1. ABSTRACT

A Solid Phase Extraction (SPE) technique is described for the selective separation of americium, curium, strontium, plutonium and uranium from soil and vegetation matrices. Environmental soils are dissolved and the strontium and actinides are separated from nitric acid using the SPE (TRU & TEVA) columns in a serial configuration. Sr-90 is separated by classical sulfate precipitation and then the Y-90 daughter is allowed to grow in before being quantified by beta proportional counting. The actinides are co-precipitated with neodymium fluoride, mounted and quantified by alpha spectrometry.

2. APPLICABILITY

This method is designed to selectively separate strontium and actinides from environmental soil samples up to 10 grams and vegetation samples up to 120 grams in size. Isotopic tracers are added to determine yield. The samples are digested in a combination on nitric and hydrofluoric acids followed by a lithium meta-borate fussion to achieve total dissolution. Other sample matrixes and sizes may be run by this procedure. Adjustments in reagent amounts and dish/beaker sizes may be made for these samples.

A Job Safety Analysis (JSA) was developed for this method in accordance with a determination made using MCP-3562, *Hazard Identification, Analysis and Control of Operational Activities*, and MCP-3480, *Environmental Instructions for Facilities, Processes, Materials and Equipment.*

Sections 7.1 through 7.5 may be used for the initial dissolution and preconcentration and then the elements of interest may be separated by other procedures.

3. DISCUSSION

Vegetation samples are ashed and then treated the same as soil samples. Up to 120 grams of dry vegetation samples may be used. Actinides are separated from environmental soil samples up to 10 grams in size as well as highly radioactive soils containing mixed fission products using this method. Isotopic tracers are added to the dry soil and mixed. The soils are digested in a combination of nitric and hydrofluoric acids followed by a lithium meta-borate fusion. The fusion cake is dissolved in dilute nitric acid and lanthanides, actinides and some strontium are concentrated with a hydroxide precipitation. The rest of the strontium is collected using a carbonate precipitation. The matrix is adjusted to 4M nitric acid and the plutonium oxidation state is adjusted to +4

using ascorbic acid and sodium nitrite. This solution is passed through one TEVA and two TRU columns stacked in tandem.

The strontium passes through all the columns and is collected and purified using strontium sulfate and yttrium oxalate precipitations.

The TEVA columns remove thorium and plutonium from the sample. Thorium is eluted with 6M HCl and the plutonium is reduced and eluted using 0.5M HCl containing $TiCl_3$.

The remaining actinides and lanthanides are removed from the sample by the TRU columns. Some other elements in the +3 state (such as yttrium) are also retained on the TRU column. The americium and retained +3 elements (lathanides, actinides and rare earths) are eluted with 9M HCl and 4M HCl. The uranium is eluted with 0.1M ammonium bioxalate.

Each actinide is reduced and coprecipitated with neodymium as the fluoride. The precipitate is filtered on a 0.1 micron polypropylene filter paper and quantified on an alpha spectrometer.

Other actinide and lanthanide isotopes not specifically mentioned in this procedure may be analyzed by selecting the appropriate final prep and using the proper counting method (i.e. Pu241 on Pu prep by LSC and SM151 on Am prep by LSC). Also, if an appropriate tracer is not available, a tracerless analysis may be done. Consult the technical leader.

4. SAFETY PRECAUTIONS

4.1 Use appropriate gloves and exercise caution to avoid contact. Hot surfaces may be present [JSA]

4.2 Use care and appropriate PPE when handling. Acids and bases may cause chemical burns. [JSA]

4.3 Handle radiological samples as specified on the applicable Radiological Work Permit (RWP). RCT coverage may be required. [JSA]

4.4 Use care to limit personal exposure. The solutions being analyzed may be highly radioactive [JSA]

NOTE: *When tracers must be added to the samples this activity shall be in an RBA under a current RWP. [JSA]*

4.5 Handle all chemicals in strict accordance with MCP-3635, *Chemical Hygiene Plan.* [JSA]

NOTE: *After samples have been concentrated, dried, muffled, desiccated, filtered and dried or other method or procedure that may have changed the concentration of radioactivity, an RCT must survey prior to moving sample to avoid the spread of contamination. [JSA]*

4.6 Use care and proper PPE to avoid contact. Ensure concentrated HF burn gel is available at the work area. Contact with concentrated HF can result in severe burns. [JSA]

4.7 Seek more information on safety from the Material Safety Data Sheets (MSDS), laboratory supervision, and industrial Safety Personnel.

5. APPARATUS AND REAGENTS

5.1 Apparatus

5.1.1 0.100 μm polypropylene filters, 25 mm

5.1.2 Alpha spectroscopy system with multichannel analyzer

5.1.3 Centrifuge with 50-mL tubes

5.1.4 Infrared heat lamp or vacuum oven

5.1.5 Muffle furnace or vacuum oven

5.1.6 Pipettes, Eppendorf or equivalent, assorted sizes, plus tips

5.1.7 Platinum (Pt) dish

5.1.8 Polypropylene beakers, assorted sizes

5.1.9 Pyrex beakers, assorted sizes

5.1.10 Stirring hot plate, with stir bars

5.1.11 TEVA extraction columns available from EIChroM Industries, Inc. (Evanston, IL)

5.1.12 TRU extraction columns available from EIChroM Industries, Inc. (Evanston, IL)

5.1.13 Vacuum manifold and filtering apparatus.

5.2 Reagents

NOTE: *Only Analytical Reagent Grade chemicals and high resistivity water is used for preparation of all reagents.*

5.2.1 Acetic acid, glacial

5.2.2 Aluminum nitrate solution (50% by weight): 500 g of $Al(NO_3)_3 \bullet 9H_2O$, per 1 L of water

5.2.3 Ammonium bioxalate, $(NH_4)HC_2O_4$, 0.1M: Dissolve 7 g of ammonium oxalate, $(NH_4)_2C_2O_4 \bullet H_2O$ and 3.5 g of oxalic acid ($HOOCCOOH \bullet 2H_2O$) in 1 L of water

5.2.4 Ammonium hydroxide, NH_4OH

5.2.5 2M ammonium thiocyanate +0.1M acetic acid: 152 g of NH_4SCN and 6 mL acetic acid diluted to 1 L with water

5.2.6 0.4M ammonium thiocyanate: Dissolve 30.2 g of NH_4SCN in 1 L of water

5.2.7 Ascorbic acid solution, 10%: Prepare fresh before each use by dissolving 1 g in 10 mL of water

5.2.8 Hydrochloric acid, HCl:

- 12M: concentrated (38%)
- 9M: 750 mL concentrated HCl diluted to 1 L with water
- 6M: 500 mL concentrated HCl diluted to 1 L with water
- 4M: 330 mL concentrated HCl diluted to 1 L with water
- 1M: 83 mL concentrated HCl diluted to 1 L with water
- 0.5M: 42 mL concentrated HCl diluted to 1 L with water

5.2.9 Hydrofluoric acid, concentrated HF, concentrated (49%)

5.2.10 Lithium metaborate, $LiBO_2$

5.2.11 Lithium sulfate

5.2.12 Neodymium solution, 0.5 mg/mL: Dissolve 0.583 g of neodymium oxide with 20 mL of 4M HCl and dilute to 1 L with water

5.2.13 Nitric acid, HNO_3:
- 16M: concentrated (69%)
- 4M: 250 mL concentrated HNO_3 diluted to 1 L with water
- 2.5M: 156 mL concentrated HNO_3 diluted to 1 L with water
- 2.0M: 125 mL concentrated HNO_3 diluted to 1 L with water

5.2.14 Oxalic acid solution, 0.03M in 1M HCl: Add 83 mL of concentrated HCl to 500 mL of H2O and mix, then add 3.8 g oxaclic acid (HOOCCOOH•2H2O) and dilute to 1 L with water. Shake to dissolve the oxalic acid.

5.2.15 Reagent alcohol

5.2.16 Sodium nitrite solution, 5% $NaNO_2$: Prepare fresh before each use by dissolving 0.5 g in 10 mL of water

5.2.17 Sodium sulfate, Na_2SO_4

5.2.18 Strontium carrier 100mg/mL, dissolve 30g of strontium chloride in 100 mL of water

5.2.19 Strontium chloride,0.1%: Dissolve 5g of strontium chloride, $SrCl_2 \cdot (6H_2O)$, in 500 mL of water

5.2.20 Titanium trichloride, $TiCl_3$, 20% solution, commercially available.

5.2.21 Tracers, Recommended amounts:
Am-243: 0.500 mL of .104 dps/ml,
Pu-242: 0.100 mL of .8594 dps/ml,
U-232: 0.500 g of 0.100 dps/ml and Sr-85: ~1900 dpm.

6. SAMPLE HANDLING

6.1 Check water samples for a pH of 2 or less. If pH is greater than 2, add 5mL of concentrated nitric acid and wait 24 hours. Repeat if pH is still above 2.

7. PROCEDURES

NOTE 1: *Not all sections are required to be performed. Sections may be repeated as needed in support of operational flexibility.*

NOTE 2: *All steps within a given section are to be performed in sequence unless other instructions are provided.*

7.1 Sample Setup

WARNING

Tracers must be added to the samples in an RBA under a current RWP. [JSA]
If higher activities than those listed below need to be added, supervision must be contacted before proceeding.

7.1.1 Laboratory Analyst: Weigh soil sample (usually 10 grams) into a 250 mL Pt dish and record weight.

7.1.2 Weigh vegetation sample (up to 120 grams) into a beaker and record weight.

7.1.3 Add appropriate tracers. (Recommended amounts: Am-243: 0.500 mL of .104 dps/mL, Pu-242: 0.100 mL of .8594 dps/mL, U-232: 0.500 g of 0.100 dps/mL and Sr-85: ~1900 dpm).

7.1.4 Ash vegetation sample in a muffle furnace at 520°C using a 1°C/minute heat-up rate.

7.2 Acid Digestion

7.2.1 Laboratory Analyst: Transfer ashed vegetation sample to a 250-mL Pt dish using 2M HNO_3 as necessary to wash the beaker.

7.2.2 Slowly add 2M HNO_3 until the sample is wet.

7.2.3 Slowly add concentrated HF until the sample is covered.

7.2.4 Slowly take the samples to dryness on a hotplate.

7.2.5 Wash down the sides of the Pt dish with 2M HNO_3.

7.2.6 Add concentrated HF until the sample is covered.

7.2.7 Slowly take the samples to dryness on a hotplate.

7.2.8 Wash down the sides of the Pt dish with concentrated HF until the sample is covered.

7.2.9 Slowly take the samples to dryness on a hotplate.

7.2.10 Wash down the sides of the Pt dish with concentrated HNO_3.

7.2.11 Slowly take the samples to dryness on a hotplate.

7.2.12 Wash down the sides of the Pt dish with 2M HNO_3.

7.2.13 Slowly take the samples to dryness on a hotplate.

7.2.14 Wash down the sides of the Pt dish with 2M HNO_3.

7.2.15 Slowly take the samples to dryness on a hotplate.

7.3 Fusion

7.3.1 Laboratory Analyst: Heat the sample in a muffle furnace at 520° C for about 3 minutes.

7.3.2 Cool and add 9 grams of lithium meta-borate($LiBO_2$).

7.3.3 Fuse the sample by heating in a muffle at 1020° C. Swirl the melt occasionally until a uniform clear melt is obtained.

7.3.4 Let the sample cool.

7.4 Dissolving

7.4.1 Laboratory Analyst: Put a small stir bar in the Pt dish.

7.4.2 Place the Pt dish in a 1000 mL beaker and cover the melt with about 600 mL of water.

7.4.3 Add 25 mL of concentrated HNO_3.

7.4.4 Heat on a stirring hotplate until fusion cake is dissolved.

7.4.5 Remove the Pt dish.

7.5 Concentrating

7.5.1 Laboratory Analyst: Add 0.5 mL of 10% $FeCl_3$ solution to sample while stirring.

7.5.2 Slowly add 50% NaOH to sample to establish a pH of 9 to 10 while stirring. (A rust-colored precipitate should form.) Continue stirring sample for 10 minutes.

7.5.3 Remove the stir bar, and let the precipitate settle (usually overnight).

7.5.4 Decant and save the solution for Sr90 analysis.

7.5.5 Transfer the precipitate to a 250-mL centrifuge tube with water.

7.5.6 Centrifuge and decant the solution.

7.5.7 Combine solutions from Steps 7.5.4 and Steps 7.5.6 and save for Sr-90 analysis ($SrCO_3$ preconcentration in procedure ACMM-3815,).

7.5.8 Dissolve the precipitate with 5 mL of concentrated HNO_3 and transfer solution to a 250 mL beaker and dilute to about 100 mL.

7.6 Actinide Separation

7.6.1 Laboratory Analyst: Add 20 mL of 50% $Al(NO_3)_3 \bullet 9H_2O$ solution.

7.6.2 Add 2 mL of 10% ascorbic acid and heat near boiling until sample turns yellow or for 10 minutes. Remove samples from heat.

7.6.3 Carefully add 2 mL of 5% $NaNO_2$ and heat at or near boiling for 10 minutes.

7.6.4 Cool to room temperature and adjust volume to 140 mL with water before loading onto columns.

7.6.5 Stack a TEVA with a reservoir extension above two TRU columns with reservoirs. Make two sets for each soil sample.

7.6.6 Condition the TEVA and TRU columns with a 7 mL of 4M HNO_3.

7.6.7 Split the soil samples into two 70 mL samples.

7.6.8 Load the samples onto the columns.

7.6.9 Once the samples have passed through all three columns, rinse columns with 5 mL of 4M HNO_3. Collect the load solution and the rinse for Sr-90 analysis for later use in Section 7.12.

7.6.10 Rinse the columns with an additional 7.5 mL of 4M HNO_3. Collect the rinse as waste.

7.6.11 Separate the columns.

7.7 TEVA Columns(Pu analysis)

7.7.1 Laboratory Analyst: Elute Thorium from TEVA columns with two 7.5 mL aliquots of 6M HCl. Collect this "Thorium fraction" as waste.

7.7.2 Elute Plutonium from the first TEVA columns with 15 mL of 0.5M HCl + 0.20 mL of $TiCl_3$. (Mix the HCl and the $TiCl_3$ just before pouring through columns). Collect this "Plutonium fraction" in centrifuge tubes and save for final precipitation and mounting for later use in Section 7.11.

7.8 TRU Columns(Am analysis)

7.8.1 Laboratory Analyst: Rinse the TRU columns twice with 7.5 mL of 4M HNO_3. Collect the rinse as waste.

7.8.2 Elute Americium from the TRU columns with 2 mL of 9M HCl followed by 15 mL of 4M HCl. Collect this "Americium fraction" in centrifuge tubes and save for the "rare earth separation" for later use in Section 7.10.

7.9 TRU Columns(U analysis)

7.9.1 Laboratory Analyst: After the Am is eluted, rinse only the first TRU column with two 10-mL aliquots of 0.03M oxalic acid in 1M HCl. Collect the rinse as waste.

7.9.2 Elute Uranium from the TRU columns with 20 mL of 0.1M ammonium bioxalate. Collect this "Uranium fraction" in centrifuge tubes and save for the "final precipitation and mounting" for later use in Section 7.11.

7.10 Separation of Americium From Rare Earths

7.10.1 Laboratory Analyst: Combine all "americium fractions" for each sample in a beaker. (4 for soil and 2 for vegetation).

7.10.2 Evaporate the samples to dryness.

7.10.3 Dissolve the residue in 10 mL of (2M ammonium thiocyanate +0.1M Acetic acid) solution by gently heating. Allow the samples to cool to room temperature.

7.10.4 Condition a new TEVA column with 10 mL of (2M ammonium thiocyanate +0.1M Acetic acid) solution.

7.10.5 Load the sample onto the TEVA column.

7.10.6 Add 10 mL of (2M ammonium thiocyanate +0.1M Acetic acid) solution to the original beakers, and heat until just boiling. Allow to cool to room temperature and load onto the TEVA column.

7.10.7 Wash the TEVA column with 10 mL of (2M ammonium thiocyanate + 0.1M Acetic acid) solution.

7.10.8 Elute Americium with 20 mL of (0.2M Ammonium Thiocyanate + 0.25 M HCl. Make fresh each day by combining equal volumes of 0.4 M Ammonium Thiocyanate and 0.5M HCI). Collect the eluant in centrifuge tubes and continue with the "final precipitation and mounting."

7.11 Final Precipitation and Mounting

7.11.1 Laboratory Analyst: For U analysis only, add 0.5 mL of $TiCl_3$ to each tube and mix, and let stand at least 5 minutes.

7.11.2 For Pu analysis only, if the Ti purple color does not persist from the elution process add 0.2 mL of $TiCl_3$, mix and let stand at least 5 minutes.

7.11.3 To all fractions (U, Pu, and Am), add 0.2 ml of the 0.5 mg/mL Nd solution to each centrifuge tube and mix. For each soil sample, there should be two tubes for Pu, two tubes for U, and one tube for Am. For each vegetation sample, there should be one tube for Pu, one tube for U, and one tube for Am.

