

Uranium Sorption on α -alumina

Experiments B-8005, B-8006, and B-8007

U-233 Alpha Spectrometry Analysis Procedure

Preparation:

1. All glass should be washed in a hot acid bath (4 liter beaker with cover glass) of fuming nitric acid over night (> 4 hours). Once the temperature of the acid bath is near room temperature, the acid washed glass should be quickly inserted into nanopure H₂O in another large beaker inside the fumehood. Two pairs of gloves and goggles should be used during this operation as there is a possibility of splashing and nitric acid is a real hazard. The rinsed glassware should then be rinsed at least three more times in the sink with nanopure water. The rinsed dishes can either be air dried on a covered tray or placed in the drying oven.

1 column + 1 100ml glass beaker / sample

Waste Disposal:

1. Used ion exchange resins will be stored in nonbreakable, screw-top containers. Containers will be clearly labelled. Radioisotope storage containers will be labelled with the following information: a) radioisotope; b) physical form; c) type of emission; d) activity in Curies; and e) dose rate at container surface. The exchange resins will be regenerated to reduce the level of radioactivity and to reduce the volume that will be disposed. Responsibility for regeneration and disposal of the ion exchange resins will be assumed by the RPC.
- 2 Disposal of the solutions containing several isotopes (*i.e.* solutions containing both ²³²U and ²³³U) down the sewer is restricted by the release limits set forth in TRC 21.303 Appendix 21-A (Note 1). This note states that the release is limited so that the sum of the the ratios in the solution to that of the limiting concentration for each isotope in the solution will be < 1. For example, in the case of two isotopes (²³²U and ²³³U) present in concentrations C_{232U} and C_{233U} with maximum permissible concentrations MPC_{232U} and MPC_{233U} :
$$(C_{232U}/MPC_{232U}) + (C_{233U}/MPC_{233U}) \leq 1.$$
 Note that the limits for MPC_{232U} and MPC_{233U} are 0.8 nCi/ml and 0.9 nCi/ml, respectively.
3. All waste solutions derived during ion exchange column manipulations either contain high concentrations of N (nitrate and ammonium (NH₄), which readily converts to nitrate) or acid and require liberal dilution prior to and during disposal via the sink.

Analytical Procedure:

A. Spiking and co-precipitation

1. Spike all samples in a rack requiring the same spike at one time (*i.e.* all spike 25 C at same time). Use the centrifuge tube stand in glass beaker to hold the tube being spiked. Use the syringe stand to hold the pasteur pipet between sample spikings. Tare a pre-folded sample boat (plastic) on balance. Using a pasteur pipet (a new one for each time a series of samples will be spiked with a different ²³²U solution) and a small rubber bulb add predetermined mass of spike solution to sample boat and record weight. Error in spike mass should be to the

low side. Dispose of pasteur pipet in special radioactive wastebasket after samples have been spiked.

2. Transfer spike quantitatively to sample centrifuge tube using squirt bottle of 0.1 N HNO₃. Use enough of 0.1 N HNO₃ during each spike transfer (~ 5 ml) to obtain roughly equal volumes in the centrifuge tubes. Dispose of sample boat into special radioactive wastebasket.
3. Homogenize sample after addition of spike by replacing lid and swirling the centrifuge tube. Allow spike to equilibrate at least 24 hours before next step.
4. Add carrier to one row of tubes in a rack at a time. Add 1 ml of Fe carrier using Eppendorf fixed volume pipet and disposable tips. Homogenize sample after addition of carrier by replacing lid and swirling the centrifuge tube. Allow sample to equilibrate for 24 hours.
5. Need
full
day
↓ Start step B1 now and continue with step B2 simultaneously with the following steps of A (A5 - A7) so that once you have completed step A7 you can immediately proceed with step B3. Bring the pH up to 7 with the addition of concentrated NH₄OH from the reagent bottle using 6 to 7 drops from the plastic pipet attached to the NH₄OH reagent bottle. This is strongly exothermic and the solution should be gently swirled during the addition of the base. Note that the NH₄OH should be from a closed reagent container (eg. new 2 l bottle) since this will ensure that minimal CO₂ will be present in the base which would lower yield. This step precipitates about 2.5 ml of Fe(OH)₃.
6. The solution can then be centrifuged (labeled 50 ml centrifuge tubes) and the supernate is discarded into a waste beaker.
7. The Fe(OH)₃ precipitates are washed with about 10 ml of ultrapure water and agitated using the hand homogenizer, centrifuged and washings discarded. This step is repeated once. This is necessary to get rid of the excess NH₄.

