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RiO5 METHOD (40)

Anderson Lab Protocol for Dissolved ^{232}Th, ^{230}Th, and ^{231}Pa

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^{232}Th, ^{230}Th, and ^{231}Pa — dissolved — water samples

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Disclaimer

It is the responsibility of the analyst to follow established safety and health practices. Although each laboratory identified as the source has tested the methods, each user should perform an individual validation procedure.

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1 SCOPE

This method is used for the measurement of dissolved ^{232}Th, ^{230}Th, and ^{231}Pa from water samples. Samples are collected in acid-cleaned 5-liter cubitainers, and acidified at sea to pH=2 using Optima grade 6M hydrochloric acid. The following method is for radionuclide analysis once the samples have been returned to Lamont-Doherty. This procedure is for analyzing one batch – which includes 15 samples, 2 procedural blanks, 2 seawater standards, and one column blank. All steps with open samples should take place in a laminar flow bench. All reagents used should be Optima grade.

2 EQUIPMENT and CHEMICAL REAGENTS

2.1 Equipment and consumables

At Sea:

- 5 liter cubitainers
- Teflon-lined Tygon Tubing
- Pall Acropak500 capsule filters (0.8µm/0.45µm)
- Parafilm to seal cubitainers, and plastic bags and tie wraps to double bag samples after acidification.

In Lab:

- 250ml Polycarbonate Centrifuge bottles (ours are from Fisher Scientific).
- 7ml and 15ml vials, and 50ml centrifuge tubes from Savillex.
- Centrifuge with rotor and inserts to handle 250ml centrifuge bottles and 50ml centrifuge tubes (maximum speed 2000-3000 rpm).
- Acid resistant hotplates (we've successfully used silicone heating pads and Teflon-coated Aluminum plates with Temperature controllers for in-house made hotplates that are more robust and cost efficient compared to commercial units).
- Plastic ion exchange columns to hold 1 ml resin bed with reservoir of 5ml or greater (Bio-rad and Evergreen Scientific are two suppliers that we've used).
- Laminar flow benches. The most difficult challenge we have encountered is keeping the ^{232}Th blanks under control. We try to do as much work as possible in laminar flow benches. (We still use Envirco 100 Plus units that are no longer made).
- Four- or Five-place analytical balance for weighing spikes.
- Top-loading balance able to weigh 5 kg samples to ±1g.
- Adjustable pipettes (10-200µl, 100-1000µl, and 1-5 ml) We have used Finpipette and Eppendorf, with a slight preference for the Eppendorf models.
- Savillex DST-1000 sub-boiling stills. We have two, one for distilling trace metal grade Nitric Acid and one for distilling trace metal grade Hydrochloric Acid.

2.2 Tracers

- ^{229}Th- ~10pg/g solution. We add 100mg to samples (~1pg ^{229}Th).
- ^{233}Pa-The parent isotope ^{237}Np is long-lived ($t_{1/2}$=2.144 x10^{6} years). We have ~60 µCi of ^{237}Np, which is milked every 6 months or so to separate the daughter, ^{233}Pa ($t_{1/2}$= 26.967 days). The Pa tracer is purified from it's long-lived daughter, ^{233}U. Isobaric interference issues can arise if care is not taken to purify Pa from U. Initially the spike concentration is ~2pg/g. Samples are spiked with 100-200 fg ^{233}Pa, so the volume of spike added to samples increases with the age of the spike, doubling each month that the spike is used. We limit the amount of 233Pa we introduce to the mass spec because the dark noise on the detector can increase due to radioactive decay of Pa deposited at the detector end of the mass spec.

2.3 Chemical reagents

- Trace metal grade Nitric Acid, redistilled with Savillex DST-1000, with a final molarity of 16 Molar
- Trace metal grade Hydrochloric Acid, redistilled with Savillex DST-1000, with a final molarity of 10.5 Molar
- Optima grade (Seastar) Perchloric Acid
- Optima grade (Seastar) Hydrofluoric Acid
- Optima grade (Seastar) Ammonium Hydroxide
- Iron salt (Ferric Chloride and Ferric Nitrate have been used)

2.4 Solutions

- ~50mg Fe/ml Iron carrier in 8 Molar Nitric Acid (cleaned to remove ^{232}Th prior to addition to samples)
- 6 Molar Hydrochloric Acid
- Concentrated Hydrochloric Acid/0.14 Molar Hydrofluoric Acid
- 8 Molar Nitric Acid
- Concentrated Nitric, Hydrochloric, Perchloric and Hydrofluoric Acid
- Concentrated Ammonium Hydroxide
- Milli-Q water

3 PROCEDURE

Day 1: Add spikes and Fe carrier

1. Transfer ~60mL of the sample into a tared plastic bottle, for possible future analysis of uranium isotopes or small-volume ^{232}Th analysis.
2. Label 20x acid-cleaned 2 mL graduated microcentrifuge tubes and 18x acid-cleaned screw caps without O-rings.

