Rapid Determination of Actinides in Vegetation Samples

AN-1406-10

Summary of Method U, Pu, Am and Cm are separated and concentrated from 5-10 gram vegetation samples. Samples are muffled in zirconium crucibles 2-4 hours to destroy organic content. The residue is wet ashed with HNO_3-H_2O_2 and then fused with 15g NaOH at 600°C for ten minutes. The fusion cakes are dissolved in water, transferred to 250mL centrifuge tubes and precipitated twice to facilitate matrix removal. Actinides are separated on stacked 2mL cartridges of Eichrom TEVA, TRU and DGA resins. Actinides are measured by alpha spectrometry following CeF_3 microprecipitation onto Eichrom Resolve® Filters. Chemical yields of tracers ranged from 90-101% for ^{242}Pu, 84-93% for ^{243}Am, and 81-87% for ^{232}U. Measured values agreed to within 1-3% of reference values for Pu isotopes, 3-9% for Am and Cm isotopes, and 2-15% for U isotopes for 16 hour count times. A single operator can prepare batches of 12 samples for the measurement of actinides in less than 8 hours.

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 nitrate)
Lanthanum and Cerium Carriers (10mg/mL)
^{242}Pu (or ^{236}Pu if meas. Np), ^{243}Am and ^{232}U tracers
Oxalic acid/Ammonium oxalate
Hydrofluoric Acid (49%) or Sodium Fluoride

3.2M $(NH_4)_2HPO_4$	2M $Al(NO_3)_3$
10% (w:w)$TiCl_3$	Boric acid
Sodium Hydroxide	Sodium Nitrite
Denature Ethanol	Sulfamic Acid
Ascorbic Acid	Hydrogen Peroxide (30%)
Nitric Acid (70%)	Hydrochloric Acid (37%)
Deionized Water	1.25M $Ca(NO_3)_2$

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)
50mL and 250mL Centrifuge Tubes
250mL Zirconium crucibles with zirconium lids
Alpha Spectrometry System

Centrifuge	Muffle Furnace
Hot Plate	Heat Lamp
Analytical Balance	Vacuum Pump

Figure 1. Sample Preparation

5-10g Vegetation sample + Tracers in zirconium crucible.

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Muffle at 600°C.
2 hours if 5g sample.
4 hours if 10g sample.

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Wet ash on hotplate with 5mL 70% HNO_3 and 5mL 30% H_2O_2.

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Fuse samples with 15g NaOH at 600°C for 10 minutes.

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Dissolve fusion cake with H_2O and transfer to 250mL centrifuge tube.

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Add 10mL 3M HNO_3 to crucible and heat to dissolve residue. Transfer to the same 250mL centrifuge tube.

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Add 125mg Fe, and 4mg La. Dilute to 180mL. Mix.

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Add 4mL 1.25M $Ca(NO_3)_2$, 5mL 3.2M $(NH_4)_2HPO_4$, and 10mL 10% $TiCl_3$. Mix. Cool in ice bath for 10min.

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Centrifuge at 3500rpm. Decant Supernate.

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Dissolve precipitate in 150mL 1M HCl.
Add 1mg La, 1mL 1.25M $Ca(NO_3)_3$, 6mL 10% $TiCl_3$. Mix. Add 20mL 49% HF.

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Centrifuge at 3500rpm. Decant Supernate.

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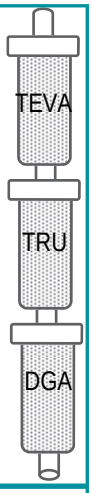
Dissolve precipitate in 5mL 3M HNO_3-0.25M Boric acid, 7mL 70% HNO_3, and 7mL 2M $Al(NO_3)_3$. Adjust valence states with 0.5mL 1.5M Sulfamic acid, 10uL 50mg/mL Fe carrier, and 1.25mL 1M Ascorbic acid. Mix. Add 1mL 3.5M $NaNO_2$ and 1.5mL 70% HNO_3. Mix.

Figure 2. Actinide Separation on TEVA - TRU - DGA*

(1) Precondition stacked 2mL TEVA, TRU, DGA with 10mL 3M HNO_3.
(2) Load sample solution.
(3) Rinse sample tube with 5mL 6M HNO_3.** Add tube rinse to cartridges.
(4) Rinse cartridges with 10mL 3M HNO_3 .
(5) Separate TEVA, TRU, and DGA cartridges.



