AN-1427-10

Rapid Determination of Plutonium in Large Rice Samples

Summary of Method Plutonium is separated and measured from up to 1.5kg rice samples. Rice samples are muffled and wet ashed to reduce volume and destroy organic content. The residue is then fused with sodium hydroxide. Precipitation steps remove additional matrix and prepare plutonium for separation on Eichrom TEVA resin. Plutonium is measured by alpha spectrometry following cerium fluoride microprecipitation onto Eichrom Resolve® Filters. Plutonium recovery through the method, determined using ^{242}Pu tracer, was 87 ± 4% for 1kg samples. Measured values for ^{239}Pu and ^{238}Pu agreed within 6% of reference values, even when refractory ^{239}Pu was present in the sample. Sample preparation can be completed in less than 48 hours.

Reagents

TEVA Resin, 2mL Cartridges (Eichrom TE-R50-S)
Iron carrier (50mg/mL Fe, as ferric iron nitrate)
La carrier (10mg/mL)
Ce carrier (1mg/mL)

Deionized Water	1.25M $Ca(NO_3)_2$
3.2M $(NH_4)_2HPO_4$	2M $Al(NO_3)_3$
10% (w:w) $TiCl_3$	HNO_3 (70%)
HCl (37%)	NaOH
HF (49%) or NaF	Boric acid
H_2O_2 (30%)	$NaNO_2$
Denatured ethanol	Sulfamic Acid
Ascorbic Acid	^{242}Pu tracer

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
Stainless Steel Planchets with adhesive tape
Alpha Spectrometry System

Centrifuge	Heat Lamp
Muffle Furnace	Hot Plate
Analytical Balance	Vacuum Pump
600mL glass beakers	

Figure 1. Sample Preparation

Rice Sample + tracers in 600mL glass beaker(s). Multiple beakers may be needed for large samples.

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Muffle for 5 hours at 350°C, then 550°C for 12 hours.

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Carefully wet ash with enough 1:1 (v:v) 70% HNO_3:30% H_2O_2 to cover sample.

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Heat to dryness. Muffle 550°C for 6-12 hours.

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Transfer residue to Zr crucible. Rinse beaker with 70% HNO_3. Add rinse to crucible. Wet ash with 1:1 70% HNO_3:30% H_2O_2. Heat to dryness.

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Repeat wet ash until no black char remains (violet residue common).

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Fuse samples with 15g NaOH at 600°C for 20-30 minutes.

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Dissolve fusion cake with H_2O. Transfer to 250mL c-tube.

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Add 10mL 3M HNO_3 to crucible. Heat to dissolve residue. Transfer to same 25mL c-tube.

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Add 125mg Fe and 10mg La to c-tube. Dilute to 180mL.

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Add 2mL 1.25M $Ca(NO_3)_2$, 1mL 3.2M $(NH_4)_2HPO_4$, 6mL 10% $TiCl_3$. Mix. Cool in ice bath for 10min.

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Centrifuge at 3500rpm. Decant Supernate.

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Partially dissolve precipitate in 100mL 1.5M HCl. Some solids will remain. Dilute to 170mL. Add 5mL 10% $TiCl_3$ and 22mL 49% HF. Mix.

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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 6M HNO_3, and 7mL 2M $Al(NO_3)_3$. Cool to room temperature.

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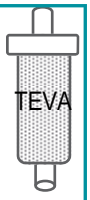
Fix valence states. Mix between each addition of: 0.5mL 1.5M sulfamic acid, 40uL 50mg/mL Fe, 1.5mL 1M ascorbic acid, 1mL 3.5M $NaNO_2$.

Figure 2. Plutonium Separation on TEVA Resin and Source Preparation

(1) Precondition 2mL TEVA, 5mL 3M HNO_3.



(2) Load sample solution.

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

(4) Rinse TEVA cartridge with:
- -15mL 3M HNO_3
- -20mL 9M HCl (Th removal)
- -5mL 3M HNO_3

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

-If measuring Pu by ICP-MS, Pu may be stripped from TEVA with 20mL of 0.05M HCl-0.025M HF-0.02M hydroxylamine-HCl.

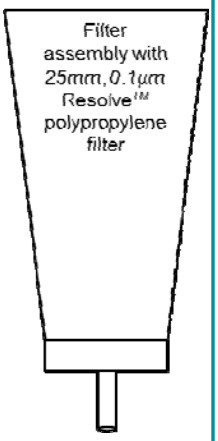
-If preparing Pu sources for alpha spectrometry by electrodeposition, strip Pu with 20mL 0.1M HCl-0.025M HF-0.02M rongalite (sodium-hydroxymethanesulfinate).

(6) Add 0.5mL 30% H_2O_2 for Uranium decontamination in rare earth fluoride precipitation alpha source

(7) Add 50ug Ce carrier to all samples. Mix well.

(8) Add 1mL 49% HF. Mix well. Wait 15-20 minutes.

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



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

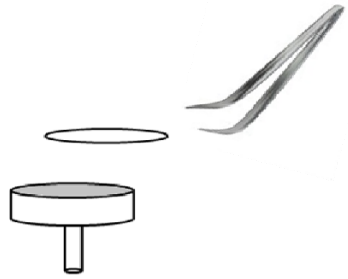
(11) Filter sample.

(12) Rinse sample tube with 5mL DI water and add to filter.

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

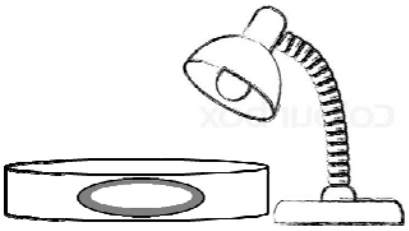
(14) Draw vacuum until filter is dry.

(15) Remove filter from funnel assembly and mount filter on stainless steel planchet with 2-sided tape.



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

(17) Measure plutonium by alpha spectrometry.



*Adding 50uL of 30% H_2O_2 to tube rinse can improve Uranium decontamination.

Method Performance

Sample (kg)	Replicates	^{242}Pu Tracer % Yield	Reference (mBq/kg) ^{239}Pu	Reference (mBq/kg) ^{238}Pu	Measured (mBq/kg) ^{239}Pu	Measured (mBq/kg) ^{238}Pu	% Bias ^{239}Pu	% Bias ^{238}Pu
1.0	8	87 ± 4	12.5	10.6	11.8 ± 1.0	10.5 ± 0.7	-5.6	-0.7

MDA for 1 kg sample, 30hours count time, 0.37uBq/kg

References

1) Sherrod L. Maxwell, Brian K. Culligan, Jay B. Hutchinson, "Rapid fusion method for determination of plutonium isotopes in large rice samples," *J. Radioanal. Nucl. Chem.,* 298(2), 1367-1374 (2013).