Rapid Determination of Pu, Am, and Cm in 80L Seawater Samples

AN-1424-10

Summary of Method Plutonium, Americium, and Curium are separated and concentrated from up to 80L samples of seawater with a hydrous titanium oxide precipitation, enhanced with lanthanum and ferric iron. A second precipitation with lanthanum fluoride removes additional matrix ions, and Pu and Am+Cm are separated from potentially interfering radionuclides in the sample using stacked 2mL cartridges of Eichrom TEVA and DGA Resins. Isotopic Pu and Am+Cm are measured by alpha spectrometry following cerium fluoride microprecipitation onto Eichrom Resolve® Filters. Chemical yields are determined by recovery of ^{243}Am and ^{242}Pu tracers. Recoveries of ^{243}Am average 94 ± 3%, while ^{242}Pu average 86 ± 4%. Measured values of ^{239}Pu, ^{241}Am, and ^{244}Cm typically agree to within 10% of reference values. A single operator can process batches of 12 samples through alpha source preparation in 6-8 hours. Alpha spectrometry count times will vary depending on desired detection limit and data quality objectives.

Reagents

TEVA Resin, 2mL Cartridges (Eichrom TE-R50-S)
DGA Resin, 2mL Cartridges (Eichrom DN-R50-S)
Ammonium Hydroxide (listed as 28% NH_3 or 56% NH_4OH)
Nitric Acid (70%)
Hydrochloric Acid (37%)
Hydrofluoric Acid (49%) or Sodium Fluoride
Deionized Water
Iron Carrier (50mg/mL Fe, as ferric nitrate)
Lanthanum and Cerium Carriers (1mg/mL)
^{243}Am and ^{242}Pu tracers

10% (w:w) $TiCl_3$	H_2O_2(30%)
2M $Al(NO_3)_3$	Boric acid
Sulfamic Acid	Ascorbic Acid
$NaNO_2$	Denatured Ethanol

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 250-500mL Centrifuge Tubes
Centrifuge
Stainless Steel Planchets with adhesive tape
Alpha Spectrometry System
Analytical Balance
Vacuum Pump
Heat Lamp

Figure 1. Sample Preparation

1-80L Sample of Seawater.
Acidify to pH 2 with 70% HCl.
Add tracers. Mix well.

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Add 15mg La, 50mg Fe/L sample and
1mL 10% $TiCl_3$/L sample. Mix well.

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Add 2.5mL 56% NH_4OH/L sample.
Mix well. Allow precipitate to settle.
Decant supernate to <1-2L.

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Transfer remaining supernate and precipitate to
250-500mL centrifuge tubes. Centrifuge
3000rpm for 10 minutes. Decant supernate.
Repeat until all sample processed.

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Partially dissolve precipitate in 120mL 1M HCl.
Some solids will remain.
Add 15mL 10% $TiCl_3$. Mix. Add 50mL 49% HF. Mix.
Wait 15 minutes. Centrifuge. Decant Supernate.

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Dissolve precipitate with 10mL 3M HNO_3-0.25M boric
acid, 12mL 2M $Al(NO_3)_3$ and 9mL 7M HNO_3.

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Load solution to valence adjustment
and TEVA-DGA separation.

Figure 2. TEVA-TRU Separation and Alpha Source Preparation

(1) Adjust valence states of actinides by adding the following reagents in the order listed (mix between steps):
- -0.2mL 1.5M Sulfamic acid
- -0.01mL 50mg/mL Fe carrier
- -1.5mL 1M Ascorbic acid
- -1mL 3.5M $NaNO_2$

(2) Precondition stacked 2mL TEVA + DGA cartridges with 5mL 3M HNO_3.

(3) Load sample solution at ~1mL/min.

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

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

(6) Separate TEVA and DGA cartridges.

(7) Rinse TEVA with 15mL 9M HCl.

(8) Rinse TEVA with 12mL 3M HNO_3.

(9) Strip Pu and Np from TEVA with 20mL 0.1M HCl-0.05M HF-0.01M $TiCl_3$. Add 0.5mL 30% H_2O_2.

