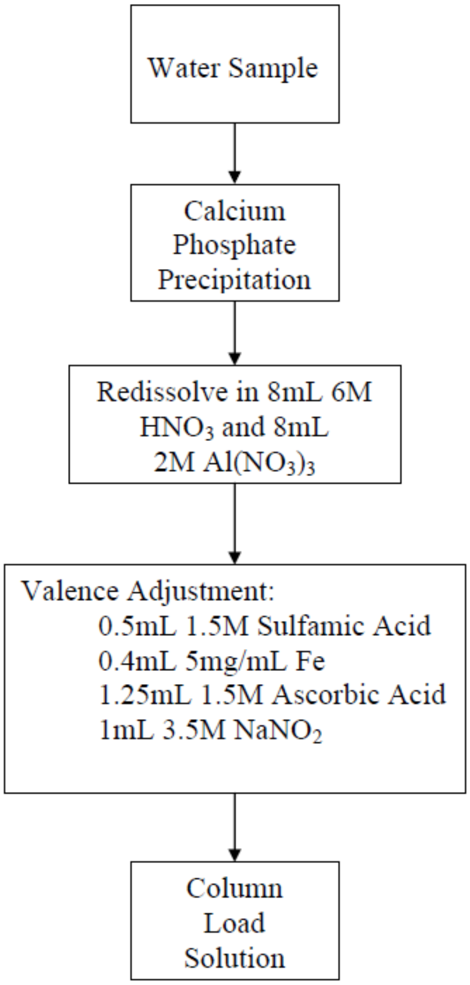


Figure 2 Rapid Water Column Separation

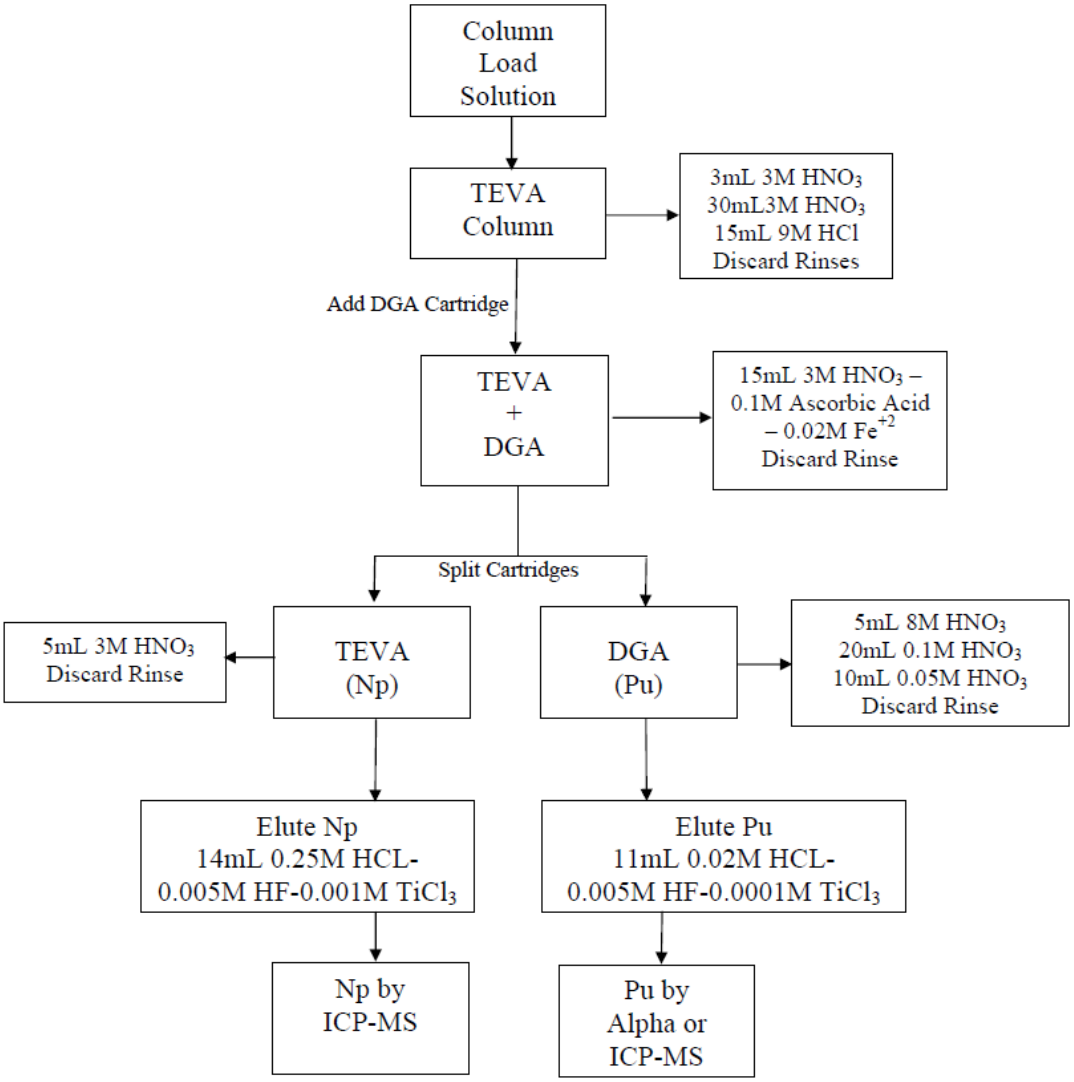