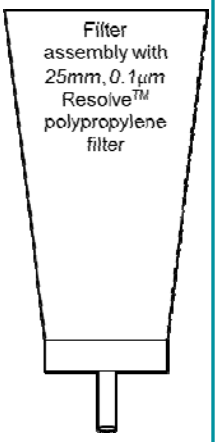
(6) Rinse TEVA cartridge with:
-10mL 3M HNO_3
-20mL 9M HCl(remove Th)
-5mL 3M HNO_3
(7) Strip Pu(Np) from TEVA with 20mL 0.1M HCl-0.05MHF-0.01M $TiCl_3$.

(8) Rinse DGA with 8mL 0.1M HNO_3.
(9) Place TRU cartridge above DGA .
(10) Strip Am/Cm from TRU onto DGA with 15mL 3M HCl.
(11) Separate TRU and DGA. Set TRU aside for U recovery.
(12) Rinse DGA with:
-5mL 3M HCl
-3mL 1M HNO_3
-15mL 0.05M HNO_3

(13) Strip Am and Cm from DGA with 10mL 0.25M HCl.

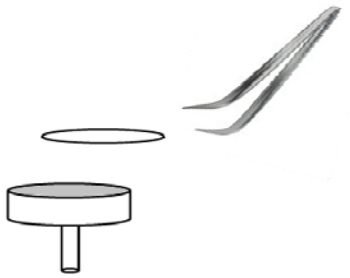
(14) Rinse TRU cartridge with 15mL 4M HCl-0.2M HF-0.002M $TiCl_3$.
(15) Strip U from TRU with 15mL of 0.1M ammonium bioxalate.
(16) Add 0.5mL 10% $TiCl_3$ to U samples, 0.5mL 30% H_2O_2 to Pu, and 0.2mL 30% H_2O_2 Am/Cm samples.

(17) Add 50-100ug Ce carrier to all samples. Mix well. Add 1mL 49% HF. Mix well. Wait 15-20 minutes.
(18) Set up Resolve® Filter Funnel on vacuum box.
(19) Wet filter with 3mL 80% ethanol followed by 3mL DI water.
(20) Filter sample.
(21) Rinse sample tube with 5mL DI water and add to filter.

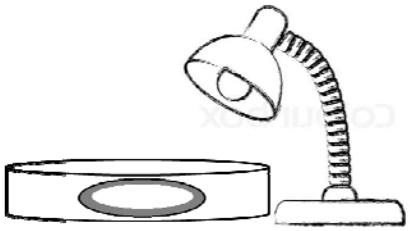


(22) Rinse filter funnel with 3mL DI water and 2mL 100% ethanol.

(23) Draw vacuum until filter is dry.
(24) Remove filter from funnel assembly and mount filter on stainless steel planchet with 2-sided tape.



(25) Dry filter under heat lamp for 3-5 minutes.
(26) Measure actinides by alpha spectrometry.



*Radiostrontium may also be measured by adding a 2mL + 1mL Sr Resin cartridge below DGA and following separation scheme in Eichrom application note AN-1405, "Rapid Determination of Sr in Vegetation Samples."
**Adding 50uL of 30% H_2O_2 to the tube rinse can help improve U recovery and decontamination in Pu/Np fractions.

Performance of Actinides in Vegetation Method

5 gram Samples					
Nuclide	Replicates	Reference (mBq/g)	Measured (mBq/g)	% Bias	% Tracer Recovery
^{238}Pu	6	29.4	30.1 ± 3.7	2.4	101 ± 6
^{239}Pu	6	56.8	57.0 ± 4.8	0.3	101 ± 6
^{241}Am	6	48.0	48.5 ± 4.6	1.0	93 ± 7
^{244}Cm	6	6.28	5.9 ± 0.6	-6.1	93 ± 7
^{234}U	6	69.2	81 ± 7	17	87 ± 7
^{238}U	6	71.8	83 ± 10	16	87 ± 7

10 gram Samples					
Nuclide	Replicates	Reference (mBq/g)	Measured (mBq/g)	% Bias	% Tracer Recovery
^{238}Pu	2	27.4	28.1 ± 0.4	2.6	90 ± 15
^{239}Pu	2	32.8	32.4 ± 0.9	-1.2	90 ± 15
^{241}Am	2	31.2	30.8 ± 0.0	-1.3	84 ± 12
^{234}U	2	41.6	41.3 ± 1.3	-0.7	81 ± 12
^{238}U	2	43.2	42.0 ± 0.3	-2.8	81 ± 12

References

1) Sherrod L. Maxwell, Brian K. Culligan, Gary W. Noyes, "Rapid separation of actinides and radiostrontium in vegetation samples," *J. Radioanal. Nucl. Chem., 286(1), 273-282* (2010).