

Rapid Determination of Actinides in Limestone and Marble

Summary of Method Actinides are separated and concentrated from 1.5 gram samples of limestone or marble. Samples are finely ground and fused in a zirconium crucible for 15 minutes at 600°C with 15 grams of sodium hydroxide. The fusion cake is dissolved in water, and actinides are concentrated and separated from the matrix using a calcium phosphate precipitate enhanced with iron. A secondary precipitation with calcium fluoride removes additional matrix (including silicates) and decreases the volume of precipitate. The calcium fluoride precipitate is dissolved with nitric acid-boric acid-aluminum nitrate to form the load solution. Analytes are separated from remaining matrix and potentially interfering radionuclides using stacked TEVA, TRU, and DGA Resin cartridges. Actinides are measured by alpha spectrometry after CeF₃ microprecipitation onto Resolve[®] Filters. Simultaneous separation of radiostrontium can be achieved by using the separation method in AN-1604.

Reagents

Sr Resin, 2mL Cartridges (Eichrom SR-R50-S)*
 Sr Resin, 1mL Cartridges (Eichrom SR1ML-R50-S)*
 TRU Resin, 2mL Cartridges (Eichrom TR-R50-S)
 TEVA Resin, 2mL Cartridges (Eichrom TE-R50-S)
 DGA Resin, 2mL Cartridges (Eichrom DN-R50-S)
 Strontium*, Lanthanum and Cerium Carriers (10mg/mL)
 Iron Carrier (50mg/mL Fe, as ferric nitrate)
²⁴²Pu (or ²³⁶Pu if Np is measured) tracer
²⁴³Am and ²³²U tracers 10% TiCl₃
⁹⁰Sr standard* HF(49%)
 30% H₂O₂ Nitric Acid (70%)
 Hydrochloric Acid (37%) Deionized Water
 1.25M Ca(NO₃)₂ 3.2M (NH₄)₂HPO₄
 2M Al(NO₃)₃ Oxalic acid
 Boric acid Sodium Hydroxide
 Ascorbic acid NaNO₂ Sulfamic acid

*Only needed if Sr is measured.

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
 Cupped Stainless Steel Planchets (~5mL volume)*
 250mL Zirconium crucibles with zirconium lids
 Alpha Spectrometry System
 Stainless Steel planchets with two sided tape
 Centrifuge Gas Flow Proportional Counter*
 Muffle Furnace Hot Plate/Heat Lamp
 Analytical Balance Vacuum Pump

Figure 1. Sample Preparation

1.5g finely ground sample in zirconium crucible

Add 4mg Sr carrier* and Pu/U/Am tracers.

Heat samples to dryness on hot plate.

Add 15g of NaOH.

Cover crucibles with zirconium lid and place in muffle furnace at 600°C for 15-20 minutes.

Carefully remove samples from furnace and cool in fume hood.

Add 25-50mL of water and heat on hot plate to dissolve fusion cake.


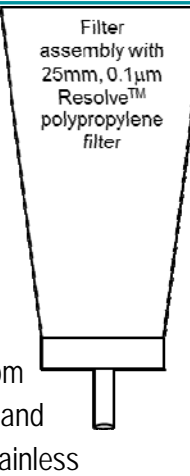
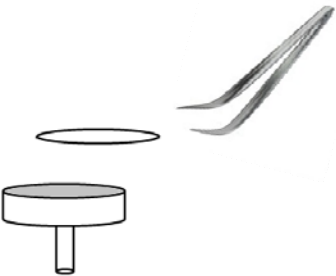
Transfer to a 250mL centrifuge tube. Rinse crucible with water. Dilute to 160mL with water.

Add 20mL conc. HCl (omit if Sr meas.), 125mg Fe, 5mg La. Mix. Add 5mL 3.2M (NH₄)₂HPO₄ (8.5mL if Sr meas.). Mix. Centrifuge 10min. Decant supernate.

Dissolve precipitate in 80mL 1.5M HCl. Dilute to 170mL. Add 4mL 10% TiCl₃ and 15mL 49%HF. Mix. Cool in ice bath 10min. Centrifuge 10min. Decant supernate.

Dissolve precipitate in 7mL 3M HNO₃-0.25M Boric acid, 7.5mL 7M HNO₃, and 7mL 2M Al(NO₃)₃. Adjust valence with 1mg Fe, 1.5mL 1M Ascorbic acid. Mix. Add 1mL 3.5M NaNO₂.

