AN-1804-10

Rapid Determination of Pu/Np and Am/Cm in Granite

Summary of Method Pu/Np and Am/Cm are separated and measured from 1 gram samples of granite. Samples are finely ground and fused in a zirconium crucible for 15 minutes at 600°C with 15 grams of NaOH. 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 2 mL TEVA and DGA Resin cartridges. Actinides are measured by alpha spectrometry after CeF_3 microprecipitation onto Resolve(R) Filters. An additional separation of Am/Cm from rare earth elements using TEVA resin and ammonium thiocyanate may be required for samples with significant rare earth content. The rugged sample preparation technique enables high tracer recovery and excellent analytical results, even when refractory materials are present.

Reagents

TEVA Resin, 2 mL Cartridges (Eichrom TE-R50-S)
DGA Resin, 2 mL Cartridges (Eichrom DN-R50-S)
Lanthanum and Cerium Carriers (10 mg/mL)
Iron Carrier (50 mg/mL Fe, as ferric nitrate)
^{242}Pu (or ^{236}Pu if Np is measured) tracer
^{243}Am tracer
Ammonium Thyiocyanate
30% H_2O_2
Hydrochloric Acid (37%)
1.25M $Ca(NO_3)_2$
2M $Al(NO_3)_3$
Sodium Hydroxide
$NaNO_2$
10-20% $TiCl_3$
HF(49%)
Nitric Acid (70%)
Deionized Water
3.2M $(NH_4)_2HPO_4$
Boric Acid
Ascorbic Acid

Equipment

Vacuum Box (Eichrom AR-24-BOX or AR-12-BOX)
Cartridge Reservoir, 20 mL (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)
50 mL and 250 mL Centrifuge Tubes
250 mL Zirconium crucibles with zirconium lids
Alpha Spectrometry System
Stainless Steel planchets with two sided tape
Centrifuge
Muffle Furnace
Hot Plate/Heat Lamp
Analytical Balance
Vacuum Pump

Figure 1. Sample Preparation

1 g finely ground sample in zirconium crucible
Add ^{242}Pu or ^{236}Pu and ^{243}Am tracers.

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Heat samples to dryness on hot plate.

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Add 15 g of NaOH.
Cover crucibles with zirconium lids.
Fuse at 600°C for 15-20 minutes.

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Carefully remove samples from furnace and cool in fume hood. Add 25-50 mL of water and heat on hot plate to dissolve fusion cake.

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Transfer to a 250 mL centrifuge tube. Rinse crucible with water. Dilute to 180 mL with water.

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Cool to room temperature. Add 125 mg Fe, 4 mg La, and 50 mg Ca. Mix. Add 5 mL 3.2M $(NH_4)_2HPO_4$. Mix. Add 4 mL 20% $TiCl_3$. Mix. Centrifuge 10 min. Decant supernate.

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Dissolve precipitate in 80 mL 1.5M HCl. Dilute to 170 mL. Add 2 mL 20% $TiCl_3$, 25 mg Ca, and 20 mL 49% HF. Mix. Cool in ice bath 10 min. Centrifuge 10min. Decant supernate.

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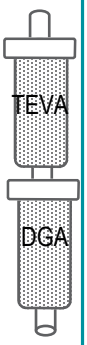
Dissolve precipitate in 7 mL 3M HNO_3-0.25M H_3BO_3, 6 mL 7M HNO_3, and 7 mL 2M $Al(NO_3)_3$.
Adjust valence with 1 mg Fe, 1.25 mL 1M ascorbic acid. Mix. Wait 5-10 min. Add 1 mL 3.5M $NaNO_2$ and 1.5 mL 70% HNO_3.

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

(1) Precondition stacked 2 mL TEVA and DGA cartridges with 10 mL 3M HNO_3.



(2) Load sample solution.

(3) Rinse sample tube with 5 mL 6M HNO_3. Add tube rinse to cartridges.*

(4) Rinse cartridges with 10 mL 3M HNO_3.

(5) Separate TEVA and DGA cartridges.

(6) Rinse TEVA cartridge with:
- -15 mL 3M HNO_3 (U decon.)
- -20 mL 9M HCl (Th)
- -5 mL 3M HNO_3

(7) Strip Pu (and Np) from TEVA cartridge with 20 mL 0.1M HCl-0.05MHF-0.01M $TiCl_3$.

