RARE EARTH FLUORIDE MICROPRECIPITATION

(SOURCE PREPARATION)

1. SCOPE

1.1. This is a procedure for preparing sources for the measurement of actinides by alpha spectrometry or beta emitting rare earths by gas flow proportional counting. This method is meant to be used in conjunction with the appropriate separation method for the nuclide or nuclides to be measured.

1.2. This method utilizes CeF_3 for the preparation of sources suitable for the measurement of actinide radionuclides via alpha spectrometry. Nearly identical performance can be achieved using an equal mass of LaF_3 or NdF_3 in place of CeF_3.

1.3. This method does not address all aspects of safety, quality control, calibration or instrument set-up. However, enough detail is given for a trained radiochemist to achieve accurate and precise results for the analysis of the analyte(s) from the appropriate matrix, when incorporating the appropriate agency or laboratory safety, quality and laboratory control standards.

2. INTERFERENCES

2.1. High levels of rare earth elements present in the sample can produce thick deposits that will degrade alpha spectra resolution through self-attenuation. This is normally only important for Am/Cm fractions, from which normal TRU or DGA separations chemistry may not adequately separate rare earth elements. If high levels of rare earth elements are suspected in the sample, Am/Cm-rare earth separation, via Eichrom Method SPA03, should be performed.

2.2. High masses (>5-10 ug/cm^2) of analyte can lead to poor microprecipitation yields and thick deposits that will degrade alpha spectra resolution (normally only a concern with $^{238/234}$U and ^{232}Th due to their very long half-lives). Sample aliquots should be adjusted to keep analyte masses to <5-10ug.

2.3. Actinides with unresolvable alpha energies such as ^{241}Am and ^{238}Pu, ^{237}Np and ^{234}U, or ^{232}U and ^{210}Po must be chemically separated to enable measurement. An appropriate separation method should be used prior to alpha source preparation.

2.4. U(VI) must be reduced with $TiCl_3$ to U(IV) in order to carry uranium with the CeF_3 precipitate. Additional uranium decontamination of Pu, Np, Th or Am/Cm fractions can be achieved by adding a small volume of 30% H_2O_2, ensuring that uranium is present as U(VI).

2.5. Peak resolution of the alpha sepctra obtained from CeF_3 precipitation sources is inversely proportional to the mass of Ce, while chemical recovery of analytes is directly proportional to the mass of Ce. Therefore, the mass of Ce must be balanced to maximize recovery and peak resolution. For uranium fractions, 100ug of Ce is recommended. For Pu, Np and Am/Cm fractions 50ug of Ce is recommended. For Th samples, where resolution of ^{229}Th and ^{230}Th peaks can be difficult, 40ug of Ce is recommended.

3. APPARATUS

- Centrifuge tubes, 50 mL
- Heat lamp
- Petri dishes, plastic, 5 ½ x 1 cm
- Planchets, stainless-steel, flat with double-sided tape, 1.25 inch diameter (A.F. Murphy stock: F-2, stainless, double-sided tape, or equivalent).
- Tweezers, stainless-steel
- Vacuum box liner, Eichrom Part: AR-24-Liner or AR-12-Liner
- Vacuum box system, Eichrom Part: AR-24-Box or AR-12-Box
- Vacuum box yellow outer tips- Eichrom Part: AR-1000-OT
- Vacuum pump, 115 V, 60 Hz Fisher Part: 01-092-25 (or equivalent replacement) or house vacuum
- One of the following:
    - Resolve™ filter- 0.1 micron 25 mm polypropylene, Eichrom Part: RF-100-25PP01 and filter apparatus- Pall 25mm polysulfone filter apparatus with polycarbonate base, metal screen and 50 mL reservoir (Pall Part: 4203)
    - Resolve™ filter- 0.1 micron 25 mm polypropylene in disposable funnel, Eichrom Part: RF-DF-25-25PP01

4. REAGENTS

Note: Analytical grade or ACS grade reagents and trace metal grade (or equivalent) acids are recommended.

