RiO5 METHOD (37)

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Cs, Pu, Am, Th (transuranics)—Electroplating—Sediment sample

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1 SCOPE

This method specifies the minimum requirements and laboratory methods for the measurement of Cs, Th, ^{239,240}Pu, ^{241}Am (transuranics) in sediments (*Anderson and Fleer, 1982*). This is a multi-day laboratory schedule that can be simplified considerably if only one radionuclide must be measured. The final step for several radionuclides involves electroplating a thin source on counting disks and detection by spectrometric methods. For details on plating and radioanalytical methods, refer to other recipes.

2 EQUIPMENT CHEMICAL REAGENTS

2.1 Equipment

- Analytical balance
- Lab hot plate
- Laboratory centrifuge
- Electoplating cells and equipment
- Drying oven
- ECONOCOLUMN equipped with metering valve and filling funnel.

2.2 Tracers

- Pu-242, Cs-134, Th-229, Am-243 tracer solutions having concentrations dependent on anticipated values of sample matrix.

2.3 Chemical reagents

- BIO-RAD AG 1x4 or 1x8 anion exchange resin
- See text of Procedure for other materials and chemical reagents.

2.4 Solutions

- 10% $NaHSO_4$
- See text of Procedure for other solutions.

3. PROCEDURE

SCHEDULE:

DAY 1	Preparation (1 hour)	
DAY 2	Cs, Pu, Am, Th	Consecutive days
DAY 3	Cs, Pu, Am, Th	
DAY 4	Pu	
DAY 5	Pu, Am	
DAY 6	Am	Consecutive days
DAY 7	Am	

(N.B. Days other than those indicated do not have to be consecutive)

DAY 1

1. Weigh sample 5-10 g and transfer to 400 ml heavy-duty beaker,
2. Add 5 drops l-octanol.
3. Add tracers relevant to the radionuclides under study (i.e, Pu-242, Cs-134, Th-229, Am-243).
4. Add 30 ml16 M (conc.) HNO_3, (5 x 6ml from dispenser).
5. After the reaction subsides, add 10 ml12 M (conc) HCI.
6. Cover and allow to stand overnight. This allows sufficient time for isotopic equilibration.
7. At this stage 0.5 ml 30% H_20_2, to maintain Pu in Pu(IV).

DAY 2

1. Boil sediment/acid mixture gently (covered) for 1 hour (large hot-plate setting 250). Allow to cool.
2. Pour into 50 ml polyethylene centrifuge tubes with caps.
3. Equalize tube pair weights with 16 M HNO_3.
4. Centrifuge (small centrifuge @ 1/2 max. setting for 20 mins).
5. Decant to 250 ml heavy-duty beakers.
6. Add 10 ml 16 M HNO_3, to sediment remaining in tubes, cap and shake. Transfer to original 400 ml leaching beaker.
7. Repeat 6 twice.
8. Add 5 drops l-octanol to 400 ml leaching beaker, 10 ml12 M HCl and boil gently (covered) for 1 hour. Allow to cool.
9. Repeat steps 2-5 inclusive.
10. Boil leachates in 250 ml beakers down to approximately 25 ml. Allow to cool. (Large hot-plate setting 450). This removes HCl and leaves the leachate as essentially 16 M HNO_3.
11. Transfer to clean centrifuge tubes, rinse beaker with 3x2 ml16 M HNO_3 equalize tube pair weights with 16 M HNO_3 centrifuge as in 4.
12. Decant to 250 ml beakers, dilute the liquid with an approximately equal volume of "Super Q". This ensures the liquid is 7-9 M HNO_3, in preparation for columns.
13. Add 0.5g AMP to each beaker. Stir for 30 mins.
14. Allow to settle for a standard period (16-48 hours).

DAY 3

1. Decant supernatant to a clean 250 ml beaker.
2. Using "Super Q" , wash precipitate into a counting tube. Place in low oven to dry.
3. Using the solution from # 12 or supernatant from Cs precipitation, add 1 g $NaNO_2$, to each sample (CAUTION), heat to 80-90°C for 1 hour. This ensures the Pu is as Pu (IV) for adsorption on the column as $Pu(N03)_6^{2-}$ complexes. Add 3-4 drops 30% H_20_2. let stand 5 minutes.
4. Prepare a 6.4 cm depth of BIO-RAD AG 1x4 or 1x8 anion exchange resin in a 1 cm diameter ECONOCOLUMN equipped with metering valve and filling funnel.
5. Top with 0.5 cm silica gel (fine. acid-washed) through SQ and drain to top of gel. Add glass beads to give 0.5 cm depth.
6. Condition the column with 25 ml 8 M HN03, discard this rinse.
7. Load the feedstock onto the columns at max. flow rate and collect the elute in 250 ml beakers.
8. Rinse original beakers with 3 small volumes of 8 M HNO_3 draining to top of bed each time. Column will stop automatically at silica gel layer.
9. Wash column with 60 ml 8 M $HN0_3$, still collecting the elute in the beaker. Add acid in 6x10ml aliquots. This removes Fe, Am and U from the column.
10. Remove and store beakers for Am analysis Day 5.
11. Wash column with 50 ml 12 M HCl collecting elute in clean 100 ml beakers. Add acid in 5x10 ml aliquots.
12. Remove beakers, add 1 ml 10% $NaHSO_4$, and evaporate solution on hotplate. Store beakers for Th analysis on Day 5.
13. Add 1 ml1.2 M HCl to column and drain to top of bed.
14. Elute Pu into 40 ml beakers with 25 ml 1.2 M HCl containing 0.5 ml 30% H_20_2 (prepared fresh). Max. flow rate 3 ml/min.
15. Evaporate down to ~3 ml (This creates the solution, 9 M HCl)