B. Uranium-thorium separation

1. Prepare a labeled (Sample ID) anion ion exchange column (8 -10 cm high, 1 cm diameter) by placing a glass wool plug in the bottom of the column and adding a slurry (in ultrapure water) of Dowex 1 x 8 100-200 mesh chloride form ion exchange resin. Use the teflon column holders and collect the waste liquid in a plastic beaker (100 ml or greater).
2. Add 30-40 ml of 8 N Ammonium Nitrate - 0.1 N Nitric acid into anion exchange column and elute into plastic waste beaker.
3. The samples will be lowered to pH =1 using 250 µl of 1.0 N HNO₃ and diluting to 5.0 ml with 0.1 N HNO₃ using squirt bottle. Make sure Fe(OH)₃ is entirely dissolved (agitate) prior to adding the ammonium nitrate. Next, saturate the solution with 5.9 g of ammonium nitrate and shake until all is dissolved. This reaction is highly endothermic.
4. Add the sample onto the column and allow to drain into 100 ml plastic beaker. Elute Fe into the beaker using 80 ml, added in 20 ml increments using squirt bottle, of 8 N NH₄NO₃ - 0.1 N HNO₃. Rinse the centrifuge tube with the 20

ml aliquot and pour onto column and mark the level of the fluid. Test for the presence of Fe after 70 to 80 ml have drained by placing a drop of NH_4CSN on the convex side of watch glass and allowing a drop of the eluate to come in contact with ammonium cyanide. If Fe is present then the solution will turn red. Continue to eluate the Fe until there is no red upon testing for Fe. Empty the contents of the 100 ml plastic beaker into a waste beaker.

5. Next add 100 ml, in 20 ml aliquots, of 8 N HCL acid and elute the thorium into the same beaker. Dispose of solution in beaker down the sink with liberal flushing.
6. Using a squirt bottle, add no more than 5 ml of 0.1 N nitric acid to the column and allow to **drain into waste beaker**. The column changes color slightly from orange to slightly yellow. Next, add 50 ml of 0.1 N nitric acid in 10 ml increments and drain the uranium into a labeled and acid washed cleaned **100 ml glass beaker**. The solution is then placed on a hot plate to reach just to dryness. Allow beaker to cool moderately and then immediately proceed with step C1. As long as the beaker is slightly warm and 0.001 N HNO_3 is added the U is more easily put into solution and the pH is closer to the desired pH.

Stop point
for overnight

C. Solvent extraction and plating

1. A total of 4 pasteur pipets are used in the following steps and it is imperative to keep them separate by labeling the rubber bulbs used with them. The dried U eluate is taken up with two ml of 0.001 N HNO_3 (pH 3) issued from a squirt bottle. Using a new pasteur pipet (W on bulb) carefully and completely wash the beaker with the acid. Transfer the acid solution to a labeled glass 12 ml centrifuge tube. Repeat this step twice more with 0.5 - 1 ml of the acid.
2. Add two drops of Methyl Orange indicator solution using a pasteur pipet (MO on bulb) to solution in centrifuge tube. Bring pH up to 3.0 with dilute 0.1 N NaOH solution using a pasteur pipet (NaO on bulb) by adding a few drops at a time and homogenizing the contents of the tube with pasteur pipet used to transfer the U eluate (W on bulb). The color should change from pink to slightly orange. The colors can be seen in test tube set which covers the pH range. If steps in B were done properly the total volume should be 5-6 ml.
3. Add 1-2 ml of the 0.4 M TTA in benzene solution to the centrifuge tube.
4. Homogenize and extract the U using the same pasteur pipet used in step C1 (W on bulb). The TTA solution should be red or orange (depending on U concentration) and this should be quickly evident (within 30 seconds to 1 minute).
5. Solution is centrifuged for 1-2 minutes, making sure that the tube is covered with Parafilm.
6. Carefully clean a stainless steel planchet and label it with a sharp pointed object. The label should have sample ID, date, initials of the person plating and U. Label a glassine stamp envelope with the same information. The mounting ring

Can be
done with
several samples
at a time

should be on the hot plate and the hot plate should be set to red mark (~3). Place the plate, labeled side down, on the mounting ring just prior to next step.

7. The TTA solution is carefully separated using a clean pasteur pipet (P on bulb), taking care not to include any of the HNO_3 solution. This is most easily accomplished by slightly tilting the tube so that the TTA bulges on top of the acid. A total of two aliquots using the pasteur pipet (P on bulb) are used to retrieve all the TTA.
8. The TTA is evaporated drop-wise (vertically) on heated steel plates that have been placed on mounting ring, making sure that spattering is avoided.
9. Remove the plate from the mounting ring and repeat the TTA extraction (Steps 3 - 8).
10. Pass the plate through the flame of a propane flame inside the fume hood to burn off the organic deposit. Allow the plate to cool on the edge of the hot plate.
11. Place plates in labeled glassine stamp envelopes and count samples ASAP after plating, recording the channel in which the sample is counted on the envelope.

