AN-1425-10

Rapid Determination of Actinides in 10g Emergency Food Samples

Summary of Method U, Pu, Np, Am and Cm are separated and concentrated from 10 gram food samples. Samples are muffled at 600°C in zirconium crucibles 2 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 sequentially with hydrous titanium oxide and lanthanum fluoride 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 93-98% for ^{236}Pu, 85-93% for ^{243}Am, and 78-89% for ^{232}U. Measured values typically agreed to within 10% of reference values. Sample preparation for batches of 12 samples can be completed by a single operator in <8 hours. Alpha spectrometry count times will depend on detection limit and data quality objectives.

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)
Deionized Water
1.25M $Ca(NO_3)_2$
Iron carrier (50mg/mL Fe, as ferric iron nitrate)
^{242}Pu (or ^{236}Pu if meas. Np), ^{243}Am and ^{232}U tracers
Oxalic acid/Ammonium oxalate
La and Ce carriers (1mg/mL)
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

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

10g Food sample + tracers in zirconium crucible .

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Muffle at 600°C for 2 hours.

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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 10minutes.

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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 5mg La to c-tube. Dilute to 180mL.

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

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Centrifuge at 3500rpm. Decant Supernate.

↓

Partially dissolve precipitate in 60mL 1M HCl. Some solids will remain. Dilute to 170mL. Add 1mg La, 1mL 1.25M $Ca(NO_3)_3$, 3mL 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 $Al(NO_3)_3$.

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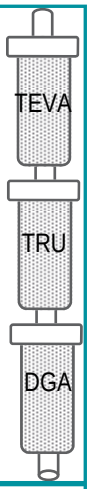
Fix valence states. Mix between each addition of: 0.5mL 1.5M sulfamic acid, 10uL 50mg/mL Fe, 1.5mL 1M ascorbic acid, 1mL 3.5M $NaNO_2$, 1.5mL 70% HNO_3.

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

(1) Precondition stacked 2mL TEVA, TRU, DGA cartridges with 10mL 3M HNO_3.
(2) Load sample solution.
(3) Rinse sample tube with 5mL 3M 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
-5mL 3M HNO_3
(7) Strip Pu (and Np) from TEVA cartridge with 20mL 0.1M HCl-0.05MHF-0.01M $TiCl_3$.

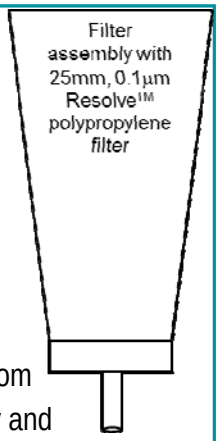
(8) Rinse DGA cartridge with 10mL 0.1M HNO_3.
(9) Place TRU cartridge above DGA.
(10) Strip Am/Cm from TRU onto DGA with 15mL 3M HCl .
(11) Separate TRU cartridge from DGA cartridge.

(12) Rinse DGA cartridge sequentially 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.

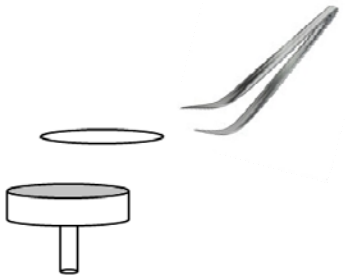
(14) Rinse TRU cartridge with 15mL 4M HCl-0.2M HF-0.002M $TiCl_3$.
(15) Strip U from TRU with 15mL of 0.1M ammonium bioxalate.
(16) Add 0.5mL 10% $TiCl_3$ to U samples, 0.5mL 30% H_2O_2 to Pu, and 0.2mL 30% H_2O_2 to Am/Cm samples.

(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.

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

Method Performance Actinides in 10 Gram Food Samples (16 hour count times)

Sample	Replicates	Analyte	Tracer	% Tracer Recovery	Analyte (mBq/g) Reference	Analyte (mBq/g) Measured	% Bias
Baby Food	5	^{238}Pu	^{236}Pu	93.5 ± 7.5	2.9	2.9 ± 0.1	-0.7
	5	^{239}Pu	^{236}Pu	93.5 ± 7.5	3.6	3.3 ± 0.4	-7.9
	5	^{237}Np	^{236}Pu	93.5 ± 7.5	3.7	3.4 ± 0.2	-8.1
	5	^{241}Am	^{243}Am	84.6 ± 6.3	5.1	5.0 ± 0.1	-3.5
	5	^{244}Cm	^{243}Am	84.6 ± 6.3	3.5	3.7 ± 0.3	4.4
	5	^{238}U	^{232}U	78 ± 10	5.7	5.6 ± 0.4	-1.5
	5	^{234}U	^{232}U	78 ± 10	5.9	5.9 ± 0.2	-0.3

Sample	Replicates	Analyte	Tracer	% Tracer Recovery	Analyte (mBq/g) Reference	Analyte (mBq/g) Measured	% Bias
Apples	5	^{238}Pu	^{236}Pu	98 ± 12	2.9	2.9 ± 0.1	-0.5
	5	^{239}Pu	^{236}Pu	98 ± 12	3.6	3.6 ± 0.4	-0.9
	5	^{237}Np	^{236}Pu	98 ± 12	3.7	3.3 ± 0.1	-11.5
	5	^{241}Am	^{243}Am	93.4 ± 8.5	5.1	4.9 ± 0.3	-2.8
	5	^{244}Cm	^{243}Am	93.4 ± 8.5	3.5	3.7 ± 0.5	6.3
	5	^{238}U	^{232}U	89 ± 10	5.7	5.6 ± 0.3	-1.2
	5	^{234}U	^{232}U	89 ± 10	5.9	5.5 ± 0.4	-6.4

References

1) Sherrod L. Maxwell, Brian K. Culligan, Angel Kelsy-Wall, Patrick J. Shaw, "Rapid separation of actinides and in emergency food samples," *J. Radioanal. Nucl. Chem.,* 292(1), 339-347 (2011).