1. ABSTRACT

This method provides instructions for the determination of certain actinide nuclides and strontium-90 in filters and solids. Solid phase extraction is used to separate the radionuclides of interest after acid digestion and lithium metaborate fusion.

2. APPLICABILITY

This method is designed to selectively separate actinide nuclides and strontium-90 from filters, up to 2 grams of soil, or up to 1 gram of ash (15 to 50 grams of unashed) from vegetation, biota, or other organic material.

A Job Safety Analysis (JSA) was developed for this procedure 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, Material and Equipment*.

3. DISCUSSION

Samples that need to be ashed (organic filters, vegetation, biota, and other organics) can be weighed into a glass beaker or a platinum (Pt) dish and then ashed. If practical, tracers are added before ashing or before the acid digestion, otherwise they are added at the appropriate time and place in the method.

4. SAFETY PRECAUTIONS

4.1 Thermal Hazards

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

4.2 Chemical Handling

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

4.2.2 Ensure an Hydrofluoric acid (HF) burn kit is located in the work area. [JSA]

4.3 Radioactive Materials and Sample Hazards

4.3.1 Handle radiological samples as specified on the applicable Radiological Work Permit (RWP). (See MCP-7, *Radiological Work Permit*). [JSA]

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

4.3.3 Handle samples not previously identified as radioactive, which are determined to be radioactive under the appropriate RWP. [JSA]

4.3.4 Ensure an RCT surveys the samples after samples have been concentrated, dried, muffled, desiccated, filtered and dried, or after any other method or procedure that may have changed the concentration of radioactivity, and prior to moving it to avoid the spread of contamination. [JSA]

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 Avery stickers, ¾ inch, or equivalent

5.1.4 Balance capable of reading 0.001 to 200 grams

5.1.5 Beakers, Pyrex, assorted sizes

5.1.6 Centrifuge

5.1.7 Centrifuge tubes, 50 mL conical polypropylene

5.1.8 Hot Plate, stirring

5.1.9 Infrared heat lamp, 250 watt

5.1.10 Metricel filter, or equivalent

5.1.11 Muffle furnace

5.1.12 Partitioned petri dish

5.1.13 Pipettes, Eppendorf or equivalent, assorted sizes, with tips

5.1.14 Platinum(Pt) dishes, 30 mL

5.1.15 Stir bars

5.1.16 Tongs

5.1.17 Vacuum manifold and filtering apparatus for 25-mm filters.

5.2 Reagents

Use Analytical Reagent Grade chemicals and ASTM Type II water or better 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, $(NH_4)HC_2O_4$, 0.1 M: Dissolve 14 g of ammonium oxalate, $(NH_4)_2C_2O_4\ H_2O$, and 7 g of oxalic acid, $H_2C_2O_4.\ 2H_2O$ in 2 L of water.

5.2.4 Ammonium hydroxide, NH_4OH, concentrated.

5.2.5 Ascorbic acid solution, 10%: Dissolve 2 g in 20 mL of water. Prepare fresh before each use.

5.2.6 5% $NaNO_2$: Dissolve 1 g sodium nitrite in 20 mL of water.

5.2.7 Neodymium carrier: 0.5mg/mL: Dissolve 0.583 g of neodymium oxide with 20 mL of 4M HCl and dilute to 1 liter with water.

5.2.8 Hydrochloric acid: HCl

12M: concentrated (38%, 12M)

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 Reagent Alcohol (Fisherbrand A995-4)

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

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

5.2.12 Hydrofluoric acid, HF, concentrated (49%)

5.2.13 Lithium metaborate, $LiBO_2$

5.2.14 Lithium sulfate, $LiSO_4$

5.2.15 Nitric acid, HNO_3,

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

5.2.16 Oxalic acid, 0.03M in 1M HCl: Add 83 mL of concentrated HCl to approximately 500 mL of H_2O and mix; then add 3.8 g of oxalic acid, HOOCCOOH 2 H_2O, and dilute to 1 L. Shake to dissolve the oxalic acid.

