

Alpha Spectrometry Source Preparation: Rare Earth Fluoride Microprecipitation

Summary of Method Rare earth fluoride microprecipitation is an alternative to electrodeposition for alpha spectrometry source preparation, which provides adequate alpha peak resolution for most analytical applications, while greatly reducing the time for sample preparation. Alpha spectrometry sources can often be prepared directly from the eluate used to recover the actinide fraction from the chromatographic column used to separate the actinides from the sample matrix and potentially interfering nuclides. The direct precipitation eliminates the numerous evaporation and digestion steps normally required for electrodeposition, reducing the alpha spectrometry source preparation time from 3-8 hours to 30-60 minutes and eliminating the emission of corrosive acid fumes through the laboratory fume hood vents.

Lanthanum, cerium or neodymium carrier and hydrofluoric acid are normally used to produce the rare earth fluoride precipitate. Ammonium bifluoride may be used instead of HF. Additionally, for laboratories which are restricted from the use of fluoride, $\text{Ce}(\text{OH})_4$ precipitation (AN-1807) may be a suitable alternative.

Rare earth fluoride precipitates will nearly quantitatively carry trivalent and tetravalent actinides, while rejecting pentavalent and hexavalent actinides. Therefore, the addition of TiCl_3 is required to reduce U(VI) to U(IV) to prepare uranium samples. Samples of the other actinides may be further purified from U during the rare earth fluoride precipitation by the addition of H_2O_2 , which will ensure U(VI) that will not be carried on rare earth fluorides.

Eichrom's Resolve Filters (RF-DF25-25PP01) are manufactured specifically for alpha spectrometry source preparation. The manufacture and quality control procedures ensure a uniform surface for the collection of the rare earth fluoride precipitate, reducing self attenuation of the alpha emissions, which can degrade peak resolution. Other filter membranes may not be suitable for alpha source preparation or may require the addition of substrate to achieve adequate resolution.

Sources prepared by rare earth precipitation typically sit closer to the detector in alpha spectrometry systems than electrodeposition sources. The difference in distance from the source to the detector can lead to a 5-10% higher efficiency for the measurement of microprecipitation sources. Since most laboratories calibrate their alpha spectrometry systems with electrodeposited sources, the efficiency difference must be considered when determining the absolute recovery of the chemical yield tracers.

Rare earth fluoride microprecipitation onto Eichrom Resolve Filters produces alpha spectra which are suitable for most analytical applications. However, electrodeposition may be required for some applications, such as the preparation of calibration sources and the measurement of nuclides with difficult to resolve alpha peaks.

Reagents

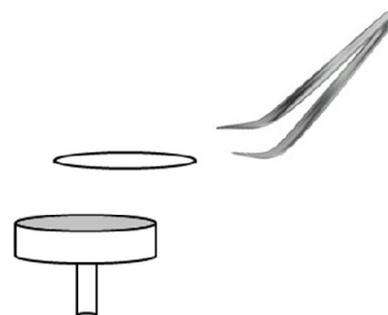
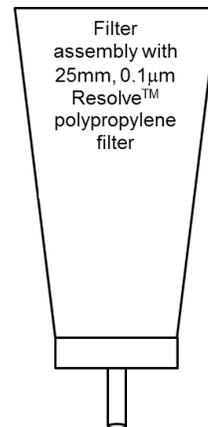
Lanthanum, Cerium or Neodymium Carrier (10 mg/mL)
HF(49%)
30% H_2O_2
Deionized Water
Denatured Ethanol
10-20% TiCl_3 (for Uranium fractions)

Equipment

Vacuum Box (Eichrom AR-24-BOX or AR-12-BOX)
Yellow Outer Tips (Eichrom AR-1000-OT)
Resolve Filters in Funnel (Eichrom RF-DF25-25PP01)
50 mL Centrifuge Tubes
Alpha Spectrometry System
Stainless Steel planchets with two sided tape
Heat Lamp
Vacuum Pump