DAY 4

1. Add to the solution 20 ml HCl, heating gently if necessary.
2. Add 0.5 g $NaNO_2$, to each sample and heat at 80-90°C for 1 hour. Add 3-4 drops 30% H_20_2
3. Allow to cool.
4. Prepare a 3.5 cm resin bed in columns. Top with silica gel 0.5 cm and g1ass beads 05 cm as previously.
5. Wash column with 3x5 ml12M HCl aliquots.
6. Introduce the sample and drain to the top of the bed.
7. Rinse the beaker with 3x5 ml 9 M HCl, introducing the rinses to the column, draining to the top of the bed each time and keeping the flow rate below 3 ml/min.
8. Wash column with an additional 10 ml 9 M HCl.
9. Wash column with 60 to 100 ml 8 M HNO_3. Add acid in 6-l0xl0 ml aliquots. Max. rate 1 ml/ min.
10. Add 0.5 ml 1.2 M HCl. Discard liquid in beakers.
11. Elute Pu into 40 ml beakers with 10 ml 1.2 M HCl containing 0.2 ml 30% H_20_2 (prepared fresh). Max. flow rate 1 ml/min.
12. Add 1 ml 10% $NaHSO_4$, and evaporate solution on hotplate.

DAY 5

1. Dissolve the residue in a minimum of 16 M HNO_3. Add 0.5 ml18 M H_2S0_4.
2. Evaporate the solution on a hotplate (low setting). Do not allow the samples to go dry. Final volume should be0.3-0.5 ml. This cannot be easily measured so put 0.5 m1

18 M H_2S0_4, in a separate beaker so as to better judge when all the HNO_3, has been removed.
3. Remove from heat and cool. add approximately 3 ml SQ, rinsing down the beaker walls as the water is added.
4. Add 2 drops of 0.04 % thymol blue to each sample.
5. With swirling, neutralise each sample to a salmon / straw colour with conc. NH_4OH (approx.1 -1.5 ml NH_4OH). If colour changes to yellow or blue back titrate with 1:99 H_2S0_4.
6. Pour the sample into its plating cell. Rinse beaker with 3x2 ml l:99 H_2S0_4~dd 2 M NH_4OH slowly to the salmon/pink colour with swirling of the bottle. Increase volume in plating cell to approximately 1/2 full using SQ.
7. Insert anodes and holders into plating cells. Gauge disc should be level with the bottle shoulder. Clip anode rod with alligator clip.
8. Set up the power supply (see power supply section). It can be done any time.
9. Turn on all cell switches.
10. Turn on main power and allow to plate at 1.1 A for 90 mins. (up 2 hours)~Voltage across each cell may be checked with a multimeter plugged into the jack sockets next to the switch on the deposition stand. Switch pos.= 0, off. Select cell number by rotating this switch. Initially, 4 cells will operate at the full 50 V supplied and run at approx. 0.8 A. After about 10 minutes, current rises to 1.1 A and near the end of plating each cell voltage requirement drops to 10 V.(to stop solution from going hot cover bottles with wet cotton gaze.

11. At the end of 90 mins., before turning the power off any cell, add 1 ml conc. NH_4OH through the anode vent with a disposable pipette (1st cell).
12. Plate for 1 minute. Switch off the cell at the deposition stand. Unto clip and quickly remove anode and holder. Quickly unscrew cell at the copper contact. Pour solution into labelled beaker
13. Disassemble the cell, remove the disc and rinse with SQ and then with acetone. Place disc on hotplate until slightly discoloured. Do not allow too much oxidation of the metal surface
14. Repeat procedure for other cells.
15. Wait two weeks (or longer) and count by alpha- spectrometry. This time period allow for the production of Ra-224 from its parent Th-228. Any Th-228 present on the disc interferes with Pu determination as it appears in the same region as Pu-238.
16. Store solution from step 11 in case of faulty plating.
17. Following step 10 of Day 3, gently evaporate the solution on a hotplate until salts begin to form. Pour the sample into a large beaker and dilute to 1 litre with SQ.
18. Adjust the pH of the solution to approx.1.5 with conc.NH_4OH. Add 50 g of oxalic acid, stir to dissolve, warming if necessary. If at this stage a precipitate appears (pH not greater than 2).
19. Let precipitate form and settle overnight.