5.2.17 Below is a list of radionuclide tracer solutions and the approximate activities that are needed. The QC lab at INTEC can provide these solutions:

A	Am-243	0.1 Bq/mL
B	Pu-242	0.1 Bq/mL
C	U-232	0.1 Bq/mL
D	Sr-90	1.5 Bq/mL
E	Am-241	0.1 Bq/mL
F	Pu-240	0.1 Bq/mL
G	U-238	0.1 Bq/mL
H	Sr-85	30. Bq/mL

5.2.18 Strontium Chloride, $SrCl_2$ ($6H_2O$)

- 1.0% $SrCl_2$, dissolve 1 g of strontium chloride in 100 mL of water
- Sr 100mg/ml, dissolve 30 g of strontium chloride in 100 mL of water

5.2.19 Titanium chloride, 20%, commercially available

6. SAMPLE HANDLING

None

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 Tracers and Ashing

NOTE: *Actual volumes of tracer solutions required will depend upon the activity of the solutions available.*

7.1.1 Select the appropriate tracer(s) to be used:

A. Am-243: 0.500

B. Pu-242: 0.100

C. Sr-85: 1.0 mL

D. U-232: 0.500 mL.

7.1.2 For soil samples, perform the following:

7.1.2.1 Weigh up to 2 g of soil sample into a 30 mL Pt dish.

7.1.2.2 Add tracer(s) identified in Step 7.1.1 and record the volume added in the preparation log.

7.1.2.3 GO TO Section 7.2 to complete the acid digestion.

7.1.3 For glass fiber filters, perform the following:

7.1.3.1 Place sample into a 30 mL Pt dish.

7.1.3.2 Add tracer(s) identified in Step 7.1.1 and record the volume added in the preparation log.

7.1.3.3 GO TO Section 7.2 to complete the acid digestion.

7.1.4 For organic based filters such as RESP and SESP filters, perform the following:

7.1.4.1 Place the filter in a 100 mL beaker dish.

7.1.4.2 Add tracer(s) identified in Step 7.1.1 and record the volume added in the preparation log.

7.1.4.3 Take sample to dryness on a hotplate.

7.1.4.4 Ash the sample by placing it in a muffle furnace and slowly (1°C per minute) increasing temperature until it reaches 520°C.

7.1.4.5 Hold the temperature at 520°C until all organics are oxidized (normally overnight).

7.1.4.6 GO TO Section 7.2 to complete the acid digestion.

7.1.5 For biota, vegetation, and other organic material, perform the following:

7.1.5.1 IF the biota matrix is deer mouse,
THEN perform a Hanta Virus treatment.

7.1.5.2 GO TO Step 7.1.5.4.

7.1.5.3 IF the matrix is otherwise,
THEN continue to Step 7.1.5.5.

7.1.5.4 Use care and proper PPE to avoid contact with biota material and inhalation of airborne particulate.

7.1.5.4.1 Cut an incision in the animal on the underside, from the neck to the anus.

NOTE: *It is recommended that the alcohol used for treatment be Fisherbrand A995-4 Reagent Alcohol. This is due to the impurity levels found in some other grades of alcohol, which can cause potential problems in the disposition of the alcohol/viscera waste.*

7.1.5.4.2 Fully immerse the animal in reagent alcohol for one week.

7.1.5.4.3 Decant the alcohol off for disposal.

7.1.5.5 Weigh the appropriate aliquot (15 to 50 grams) in a beaker.

7.1.5.6 Add tracer(s) identified in Step 7.1.1 and record the volume added in the preparation log.

7.1.5.7 Take sample to dryness on a hotplate.

7.1.5.8 Ash the sample by placing it in a muffle furnace and slowly increasing temperature until it reaches 520°C.

7.1.5.9 Hold the temperature at 520°C until all organics are oxidized, (normally 48 hrs.).

7.1.5.10 Allow sample to cool to room temperature.

7.1.5.11 GO TO Section 7.2 to complete the acid digestion.

7.2 Acid Digestion

WARNING

HF can cause severe burns.