Figure 1. Rare Earth Fluoride Alpha Spectrometry Source Preparation

<p style="text-align: center;">Uranium Samples*</p> <p>(1) Obtain a purified sample of U in a 50 mL centrifuge tube using an appropriate separation method. Samples are typically in 10-20 mL of 1M HCl or 0.1M ammonium bioxalate. Other matrices and volumes should be tested prior to application. Concentrations of >0.1M HNO₃ may interfere with uranium reduction by TiCl₃ and lead to poor recoveries in the rare earth fluoride precipitation.</p> <p>(2) Add 0.25 mL of 20% TiCl₃ and 100 µg of La, Ce or Nd carrier. Mix.</p> <p>(3) Add 1 mL 49% HF. Mix well. Wait 15-20 minutes. Proceed to step (4).</p>	<p style="text-align: center;">Pu/Np Samples*</p> <p>(1) Obtain a purified sample of Pu/Np in a 50 mL centrifuge tube using an appropriate separation method. Samples are typically in 15-20 mL of dilute HCl-HF with a reducing agent.</p> <p>(2) Add 50 µg of La, Ce or Nd carrier and 0.5 mL 30% H₂O₂. Mix.</p> <p>(3) Add 1 mL 49% HF. Mix well. Wait 15-20 minutes. Proceed to step (4).</p>	<p>(5) Wet filter with 3 mL 80% ethanol followed by 3 mL DI water.</p> <p>(6) Filter sample.</p> <p>(7) Rinse sample tube with 5 mL DI water. Add to filter.</p> <p>(8) Rinse funnel with 3 mL DI water and 2 mL ethanol.</p> <p>(9) Draw vacuum until filter is dry.</p> <p>(10) Remove filter from funnel. Mount filter on stainless steel planchet with 2-sided tape.</p>
<p style="text-align: center;">Thorium Samples*</p> <p>(1) Obtain a purified sample of Th in a 50 mL centrifuge tube using an appropriate separation method. Samples are typically in 10-15 mL of 6-9M HCl.</p> <p>(2) Add 50 µg of La, Ce or Nd carrier. Dilute to 30 mL with DI H₂O. Mix.</p> <p>(3) Add 1 mL 49% HF. Mix well. Wait 15-20 minutes. Proceed to step (4).</p>	<p style="text-align: center;">Am/Cm, An(III), and Ln(III) Samples*</p> <p>(1) Obtain a purified sample of Am/Cm, An(III) or Ln(III) in a 50 mL centrifuge tube using an appropriate separation method. Samples are typically in 15-20 mL of 0.1-4M HCl. Samples with high native rare earth content will require removal of rare earths using TEVA-SCN (AN-1806).</p> <p>(2) Add 50 µg of La, Ce or Nd carrier and 0.2 mL 30% H₂O₂. Mix.</p> <p>(3) Add 1 mL 49% HF. Mix well. Wait 15-20 minutes. Proceed to step (4).</p>	<p>(11) Dry filter under heat lamp for 3-5 minutes.</p> <p>(12) Measure actinides by alpha spectrometry.</p>



Typical Performance of CeF₃ Microprecipitation onto Eichrom Resolve Filters

Nuclide	µg Ce	Matrix	Yield	Resolution (FWHM)
²³⁰ Th	50	30 mL 4.5M HCl	>95%	20-30 keV
^{238/234} U	100	20 mL 1M HCl	>95%	30-40 keV
²³⁹ Pu	50	20 mL 0.1M HCl-0.05MHF-0.01MTiCl ₃	>95%	30-40 keV
²⁴¹ Am	50	15 mL 4M HCl	>95%	22-28 keV

References

- 1) Claude W. Sill, "Precipitation of Actinides as Fluorides or Hydroxides for High-Resolution Alpha Spectrometry," Nuclear and Chemical Waste Management, 7, 201-215 (1987).
- 2) ASTM C1163-14, Standard Practice for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride