AN-1429-10

Rapid Determination of Actinides in Asphalt Samples

Summary of Method Actinides are separated and measured from 1g samples of asphalt. Asphalt samples are fused in zirconium crucibles with sodium hydroxide. Sequential precipitations remove matrix prior to separation of actinides on 2mL cartridges of Eichrom TRU and DGA resins. Actinides are measured by alpha spectrometry following cerium fluoride microprecipitation onto Eichrom Resolve® Filters. Chemical recoveries averaged 91±6%, 84±12%, and 86±7%, respectively, for ^{242}Pu, ^{243}Am and ^{232}U tracers. Measured values typically agreed to within 2-6% of reference values. Batches of 12 samples can be prepared for measurement in as little as 4 hours.

Reagents

TRU Resin, 2mL Cartridges (Eichrom TR-R50-S)
DGA Resin, 2mL Cartridges (Eichrom DN-R50-S)
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 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	

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
Muffle Furnace
Analytical Balance
250mL Zirconium crucibles with zirconium lids
Stainless Steel Planchets with adhesive tape
Alpha Spectrometry System
Vacuum Pump
Heat Lamp

Figure 1. Sample Preparation

1g finely ground asphalt + tracers in 250mL Zr-crucible

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Fuse samples with 15g NaOH at 600°C for 15 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. Add to same c-tube.

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Add 125mg Fe and 5mg La to c-tube. Dilute to 180mL.

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Add 2mL 1.25M $Ca(NO_3)_2$, 5mL 3.2M $(NH_4)_2HPO_4$, 10mL 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 60-80mL 1.5M HCl.*
Dilute to 170mL with 0.01M HCl.
Add 1mg La and 5mL 10% $TiCl_3$. Mix.
Add 20mL 49% HF. Mix. Wait 10 min.

*The entire precipitate will not dissolve in HCl. Dissolution will be completed with the HF addition.

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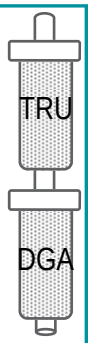
Fix valence states. Mix between each addition of: 0.5mL 1.5M sulfamic acid, 10uL 50mg/mL Fe, 1.5mL 1M ascorbic acid, 1mL 3.5M $NaNO_2$, 1.5mL 70% HNO_3.

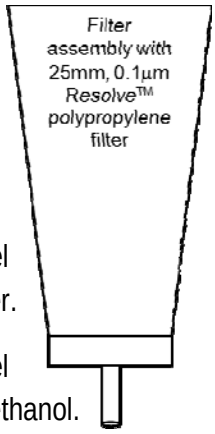
Figure 2. Actinide Separation on TRU/DGA and Source Preparation

(1) Precondition TRU/DGA resin with 5mL 8M HNO_3.
(2) Load samples.
(3) Rinse sample tube with 5mL 8M HNO_3, and add tube rinse to TRU/DGA.*
(4) Rinse TRU/DGA with:
-10mL 10M HNO_3
-15mL 4M HCl
(5) Separate TRU and DGA.

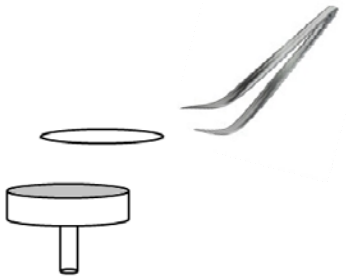


(6) Strip Pu from TRU w/ 15mL 3M HCl-0.02M $TiCl_3$. Add 0.5mL 30% H_2O_2.
(7) Rinse TRU with:
-5mL 8M HNO_3 + 50uL 30% H_2O_2
-10mL 4M HCl-0.2M HF
-10mL 4M HCl-0.2M HF-2mM $TiCl_3$
-3mL 8M HNO_3
(8) Strip U from TRU with 15mL 0.1M ammonium bioxalate. Add 0.5mL $TiCl_3$ for CeF_3 ppt.
(9) Rinse DGA with:
-12mL 3M HCl
-20mL 0.05M HNO_3
-12mL 3M HNO_3-0.25M HF

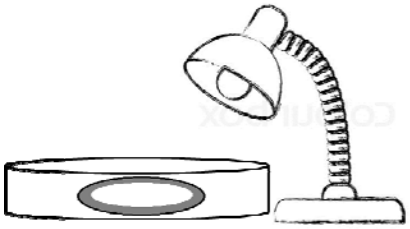
(10) Rinse DGA with 5mL 3M HCl.
(11) Strip Am/Cm from DGA with 12mL 0.25M HCl. Add 0.2mL 30% H_2O_2.
(12) Add 50-ug Ce carrier to each sample. Mix well. Add 1mL 49% HF. Mix well. Wait 15-20 minutes.
(13) Set up Resolve® Filter Funnel on vacuum box.
(14) Wet filter with 3mL 80% ethanol followed by 3mL DI water.
(15) Filter sample.
(16) Rinse sample tube with 5mL DI water and add to filter.
(17) Rinse filter funnel with 3mL DI water.
(18) Rinse filter funnel with 2mL 100% ethanol.



(19) Draw vacuum until filter is dry.
(20) Remove filter from funnel assembly and mount filter on stainless steel planchet with adhesive tape.



(21) Dry filter under heat lamp for 3-5 minutes.
(22) Measure actinides by alpha spectrometry.



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

Method Performance

Analyte	Replicates	Tracer	% Tracer Recovery	Analyte Reference (mBq/g)	Analyte Measured (mBq/g)	% Bias
^{239}Pu	8	^{242}Pu	91 ± 6	39.2	40 ± 2	2.0
^{241}Am	8	^{243}Am	84 ± 13	24.4	23 ± 3	-5.7
^{244}Cm	8	^{243}Am	84 ± 13	35.5	37 ± 5	4.2
^{238}U	8	^{232}U	86 ± 7	73.6	72 ± 8	-2.1
^{234}U	8	^{232}U	86 ± 7	73.6	72 ± 9	-2.1

References

1) Sherrod L. Maxwell, Brian K. Culligan, Jay B. Hutchinson, "Rapid determination of actinides and in asphalt samples," *J. Radioanal. Nucl. Chem.*, 299(3), 1891-1901 (2014).