USTUR 150: PRE-CONCENTRATION OF PLUTONIUM AND AMERICIUM FROM DISSOLVED TISSUE SAMPLES

Purpose	Pre-concentration of Pu and Am from tissue solutions	**Method Number**	USTUR 150
Original Date	10/1/99	**Author**	Radiochemistry Staff
Revision Number	2	**Approved By**	James T. Elliston
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SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Section 3 of this procedure.

1. Principle of Method

1.1. The radionuclides of plutonium and americium are pre-concentrated from the matrix of ashed and acid-dissolved tissue samples (USTUR 100-140).

1.2. An aliquot of the tissue sample is selected for analysis on the basis of sample mass and estimated sample alpha activity (see USTUR 100-140).

1.3. Tracers ^{242}Pu and ^{243}Am are added to the aliquot. Plutonium and americium are separated from the sample matrix by extraction chromatography.

1.4. The extractant is stripped from the column and digested with hydrogen peroxide and nitric acid.

2. Apparatus

2.1. Hotplates: magnetic stirring, adjustable to 250°C.

2.2. Watch glasses: Pyrex assorted sizes to fit beakers used, plain and ribbed.

2.3. Hotplate thermometer with range to 250ºC.

2.4. Eichrom Actinide resin column.

2.5. Bio-Rad plastic column reservoir.

2.6. Rack: to support columns.

2.7. Graduated cylinders: various sizes.

2.8. Beakers: various sizes.

2.9. Disposable plastic transfer pipet.

2.10. Bio-Rad plastic reservoir cap.

2.11. Stir bars: Teflon-coated.

3. Reagents

3.1. 18 M Ω deionized water (D.I. water).

3.2. Hydrochloric acid (concentrated 36.5-38%, reagent-grade).

3.3. Hydrochloric acid (2M). Add 200 mL of concentrated HCl to 1000 mL of D.I. water.

3.4. Ascorbic acid **ONLY (**J. T. Baker L-(+)- Ascorbic Acid, Powder #B581-07)

3.5. Hydrofluoric acid (concentrated, 48.0-51.0% reagent-grade).

3.6. 2M hydrochloric acid/0.5 M hydrofluoric acid solution. In a plastic graduated cylinder, add 167 mL of concentrated HCl and 19 mL of concentrated HF to 814 mL of D.I. water.

3.7. 2-Propanol (reagent-grade).

3.8. Hydrochloric acid (6M). Add 500 mL of concentrated HCl to 500 mL D.I. water.

3.9. Hydrogen peroxide (30%, reagent-grade).

3.10. Nitric acid (concentrated 69-71%, reagent-grade).

3.11. Calcium nitrate ($Ca(NO_3)_2 \cdot 4\ H_2O$, reagent grade).

3.12. Calcium nitrate (1.25 M). Weight out 147.6 g of calcium nitrate, dissolve in ~300 mL D.I. water and then bring to a total volume of 500 mL with D.I. water.

3.13. Sodium metavanadate ($NaVO_3$, technical grade, Aldrich).

3.14. Sodium metavanadate (0.1 M). Weigh out 0.30 g of $NaVO_3$. Dissolve in D.I. water and bring to 25 mL volume.

4. Procedure

4.1. Sample preparation.

4.1.1. Refer to procedure USTUR 100, Tissue Ashing, Sample Dissolution, Sample Aliquot Selection, and Tracer Addition.

4.1.2. A maximum of 5 g of dissolved ash can be run on the Actinide column. For optimum recoveries aliquot samples such that they contain ≤ 1 g of dissolved ash.

4.2. Sample dissolution.

4.2.1. To the previously prepared sample add 50-90 mL of 2 M HCl to completely dissolve the sample when heated to 120ºC on a hotplate. Use a magnetic stirring bar to hasten dissolution of larger samples. Cover sample with a watch glass while heating.

4.2.2. Cool sample to room temperature.

4.2.3. Weigh out 0.5 g ascorbic acid for each sample and 0.25 g ascorbic acid for each blank or quality control sample. Dissolve in D.I. water so 5 mL of solution contains approximately 0.5 g ascorbic acid.

For aliquots of 18-20 samples weigh out 10.0 g ascorbic acid and dissolve in 100 mL of D.I. water. Add 5 mL of ascorbic acid solution to each sample and 3 mL to the blanks and QA/QC samples.

NOTE: Prepare fresh just before use. Once the ascorbic acid is added to the samples, the separation MUST be completed in a timely manner. The columns should not be left dry for more than 20-30 minutes and preferably less.

4.2.4 Add appropriate amounts of ascorbic acid solution to samples (0.5 g) and blanks/controls (0.25 g) and swirl, see 4.2.3. Sample solutions should become colorless. If any yellow color remains, add additional small amounts of ascorbic acid solution until sample is colorless.