DAY 6
1. Discard supernatant. Wash precipitate with 0.5% oxalic acid solution. If transparent crystals of ammonium oxalate are present in the precipitate they should be dissolved in 0.5% oxalic acid (warm if necessary). Transfer precipitate by washing to centrifuge tubes. Discard all wash solutions.
2. Convert the oxalates to hydroxides by addition of 5 ml of 10 m NaOH. Break up the lumps so as to obtain a homogeneous slurry. Let stand for 5 minutes, mixing occasionally.
3. Dilute with SQ (1/2 fill tube) and centrifuge. Discard supernatant.

4. Add a few drops of 10 M NaOH, mix well, wait for 5 mins., dilute with water and centrifuge. Discard supernatant.
5. Dissolve the hydroxides with 10 ml 8 M HNO_3 add 0.1 g $NaNO_2$, and let stand for

5-10 minutes.
6. Prepare a 7 cm anion-exchange column as before and wash with 20 ml 8 M HNO_3. Transfer the sample to the column.
7. Wash column with 20 ml 8 M HNO,.(any remaining Pu and Th remain on the column)
8. Evaporate elute to dryness (evaporate very slowly at the end as the salts formed tend to spit).
9. Dissolve residue in 2 ml12 M HCl and evaporate to dryness (slowly). Repeat. Wash beaker with 2 ml SQ and evaporate to dryness.
10. Prepare a 3.5 cm anion- exchange column as before. Wash with 10 ml 1.5 M HCl.
11. Dissolve residue in 1 ml1.5 ml HCl and transfer to the column.(Pb and Po remain on the column).
12. Wash column with 20 ml1.5 M HC!. Evaporate eluate to dryness (slowly).

DAY 7
1. Add 10 ml 1 M HNO_3/93%CH_3OH solution to residue and boil to dissolve (salts tend to precipitate out again as it cools).
2. Prepare a 7 cm anion - exchange column as before and wash with 20 ml 1 M HNO_3/93% CH_3OH solution. Transfer the sample to the column. Wash with 10 ml 1 M HNO_3/93% CH_3OH solution. (This step removes any Fe remaining after its removal during the oxalate precipitation step).
3. Wash column with 20 ml 0.1 M HCl/0.5 M NH_4SCN/80% CH_3OH solution (this removes lanthanides).
4. Elute Am (and Cm) from the column with 20 ml1.5 M HCl/86% CH_3OH solution.
5. To the elute add a few drops of 16 M HNO_3, and heat gently on hotplate. Before dryness; remove from heat and (very carfully) add a few drops of 16 M HNO_3 Repeat. Take solution to dryness.
6. Dissolve residue in a minimum of 16 M HNO_3, and follow through the electroplatimg procedure (Day 5, steps 1-15).

DAY 8
1. Following step 12 of Day 3, dissolve the residue in 20 M 8 M HNO_3.
2. Prepare a 3.5 cm anion - exchange column as before and wash with 10 ml 8 M HNO_3.
3. Transfer the sample to the column. Wash the beaker with 2x2 ml 8 M HNO_3 and pass through the column.
4. Wash column with 25 ml 8 M HNO_3. Discard washes.
5. Elute Th into 40 ml beakers with 30 ml HCl. Add 1 ml 10 % $NaHSO_4$, and evaporate on hotplate.
6. Dissolve residue in a minimum of 16 M HNO_3, and follow through the electroplating procedure (Day 5, steps 1-15).

Power Supply
1. To set constant current, short out the power supply (connect neg. to pos. poles). Turn current and voltage all way down then bring voltage knob up slightly. Turn on main power select 4 A meter display .Bring current up to 1.1 A. Turn main power off.
2. Disconnect" short " wire. Select 70 V meter display with power supply terminals open, turn on main power. Set voltage to 50 V. Turn off main power. Allow to discharge for 5 minutes.

3. Connect power supply to electrodeposition stand, red to red, black to black.

Plating Cells

1. Clean 30 ml polyethylene bottles with 0.5 N HCl. Rinse with SQ. Remove bottle base with a scalpel, taking off as little of the bottle wall as possible.
2. Clean anodes and holder in 0.5 N HCl rinse with SQ.
3. Remove paper backing from stainless steel discs. Avoid touching the surface protected by the paper, this is the side onto which the Pu will be deposited. Degrease the discs with acetone.
4. Place the discs into electrode cap assemblies, polished side up, centering the discs. Screw in bottles tightly, add SQ and let stand. Check for leaks (water inside threaded copper contact).
5. Mount bottle on deposition stand, screw in.

Blank Plating Solution

1 ml 18 M H_2SO_4 + 6 ml SQ titrate with conc. NH_4OH to salmon/pink colour.
Store in polyethylene bottle.

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