DD. Cleaning up

1. The solution remaining in the centrifuge tube should be placed into a glass waste beaker. The centrifuge tube should be rinsed with 0.1 N HNO_3 and the rinse should also be placed into the waste beaker. This beaker should remain inside the fumehood. The volume of the solution should be reduced by gentle heating until dry.
2. The used anion exchange resin should be rinsed with water from a squirt bottle into the used resin bottle (see instructions above).
3. All glassware should then be washed usingalconox. The glassware should be rinsed with the single pass water. The glassware is then ready for the fuming nitric acid bath.

	B-8005 #ptu #a SAMPLE NAME						
STEP	8.50a	8.75a					
Column prep.	X	X					
Fe(OH) ₃ precip, pH→~7	X	X					
Wash and Centrifuge (2X)	X	X					
pH→1, (.25 ml 1.0N HNO ₃ +2.0 ml 0.1N) NH ₄ NO ₃ add.(5.9 g)	X	X					
Sample to column, 70-80 ml to wash Fe off	X	X					
100 ml 8N HCl, Th wash off	X	X					
≤5 ml wash 0.1N HNO ₃ (discard) 50 ml 0.1N HNO ₃ — save U	X	X					

	B-8005 *PHI* a SAMPLE NAME							
STEP	8.50% _a	8.75% _a						
Heat to near dryness	X	X						
Wash beaker— 2ml 0.001N Nitric, repeat 2X	X	X						
1-2 MI TTA, homogenize	X	X						
Centrifuge (2 min)	X	X						
Clean and label planchet, heat	X	X						
With new pipet, Separate, evaporate TTA on planchet	X	X						
Repeat extraction	X	X						
Burn off organic	X	X						
Place in labeled envelope	X	X						

	SAMPLE NAME							
STEP	B-005-1 PH6 to 1	B-007-1 PH6 to 1	B-007-1 PH6 to 1	B-007-1 PH6 to 1	B-005-1 PH6 to 1	B-007-1 PH6 to 1		
Column prep.	X	X	X	X	X	X		
Fe(OH) ₃ precip, pH→~7	X	X	X	X	X	X		
Wash and Centrifuge (2X)	X	X	X	X	X	X		
pH→1, (.25 ml 1.0N HNO ₃ +2.0 ml 0.1N) NH ₄ NO ₃ add.(5.9 g)	X	X	X	X	X	X		
Sample to column, 70-80 ml to wash Fe off	X	X	X	X	X	X		
100 ml 8N HCl, Th wash off	XXXX X	XXXX X	XXXX X	XXXX X	XXXX X	XXXX X		
≤5 ml wash 0.1N HNO ₃ (discard) 50 ml 0.1N HNO ₃ — save U	X	X	X	X	X	X	XXXX	

	SAMPLE NAME							
STEP	B-8006-1	B-8006-1	B-8005-1	B-8007-1				
Column prep.	X	X	X	X				
Fe(OH) ₃ precip, pH→~7	X	X	X	X				
Wash and Centrifuge (2X)	X	X	X	X				
pH→1, (.25 ml 1.0N HNO ₃ +2.0 ml 0.1N) NH ₄ NO ₃ add.(5.9 g)	X	X	X	X				
Sample to column, 70-80 ml to wash Fe off	X	X	X	X				
100 ml 8N HCl, Th wash off	X	X	X	X				
≤5 ml wash 0.1N HNO ₃ (discard) 50 ml 0.1N HNO ₃ — save U	✓ 10 10 10 10	✓ 10 10 10 10	✓ 10 10 10 10	✓ 10 10 10 10				

	SAMPLE NAME							
STEP	B-8006* U*a	B-8006* U*b	B-8005-C Ptlb*a2	B-8007-C Ptlb*a2				
Heat to near dryness	X	X	X	X				
Wash beaker— 2ml 0.001N Nitric, repeat 2X	X	X	X	X				
1-2 MI TTA, homogenize	X	X	X	X				
Centrifuge (2 min)	X	X	X	X				
Clean and label planchet, heat	X	X	X	X				
With new pipet, Separate, evaporate TTA on planchet	X	X	X	X				
Repeat extraction	X	X	X	X				
Burn off organic	X	X	X	X				
Place in labeled envelope	X	X	X	X				