

Rapid Determination of Actinides in Urine by ICP-MS + Alpha Spec.

Summary of Method Actinides are separated and concentrated from 100mL urine samples. Actinides are concentrated from urine samples using a calcium phosphate precipitation. Pu, Np, Am-Cm, and U are separated on 2mL cartridges of Eichrom TEVA, TRU and DGA resins. Pu-Np are measured by ICP-MS. Measured values for ^{239}Pu and ^{237}Np agreed to within 1-2% of reference values, while ^{241}Am and ^{244}Cm agreed to within 2-3%. Decontamination factors of $>10^6$ were achieved for Pu over U (^{238}U -H can interfere with the measurement of ^{239}Pu by ICP-MS). Sample preparation for batches of 12 samples can be completed by a single operator in <8 hours.

Reagents

TEVA Resin, 2mL Cartridges (Eichrom TE-R50-S)
 TRU Resin, 2mL Cartridges (Eichrom TR-R50-S)
 DGA Resin, Normal, 2mL Cartridges (Eichrom DN-R50-S)
 Iron carrier (50mg/mL Fe, as ferric iron nitrate)
 ^{242}Pu (ICP-MS) or ^{236}Pu (alpha) tracer
 ^{233}U (ICP-MS) or U^{232} (alpha) tracer
 ^{243}Am tracer Ce carrier (1mg/mL)
 1.25M $\text{Ca}(\text{NO}_3)_2$ 3.2M $(\text{NH}_4)_2\text{HPO}_4$
 Deionized Water 2M $\text{Al}(\text{NO}_3)_3$
 HNO_3 (70%) HCl (37%)
 NH_4OH HF (49%) or NaF
 NaNO_2 Denatured ethanol
 Sulfamic Acid Ascorbic Acid
 Oxalic acid/Ammonium oxalate
 Hydroxylamine Hydrochloride

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)
 600mL Glass beakers
 Stainless Steel Planchets with adhesive tape
 Alpha Spectrometry System
 ICP-MS System
 50mL and 250mL Centrifuge Tubes
 Centrifuge
 Heat Lamp
 Hot Plate
 Analytical Balance
 Vacuum Pump