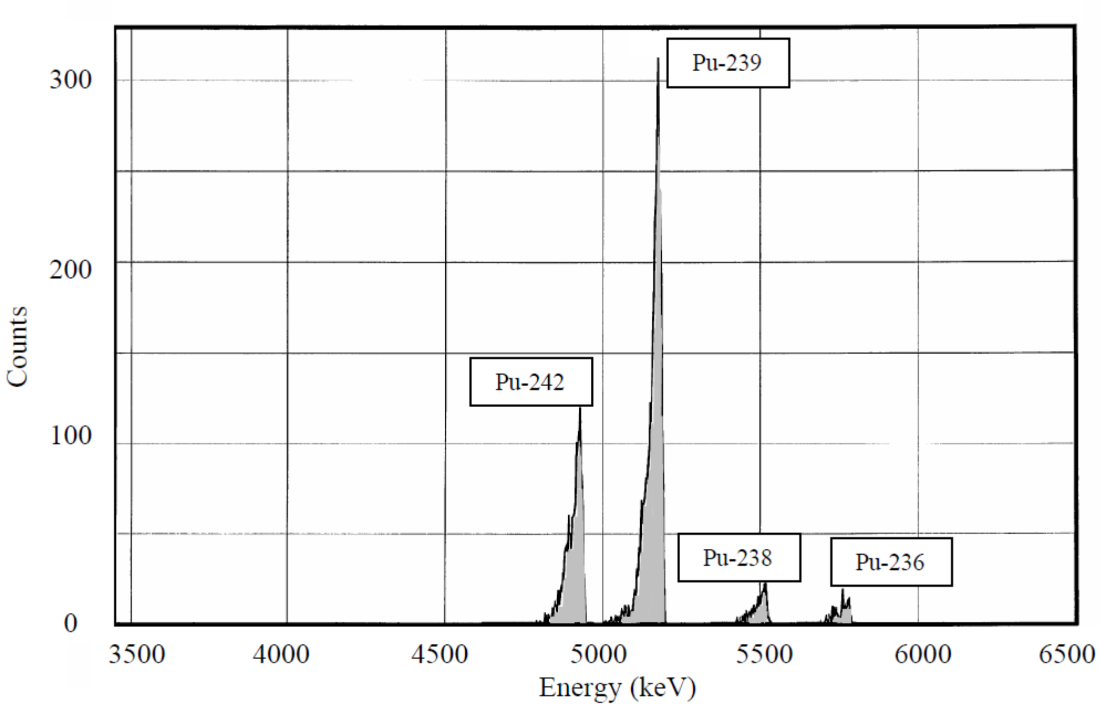


Figure 3 Alpha Spectra for Pu isotopes



Tracer Yield = 93.9%, Count Time = 16 h, Tracer FWHM = 25.8keV