

ELECTRODEPOSITION OF ACTINIDES

(SOURCE PREPARATION)

1. SCOPE

- 1.1. This is a procedure for preparing sources for the measurement of actinides by alpha spectrometry using electrodeposition onto stainless steel planchets. 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 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. Samples must be evaporated to dryness and dissolved in the plating electrolyte solution. It is important to remove residual acid, oxidizing agents, and organic material which can interfere with the electrodeposition. However, care must be taken to prevent forming difficult to dissolve oxides and/or loss of analyte to the surface of the glass beaker by heating samples to high or for too long or without sulfuric acid/ NaHSO_4 . This is particularly important for thorium and plutonium samples.
- 2.2. High levels of rare earth elements or iron present in the sample can interfere with the electrodeposition and/or produce thick deposits that will degrade alpha spectra resolution through self-attenuation.
- 2.3. High masses ($>5\text{-}10\text{ ug/cm}^2$) of analyte can lead to thick deposits that will degrade alpha spectra resolution (normally only a concern with $^{238/234}\text{U}$ and ^{232}Th due to their very long half-lives).
- 2.4. The electrodeposition process will produce OH^- , increasing the pH of the plating solution. Ideally, the plating solution should remain at pH 2-4. Higher pH can lead to low deposition yields or poorly

adhered deposits. Increase in pH can be exacerbated by high deposition currents or impurities in the plating solution.

- 2.5. The method will deposit any element present in the sample which is capable of cathodic electrodeposition. Therefore, appropriate separation techniques must be employed to separate matrix elements and actinides with overlapping alpha emission energies, such as $^{232}\text{U}/^{210}\text{Po}$, $^{241}\text{Am}/^{238}\text{Pu}$ and $^{237}\text{Np}/^{234}\text{U}$.

3. APPARATUS

- Electrodeposition cell assembly - consisting of disposable plastic vial, cap assembly containing stainless steel for plating planchet (cathode) and Teflon cover with platinum electrode (anode)
- Petri dishes, plastic, 5 ½ x 1 cm
- Planchets, stainless-steel, 3/4 inch diameter (F.A. Murphy, Part: F-A, stainless steel, or equivalent)
- Tweezers, Stainless-steel
- Variable DC power supply

4. REAGENTS

Note: Analytical grade or ACS grade reagents are recommended.

<i>Ammonium hydroxide (56% NH₄OH or 28% NH₃), concentrated NH₄OH</i>
<i>Ammonium sulfate, (NH₄)₂SO₄</i>
<i>Anhydrous denatured ethanol, C₂H₅OH</i>
<i>Deionized water, all reagents are prepared using deionized water</i>
<i>Sodium hydrogen sulfate, NaHSO₄</i>
<i>Sulfuric acid (98%), concentrated H₂SO₄</i>
<i>Thymol Blue pH Indicator (0.04%)</i>

- 4.1. *Ammonium hydroxide (5wt%)* - Dissolve 50g ammonium hydroxide in 950g water.
- 4.2. *Sodium hydrogen sulfate (5wt%)* - Dissolve 50g of N_HSO₄ in 950g of water.
- 4.3. *Ammonium sulfate (1M)* - Dissolve 132g of ammonium sulfate in 850g of water. Dilute to 1L with water.

- 4.4. Sulfuric acid (10%) – **Carefully** add 100g of 98% H₂SO₄ to 900g of water.

5. PROCEDURE

Note: Electrodeposition efficiency and peak resolution may be improved by cleaning and/or electro polishing planchets as described in reference 2.

- 5.1. Place actinide solutions from separation method (in glass beakers) onto a hotplate. Add 2mL of concentrated H₂SO₄ and 2mL of 5wt% NaHSO₄. Evaporate to dryness but do not bake samples.
- 5.2. Add 5mL 10% H₂SO₄ to each evaporated actinide solution. Mix each solution until the entire residue is dissolved. Heat if necessary.
- 5.3. Inscribe 3/4 inch stainless steel planchets with sample number, radionuclide, and plating date. Wipe clean with acetone.
- 5.4. Assemble each planchet in an electrodeposition cell as the cathode. Rinse the cell several times with water.
- 5.5. Test cell for leaks:
 - 5.5.1. Wipe the outside of the assembled cell dry, add water to each cell and allow to stand for a short period of time to check for leaks.
 - 5.5.2. If a leak is found, re-tighten the cap assembly and observe.
 - 5.5.3. If the leak is still present, disassemble the cell, clean all surfaces with acetone and then water. Reassemble the cell and test again.
 - 5.5.4. If the cell continues to leak, replace the plastic vial and cap, and test again.
- 5.6. Add 5mL of 1M (NH₄)₂SO₄ to each solution from 5.2. Mix. Add 1-2 drops of 0.04% thymol blue pH indicator. Adjust to the pale pink/straw colored pH 2 endpoint with H₂SO₄ and NH₄OH.
- 5.7. Transfer to an electrodeposition cell. Rinse beaker with 1-2mL of 1M (NH₄)₂SO₄, adding the rinses to the cell.

Note: Adding 1mL of 0.25M ammonium oxalate to each cell can reduce the impact of traces iron and some other remaining matrix impurities. However, the ammonium oxalate can also reduce electrodeposition yields of some actinides.

- 5.8. Insert the platinum anode into the solution and connect the electrodes to the variable DC power supply.
- 5.9. Turn on the power supply and adjust the voltage until a current to 0.5A is achieved. Electrodeposit for 5 minutes.

Note: The formation of bubbles from the anode and cathode, due to the electrolysis of water should be observed. If no bubbles are observed check the electrode connections.

- 5.10. Adjust the voltage until a current of 1.0-1.2A is achieved and electrodeposit for 90-120 minutes.

Note: The formation of bubbles at the anode and cathode should become more vigorous. However, if excessive heat is generated, reduce the plating current.

Note: The plating solution should remain relatively colorless during the electrodeposition. If a rusty brown precipitate forms during plating, ensure that the electrodes are not connected backwards.

Note: The current may increase as the electrodeposition proceeds. Adjust to keep a constant 1.0-1.2A as necessary.

- 5.11. Add 1mL of concentrated NH_4OH to stop the reaction, continuing deposition for 1 minute after the NH_4OH addition.
- 5.12. Turn off power, remove electrodes and decant electrolyte to waste.
- 5.13. Remove each planchet and rinse with a small volume of ethanol.
- 5.14. Dry each planchet on a hot plate for 5 minutes at approximately 200°C . Allow the planchets to cool.
- 5.15. Store each planchet in a covered, labeled Petri dish.
- 5.16. Count samples using alpha spectrometry.
- 5.17. 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) I.K. Kressin, "Electrodeposition of plutonium and americium for high resolution alpha spectrometry," *Analytical Chemistry*, 49, 842-846 (1977).
- 3) N.A. Talvitie, "Electrodeposition of Actinides for Alpha Spectrometric Determination," *Analytical Chemistry*, 44(2), 280-283 (1972).
- 4) I.M. Fisenne, "Electrodeposition of the actinides: Mitchell Method," Environmental Measurements Laboratory, U. S. Department of Energy, HASL-300, 28th Edition, G-01, Vol 1, February (1997).
- 5) I.M. Fisenne and P.M. Perry, "Electrodeposition of the actinides: Talvite Method," Environmental Measurements Laboratory, U. S. Department of Energy, HASL-300, 28th Edition, G-02, Vol 1, February (1997).