7.11.4 Add at least 5 mL of concentrated HF, and mix.

7.11.5 Set up the filtration apparatus with a 0.1 micron polypropylene filter. Wet the filter with reagent alcohol.

7.11.6 Filter the sample, washing first with a small amount of water and then with a small amount of reagent alcohol. (Note that the U and Pu soil samples each consist of two centrifuge tubes and that the sample in both of these centrifuge tubes should be filtered through one filter).

7.11.7 Mount the filter (precipitate side up) to a round self-adhesive numbered label with the ID of the sample written on it.

7.11.8 Dry the filters, and place them in the alpha chamber for counting. Consult the operator's manual for instrument operating instructions.

7.12 Sr-90

7.12.1 Laboratory Analyst: Generally, each sample will have four 50 mL centrifuge tubes containing the "Sr fraction". Add and dissolve 3.5 grams of $Li2SO_4$ in each tube.

7.12.2 To each tube, add 0.1 mL of 100 mg/mL Sr carrier, mix and wait at least 5 minutes (A strontium sulfate precipitate will form).

7.12.3 Add five 3 mL aliquots of 0.1% SrCl2, mixing and waiting at least 3 minutes after each addition.

7.12.4 Allow to sit overnight.

7.12.5 Centrifuge, decant, and save the supernate.

7.12.6 With the strontium sulfate precipitate, continue with the Sr90 analysis in ACMM-3815 Section 7.9.

8. QUALITY CONTROL REQUIREMENTS

8.1 Analyze a blank with each batch. Blank values are used during calculations for accurate results.

8.2 Analyze a control sample with each batch. Repeat any control that is beyond 20% of known values or beyond the acceptance criteria specified by the customer.

8.3 Analyze any additional QC samples as required by project requirements.

9. CALCULATIONS

The SUN/Analytical computer is programmed to calculate the activity of each isotope. The method requires that a daily control be passed before the analyst can enter results. If hand calculations are necessary, they can be performed according to the following equations.

NOTE: *If the following equation is used, the appropriate dilution factors must be used as applicable.*

$$Pu\text{ - }238\ d/s/g = \frac{cnts\ @\ 5.499\ MEV * SA}{cnts\ @\ 5.74\ MEV * W}$$

Example:

Where:

cnts @ 5.499 MEV = total counts in Pu-238 peak

cnts @ 4.91 MEV = total counts in Pu-242 spike peak

SA = spike acitvity added in d/s

W = weight of sample in grams.

Convert to other units if requested by the customer.
Other isotopes are calculated in the same manner using the counts at the appropriate energy and the counts from the appropriate tracer.

10. RECORDS

Records Description	Uniform File Code	Disposition Authority	Retention Period
Data printouts Data reports Electronic data files Preparation Logbook	7101	MCP-2007, *Analytical Records Management*	

11. REFERENCES

11.1 Analytical Chemistry, Horwitz E.P., Dietz M. L., Fisher D. E., 1991.

11.2 The Chemistry of Plutonium, Cleveland J. M., 2nd edition - 1979.

11.3 Nuclear and Radiochemistry, Friedlander G., Kennedy J. W., 3rd edition - 1981.

11.4 MCP-2001, *Control of Analytical Methods and Procedures*

11.5 MCP-2007, *Analytical Records Management*

11.6 MCP-3562, *Hazard Identification, Analysis & Control of Operational Activities*

11.7 MCP-3635, *Chemical Hygiene Plan*

11.8 MCP-3480, *Environmental Instructions for Facilities, Processes, Materials and Equipment*

12. SUPPLEMENTAL INFORMATION

12.1 History of ACMM-3804

Revision	Author(s)	Date
0	Bob Hague	May 2000
1	John Eisenmenger	October 2001

12.2 Revision Summary

Revision 1 changes include corrections for technical accuracy and miscellaneous editorial changes.

13. APPROVAL SIGNATURE BLOCK

POSITION TITLE	SIGNATURE	DATE
Method Author		10-16-01
Responsible ALD Tech Leader		10-16-01
Responsible ALD Supervisor	for Gary Mclaughlin	10-16-01
ALD QA Officer	for Sheila Sedlacek	10/17/01
ALD Manager		10/17/01
ALD Facility Manager		10/16/01

APPENDIX A

Procedure Basis

Step(s)	Basis/Summary	Source
4.1 through 4.6 including notes in Section 4.	Controls are implemented to adequately mitigate hazards identified by JSA.	JSA # ACMM-3804, Note 2

APPENDIX B

Diagram of Separation Columns