NOTE: This reduces Fe^{3+} in the sample to Fe^{2+} which is not extracted by actinide resin. Also Pu^{4+} is reduced to Pu^{3+} for extraction.

4.3. Extraction separation.

4.3.1. Remove cap from actinide column and fit a Bio-Rad reservoir into top.

NOTE: Column resin should be covered with several milliliters of liquid, if it is dry, discard the column.

4.3.2. Snap bottom tip from column and allow storage solution to drain.

4.3.3. When column has drained, add 5 mL of 2M HCl and allow the 2 M HCL to drain completely from the column.

4.3.4. Add the prepared sample solution to the column, rinse the beaker twice with approximately 5 mL of 2 M HCl and adding each rinse to the column and allow the column to drain completely.

NOTE: Document any slow running column(s).

4.3.5. When the column has drained, wash it with 5 mL 2 M HCl, and allow it to drain completely.

4.3.6. Rinse the column with 5 mL of 2 M HCl/0.5 M HF solution. Use a disposable transfer pipet to get any droplets left in column tops and reservoir and add to column rinse. Allow the column to drain completely.

4.3.7. Rinse the column with 5 mL of deionized water and allow it to drain.

4.3.8. Place a clean, labeled 150 mL beaker under the column. Strip the extractant by adding 15 mL of 2-propanol to the column. Place the reservoir cap loosely on the reservoir to slow evaporation of alcohol. Allow the column to drain completely.

NOTE: This step is slow because the extractant loaded onto the column resin is being stripped off. It generally takes two hours to drain the column.

4.3.9. Add 5 mL of 6 M HCl to the column after alcohol has drained, collecting it in the sample beaker.

4.3.10. Place a ribbed watch glass on the sample beaker. Evaporate the sample to dryness on a hotplate set between < 50ºC (use a hotplate thermometer).

4.4. Digestion of Actinide Extractant

The extractant must be totally broken down in order to be able to separate Pu and Am. The extractant-actinide complex is quite strong and will interfere with subsequent separation procedure.

4.4.1 Add 3 mL of 1.25 M $Ca(NO_3)_2$ and 0.1 mL of 0.1 M $NaVO_3$ to the sample beaker.

4.4.2 Evaporate the sample to dryness at 75-90ºC with a ribbed watchglass on the beaker.

4.4.3 Remove the beaker from the hotplate and cool to room temperature. Bring the hotplate temperature to 150ºC, using a hotplate thermometer.

NOTE: The temperature must not be above 150ºC or excessive spattering occurs in the following steps.

4.4.4. Add 6 mL of 30% H_2O_2 to the sample and cover with a ribbed watchglass.

NOTE: DO NOT rinse the sides of the beaker down with the peroxide. It causes the extractant to "climb" the walls of the beaker.

4.4.5. Evaporate the sample to dryness at 150ºC.

4.4.6. Repeat steps 4.4.4-4.4.5 an additional three times. Bring the sample to room temperature before adding each addition of 30% H_2O_2.

NOTE: There will be some spattering, particularly during the first two additions of peroxide. Do not rinse the beaker down with the next addition of peroxide. If spatters occur on the watchglass, it can be rinsed, but allow the peroxide to drip directly into beaker instead of down the beaker wall.

4.4.7 Bring the sample to room temperature after the last peroxide addition is dried down.

4.4.8. Bring the hotplate temperature up to 200-250ºC, using a hotplate thermometer.

4.4.9. Add 20 mL of concentrated HNO_3 to the sample. Use portions of the $HN0_3$ to rinse the ribbed watchglass or any spatters that are directly on the rim of the beaker. Mark the ribbed watchglass with the sample number and set aside on a clean paper towel.

NOTE: It is not necessary to rinse the sides of the beaker since the refluxing in the next step will take care of it.

4.4.10. Place a plain watchglass on the sample beaker and reflux the sample for a minimum of one hour at 225ºC.

4.4.11. Turn the hotplate down to 150ºC, after refluxing. Leave the sample on the hotplate.

4.4.12. Once the hotplate has reached 150ºC, trade the plain watchglass for the appropriate ribbed watchglass.

4.4.13. Bring the sample to dryness at 150ºC and then remove from the hotplate and cool to room temperature.

4.4.14. Add 6 mL 30% H_2O_2 to the sample and bring to dryness at 150ºC with a ribbed watchglass on the beaker.

4.4.15. Cool the sample to room temperature and store with a plain watchglass on the beaker (or parafilm) until ready for analysis.

4.4.16. Proceed to USTUR 220 for separation of Pu and Am.

5. Source Materials

5.1. Hongguo Qu, et al, J. Radioanalytical and Nuclear Chem. 234(1-2), 175 (1998).