(10) Rinse DGA with 15mL 3M HCl.

(11) Rinse DGA with 4mL 1M HNO_3.

(12) Rinse DGA w/ 30mL 0.05M HNO_3.

(13) Rinse DGA with 16mL 3M HNO_3-0.25M HF.

(14) Rinse DGA with 8mL 3M HCl.

(15) Strip Am+Cm from DGA with 20mL 0.25M HCl. Add 0.2mL 30% H_2O_2.

(16) Add 50-100ug Ce carrier. Mix well. Add 1mL 49% HF. Mix well. Wait 15-20 minutes.

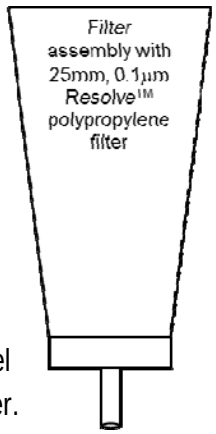
(17) Set up Resolve® Filter Funnel on vacuum box.

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

(19) Filter sample.

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

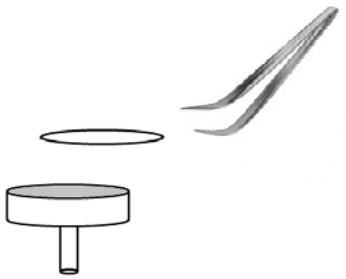
(21) Rinse filter funnel with 3mL DI water.



(22) Rinse filter funnel with 1-2mL 100%ethanol.

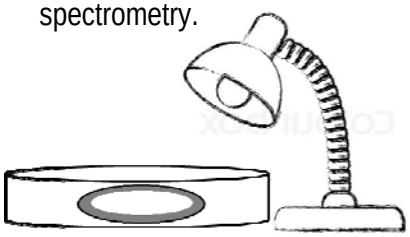
(23) Draw vacuum until filter is dry.

(24) Remove filter from funnel assembly and mount filter on stainless steel planchet with adhesive tape.



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

(26) Measure actinides by alpha spectrometry.



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

Method Performance Pu, Am and Cm from Seawater

Analyte	Volume, L	Replicates	Tracer	% Tracer Recovery	Analyte(mBq/L) Reference	Analyte(mBq/L) Measured	% Bias
^{239}Pu	16	2	^{242}Pu	90 ± 1	4.22	4.67 ± 0.05	11
^{239}Pu	25	2	^{242}Pu	84.6 ± 0.2	3.22	3.3 ± 0.1	2.5
^{239}Pu	40	2	^{242}Pu	86 ± 2	0.81	0.82 ± 0.02	1.2
^{239}Pu	80	2	^{242}Pu	85 ± 5	0.40	0.37 ± 0.01	-7.5
^{241}Am	16	2	^{243}Am	95 ± 4	3.31	3.1 ± 0.1	-6.3
^{241}Am	25	2	^{243}Am	93.1 ± 0.1	2.12	1.9 ± 0.1	-10
^{241}Am	40	2	^{243}Am	96 ± 2	0.53	0.51 ± 0.02	-3.8
^{241}Am	80	2	^{243}Am	93 ± 4	0.27	0.25 ± 0.01	-7.4
^{244}Cm	16	2	^{243}Am	95 ± 4	2.16	2.1 ± 0.2	-2.8
^{244}Cm	25	2	^{243}Am	93.1 ± 0.1	1.35	1.3 ± 0.1	-3.7
^{244}Cm	40	2	^{243}Am	96 ± 2	0.85	0.78 ± 0.04	-8.2
^{244}Cm	80	2	^{243}Am	93 ± 4	0.42	0.41 ± 0.01	-2.3

16 hour count times

References

1) Sherrod L. Maxwell, Brian K. Culligan, Jay B. Hutchinson, Robin C. Utsey, Daniel R. McAlister, "Rapid determination of actinides in seawater samples," *J. Radioanal. Nucl. Chem., 300(3), 1175-1189* (2014).