eichrom

Rapid Determination of Pu, Np, Am and Cm in 100g Soil Samples

AN-1431-10

Summary of Method Pu(Np) and Am-Cm are separated and concentrated from 100-200 gram soil samples. Samples are muffled at 550°C to destroy organic content and wet ashed and leached with HNO₃ and HCI. The filtered leachates are evaporated to dryness and fused with NaOH in Zr crucibles. Sequential precipitations facilitate matrix removal. Actinides are separated on stacked 2mL cartridges of Eichrom TEVA, TRU, and DGA resins. Native rare earths from the samples are removed from Am-Cm using TEVA Resin and ammonium thiocyanate. Actinides are measured by alpha spectrometry following CeF₃ microprecipitation onto Eichrom Resolve[®] Filters. Chemical yields of tracers ranged

from 93-98% for ²³⁶Pu and 85-93% for ²⁴³Am. Measured values typically agreed to within 10% of reference values. Sample preparation for batches of 12 samples can be completed by a single operator in <8 hours.

Figure 1. Sample Preparation

Dry 100-200g soil at 110°C. Blend and Size. Aliquot sample to 1L glass beaker. Add tracers. Muffle at 550°C for 4 hours. Cool. Add 75mL 70% HNO₃ and 25mL 37% HCl. Heat to dryness on hotplate. Add 75mL 70% HNO₃. Warm sample. Transfer solids and liquid to 250mL centrifuge tube. Add 25mL 70% HNO₃ to beaker. Warm beaker. Transfer solids and liquid to 250mL centrifuge tube. Centrifuge 3500 rpm, 10 min. Filter leachate through 25mm 0.45um filter. Transfer leachate to 600mL beaker. Add 25mL 70% HNO₃ to solids. Mix. Centrifuge. Filter leachate into same 600mL beaker. Repeat once. Add 25mL warm 4M HCl to solids. Mix. Centrifuge. Filter leachate into same 600mL beaker. Repeat once. Evaporate supernate in 600mL beaker to dryness. Wet ash with 15mL 70% HNO₃ to dryness. Repeat once. Transfer solids to 250mL Zr crucibles. Rinse beakers with 70% HNO₃. Transfer to same crucible. Heat crucibles to dryness. Add 20g NaOH to each crucible. Fuse at 600°C for 20min. Dissolve fusion cakes with water. Transfer to 250mL c-tubes. Rinse crucibles with 10mL 3M HNO₃. Heat to dissolve residue. Transfer to same c-tube. Continue to precipitation steps.

Reagents

TEVA Resin, 2mL Cartridges (Eichrom TE-R50-S) TRU Resin, 2mL Cartridges (Eichrom TR-R50-S) DGA Resin, 2mL Cartridges (Eichrom DN-R50-S) Iron carrier (50mg/mL Fe, as ferric iron nitrate) ²⁴²Pu (or ²³⁶Pu if meas. Np), and ²⁴³Am tracers

La carrier (10mg/mL) Deionized Water 10% (w:w) TiCl₃ HCI (37%) HF (49%) or NaF H₂O₂ (30%) Denatured ethanol Ascorbic Acid Formic Acid Ce carrier (1mg/mL) 2M AI(NO₃)₃ HNO₃ (70%) NaOH Boric acid NaNO₂ Sulfamic Acid Ammonium Thiocyanate

Equipment

Vacuum Box (Eichrom AR-24-BOX or AR-12-BOX) Cartridge Reservoir, 20mL (Eichrom AR-200-RV20) Inner Support Tubes-PE (Eichrom AR-1000-TUBE-PE) Yellow Outer Tips (Eichrom AR-1000-OT) Resolve Filters in Funnel (Eichrom RF-DF25-25PP01) 1L and 600mL Glass beakers 250mL Zirconium crucibles with lids Stainless Steel Planchets with adhesive tape Alpha Spectrometry System 50mL and 250mL Centrifuge Tubes 25mm 0.45um filters Centrifuge Heat Lamp Muffle Furnace Hot Plate Analytical Balance Vacuum Pump

