Rapid Separation of Actinides and Radiostrontium in Vegetation Samples

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Abstract

A new rapid method for the determination of actinides and radiostrontium in vegetation samples has been developed at the Savannah River Site Environmental Lab (Aiken, SC, USA) that can be used in emergency response situations or for routine analysis. The actinides in vegetation method utilizes a rapid sodium hydroxide fusion method, a lanthanum fluoride matrix removal step, and a streamlined column separation process with stacked TEVA, TRU and DGA Resin cartridges. Lanthanum was separated rapidly and effectively from Am and Cm on DGA Resin. Alpha emitters are prepared using rare earth microprecipitation for counting by alpha spectrometry. The purified ^{90}Sr fractions are mounted directly on planchets and counted by gas flow proportional counting. The method showed high chemical recoveries and effective removal of interferences. The actinide and ^{90}Sr in vegetation sample analysis can be performed in less than 8 hours with excellent quality for emergency samples. The rapid fusion technique is a rugged sample digestion method that ensures that any refractory actinide particles or vegetation residue after furnace heating is effectively digested.

Introduction

There is an increasing need to develop faster analytical methods for emergency

response, including emergency vegetation samples [1-3]. There are a number of analytical methods reported that use ion exchange/extraction chromatography plus alpha spectrometry to determine actinides in environmental samples. Wang et al reported a sequential method to determine actinides and strontium in environmental samples [4]. 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 Cerenkov counting, while all actinide fractions were electrodeposited for counting by alpha spectrometry. The chemical recoveries using this method on environmental samples were as follows: plutonium (61-85%), americium (42-65%), uranium (56-73%), and Strontium (67-83%). A large number of sequential steps were required, but the accuracy of the actinide and strontium results versus reference values was very good.

Ageyev et al reported a method for environmental samples including vegetation samples [5]. 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 $LaOH_2$, rereedissolved 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-isoo-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.

Vioque et al reported the determination of Pu isotopes in vegetation samples that included ashing the sample for 24 hours at 550˚C, leaching with 8M HNO_3 for 8 hours, followed by iron hydroxide precipitation, and column separation using a large AG 1x8 ion exchange column [6]. The sample was loaded from 8M HNO_3 and Pu was eluted with 10M HCl-NH_4I. The eluant was evaporated, wet-ashed and electrodeposited for alpha spectrometry counting. The Pu tracer yields averaged ~60% for soils, and 45% (range 21% to 71%) for peat. The large anion resin column required relatively large volumes of rinse and eluant solutions. The overall results versus reference values were very good but the method would not be considered rapid.

Epov reported a new method for Pu isotopes in leaves or grass using a new online flow injection inductively couple mass spectrometry method after microwave digestion [7]. The sample was initially ashed at 900˚C for 30 minutes, the heated in a microwave with nitric acid, hydrogen peroxide and hydrofluoric acid for 35 minutes The samples were evaporated to dryness and redissolved in 8M HNO_3. Uranium and rare earth removal are

very important when preparing vegetation samples for ICP-MS analysis. Dynamic reaction cell was used to minimize $^{238}U\ H^{+}$ interference on ^{239}Pu. AGMP-1M ™ anion resin was found in this work to perform better than TRU Resin due to avoid Fe^{3+} and rare earth interferences. TEVA Resin, however, which does not have as much a uranium tailing problem as anion resin such as AGMP-1M, does not appear to have been tested. Tracer recoveries were very high, typically greater than 90%, but the method was designed for Pu isotopes only.

A new method has been developed in the Savannah River Site Environmental Lab (Aiken, SC, USA) that has reduced the sample preparation time for vegetation samples to <8 hours. This method for the determination of actinides and radiostrontium in vegetation samples can be used in emergency response situations or for routine analysis. The vegetation samples analyzed using a rapid furnace heating step, a rapid sodium hydroxide fusion, followed by precipitation steps including a lanthanum fluoride matrix removal step, followed by a stacked column consisting of TEVA Resin + TRU Resin + DGA Resin. Lanthanum, which follows Am on TRU Resin and DGA Resin, was removed on DGA Resin using a dilute nitric acid rinse. Lanthanum was separated rapidly and effectively from Am and Cm on DGA Resin. Vacuum box technology and rapid flow rates are used to reduce analytical time. Alpha sources are prepared using cerium fluoride microprecipitation for counting by alpha spectrometry. Radiostrontium was collected, separated from ^{90}Y and matrix interferences using Sr Resin, and counted using a gas proportional counter. This new method showed high chemical recoveries and effective removal of interferences. While not automated, the method allows for simple vacuum box separation of up to 24 samples simultaneously.

This approach was used because previous experience in this laboratory has shown that for some vegetation samples prepared by high temperature ashing and by wet-ashing with nitric acid and hydrogen peroxide on a hot plate that incomplete digestion can occur. Significant amounts of residual solids can adversely affect tracer yields and method performance.

Experimental

Reagents

The resins employed in this work are TEVA Resin®(Aliquat ™336), TRU-Resin® (tri-n-butylphosphate (TBP) and octyl (phenyl) N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)), DGA Resin (N,N,N',N'-tetraoctyldiglycolamide), and Sr Resin (4, 4', (5') di-t-butylcyclohexane-18-crown-6), available from Eichrom Technologies, Inc., (Lyle, Illinois, USA). Nitric 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 tracers ^{242}Pu, ^{243}Am, and ^{232}U that were obtained from Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 0.37 Bq ml^{-1} were employed to enable yield corrections. ^{244}Cm was obtained from Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 0.37 Bq ml^{-1}. ^{232}U tracer was prepared to be self-cleaning, removing its ^{228}Th daughter using barium sulfate precipitation [8].

Procedures

Column preparation. TEVA, TRU, DGA and Sr-Resin columns were 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.