Figure 1. Sample Preparation

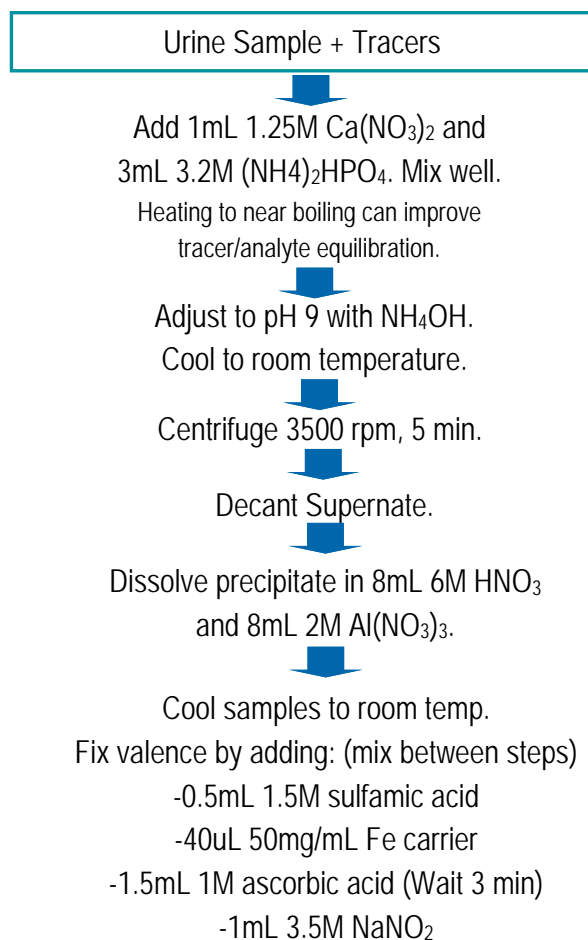

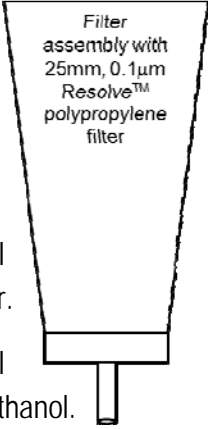



Figure 2. Actinide Separation on TEVA - DGA

<p>(1) Precondition 2mL TEVA+TRU with 10mL 6M HNO₃.</p> <p>(2) Load Sample.</p> <p>(3) Rinse centrifuge tube with 5mL 6M HNO₃. Add to TEVA-TRU.*</p> <p>(4) Rinse TEVA+TRU with 5mL 3M HNO₃.</p> <p>(5) Separate TEVA and TRU.</p>		<p>(12) Rinse DGA with:</p> <ul style="list-style-type: none"> -5mL 8M HNO₃ -20mL 0.1M HNO₃ -10mL 0.05M HNO₃. <p>(13) Strip Pu from DGA with 11mL 0.02M HCl-0.005M HF-0.01M Hydroxylamine hydrochloride.</p>	<p>(20) Wet filter with 3mL 80% ethanol followed by 3mL DI water.</p>
<p>(6) Rinse TEVA with:</p> <ul style="list-style-type: none"> -30mL 3M HNO₃ -15mL 9M HCl (Th removal) 	<p>(14) Strip Am/Cm from TRU with 15mL 4M HCl.</p> <p>(15) Rinse TRU resin with 15mL 4M HCl-0.2MHF.</p> <p>(16) Strip U from TRU with 15mL 0.01M ammonium bioxalate.</p>	<p>(21) Filter sample.</p> <p>(22) Rinse sample tube with 5mL DI water and add to filter.</p> <p>(23) Rinse filter funnel with 3mL DI water.</p> <p>(24) Rinse filter funnel with 2mL 100% ethanol.</p>	
<p>(7) Add DGA below TEVA.**</p> <p>(8) Strip Pu/Np from TEVA to DGA with 15mL 3M HNO₃-0.1M Ascorbic acid-0.02M Fe²⁺.</p> <p>(9) Separate TEVA and DGA.</p> <p>(10) Rinse TEVA with 5mL 3M HNO₃.</p> <p>(11) Strip Np from TEVA with 14mL 0.25M HCl-0.005M HF-0.01M Hydroxylamine hydrochloride.</p>		<p>(17) Measure Np, Pu and U by ICP-MS.</p> <p>(18) Add 50ug Ce carrier and 0.5mL 30% H₂O₂ to each Am-Cm sample. Mix well. Add 1mL 49% HF. Mix well. Wait 15-20 min.</p> <p>(19) Set up Resolve® Filter Funnel on vacuum box.</p>	<p>(25) Draw vacuum until filter is dry.</p> <p>(26) Remove filter from funnel assembly and mount filter on stainless steel planchet with adhesive tape.</p> <p>(27) Dry filter under heat lamp for 3-5 minutes.</p> <p>(28) Measure actinides by alpha spectrometry.</p>

* Adding 50uL of 30% H₂O₂ to the 6M HNO₃ tube rinse can help improve U recoveries and decontamination in the Np and Pu fractions.

** Adding a 1mL UTEVA cartridge between TEVA and DGA can help improve uranium decontamination.

References

- 1) Sherrod L. Maxwell, Vernon D. Jones, "Rapid determination of Actinides in urine by ICP-MS and alpha spectrometry: A hybrid approach," *Talanta*, 80(1), 143-150 (2009).
- 2) Sherrod L. Maxwell, Brian K. Culligan, Vernon D. Jones, Sheldon T. Nichols, Gary W. Noyes, Maureen A. Bernard, "Rapid Determination of ²³⁷Np and Plutonium Isotopes by ICP-MS and Alpha Spectrometry," *Health Physics*, 101(2), 180-186 (2011).