Cerium nitrate hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$
Deionized water, all reagents are prepared using deionized water
Ethanol denatured, C_2H_3OH
Hydrofluoric acid (49%), concentrated HF
Hydrogen peroxide (30%), concentrated H_2O_2
Titanium (III) chloride(10wt%) solution in 20-30wt% HCl

4.1. *Cerium carrier (500μg/mL)*- Dissolve 0.155g $Ce(NO_3)_3 \cdot 6H_2O$ in 50 mL water and dilute to 100mL with water.

4.2. *Ethanol, 80%*- Add 80mL anhydrous denatured ethanol to 20mL water.

5. PROCEDURE

5.1. Perform any necessary sample pretreatments as specified in Table I. Mix sample.

Table I. Preparation of Samples for CeF_3 Micro precipitation

Analyte	*Matrix*	*Pre-treatment**	*Ce (ug)*	*HF (mL)*
Ac	*10mL 0.35M HNO_3*	*None*	*100*	*1.0*
Ac	*15mL 2M HCl*	*None*	*100*	*1.0*
Am/Cm	*15mL 4M HCl*	*Dilute 2x*	*50*	*3.0*
Am/Cm	*15mL 0.25M HCl*	*None*	*50*	*1.0*
Am/Cm	*20mL 1M HCl*	*None*	*50*	*1.0*
Np	*10mL 0.1 ammonium bioxalate*	*None*	*50*	*1.0*
Np/ Pu	*20mL 0.1M HCl-0.05M HF-0.01M $TiCl_3$*	*None*	*50*	*1.0*
Pu	*20mL 0.1M HCl-0.05M HF-0.01M $TiCl_3$*	*None*	*50*	*1.0*

Pu	*10mL 0.1M ammonium bioxalate*	*None*	*50*	*1.0*
Pu	*25mL 0.05M HNO3-0.05M HF-0.02M $TiCl_3$*	*None*	*50*	*1.0*
Th	*15mL 9M HCl*	*Dilute to 40mL*	*40*	*3.0*
U	*15mL 1M HCl*	*None*	*100*	*1.0*
U	*10mL 0.1M ammonium bioxalate*	*None*	*100*	*1.0*
Y	*15mL 8M HNO_3*	*Dilute 2x*	*100*	*3.0*

*Adding 0.5mL of 30% H_2O_2 to each Np, Pu, Th, Am/Cm sample can improve uranium decontamination.

5.2. Add the amount of cerium carrier recommended in Table I to each sample.

Note: For samples containing significant mass of uranium or thorium (>10μg), additional cerium carrier may be needed (up to an additional 0.1mL cerium carrier) to completely carry the analytes with the CeF_3 precipitate. Alternatively, samples aliquots can be adjusted to limit uranium and thorium content to less than 10μg.

5.3. **For uranium samples only**, add 0.5 mL of titanium chloride. This will reduce uranium to U(IV), which will co-precipitate with CeF_3. U(VI) will not co-precipitate with CeF_3.

5.4. Add the amount of concentrated HF specified in Table I to each centrifuge tube. Cap tubes and swirl to mix. Let the solutions sit for 15-30 minutes before filtering.

- **Option 1:** Place an Eichrom 0.1 micron 25 mm polypropylene filter on a Pall filter apparatus, with 50 mL polysulfone funnel. Insert the stem of the filter apparatus into a vacuum box yellow outer tip. Insert the yellow outer tip into a hole on a 12 or 24 hole Eichrom vacuum box. Repeat for each filter assembly available. Plug unused vacuum box holes with scotch tape or vacuum box tip assembly with appropriate plug.

- **Option 2**: Make sure that an Eichrom 0.1 micron 25 mm polypropylene filter in disposable funnel assembly is fit together tightly with the filter properly set in the bottom of the funnel. Insert the stem of the disposable filter into a yellow outer tip. Insert the yellow outer tip into a hole on a 12 or 24 hole Eichrom vacuum box. Repeat for each filter assembly to be used. Plug

unused vacuum box holes with scotch tape or vacuum box tip assembly with appropriate plug.