7.2.1 Use care and proper PPE to avoid contact. Ensure HF burn gel is available at the work area. [JSA]

7.2.2 IF the sample is in a glass beaker,
THEN transfer the sample to a 30 mL Pt dish.

7.2.3 Rinse the beaker with 2M HNO_3.

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

7.2.5 Ensure HF burn gel is near at hand. [JSA]

7.2.6 Slowly 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 2M HNO_3.

7.2.9 Add concentrated HF until the sample is covered.

7.2.10 Slowly take the sample to dryness on a hotplate.

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

7.2.12 Slowly take the samples to dryness on a hotplate.

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

7.2.14 Slowly take the samples to dryness on a hotplate.

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

7.2.16 Slowly take the samples to dryness on a hotplate.

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

7.2.18 Slowly take the samples to dryness on a hotplate.

7.3 Fusion

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

7.3.2 Add 1.4 grams of lithium meta-borate ($LiBO_2$).

7.3.3 Fuse the sample by heating in a muffle furnace at 1,020°C, swirling the melt occasionally until a uniform clear melt is obtained.

7.4 Dissolving the Melt

7.4.1 Put the Pt dish in a 100 mL beaker containing ~50mL water.

7.4.2 Add 5 mL concentrated HNO_3.

7.4.3 Add 14 mL of 50% $Al(NO_3)_3 \bullet 9H_2O$ solution.

7.4.4 Add water until the Pt dish is completely covered.

7.4.5 Add a small stir bar and heat on a stirring hotplate until sample has dissolved.

7.4.6 Remove the Pt dish and rinse it with water.

7.5 Actinide Separation

7.5.1 Add 2 mL of 10% ascorbic acid and heat near boiling until sample turns yellow or for 10 minutes, then remove sample from heat.

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

7.5.3 Adjust volume to 60-70 mL, with water and cool to room temperature before loading onto columns.

7.5.4 Stack a TEVA with a reservoir extension above a TRU column with a reservoir.

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

7.5.6 Load the samples onto the columns.

7.5.7 Rinse columns with 5 mL of 4M HNO_3, after the samples have passed through the columns.

7.5.8 Collect the load solution and the rinse for Sr analysis for use in Section 7.10.

7.5.9 Rinse the columns with an additional 7.5 mL of 4M HNO_3.

7.5.10 Collect the rinse as waste.

7.5.11 Separate the columns.

7.5.12 GO TO the appropriate section (7.6, 7.7, or 7.8) to proceed with elution.

7.6 TEVA Columns (Pu analysis)

7.6.1 Elute Thorium from TEVA columns with two 7.5 mL aliquots of 6M HCl.

7.6.2 Collect this "Thorium fraction" as waste.

7.6.3 Elute Plutonium from the TEVA columns with 15 mL of 0.5M HCl and 0.20 mL of $TiCl_3$. (Mix the HCl and the $TiCl_3$ just before pouring through columns).

7.6.4 Collect this "plutonium fraction" in centrifuge tubes and save for final precipitation and mounting for use in Section 7.9.

7.6.5 GO TO the appropriate section (7.7, 7.8, or 7.9) to continue.

7.7 TRU Columns (Am analysis)

7.7.1 Rinse the TRU columns twice with 7.5 mL of 4M HNO_3.

7.7.2 Collect the rinse as waste.

7.7.3 Elute Americium from the TRU columns with 2 mL of 9M HCl followed by 15 mL of 4M HCl.

7.7.4 Collect this "americium fraction" in centrifuge tubes and save for the final precipitation and mounting for use in Section 7.9.

7.7.5 GO TO the appropriate section (7.8 or 7.9) to continue.

7.8 TRU Columns (U analysis)

7.8.1 After the Am is eluted, rinse the TRU columns with two 10-mL aliquots of 0.03M oxalic acid in 1M HCl.

7.8.2 Collect the rinse as waste.

7.8.3 Elute Uranium from the TRU columns with 20 mL of 0.1M ammonium bioxalate.

7.8.4 Collect this "Uranium fraction" in centrifuge tubes and save for the final precipitation and mounting.

7.9 Final Precipitation and Mounting

7.9.1 Add 0.5 mL of 20% $TiCl_3$ to each tube for U analysis only.

7.9.2 Mix and let stand at least 5 minutes.

7.9.3 For Pu analysis only: IF the Ti purple color does not persist from the elution process,
THEN add 0.2 mL of $TiCl_3$.

