

Rapid Fusion Method for Refractory Th, U, and Pu in Soils

Summary of Method U, Th and Pu are separated and concentrated from 1-2 gram soil samples. Samples are fused with NaOH at 600°C in zirconium crucibles. The fusion cakes are dissolved in water, transferred to 250mL centrifuge tubes and precipitated sequentially with Fe/Ti-hydroxide and lanthanum fluoride to facilitate matrix removal. U, Th, and Pu are separated on stacked 2mL cartridges of Eichrom TEVA and TRU resins. U, Th, and Pu are measured by alpha spectrometry following CeF₃ microprecipitation onto Eichrom Resolve® Filters. Batches of 12-24 samples can be prepared for alpha spectrometry in less than 8 hours. Method ruggedness has been demonstrated with successful analysis of high fired refractory material from MAPEP 30 soil standards. For one gram soil samples and 16 hour count times, MDA for this method is ~500uBq/g.

Reagents

TEVA Resin, 2mL Cartridges (Eichrom TE-R50-S)

TRU Resin, 2mL Cartridges (Eichrom TR-R50-S)

Iron carrier (50mg/mL Fe, as ferric iron nitrate)

²⁴²Pu, ²³²U and ²²⁹Th tracers

Oxalic acid/Ammonium oxalate

La carrier (10mg/mL) Ce carrier (1mg/mL)

Deionized Water 1.25M Ca(NO₃)₂

3.2M (NH₄)₂HPO₄ 2M Al(NO₃)₃

10% (w:w) TiCl₃ HNO₃ (70%)

HCl (37%) NaOH

HF (49%) or NaF Boric acid

H₂O₂ (30%) NaNO₂

Denatured ethanol Ascorbic Acid

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

Centrifuge

Heat Lamp

Muffle Furnace

Hot Plate

Analytical Balance

250mL Zirconium crucibles with zirconium lids

Stainless Steel Planchets with adhesive tape

Alpha Spectrometry System

Vacuum Pump

Figure 1. Sample Preparation

1-2g finely ground soil + tracers in zirconium crucible.

Place in Furnace at 250°C. Ramp to 600°C. Heat 30 min.

Cool. Add 15g NaOH. Fuse at 600°C for 15-20 minutes.

Dissolve fusion cake with 2x 50mL H₂O. Transfer to 250mL c-tube.

Add 10mL 3M HNO₃ to crucible. Heat to dissolve residue.
Transfer to same 250mL c-tube.

Add 150mg Fe and 5mg La to c-tube. Dilute to 180mL.

Add 2mL 1.25M Ca(NO₃)₂, 3mL 3.2M (NH₄)₂HPO₄,
10mL 10% TiCl₃. Mix. Cool in ice bath for 10 min.

Centrifuge 10min. Decant Supernate.

Partially dissolve precipitate in 80mL 1.5M HCl.

Some solids will remain. Dilute to 170mL.

Add 1mg La, 0.5mL 1.25M Ca, and 6mL 10% TiCl₃.
Mix. Add 25mL 49% HF. Cool in ice bath for 10 min.


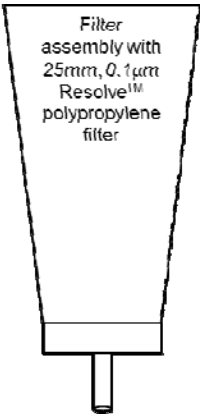
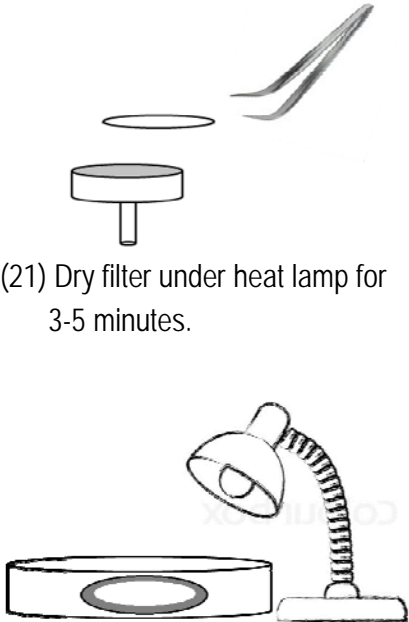
Centrifuge 10min. Decant Supernate.

Dissolve precipitate in 10mL 3M HNO₃-0.25M Boric
acid, 6mL 7M HNO₃, and 8.5mL 2M Al(NO₃)₃.
Warming samples can help complete dissolution.

Cool samples to room temperature.

Fix valence states. Mix between each addition of:
20uL 50mg/mL Fe
1.5mL 1M ascorbic acid
1mL 3.5M NaNO₂.

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

<p>(1) Precondition stacked 2mL TEVA and TRU cartridges with 10mL 3M HNO₃. (2) Load sample solution. (3) Rinse sample tube with 5mL 3M HNO₃ + 30uL 30% H₂O₂. Add to cartridges. (4) Rinse cartridges w/ 10mL 3M HNO₃. (5) Separate TEVA-TRU cartridges.</p>		<p>(10) Rinse TRU cartridge with: - 5mL 8M HNO₃ - 20mL 4M HCl-0.2M HF-0.002M TiCl₃ - 10mL 8M HNO₃ (11) Strip U from TRU with 15mL of 0.1M ammonium bioxalate. (12) Add 100ug Ce and 0.5mL 10% TiCl₃</p>	<p>(19) Draw vacuum until filter is dry. (20) Remove filter from funnel assembly and mount filter on stainless steel planchet with 2-sided tape.</p>
<p>(6) Rinse TEVA cartridge with 10mL 3M HNO₃. (7) Strip Th with 15mL 9M HCl. Dilute to 30mL. Add 0.5mL 30% H₂O₂ and 40ug Ce. (8) Rinse TEVA with: - 5mL 9M HCl - 5mL 3M HNO₃ (9) Strip Pu (and Np) from TEVA with 20mL 0.1M HCl-0.05MHF-0.01M TiCl₃. Add 0.5mL 30% H₂O₂ and 50ug Ce. Mix.</p>	<p>(13) Add 1mL 49% HF to all samples. Mix well. Wait 15-20 minutes. (14) Set up Resolve® Filter Funnel on vacuum box. (15) Wet filter with 3mL 80% ethanol followed by 3mL DI water. (16) Filter sample. (17) Rinse sample tube with 5mL DI water and add to filter. (18) Rinse filter funnel with 3mL DI water and 2mL 100% ethanol.</p>		<p>(21) Dry filter under heat lamp for 3-5 minutes. (22) Measure actinides by alpha spectrometry.</p> 

Method Performance

Sample	replicates	analyte	tracer	% tracer recovery	mBq/g reference	mBq/g measured	% bias
1g Soil	12	²³⁸ U	²³² U	86 ± 8	83.0	85 ± 3	± 3
1g Soil	12	²³⁴ U	²³² U	86 ± 8	81.0	80 ± 2	± 2
1g Soil	12	²²⁸ Th	²²⁹ Th	91 ± 6	51.1	50 ± 2	± 4
1g Soil	12	²³⁰ Th	²²⁹ Th	91 ± 6	96.2	98 ± 6	± 5
1g Soil	12	²³² Th	²²⁹ Th	91 ± 6	48.8	50 ± 3	± 6
1g Soil	3	²³⁹ Pu	²⁴² Pu	91 ± 6	76.8	79 ± 3	± 4
1g Soil	3	²³⁹ Pu	²⁴² Pu	91 ± 6	96.0	98 ± 5	± 4

References

1) Maxwell, Hutchinson, McAlister, "Rapid Fusion Method for the Determination of Refractory Thorium and Uranium Isotopes in Soil Samples" *Analytica Chimica Acta*, 701(1), 112-118 (2015).