3. Weigh out ^{229}Th and ^{233}Pa spikes into microcentifuge tubes in balance room (Comer 306). Add 100 μL of ^{229}Th (2012-1) – the amount of ^{233}Pa spike added will depend on the amount of time elapsed since the spike was prepared. For each standard, weigh out a 100 μL aliquot of either SW STD 2010-1 or SW STD 2015-1 (you will run one of each).
4. Weigh 5L seawater samples.
5. Add 500 μL of 0.024M HCl to each microcentrifue tube containing spikes, cap, shake well, and add to the appropriate seawater sample.
6. Rinse microcentrifuge tubes with an additional 500 μL of 0.024M HCl, add to sample
7. Add 500 μL of purified $FeNO_3$ carrier (30-50 mg Fe/mL) to each sample.
8. Let samples sit overnight so that spikes can equilibrate.

Day 2: Raise pH of samples to precipitate Fe

1. Add 10 mL concentrated NH_4OH to each sample.
2. Check pH with pH test strips.
3. Continue adding NH_4OH in 0.5-1 mL intervals and checking pH until the pH has reached 8.5-8.7. Record total volume of NH_4OH added to each sample.
4. Shake samples well, let sit overnight

Day 3: Shake samples

1. Shake samples well
2. Replace cubitainer caps with (closed!) valve caps, turn cubitainers 90 degrees so that nozzles are facing down.
3. Let samples sit overnight – the next day, there should be a layer of flocculated particulate Fe coating the bottom of the cubitainer.

Day 4: Siphon samples

1. Set up seawater waste container on the ground in a secondary containment vessel.
2. Connect Tygon tubing to the valve cap of the cubitainer, with the other end in the seawater waste container.
3. Slowly open valve (2/3-3/4 of the way open), allow seawater to pass to the waste container.
4. When the water level reaches the valve, close valve slightly.
5. With one hand on the valve, gently press the other hand on the top of the cubitainer, applying pressure. Tilt front edge of cubitainer over the edge of the lab bench while keeping valve perpendicular to the floor. Make sure none of the iron flocs are being siphoned into the waste.
6. Replace valve with original cap.
7. Swirl the cubitainer and pour up to 225 mL of sample into 250 mL centrifuge bottles
8. Weigh centrifuge bottles to ensure bottles across from each other are within ~1g.
9. Centrifuge 4 bottles at a time at 3000 rpm for 27 minutes, speed 3 up, speed 1 down
10. Decant liquid from centrifuged samples down the drain, with a kimwipe or white paper towel held on the back to monitor the red iron flocs (don't lose any!)
11. Pour any liquid remaining in cubitainer into the same 250 mL centrifuge tube, repeat centrifuging/decanting until cubitainer is empty.

12. If there is extra room in 250 mL centrifuge bottle, add 30 mL of Milli-Q (MQ) water and 1 drop NH_4OH to cubitainer, shake, and transfer to 250 mL centrifuge bottle.
13. After final centrifuge, swirl 250 mL centrifuge bottles and transfer iron flocs to 50 mL centrifuge tubes. Rinse 250 mL bottle with MQ from squirt bottle until all the Fe has been transferred to the 50 mL tube.
14. Fill 50 mL centrifuge tube up to the top line with MQ
15. Centrifuge 50 mL tubes at 3000 rpm for 12 minutes, speed 3 up, speed 1 down
16. Decant supernatant, Fe pellet will stay at bottom of tubes
17. Dissolve Fe in 1 mL concentrated HNO_3, transfer to 15 mL Savillex vial
18. Rinse 50 mL centrifuge tube with 1 mL concentrated HNO_3, transfer to 15 mL Savillex
19. Add 1mL concentrated $HClO_4$ to 15 mL Savillex, heat overnight at 100 ºC.