7.9.4 Mix and let stand at least 5 minutes.

7.9.5 To all necessary fractions (U, Pu, Am, and Th), add 0.2 mL of the 0.5 mg/mL Nd carrier to each centrifuge tube and mix.

7.9.6 Add at least 5 mL of cone HF and mix, and wait at least 15 minutes before filtering.

7.9.7 Wet a 0.1 micron Metricel filter (or equivalent) with reagent alcohol.

7.9.8 Set up the filtration apparatus with the filter.

7.9.9 Filter the sample:

7.9.9.1 Wash with a small amount of water.

7.9.9.2 Wash with a small amount of reagent alcohol.

7.9.9.3 For Am samples, Wash with two additional small aliquots of reagent alcohol.

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

7.9.11 Dry the filters.

7.9.12 Place the filters in the alpha chamber for counting.

7.10 Sr-90

7.10.1 Split each "Sr fraction" into 50 mL centrifuge tubes containing no more than 30 mL per tube.

7.10.2 Add and dissolve 3.5 grams of Li_2SO_4 in each tube.

7.10.3 Add 0.1 mL of 100 mg/mL Sr carrier to each tube.

7.10.4 Mix each and wait at least 3 minutes (A strontium sulfate precipitate will form).

7.10.5 Add five 1.5 mL aliquots of 1.0% $SrCl_2$ to each tube.

7.10.6 Mix and wait at least 8 minutes after each addition.

7.10.7 Centrifuge, decant, and discard solution.

7.10.8 Forward the sulfate precipitate to the Sr-90 analyst for further procession per ACMM-3815, *Determination Of Selected Actinides And Strontium-90 In Water.*

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.

8.4 IF the strontium yield is below 35% recovery,
THEN contact Technical Supervisor for possible reanalysis of saved fractions.

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 equations are used, the appropriate dilution factors must be used as applicable.*

9.1 Pu-238 Result Calculation

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

Where:

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

cnts @ 5.74 MEV = total counts in Pu-236 spike peak.

SA = spike acitvity added in d/s.

V = volume of sample in mL.

9.2 Pu-239 Result Calculation

$$Pu\text{-}239\ d/s/mL = \frac{cnts\ @\ 5.15\ MEV * SA}{cnts\ @\ 5.74\ MEV * V}$$

Where:

cnts @ 5.15 MEV = total counts in Pu-239 peak.

cnts @ 5.74 MEV = total counts in Pu-236 spike peak.

SA = spike acitvity added in d/s.

V = volume of sample in mL.

9.3 Am-241 Result Calculation

$$Am\text{-}241\ d/s/mL = \frac{cnts\ @\ 5.46\ MEV * SA}{cnts\ @\ 5.25\ MEV * V}$$

Where:

cnts @ 5.46 MEV = total counts in Am-241 peak.

cnts @ 5.25MEV = total counts in Am-243 spike peak.

SA = spike acitvity added in d/s.

V = volume of sample in mL.

9.4 Cm-244 Result Calculation

$$Cm\text{-}244\ d/s/mL = \frac{cnts\ @\ 5.8\ MEV * SA}{cnts\ @\ 5.25\ MEV * V}$$

Where:

cnts @ 5.8 MEV = net counts in Cm-244 peak.

cnts @ 5.25 MEV = net counts in Am-243 peak.

SA = spike activity added in d/s (Am-243).

V = volume of sample in mL

9.5 Uranium-2XX Result Calculation

$$U\text{-}2XX\ d/s/mL = \frac{cnts\ @\ U\text{-}2XX\ peak * SA}{cnts\ @\ 5.3\ MEV * V * BR}$$

Where:

U-2XX = uranium isotope of interest (i.e., U-234,235,238).

cnts @ 5.3 MEV = net counts in U-232 spike peak.

SA = spike activity added in d/s.

V = volume of sample in mL

BR = branching ratio of the uranium isotope.

9.6 Sr-90 Result Calculation

Use approved calculation program or the following equations:

Sr-90, μCi/g = (Y-YB)/(CTY*CEY*g*SY*YY*YG*YD*2.22 E6)

S^2Sr-90 = SQR(A^2+B^2+C^2+D^2+E^2+F^2+G^2)*Sr-90^2

Where: A = SQR(Y+YB)/(Y-YB)

B = SCEY/CEY

C = SG/g

D = SSY/SY

E = SYY/YY

F = SYG/YG

G = SYD/YD

and:

Y = Gross counts of Y-90

YB = Background of Y-90

CTY = Count time in minutes

g = Sample size

SG = Standard deviation of the sample size.