Sample Preparation. The MAPEP (Mixed Analyte Performance Evaluation Program) vegetation samples (5 to 10g) were added to 250 ml zirconium crucibles (Metal Technology, Inc., Albany, OR, USA). MAPEP samples were provided by Department of Energy (DOE) – Radiological and Environmental Sciences Laboratory (RESL), Idaho, USA. Replicate five gram aliquots of a ~100g MAPEP 18 vegetation sample and 10 gram MAPEP 15 and MAPEP 16 samples (entire sample) were analyzed. ^{244}Cm standard (31.4 mBq) was also added to the 5 gram aliquots taken to analyze for ^{244}Cm.

Tracers were added to each crucible. The crucibles were covered with a zirconium lid and placed in a furnace that was preheated to 600˚C. After about 10 minutes, the temperature of the furnace was increased to 700˚C for 2 hours for 5 gram samples and 4 hours for 10g samples. The crucibles were removed an allowed to cool and ~5 mLs of concentrated nitric acid and ~5 mLs of 30 wt% hydrogen peroxide were added to each crucible. The crucibles were evaporated to dryness on a hotplate on medium heat and heated for ~1 to 2 minutes at 600˚C in a furnace to dry completely.

After removing the crucibles and allowing them to cool, 15 grams of sodium hydroxide were added to each crucible. The crucibles were covered with a zirconium lid and placed into a furnace at 600˚C for ~ 10 minutes.

After removing the crucibles from the furnace, they were cooled for about 10 minutes, transferred to a hot plate and water was added to transfer the solids to 225 ml centrifuge tubes. The residual solids were removed from the crucibles by adding water

and heating the crucibles on the hot plate as needed. One hundred and twenty-five milligrams of iron (added as ferric nitrate) and four milligrams of lanthanum (as lanthanum nitrate) were added to 225 ml centrifuge tubes 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.

Four milliliters of 1.25M calcium nitrate and five milliliters of 3.2M ammonium hydrogen phosphate were added to each tube and each tube was capped and mixed well. The calcium and phosphate are added to enhance strontium recovery. Five milliliters of 20% titanium chloride were added to each tube, followed by 1 ml of 10% barium nitrate to complex any carbonate present. The samples were cooled in an ice bath to room temperature for ~10 minutes. The tubes were centrifuged at 3500 rpm for 6 minutes and the supernatant was discarded. The remaining solids were dissolved in a total volume of ~60 ml of 1.5 M HCl. This solution was diluted to ~170 ml with 0.01M HCL. After dilution, 1 mg of lanthanum as lanthanum nitrate and 1 ml 1.25M calcium nitrate were added to each sample. To ensure no actinides were in the hexavalent state and facilitate complete precipitation, 3 milliliters of 20% titanium chloride were added to each sample. Twenty milliliters of 28M hydrofluoric acid were added to each sample. The samples were placed on ice for ~10 minutes to reduce solubility and centrifuged for 10 minutes at 3500 rpm.

The supernatant was removed and the residual solids containing the actinides were dissolved in 5 ml of warm 3M HNO3-0.25M boric acid, 6 ml of 7M HNO3 and 7 ml of 2 M aluminum nitrate. The solids were transferred to 100 ml teflon beakers during this step and warmed to redissolve the solids. The aluminum nitrate was previously

scrubbed to remove trace uranium by passing approximately 250 ml of 2M aluminum nitrate through a large column (Environmental Express, Mount Pleasant, SC, USA) containing 7 ml of UTEVA Resin (Eichrom Technologies) at ~10 to 15 ml per minute. The columns were prepared from a water slurry of the UTEVA Resin.

A valence adjustment was performed on the load solution by adding 0.5 ml 1.5M sulfamic acid and 1.25 ml 1.5M ascorbic acid with a three minute wait step to reduce plutonium to Pu^{3+}. Np was not determined for these samples, but it should be noted that if ^{237}Np measurement is needed, it can assayed along with Pu in the purified Pu fraction if ^{236}Pu tracer is used [9]. If ^{237}Np separation is desired, 0.4 ml 5 mg/ml Fe as ferric nitrate can be added to facilitate ^{237}Np reduction to Np^{4+}. The ferric ions are reduced to ferrous ions by the ascorbic acid, which reduces Np effectively to Np^{4+}. Following the reduction step, 1 ml 3.5M sodium nitrite was added to oxidize plutonium to Pu^{4+}. After this oxidation step, 1.5 ml 15.8M HNO_3 was added to each sample to increase the nitrate concentration. This enhances Am/Cm retention and selects against Ca retention on DGA Resin.

Column separation. TEVA, TRU, and DGA-Resin cartridges were stacked on the vacuum box from top to bottom, in that order. Fifty milliliter centrifuge tubes were used to collect rinse or final purified fractions. Column load solutions were loaded at ~1 drop per second, rinse solutions at ~2 drops per second and column strip solutions were added at ~1 drops per second, using vacuum.

After the valence adjustment, the sample solution was loaded onto the stacked column at approximately ~1 drop per second. After the sample was loaded, a beaker rinse of ~5 ml 6M HNO_3 was transferred to the stacked column and a rinse of 10 ml 3M HNO_3 was

added directly to the stacked column. The load and beaker rinse solution was collected, transferred to a 250 ml beaker and evaporated to ~15 ml volume on a hot plate for radiostrontium analysis. The TRU Resin and DGA-Resin cartridges were removed and the TEVA cartridges were kept on the vacuum box. The TEVA cartridge was rinsed with 10 ml 3M nitric acid 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 bleed-off of extractant from the resin (which can occur after strong HCL contacts the extractant-coated 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 10 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene filters, dried, and counted by alpha spectrometry. Cerium was used to prepare alpha sources but another rare earth could have been used. Lanthanum was used instead of cerium in the matrix removal step because La retention on DGA Resin is slightly less than that of Ce. It is important to remove the rare earth added in the sample matrix removal step to ensure good alpha speak resolution in the americium fraction.