Figure 2. Actinide Separation on TEVA - TRU - DGA and Source Preparation

Dilute samples to 180mL.	(4) Rinse cartridges w/ 5mL 6M HNO ₃ .	(20) Add 50ug Ce carrier to all
Add 7mg La and 20mL 10% TiCl ₃ .	(5) Separate TEVA from TRU-DGA.	samples. Add 0.5mL 30% H ₂ O ₂ to Pu
Mix. Cool to room temperature.	(6) Rinse TEVA with:	samples and 0.2mL 30% H ₂ O ₂ to
Centrifuge 3500 rpm. 5min.	-10mL 3M HNO ₃	Am/Cm samples. Mix. Add TmL 49% HF. Mix. Wait 15-20 minutes.
Decant supernate	-20mL 9M HCI (Th removal)	(21) Set up Resolve® Filter Funnel on
Partially dissolve in 60mL 1.5M HCI.	-5ITL 310 HINO3 (7) Strin Pu from TEVA with 20ml	vacuum box.
Solids will remain. Dilute to 170mL.	0.1M HCI-0.05M HF-0.03M TiCl ₃ .	(22) Wet filter with 3mL 80% ethanol
Add 2mg La and 10mL 30% H ₂ O ₂ . Mix.	(8) Rinse TRU-DGA with 15mL 4M HCI.	followed by 3mL DI water.
Add 22mL 49% HF. Mix.	(9) Discard TRU cartridge.	(23) Filter sample.
Centrifuge 3500 rpm. 5min.	(10) Rinse DGA w/ 20mL 0.05M HNO ₃ .	(24) Rinse sample tube with 5mL DI
Decant supernate	(11) Strip Am/Cm W/ 10mL 0.25M HCI.	(25) Pinso filtor funnol with 2ml DI
Dissolve solids in 5ml 3M HNO ₂ -	(12) Add 2 mL 70% HNO $_3$ + 500L 10% H $_2$ SQ, to Am/Cm. Evaporate to drugoes	water and 2ml 100% ethanol
0.25M Boric acid, 6mL 7M HNO ₃ , and	(13) Ash to dryness with 3ml 70%	(26) Draw vacuum until filter is dry
7.5mL 2M AI(NO ₃) ₃ . Warming samples	$HNO_3 + 2mI_30\% H_2O_2$	(27) Remove filter from funnel
can improve dissolution.	(14) Dissolve Am/Cm in 5mL	assembly and mount filter on
Cool samples to room temp. Fix	4M NH₄SCN-0.1M Formic acid.	stainless steel planchet with
valence by adding: (mix between steps)	(15) Precondition 2mL TEVA with 5mL	2-sided tape.
-0.5mL 1.5M sulfamic acid	4M NH ₄ SCN-0.1M Formic acid.	(28) Dry filter under heat lamp for
-40uL 50mg/mL Fe carrier	(16) Load Am/Cm on TEVA.	3-5 minutes.
-1.5mL 1M ascorbic acid (Wait 3 min)	(17) Rinse Am/Cm beaker with 5mL	(29) Measure actinides by alpha
-1mL 3.5M NaNO ₂	4M NH₄SCN-0.1M Formic acid.	spectrometry.
(1) Precondition 2mL TEVA, TRU,	Add to TEVA.	
DGA cartridges with 10mL 8M HNO ₃ .	(18) Rinse TEVA w/ 10mL 1.5M	
(2) Load Sample.	NH₄SCN-0.1M Formic acid.	
(3) Rinse c-tube with 5mL 6M HNO ₃ .*	(19) Strip Am/Cm from TEVA with	
Add to stacked cartridges.	20mL 1M HCI.	

*Adding 50uL of 30% H₂O₂ to tube rinse can help improve U decontamination.

Method Performance							
			²⁴² Pu	²³⁸ Pu	²⁴³ Am	²⁴¹ Am	
	Sample		Tracer	Measured	Tracer	Measured	
_	Size (g)	Replicates	% Recovery	% Bias	% Recovery	% Bias	
_	100	3	86 <u>+</u> 7	-3.0	94 <u>+</u> 4	-10	
	100	3	81 <u>+</u> 15	-6.0	80 <u>+</u> 5	-13	
	200	2	82 <u>+</u> 1	2.0	93 <u>+</u> 5	-19	
	200	3	80 <u>+</u> 8	-5.0	93 <u>+</u> 5	-18	

References

1) Sherrod L. Maxwell, "Rapid method for determination of plutonium, americium, and curium in large soil samples," *J. Radioanal. Nucl. Chem.*, 275(2), 395-402 (2008).