SY = Strontium yield

SSY = St. Dev. of SY

YY = Yttrium yield

SYY = St. Dev. of YY

YG = Yttrium growth = 1-exp-(Ln 2 * T1/64)

SYG = St. Dev. YG = (Ln 2 * T1/64) * SQR ($(ST1/T1)^2$ + $(.1/64)^2$)

YD = Yttrium decay = exp-(Ln 2 * T2/64)

SYD = St. Dev. of YD = (Ln 2 * T2/64) * SQR ($(ST2/T2)^2 + (.1/64)^2$)

T1 = Time of Y-90 ingrowth in hours

ST1 = St. Dev. of T1

T2 = Time of Y-90 decay in hours

ST2 = St. Dev. of T2

CEY = Counting efficiency of Y-90 on yttrium oxalate.

SCEY = St. Dev. of CEY

SQY ( ) = Square root of the quantity in the ( )

exp- ( ) = The antilog of minus the quantity in the ( )

10. RECORDS

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

11. REFERENCES

11.1 MCP-7, *Radiological Work Permit*

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

11.3 MCP-3480, *Environmental Instructions for Facilities, Processes, Material and Equipment*

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

11.5 MCP-3635, *Chemical Hygiene Plan*

11.6 ACMM-3815, *Determination Of Selected Actinides And Strontium-90 In Water*

12. SUPPLEMENTAL INFORMATION

12.1 History of ACMM-3816

Revision	Author(s)	Date
0	R. Hague	May 2000
1	B. K. Schuetz	November 2001

12.2 Revision Summary

Revision 1 incorporates changes required for better work practices and editorial corrections.

13. APPROVAL SIGNATURE BLOCK

Position Title	Signature	Date
Method Author		11/13/01
Responsible ALD Tech Leader		11/13/01
Responsible ALD Supervisor		11/13/01
ALD QA Officer		11/13/01
ALD Manager		11/13/01
ALD Facility Manager		11/13/01

Analytical Method Analytical Laboratories Department	**DETERMINATION OF SELECTED ACTINIDE NUCLIDES AND STRONTIUM-90 IN FILTERS AND SOLIDS**	Identifier: ACMM-3816 Revision: 1 Page: **A1 of A1**

APPENDIX A

PROCEDURE BASIS

Step	Basis/Summary	Source
4.1.1	Use appropriate gloves and exercise caution to avoid contact.	JSA# ACMM-3816, NOTES 1 & 2
4.2.1	Handle all chemicals in strict accordance with MCP-3635, *Chemical Hygiene Plan.*	JSA# ACMM-3816, NOTES 1 & 2
4.2.2	Ensure an Hydrofluoric acid (HF) Burn kit is located in the work area.	JSA# ACMM-3816
4.3.1	Handle radiological samples as specified on the applicable Radiological Work Permit (RWP). (See MCP-7, *Radiological Work Permit*).	JSA# ACMM-3816, NOTES 1 & 2
4.3.2	Use care to limit personal exposure. The solutions being analyzed may be highly radioactive.	JSA# ACMM-3816, NOTES 1 & 2
4.3.3	Handle samples not previously identified as radioactive, which are determined to be radioactive under the appropriate RWP.	JSA# ACMM-3816, NOTES 1 & 2
4.3.4	Ensure an RCT surveys the samples after samples have been concentrated, dried, muffled, desiccated, filtered and dried, or after any other method or procedure that may have changed the concentration of radioactivity, and prior to moving it to avoid the spread of contamination	JSA# ACMM-3816, NOTES 1 & 2
WARNING After Section 7.2	HF can cause severe burns.	JSA# ACMM-3816
7.2.1	Use care and proper PPE to avoid contact. Ensure HF burn gel is available at the work area.	JSA# ACMM-3816, NOTES 1 & 2
7.2.5	Ensure HF burn gel is near at hand.	JSA# ACMM-3816