The DGA Resin cartridges were placed on a separate vacuum box and processed at the same time as the TEVA Resin cartridges to save time. The DGA Resin cartridges

were rinsed with 8 ml of 0.1M HNO_3 at ~1-2 drops per second to remove any residual uranium that may have passed through TRU Resin. The 0.1M HNO_3 rinse solution will also remove any strontium that may have been retained on the DGA Resin, which has a slight retention for strontium in 3M HNO_3. This rinse solution was collected and added to the 250 ml beaker along with the load and rinse solution collected previously for radiostrontium analysis.

The TRU Resin cartridges were placed above each DGA Resin cartridge. Am was stripped from TRU Resin with 15 ml 3M HCl at ~1-2 drops per second onto DGA Resin. The TRU Resin cartridges were removed. DGA Resin cartridges (alone) were rinsed with 5 ml 3M HCL, 3 ml 1M HNO_3, and 15 ml 0.05M HNO_3 at 1-2 drops per second to remove lanthanum. Am (and Cm if present) was stripped from DGA Resin with 10 ml 0.25M HCL into clean tubes at ~1 drop per second. Cerium was added as previously described to the tubes, along with 1 ml of concentrated hydrofluoric acid (49%), prior to elution. After waiting 10 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene filters (Resolve® filter-Eichrom Technologies), dried and counted by alpha spectrometry.

TRU Resin was rinsed with 15 ml 4M HCl-0.2M HF-0.002M $TiCl_3$ to remove any residual thorium and polonium that may have passed through TEVA and been retained on TRU Resin at ~1-2 drops per second. After the 4M HCl-0.2M HF-0.002M $TiCl_3$ rinse was added to TRU Resin, 5 ml 8M HNO3 was added to TEVA Resin and this rinse was discarded.

Uranium was stripped from TRU Resin using 15 ml 0.1M ammonium bioxalate at ~1 drop per second**.** Cerium was added to the tubes as previously described, along with 1

ml of concentrated hydrofluoric acid (49%), prior to elution. A 0.5 ml volume of 20 wt% titanium chloride was also added to each tube also prior to elution to reduce uranium to U^{+4}. After waiting 10 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene filters (Resolve® filter-Eichrom Technologies), dried and counted by alpha spectrometry.

The load and rinse solutions that were evaporated to ~15 ml on a hot plate were diluted to 25 ml with 8M HNO_3. If any residual solids were present these sample solutions were centrifuged @3500 rpm for ~5 minutes to remove solids. These solutions were loaded onto 3ml Sr Resin (2 ml+1 ml cartridges) at ~1 drop per second. The columns were rinsed with a 3ml 8M HNO_3 tube rinse, followed by 10 ml 8M HNO_3, 5 ml 3M HNO_3-0.05M oxalic acid, 10 ml 8M HNO_3 rinses at 1-2 drops per second. The Sr was stripped from the Sr Resin using 15 mL 0.05M HNO_3 into 50 ml tubes at ~1 drop per second. This solution was transferred to preweighed planchets and evaporated on a hot plate to dryness. Two milliliters 8M HNO_3 were used to rinse each tube and then was transferred to each planchet and dried. The dried planchets were allowed to cool and then were weighed to determine gravimetric carrier recovery. The planchets were counted by simultaneous gas proportional counting (Tennelec LB 4100). The detectors were calibrated using NIST Traceable $^{90}Sr/^{90}Y$ sources matching the sample geometry. Detector backgrounds are determined and subtracted from the sample counts. A mass attenuation correction factor was determined experimentally using prepared mounts containing $^{90}Sr/^{90}Y$ (>167 Bq) and a nominal amount of Sr carrier.

The samples are counted within 1 to 2 hours and corrected for the attenuation of the Sr carrier mass, in-growth of ^{90}Y daughter, and a factor to correct for the fact that the

counting efficiency is determined with a $^{90}Sr/^{90}Y$ source instead of a ^{90}Sr source.

While alpha spectrometry was used in this work, previous work in this lab has shown that if ICP-MS measurement is desired, alternate strip solutions may be used that are compatible with direct introduction without any significant signal suppression [10,11]. Alternately, Pu may be stripped from TEVA Resin using 15 ml 0.25M HCL-0.005M HF-0.0001M titanium (III) chloride solution. The trace of titanium reductant present is very important to achieve effective Pu removal from TEVA Resin. The 0.25M HCL solution used to strip Am from DGA Resin is already compatible with ICP-MS measurements. Uranium may be stripped from TRU Resin using 15 ml 0.01M ammonium bioxalate. A combination of ICP-MS and alpha spectrometry may be used as needed as an alternative to flow injection-ICP-MS and to allow measurement of actinide isotopes with high specific activities and low mass..

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 SRS reported values compared with the MAPEP reference values for ^{238}Pu for each MAPEP 18 vegetation sample (5g) analyzed. Results were calculated based on a per total sample basis as typically requested by the MAPEP program. The differences, which range from -11.3% to +16.7%, fall within the reported uncertainty ranges for each reported result at the 95% confidence level and MAPEP acceptance limits. MAPEP acceptance limits are typically ±20% of the reference value, although measured values greater than ±20% but less than ±30% are acceptable with a warning. 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. The average bias for ^{238}Pu was +2.4%. The average tracer recovery for ^{242}Pu was 101% (6%RSD).

Table 2 shows the SRS reported values compared with the MAPEP 18 reference values for ^{239}Pu for each vegetation sample (5g) analyzed. The differences, which range from -12.1% to +11.8%, fall within the reported uncertainty ranges for each reported result at the 95% confidence level and MAPEP acceptance limits. The average bias for ^{238}Pu was 3.1%.

Table 3 shows the SRS reported values compared with the MAPEP reference values for ^{241}Am for each MAPEP 18 vegetation sample (5g) analyzed. The differences, which range from -12.0% to +15.8%, fall within the reported uncertainty ranges for each

reported result at the 95% confidence level and MAPEP acceptance limits. The average bias for ^{241}Am was +5.6%. The average tracer recovery for ^{243}Am was 93% (7%RSD).

Table 4 shows the SRS reported values compared with the MAPEP reference values for ^{244}Cm for each MAPEP 18 vegetation sample (5g) analyzed. The differences, which range from -12.7% to +9.9%, fall within the reported uncertainty ranges for each reported result at the 95% confidence level and MAPEP acceptance limits. The average bias for ^{244}Cm was -8.6%. These results show that although there may be a slight negative bias ^{244}Cm can be determined using this method using ^{243}Am tracer for yield correction.

Table 5 shows the SRS reported values compared with the MAPEP reference values for ^{234}U for each MAPEP 18 vegetation sample (5g) analyzed. The differences range from +6.9% to +30.7%. The average bias for ^{234}U was +15.6%. The average tracer recovery for ^{232}U was 87% (7%RSD). Table 6 shows the SRS reported values compared with the NIST reference values for ^{238}U for each MAPEP 18 vegetation sample (5g) analyzed. The differences range from -2.6% to +38.7%. The average bias for ^{234}U was +14.4%. It is not known with certainty why there was a slight positive bias for ^{234}U and ^{238}U. The MAPEP vegetation sample aliquots were taken from a 100g sample that was split into 5g aliquots. MAPEP recommends that these samples not be split due to possible homogeneity problems so that may have been why the uranium was higher in some aliquots. When the 10 gram MAPEP samples (the entire sample) were analyzed, no significant positive bias was observed for uranium isotopes.

Table 7 shows the SRS reported values compared with the MAPEP reference values for ^{238}Pu for each MAPEP vegetation sample (10g) analyzed. The differences, which range from -5.9% to +3.7%, fall within the reported uncertainty ranges for each

reported result at the 95% confidence level and well within MAPEP acceptance limits. The average bias for ^{238}Pu was -0.2%. The average tracer recovery for ^{242}Pu was 90% (15%RSD). Table 8 shows the SRS reported values compared with the MAPEP reference values for ^{239}Pu for each vegetation sample (10g) analyzed. The differences, which range from -3.2% to +0.4%, fall within the reported uncertainty ranges for each reported result at the 95% confidence level. The average bias for ^{238}Pu was -3.2%. The ^{239}Pu isotope was not added to the MAPEP 16 sample and the results for this false positive test are acceptable.

Table 9 shows the SRS reported values compared with the MAPEP reference values for ^{241}Am for each MAPEP vegetation sample (10g) analyzed. The differences, which range from -5.4% to -1.1%, fall within the reported uncertainty ranges for each reported result at the 95% confidence level and well within MAPEP acceptance limits. The average bias for ^{241}Am was -3.2%. The average tracer recovery for ^{243}Am was 84% (12%RSD).

Table 10 shows the SRS reported values compared with the MAPEP reference values for ^{234}U for each MAPEP vegetation sample (10g) analyzed. The differences range from -2.9% to +1.4%. The average bias for ^{234}U was -1.5%. The average tracer recovery for ^{232}U was 81% (12%RSD). Table 11 shows the SRS reported values compared with with the MAPEP reference values for ^{238}U for each MAPEP vegetation sample (10g) analyzed. The differences range from -3.2% to -2.4%. The average bias for ^{238}U was -3.0%. The differences for the for ^{234}U and ^{238}U measured values fall within the reported uncertainty ranges for each reported result at the 95% confidence level and are well within MAPEP acceptance limits.

Table 12 shows the SRS reported values compared with the MAPEP reference values for ^{90}Sr for each MAPEP vegetation sample (5g) analyzed. The differences, which range from 1.4%% to +26.9%. The possible homogeneity issues with the 100g MAPEP vegetation sample split into 5g aliquots noted previously may have also affected the ^{90}Sr results in some aliquots. When the 10 gram MAPEP samples (entire sample analyzed), no significant positive bias was observed for ^{90}Sr. The average bias for ^{90}Sr in the 5g aliquots was 10.9%. The average stable strontium carrier recovery was 64% (4%RSD). The collection and separation of ^{90}Sr for analysis along with the actinides results in significant time savings. If $^{89/90}$Sr differentiation is needed, there are Čerenkov counting techniques for more rapid determination of ^{89}Sr and ^{90}Sr. ^{89}Sr can be measured directly by Čerenkov counting, employing methodology that takes advantage of the high Čerenkov counting efficiency of ^{89}Sr relative to ^{90}Sr [12].

Table 13 shows the SRS reported values compared with the MAPEP reference values for ^{90}Sr for each MAPEP vegetation sample (10g) analyzed. The differences, which range from -2.9%% to +2.1%, are within the uncertainty ranges for each reported result at the 95% confidence level and are well within MAPEP acceptance limits.

Figure 3 shows an example of the plutonium spectra for a MAPEP vegetation sample. The ^{242}Pu tracer recovery was 99% and the Full Width Half Maximum (FWHM) was 35 keV, showing acceptable alpha peak resolution and minimal reduction in tracer recoveries even with rapid column flow rates. The ^{239}Pu peak labeled on the spectra represents ^{239}Pu plus ^{240}Pu, since these isotopes have essentially the same alpha energy.

Figure 4 shows an example of the americium spectra for a MAPEP vegetation sample. The ^{243}Am tracer recovery was 98% and the Full Width Half Maximum (FWHM) was 49 keV, showing acceptable alpha peak resolution.

Figure 5 shows an example of the uranium spectra for a MAPEP vegetation sample. The ^{232}U tracer recovery was 90% and the Full Width Half Maximum (FWHM) was 37 keV, showing acceptable alpha peak resolution.

Conclusions

A new rapid method to determine actinides and strontium-90 in vegetation has been developed that can be used for emergency response or routine analyses. The data quality based on the analysis of MAPEP samples is good, and tracer yields and removal of interferences are very good. The rapid fusion method eliminates residual solids that can sometimes occur with simply ashing the samples at high temperature and wet ashing with acids prior to extraction chromatography.

