Alpha Spectrometry Source Preparation: Rare Earth Fluoride Microprecipitation

AN-1805-11

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, eliminating 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 reducing 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, $Ce(OH)_4$ 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-DF25-25PE01) 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 and mounted to stainless steel planchets with doubled-side tape or glue 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-DF25-25PE01)
50 mL Centrifuge Tubes
Alpha Spectrometry System
Heat Lamp
Vacuum Pump
Stainless Steel planchets with two sided tape
(A.F. Murphy part no. F-2-C)

Figure 1. Rare Earth Fluoride Alpha Spectrometry Source Preparation

Uranium Samples*

(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 HNO_3 may interfere with uranium reduction by $TiCl_3$ and lead to poor recoveries in the rare earth fluoride precipitation.

(2) Add 0.25 mL of 20% $TiCl_3$ and 100 μg of La, Ce or Nd carrier. Mix.

(3) Add 1 mL 49% HF. Mix well. Wait 15-20 minutes. Proceed to step (4).

Thorium Samples*

(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.

(2) Add 50 μg of La, Ce or Nd carrier. Dillute to 40 mL with DI H_2O. Mix.

(3) Add 3 mL 49% HF. Mix well. Wait 15-20 minutes. Proceed to step (4).

Pu/Np Samples*

(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.

(2) Add 50 μg of La, Ce or Nd carrier and 0.5 mL 30% H_2O_2. Mix.

(3) Add 1 mL 49% HF. Mix well. Wait 15-20 minutes. Proceed to step (4).

Am/Cm, An(III), and Ln(III) Samples*

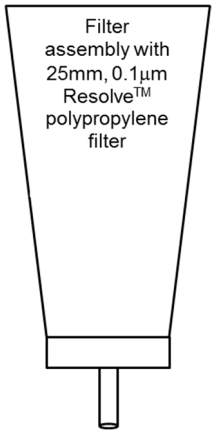
(1) Obtain a purified sample of Am/Cm, An(III) or Ln(III) in a 50 mL centrifuge tube using an appropriate separation method. Samples are typically in 15-20 mL of 0.1-4M HCl. Samples with high native rare earth content will require removal of rare earths using TEVA-SCN (AN-1806).

(2) Add 50 μg of La, Ce or Nd carrier and 0.2 mL 30% H_2O_2. Mix.

(3) Add 1 mL 49% HF. Mix well. Wait 15-20 minutes. Proceed to step (4).

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

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



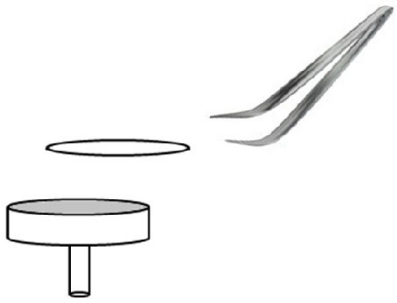
(6) Filter sample.

(7) Rinse sample tube with 5 mL DI water. Add to filter.

(8) Rinse funnel with 3 mL DI water and 2 mL ethanol.

(9) Draw vacuum until filter is dry.

(10) Remove filter from funnel. Mount filter on stainless steel planchet with 2-sided tape or glue.*



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

(12) Measure actinides by alpha spectrometry.

***Some users prefer to dry the filters before mounting. With the polyethylene Resolve Filters®, this can lead to curling, making the filters more difficult to mount. Mounting the filters prior to drying is recommended.**

Typical Performance of CeF_3 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-0.01M$TiCl_3$	>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