(8) Rinse DGA cartridge with:
- -10 mL 3M HCl
- -3 mL 1M HNO_3
- -20 mL 0.1M HNO_3 (U decon.)
- -10 mL 0.05M HNO_3
- -20 mL 3M HNO_3-0.25M HF (Th)
- -5 mL 4M HCl

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

Optional Am/Cm rare earth separation.

(10) Add 2 mL 70% HNO_3 + 50 uL 10% H_2SO_4 to Am/Cm. Evaporate to dryness.

(11) Ash to dryness with 3 mL 70% HNO_3 + 2 mL 30% H_2O_2.

(12) Dissolve Am/Cm in 5 mL 4M NH_4SCN-0.1M Formic acid.

(13) Precondition 2 mL TEVA with 5 mL 4M NH_4SCN-0.1M Formic acid.

(14) Load Am/Cm on TEVA.

(15) Rinse Am/Cm beaker with 5 mL 4M NH_4SCN-0.1M Formic acid. Add to TEVA.

(16) Rinse TEVA w/ 10 mL 1.5M NH_4SCN-0.1M Formic acid.

(17) Strip Am/Cm from TEVA with 20 mL 1M HCl.

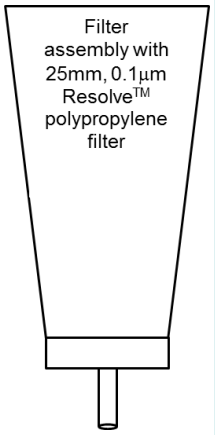
(18) Add 0.5 mL 30% H_2O_2 to Pu, and 0.2 mL 30% H_2O_2 to Am/Cm samples.

(19) Add 50ug Ce to Pu and Am/Cm samples. Mix well. Add 1 mL 49% HF. Mix well. Wait 15-20 minutes.

(20) Set up Resolve® Filter Funnel on vacuum box.

(21) Wet filter with 3 mL 80% ethanol followed by 3 mL DI water.

(22) Filter sample.

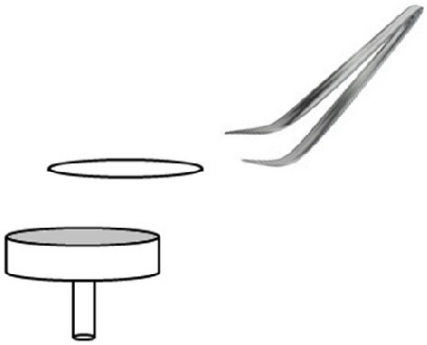


(23) Rinse sample tube with 5 mL DI water. Add to filter.

(24) Rinse funnel with 3 mL DI water and 2 mL 100 ethanol.

(25) Draw vacuum until filter is dry.

(26) Remove filter from funnel. Mount filter on stainless steel planchet with 2-sided tape.



(27) Dry filter under heat lamp for 3-5 minutes.

(28) Measure actinides by alpha spectrometry.

*Adding 50uL 30% H_2O_2 to the tube rinse can improve Uranium recoveries and decontamination in Pu(Np) fractions.

Method Performance for 1 gram Granite Samples

Analyte	Sample replicates	Reference (mBq/g)	Measured (mBq/g)	Average % Diff.	Tracer % Yield
^{239}Pu	8	29.4	29.2 ± 1.4	4.3	92.1 ± 5.5
^{239}Pu	6	21.2	20.1 ± 1.2	5.4	97.2 ± 5.8
^{238}Pu	6	25.2	25.0 ± 2.2	6.9	97.2 ± 5.8
^{237}Np	6	37.0	37.1 ± 1.7	3.5	97.2 ± 5.8
^{241}Am	4	37.0	37.7 ± 3.3	7.0	90.7 ± 5.1
^{244}Cm	4	33.1	34.4 ± 2.0	5.2	90.7 ± 5.1

References

1) Maxwell, S.L. Culligan, B. Hutchinson, J.B. Sudowe, R. McAlister, D.R. "Rapid Method to Determine Pu, Np, Am/Cm in Granite Samples," *J. Radioanal. Nucl. Chem.* 140, 102-108 (2018).