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Table Captions

Figure Captions

Figure 1 Rapid Vegetation Sample Preparation

Figure 2 Rapid Vegetation Column Separation

Figure 3 Alpha spectra showing Pu Isotopes in MAPEP Vegetation Sample

Figure 4 Alpha spectra showing Am Isotopes in MAPEP Vegetation Sample

Figure 5 Alpha spectra showing U Isotopes in MAPEP Vegetation Sample

Table 1 MAPEP Vegetation Analysis Results for ^{238} Pu (5g)

Sample ID	^{242}Pu Yield (%)	^{238}Pu Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	93	0.147	0.133 ±0.020	-9.7	MAPEP 18
2	100	0.147	0.171 ±0.026	16.7	MAPEP 18
3	109	0.147	0.130 ±0.020	-11.3	MAPEP 18
4	97	0.147	0.167 ±0.025	13.9	MAPEP 18
5	106	0.147	0.163 ±0.024	10.7	MAPEP 18
6	99	0.147	0.140 ±0.021	-4.7	MAPEP 18
Avg	101			2.4	
% RSD	6				

Table 2 MAPEP Vegetation Analysis Results for ^{239} Pu (5g)

Sample ID	^{242}Pu Yield (%)	^{239}Pu Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	93	0.284	0.282 ±0.042	-0.7	MAPEP 18
2	100	0.284	0.317 ±0.048	11.8	MAPEP 18
3	109	0.284	0.268 ±0.040	-5.6	MAPEP 18
4	97	0.284	0.303 ±0.045	6.9	MAPEP 18
5	106	0.284	0.250 ±0.038	-12.1	MAPEP 18
6	99	0.284	0.290 ±0.044	2.0	MAPEP 18
Avg	101			3.1	
% RSD	6				

Table 3 MAPEP Vegetation Analysis Results for ^{241}Am (5g)

Sample ID	^{243}Am Yield (%)	^{241}Am Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	92	0.24	0.241 ±0.036	0.4	MAPEP 18
2	85	0.24	0.278 ±0.042	15.8	MAPEP 18
3	98	0.24	0.236 ±0.035	-1.7	MAPEP 18
4	87	0.24	0.258 ±0.039	7.7	MAPEP 18
5	103	0.24	0.211 ±0.032	-12.0	MAPEP 18
6	92	0.24	0.230 ±0.035	-4.0	MAPEP 18
Avg	93			5.6	
% RSD	7				

Table 4 MAPEP Vegetation Analysis Results for ^{244}Cm (5g)

Sample ID	^{243}Am Yield (%)	^{244}Cm Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	92	0.0314	0.030±0.005	-3.2	MAPEP 18
2	85	0.0314	0.028±0.005	-10.5	MAPEP 18
3	98	0.0314	0.027±0.005	-12.7	MAPEP 18
4	87	0.0314	0.029±0.005	-8.0	MAPEP 18
5	103	0.0314	0.027±0.005	-12.7	MAPEP 18
6	92	0.0314	0.035±0.006	9.9	MAPEP 18
Avg	93			-8.6	
% RSD	7				

Table 5 MAPEP Vegetation Analysis Results for ^{234}U (5g)

Sample ID	^{232}U Yield (%)	^{234}U Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	81	0.346	0.370 ±0.056	7.0	MAPEP 18
2	81	0.346	0.452 ±0.068	30.7	MAPEP 18
3	94	0.346	0.374 ±0.056	8.1	MAPEP 18
4	93	0.346	0.403 ±0.060	16.6	MAPEP 18
5	81	0.346	0.441 ±0.066	27.5	MAPEP 18
6	90	0.346	0.370 ±0.056	6.9	MAPEP 18
Avg	87			15.6	
% RSD	7				

Table 6 MAPEP Vegetation Analysis Results for ^{238}U (5g)

Sample ID	^{232}U Yield (%)	^{238}U Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	81	0.359	0.415 ±0.062	15.6	MAPEP 18
2	81	0.359	0.432 ±0.065	20.3	MAPEP 18
3	94	0.359	0.385 ±0.058	7.1	MAPEP 18
4	93	0.359	0.411 ±0.062	14.6	MAPEP 18
5	81	0.359	0.498 ±0.075	38.7	MAPEP 18
6	90	0.359	0.350 ±0.053	-2.6	MAPEP 18
Avg	87			14.4	
% RSD	7				

Table 7 MAPEP Vegetation Analysis Results for ^{238}Pu (10g)

Sample ID	^{242}Pu Yield (%)	^{238}Pu Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	71	0.137	0.142 ±0.021	3.7	MAPEP 15
2	97	0.137	0.139 ±0.021	1.3	MAPEP 15
3	90	0.151	0.151 ±0.023	0.2	MAPEP 16
4	102	0.151	0.142 ±0.021	-5.9	MAPEP 16
Avg	90			-0.2	
% RSD	15				

Table 8 MAPEP Vegetation Analysis Results for ^{239}Pu (10g)

Sample ID	^{242}Pu Yield (%)	^{239}Pu Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	71	0.164	0.165 ±0.025	0.4	MAPEP 15
2	97	0.164	0.159 ±0.024	-3.2	MAPEP 15
3	102	N/A	0.0001 ±0.0001	N/A	MAPEP 16
4	0	N/A	0.0003 ±0.0003	N/A	MAPEP 16
Avg	68			-1.4	
% RSD	70				

NA is shown when no ^{239}Pu was present. Acceptable false positive test results.

Table 9 MAPEP Vegetation Analysis Results for ^{241} Am (10g)

Sample ID	^{243}Am Yield (%)	^{241}Am Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	71	0.156	0.154 ±0.023	-1.1	MAPEP 15
2	94	0.156	0.154 ±0.022	-5.4	MAPEP 15
3	82	N/A	0.0001 ±0.0001	N/A	MAPEP 16
4	89	N/A	0.0001 ±0.0001	N/A	MAPEP 16
Avg	84			-3.2	
% RSD	12				

NA is shown when no ^{241}Am was present. Acceptable false positive test results.

