AN-1423-10

Rapid Determination of Pu, Np, and U in 1-8L Seawater Samples

Summary of Method Plutonium, Neptunium, and Uranium are separated and concentrated from up to 8L samples of seawater with a hydrous titanium oxide precipitation, enhanced with 5mg of lanthanum and 125mg of ferric iron. A second precipitation with lanthanum fluoride removes additional matrix ions, and Uranium and Pu+Np are separated from potentially interfering radionuclides in the sample using stacked 2mL cartridges of Eichrom TEVA and TRU Resins. Isotopic U and Pu+Np are measured by alpha spectrometry following cerium fluoride microprecipitation onto Eichrom Resolve® Filters. Chemical yields are determined by recovery of ^{232}U and ^{242}Pu (or ^{236}Pu if measuring ^{237}Np) tracers. Recoveries of ^{232}U average 95 $\pm$ 6%, while ^{236}Pu average 90 $\pm$ 9%. Measured values of ^{238}U, ^{239}Pu, and ^{237}Np typically agree to within 10% of reference value. 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)
TRU Resin, 2mL Cartridges (Eichrom TR-R50-S)
Nitric Acid (70%)
Hydrochloric Acid (37%)
Hydrofluoric Acid (49%) or Sodium Fluoride
Ammonium Hydroxide (listed as 28% NH_3 or 56% NH_4OH)
Iron Carrier (50mg/mL Fe, as ferric nitrate)
Lanthanum and Cerium Carriers (1mg/mL)
^{232}U and ^{242}Pu(or ^{236}Pu if meas. ^{237}Np) tracers
Oxalic acid/Ammonium Oxalate
Deionized Water
H_2O_2(30%)
10% (w:w) $TiCl_3$
2M $Al(NO_3)_3$
Boric acid
Sulfamic Acid
$NaNO_2$
Ascorbic Acid
Denatured Ethanol
1.25M $Ca(NO_3)_2$

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

1-8L Sample of Seawater.
Acidify to pH 2 with 70% HCl.
Add tracers. Mix well.

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Add 5mg La, 125mg Fe and
10mL 10% $TiCl_3$. Mix well.

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Add 5mL 56% NH_4OH. Mix well.
Allow precipitate to settle.
Decant supernate to <1L.

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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 80mL 1M HCl.
Some solids will remain.
Add 1mg La, 25mg Ca, 5mL 10% $TiCl_3$. Mix.
Add 25mL 49% HF. Mix. Centrifuge. Decant Supernate.

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Dissolve precipitate with 5mL 3M HNO_3-0.25M boric acid,
7mL 2M $Al(NO_3)_3$ and 8mL 7M HNO_3.

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Load solution to valence adjustment
and TEVA-TRU 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 + TRU cartridges with 5mL 3M HNO_3.

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

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

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

(6) Separate TEVA and TRU cartridges.

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

(8) Rinse TEVA with 5mL 3M HNO_3.

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

(10) Rinse TRU with 20mL 4M HCl-0.2M HF.

(11) Rinse TRU with 12mL 10M HNO_3.

(12) Strip U from TRU with 15mL 0.1M ammonium bioxalate.

(13) Add 0.5mL 10% $TICl_3$ to U samples and 0.5mL 30% H_2O_2 to Pu/Np samples.

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

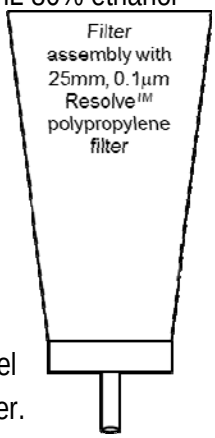
(15) Set up Resolve® Filter Funnel on vacuum box.

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

(17) Filter sample.

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

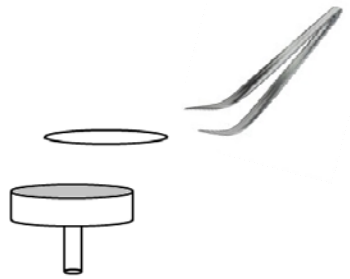
(19) Rinse filter funnel with 3mL DI water.



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

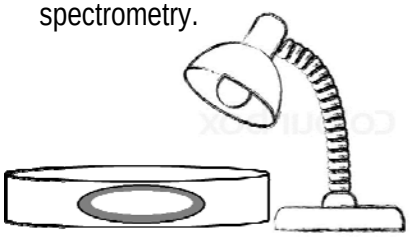
(21) Draw vacuum until filter is dry.

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



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

(24) Measure actinides by alpha spectrometry.



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

Method Performance Pu, Np and U from Seawater

Analyte	Volume, L	Replicates	Tracer	% Tracer Recovery	Analyte(mBq/L) Reference	Analyte(mBq/L) Measured	% Bias
^{239}Pu	2	5	^{236}Pu	91 ± 9	33.8	32.6 ± 1.4	-3.6
^{239}Pu	4	1	^{236}Pu	86	16.9	16.2	-4.1
^{239}Pu	8	2	^{236}Pu	87 ± 3	27.8	27.6 ± 0.5	-0.7
^{237}Np	2	5	^{236}Pu	91 ± 9	17.4	17.7 ± 1.5	1.7
^{237}Np	4	1	^{236}Pu	86	8.7	7.2	-17
^{237}Np	8	2	^{236}Pu	87 ± 3	4.4	4.2 ± 0.4	-4.5
^{238}U	2	5	^{232}U	99 ± 2	51.8	49.3 ± 1.5	-4.8
^{238}U	4	1	^{232}U	86	25.9	25.0	-3.6
^{238}U	8	2	^{232}U	92 ± 5	96.3	94 ± 3	-2.4

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).