Note: The vacuum box assembly in either option 1 or 2 can be run with individual 50mL plastic centrifuge tubes in a vacuum box rack (AR-12-RACK or AR-24-RACK) below each filter or a single vacuum box inner liner (Eichrom AR-12-LINER or AR-24-LINER). Either option is normally effective. However, using individual 50 mL centrifuge tubes provides additional insurance, should issues arise during the filtration of the CeF_3 micro precipitate.

5.5. Apply vacuum (~10in. Hg). Add 3-5 mL of 80% ethanol to wet each filter. Make sure that there are no leaks along the sides of the filter assembly. Allow all liquid to pass through filter.

5.6. Add 2-3 mL of water to each filter. Allow all liquid to pass through filter.

5.7. Add each sample to the appropriate filter funnel apparatus. Rinse centrifuge tube with 3-5mL of DI water and add to the appropriate filter funnel. Allow all liquid to pass through the filter.

5.8. Wash the sides of each filter funnel with 3-5 mL of water. Allow all liquid to pass through the filter.

Note: Take care not to forcibly spray the rinse directly onto the filter. Gently rinse the sides of the filter funnel and allow the rinse solution to fall down to the filter by gravity.

5.9. Wash the sides of each filter funnel with 2-3mL of anhydrous denatured ethanol.

Note: Take care not to forcibly spray the rinse directly onto the filter. Gently rinse the sides of the filter funnel and allow the rinse solution to fall down to the filter by gravity.

5.10. Run vacuum until all liquid has passed through filter.

5.11. Remove the reservoir portion of the filter apparatus.

5.12. Remove filters from filter assembly using tweezers to lift and grab the outer edge of each filter. Mount filters in the center of stainless planchets, with the top of the filter facing out, adhering them with double-sided tape or glue stick. Place in plastic Petri dishes, and use a heating (IR) lamp to dry (normally 3-5 minutes).

5.13. Place the lid on each petri dish and store planchets until they are analyzed by alpha spectrometry or gas flow proportional counting.

5.14. Count samples by alpha spectrometry or gas flow proportional counting.

5.15. Analyze data and perform calculations as outlined in the appropriate separation method.

6. REFERENCES

1) National Analytical Management Program (NAMP), Radiochemistry Webinar Series, "Source Preparation for Alpha Spectrometry," Michael K. Schultz, https://www.icln.org/default/assets//File/Source%20Prep%20Alpha%20Spec%20Final_1-21-13%20slide%20deck.pdf.

2) Claude W. Sill, "Precipitation of Actinides as Fluorides or Hydroxides for High-Resolution Alpha Spectrometry," *Nuclear and Chemical Waste Management*, 7, 201-215 (1987).

3) A.E. Lally and K.M. Glover, "Source Preparation in Alpha Spectrometry," *Nuclear Instruments and Methods in Physics Research*, 223, 259-265 (1984).

4) I. M. Frisenne, "Microprecipitation source preparation for alpha spectrometry," Environmental Measurements Laboratory, U. S. Department of Energy, HASL-300, 28th Edition, G-03, Vol. 1, February (1997).

1) Dilute samples as necessary and add Ce Carrier (See Table I).

2) **U Samples**, Add 0.5mL 10% $TiCl_3$

3) **Th, Np, Pu, Am/Cm samples requiring additional U decontamination:** Add 50mL 30% H_2O_2.

4) Swirl to mix.

5) Add 1-3.5mL conc. HF (see Table I).

6) Swirl to mix.

7) Wait 20-30 minutes before filtration.

8) Ensure tight fit of filter assembly.

9) Engage vacuum.

10) Wet filter with 3-5mL 80% ethanol.

11) Wet filter with 3-5mL DI water.

12) Add sample.

13) Rinse tube with 5mL DI water and add to filter assembly.

14) Allow all fluid to pass through filter.

15) Rinse filter funnel with 3-5mL DI Water.

16) Rinse filter funnel with 2-3mL ethanol.

17) Filter until dry.

18) Remove filter (lifting on edges).

19) Mount filter to stainless steel planchet.

20) Place mounted filter into petri dish.

21) Dry under heat lamp.

22) Place lid on petri dish. Store until alpha measurement.