Table 10 MAPEP Vegetation Analysis Results for ^{234} U (10g)

Sample ID	^{232}U Yield (%)	^{234}U Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	67	0.208	0.211 ±0.032	1.4	MAPEP 15
2	89	0.208	0.202 ±0.030	-2.9	MAPEP 15
3	82	0.243	0.237 ±0.036	-2.6	MAPEP 16
4	86	0.243	0.238 ±0.036	-1.9	MAPEP 16
Avg	81			-1.5	
% RSD	12				

Table 11 MAPEP Vegetation Analysis Results for ^{238} U (10g)

Sample ID	^{232}U Yield (%)	^{238}U Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	67	0.216	0.211 ±0.032	-2.4	MAPEP 15
2	89	0.216	0.209 ±0.031	-3.2	MAPEP 15
3	82	0.253	0.245 ±0.037	-3.0	MAPEP 16
4	86	0.253	0.245 ±0.037	-3.2	MAPEP 16
Avg	81			-3.0	
% RSD	12				

Table 12 MAPEP Vegetation Analysis Results for ^{90}Sr (5g)

Sample ID	Sr carrier (%)	^{90}Sr Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	64	1.273	1.39±0.28	9.5	MAPEP 18
2	66	1.273	1.58±0.32	24.2	MAPEP 18
3	60	1.273	1.33±0.27	4.2	MAPEP 18
4	67	1.273	1.34±0.27	5.6	MAPEP 18
5	65	1.273	1.29±0.26	1.4	MAPEP 18
6	64	1.273	1.62±0.32	26.9	MAPEP 18
Avg	64			10.9	
% RSD	4				

Table 13 MAPEP Vegetation Analysis Results for ^{90}Sr (10g)

Sample ID	Sr carrier (%)	^{90}Sr Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	67	1.561	1.57 ±0.31	0.6	MAPEP 15
2	70	1.561	1.55 ±0.31	-0.5	MAPEP 15
3	64	1.095	1.06 ±0.21	-2.9	MAPEP 16
4	77	1.095	1.12 ±0.22	2.1	MAPEP 16
Avg	70			-0.2	
% RSD	8				

Figure 1 Rapid Vegetation Sample Preparation

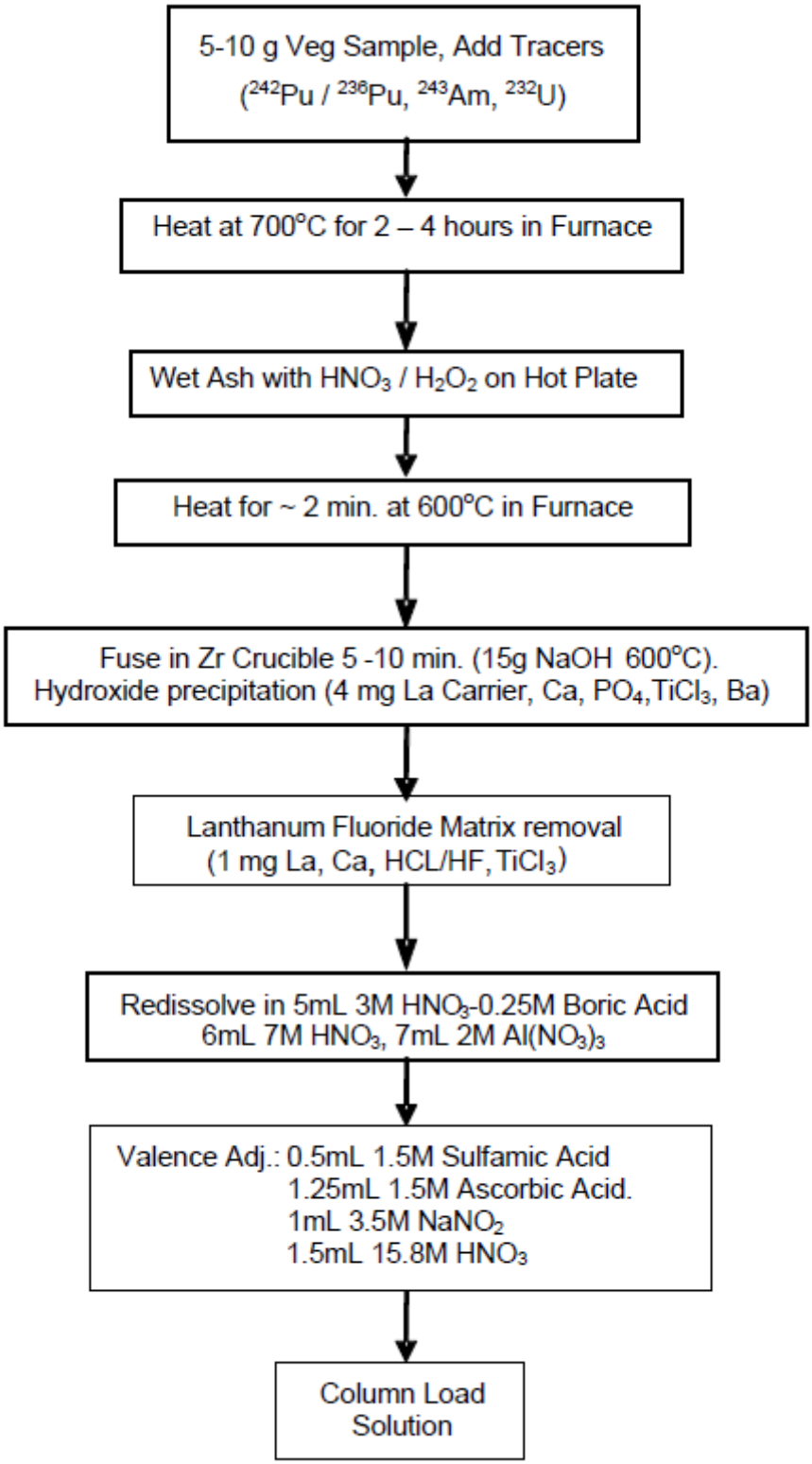
5-10 g Veg Sample, Add Tracers
(^{242}Pu / ^{236}Pu, ^{243}Am, ^{232}U)
Heat at 700°C for 2 – 4 hours in Furnace
Wet Ash with HNO_3 / H_2O_2 on Hot Plate
Heat for ~ 2 min. at 600°C in Furnace
Fuse in Zr Crucible 5 -10 min. (15g NaOH 600°C).
Hydroxide precipitation (4 mg La Carrier, Ca, PO_4,$TiCl_3$, Ba)
Lanthanum Fluoride Matrix removal
(1 mg La, Ca, HCL/HF, $TiCl_3$)
Redissolve in 5mL 3M HNO_3-0.25M Boric Acid
6mL 7M HNO_3, 7mL 2M $Al(NO_3)_3$
Valence Adj.: 0.5mL 1.5M Sulfamic Acid
1.25mL 1.5M Ascorbic Acid.
1mL 3.5M $NaNO_2$
1.5mL 15.8M HNO_3
Column Load
Solution

Figure 2 Rapid Vegetation Column Separation

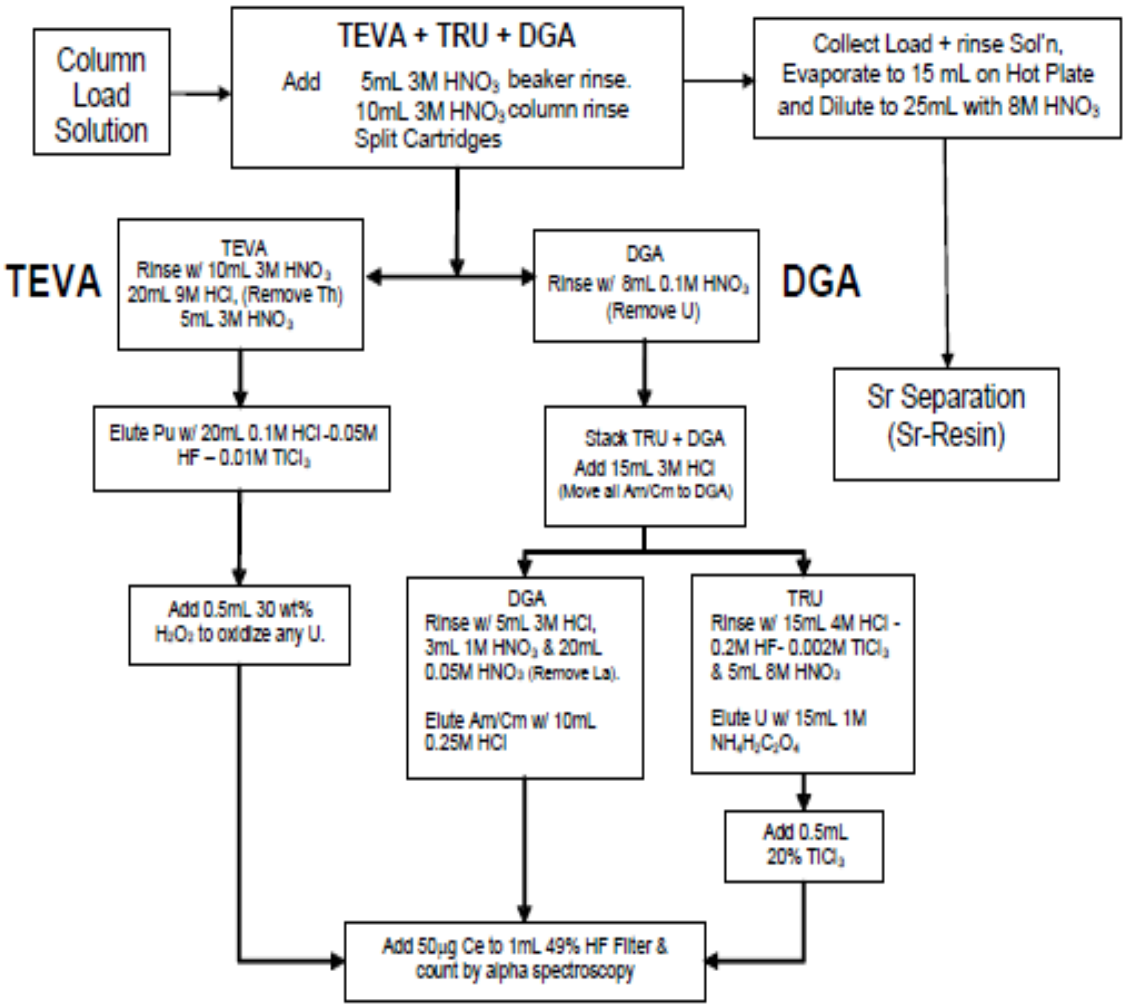

Figure 3 Alpha spectra showing Pu Isotopes in MAPEP Vegetation Sample

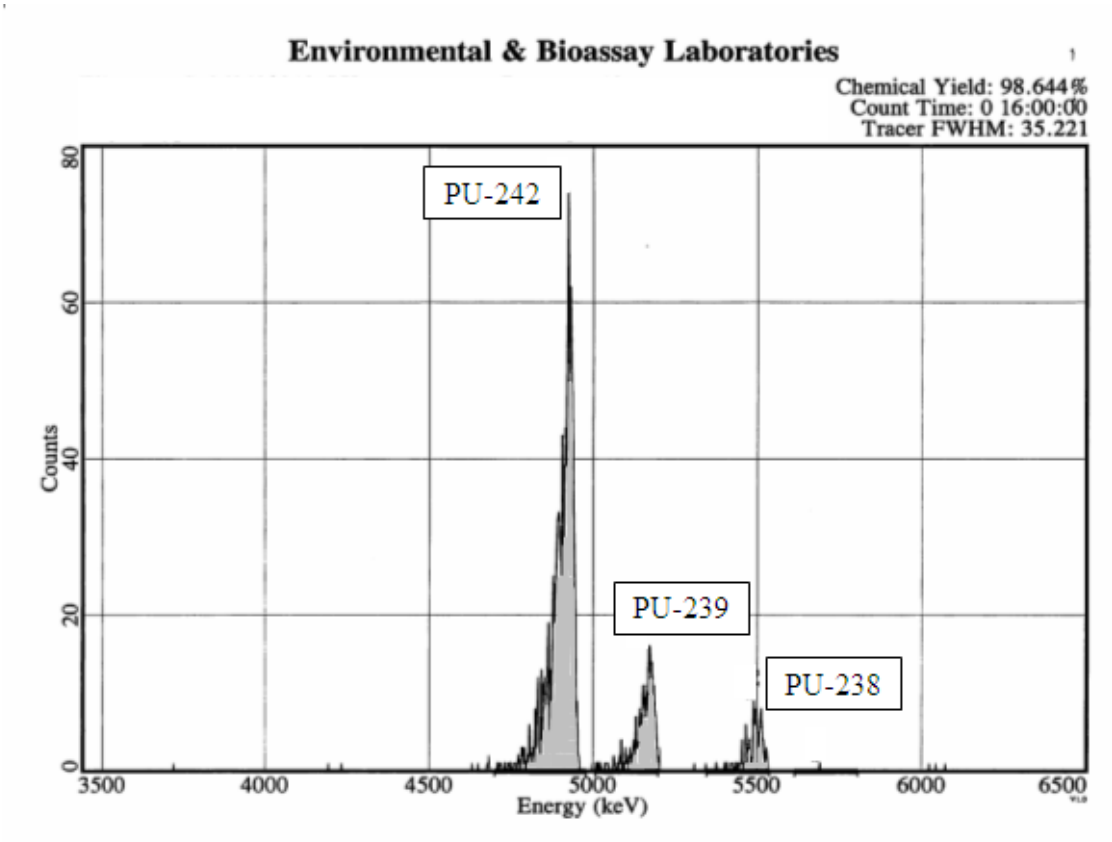