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

<p>(1) Precondition stacked 2mL TEVA, TRU, DGA cartridges with 10mL 3M HNO₃.*</p> <p>(2) Load sample solution.</p> <p>(3) Rinse sample tube with 5mL 3M HNO₃. Add tube rinse to cartridges.**</p> <p>(4) Rinse cartridges with 10mL 3M HNO₃.</p> <p>(5) Separate TEVA, TRU, and DGA cartridges.</p>		<p>(12) Rinse DGA cartridge sequentially with: -5mL 3M HCl -3mL 1M HNO₃ -15mL 0.05M HNO₃</p> <p>(13) Strip Am and Cm from DGA with 10mL 0.25M HCl.</p>	<p>(22) Rinse filter funnel with 3mL DI water and 2mL 100% ethanol.</p> <p>(23) Draw vacuum until filter is dry.</p> <p>(24) 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 -20mL 9M HCl -5mL 3M HNO₃</p> <p>(7) Strip Pu (and Np) from TEVA cartridge with 20mL 0.1M HCl-0.05MHF-0.01M TiCl₃.</p>	<p>(14) Rinse TRU cartridge with 15mL 4M HCl-0.2M HF-0.002M TiCl₃.</p> <p>(15) Strip U from TRU with 15mL of 0.1M ammonium bioxalate.</p> <p>(16) Add 0.5mL 10% TiCl₃ to U samples, 0.5mL 30% H₂O₂ to Pu, and 0.2mL 30% H₂O₂ to Am/Cm samples.</p> <p>(17) Add 50ug Ce to Pu and Am/Cm samples, 100ug Ce to U samples. Mix well. Add 1mL 49% HF. Mix well. Wait 15-20 minutes.</p>		
<p>(8) Rinse DGA cartridge with 10mL 0.1M HNO₃.</p> <p>(9) Place TRU cartridge above DGA.</p> <p>(10) Strip Am/Cm from TRU onto DGA with 15mL 3M HCl.</p> <p>(11) Separate TRU cartridge from DGA cartridge.</p>	<p>(18) Set up Resolve® Filter Funnel on vacuum box.</p> <p>(19) Wet filter with 3mL 80% ethanol followed by 3mL DI water.</p> <p>(20) Filter sample.</p> <p>(21) Rinse sample tube with 5mL DI water and add to filter.</p>	 <p>(25) Dry filter under heat lamp for 3-5 minutes.</p> <p>(26) Measure actinides by alpha spectrometry.</p>	

*Radiostrontium may also be measured by adding a 2mL + 1mL Sr Resin cartridge below DGA and following separation scheme in Eichrom Application note AN-1604-10.

**Adding 50uL 30% H₂O₂ to the tube rinse can improve Uranium recoveries and decontamination in Pu(Np) fractions.

Method Performance

Sample	replicates	analyte	tracer	% tracer recovery	mBq/g reference	mBq/g measured	% bias
1.5g limestone	6	^{239/240} Pu	²⁴² Pu	100 ± 5	29.4	30 ± 2	± 5
1.5g limestone	6	^{239/240} Pu	²³⁶ Pu	93 ± 6	23.0	24 ± 1	± 5
1.5g limestone	6	²³⁸ Pu	²³⁶ Pu	93 ± 6	28.8	29 ± 2	± 5
1.5g limestone	6	²³⁷ Np	²³⁶ Pu	93 ± 6	37.0	39 ± 3	± 7
1.5 g marble	4	^{239/240} Pu	²⁴² Pu	96 ± 3	29.4	30 ± 2	± 6
1.5 g marble	4	²⁴¹ Am	²⁴³ Am	89 ± 4	29.1	29 ± 1	± 3
1.5 g marble	4	²⁴⁴ Cm	²⁴³ Am	89 ± 4	34.8	35 ± 3	± 6
1.5 g marble	7	²³⁸ U	²³² U	93 ± 6	50.2	48 ± 1	± 4

References

1) Maxwell, Culligan, Hutchinson, Utsey, Sudowe, McAlister, "Rapid Method to Determine Actinides and Sr-89/90 in Limestone and Marble Samples," *J. Radioanal. Nucl. Chem.* accepted (2016). doi 10.1007/s10967-016-4783-8