Figure 4 Alpha spectra showing Am Isotopes in MAPEP Vegetation Sample

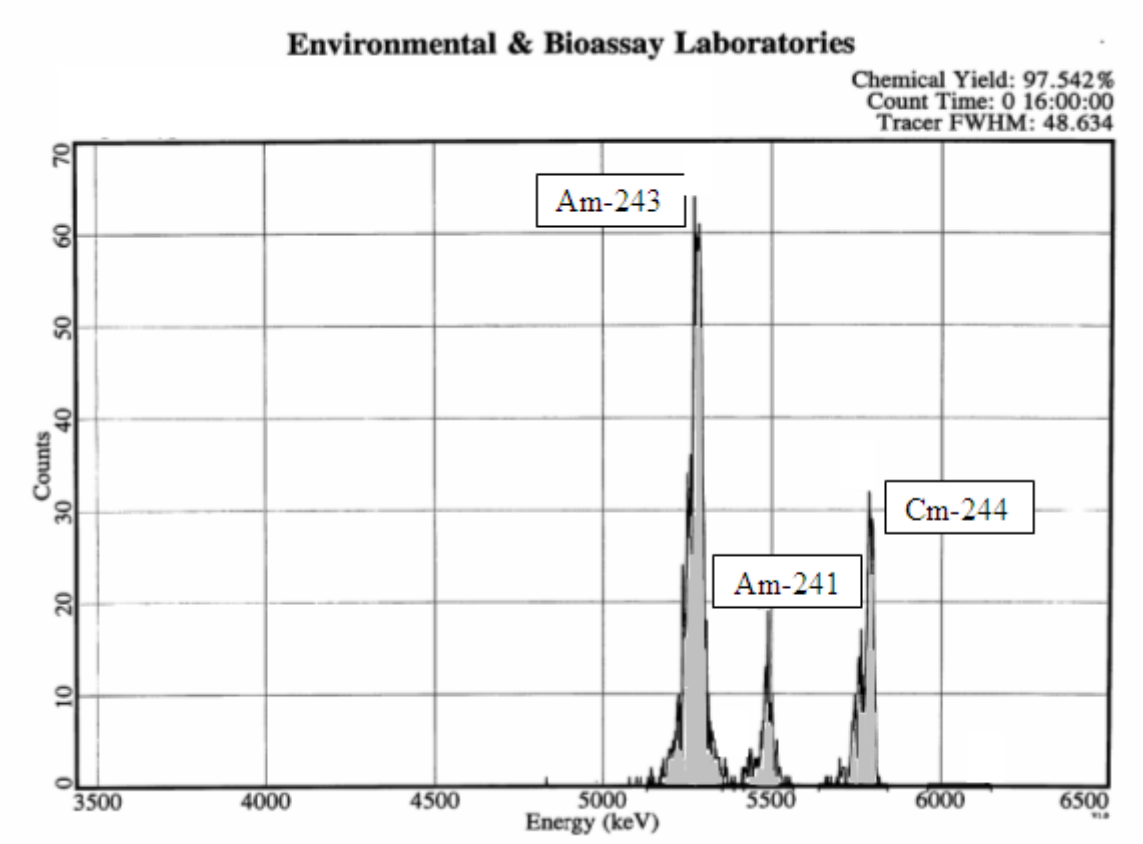

Figure 5 Alpha spectra showing U Isotopes in MAPEP Vegetation Sample