Day 5: Digestion

1. Turn heat on hot plate up to 180º, and fume $HClO_4$ for 20-30 minutes
2. Add 10 drops concentrated HF, heat to $HClO_4$ fumes (~15-20 minutes)
3. Add 5 more drops concentrated HF, heat back to $HClO_4$ fumes
4. Fume $HClO_4$ for 20-30 minutes
5. Rinse vial walls with 1 mL concentrated HNO_3
6. Heat until there is a nearly dry, "sludgey blob" of Fe in vial
7. Dissolve Fe in 5 drops concentrated HCl
8. Add 5 mL MQ, heat capped for 2-3 minutes to fully dissolve Fe
9. Transfer sample back to 50 mL centrifuge tubes
10. Rinse 15 mL Savillex vial with 5 mL MQ, transfer to 50 mL centrifuge tubes
11. Fill centrifuge tubes halfway with MQ
12. Add ~10 drops concentrated NH_4OH to re-precipitate Fe
13. Fill centrifuge tube fully with MQ
14. Centrifuge at 3000 rpm for 12 minutes, speed 3 up, speed 1 down
15. Decant supernatant – only Fe pellet should remain at bottom of centrifuge tube
16. Dissolve Fe with 1 mL concentrated HNO_3, transfer back to 15 mL Savillex
17. Rinse centrifuge tubes with 1 mL concentrated HNO_3, transfer to 15 mL Savillex
18. For the column blank and seawater standards, transfer solutions from 2 mL microcentrifuge tube to 15 mL Savillex with 2 mL concentrated HNO_3.
19. Cap 15 mL Savillex and let sit until you are ready for the first anion column

Day 6: Initial Column separation (Columns are Bio-Rad resin, AG1-X8, 100-200 mesh size)

1. Heat samples dry in 15 mL Savillex at 180º
2. Add 5 drops concentrated HCl, heat to dry at 150º
3. Add 2 drops concentrated HCl
4. Add 2 mL concentrated HCl – this is what you will load onto the columns
5. Condition the columns: First Uncap the columns and let the MQ go to waste
    a. Add 3 mL concentrated HCl/0.14M HF, to waste
    b. Add a full column reservoir of MQ, to waste
    c. Add 2x2 mL concentrated HCl, to waste
6. Put 7 mL Savillex vials underneath columns to collect Th fractions
7. Load samples from 15 mL Savillex on column, collect Th
8. Rinse 15 mL Savillex vials 2x1 mL concentrated HCl, add on column, collect Th
9. Add 2x1 mL concentrated HCl on column, collect Th
10. Cap 7 mL Savillex with Th fractions and remove from under columns

11. Take Th fractions to Comer 306 and gamma count on the NaI detector to ensure that no Pa leaked into the Th fractions. Measure background, and make sure that the gamma counts for each Th vial is within 20-30 counts of background
12. Put new 7 mL Savillex vials underneath columns to collect Pa fractions
13. Add 3x2 mL concentrated HCl/0.14M HF, collect Pa
14. Cap 7 mL Savillex with Pa fractions, remove from under columns
15. Place waste beakers beneath columns
16. Add 2 full reservoirs of MQ + 2 drops concentrated HCl to clean columns
17. Add two times the amount of Pa spike added of mix Pa to the mix Pa vial
18. Add 0.5 mL 8M HNO_3 + 2 drops concentrated $HClO_4$ to Th and Pa fractions
19. Heat Th and Pa fractions overnight at 100 ºC

Day 7: Cleanup Columns

1. Samples should be in a drop of $HClO_4$ in the 7 mL Savillex vials
2. Add 100 μL concentrated HNO_3 to Th vials, cap, and set aside
3. Add 100 μL concentrated HNO_3 to all Pa vials, heat to dry at 180º
4. Add 2 drops concentrated HCl to Pa vials, heat to dry
5. Add 2 drops concentrated HCl to Pa vials
6. Add 2 mL concentrated HCl to Pa vials
7. Condition columns
   a. Uncap columns, let MQ go to waste
   b. Add 3 mL concentrated HCl/0.14M HF, to waste
   c. Add full column reservoir of MQ, to waste
   d. Add 2x2 mL concentrated HCl, to waste
8. Load samples in concentrated HCl, to waste
9. Rinse vials 2x1 mL concentrated HCl, to waste
10. Add 1 mL 8M HNO_3 to Pa vials, cap, heat for 30 minutes at 130º to reflux acid and clean vials
11. Add 3x1 mL concentrated HCl on column, to waste
12. Remove Pa vials from hot plate, dump acid in them to waste, and rinse well with MQ
13. Place Pa vials under columns
14. Add 3x2 mL concentrated HCl/0.14M HF, collect Pa
15. Remove Pa vials from under columns
16. Put Th vials in 100 μL of concentrated HNO_3 on hot plate at 180º
17. Heat Th samples to dry
18. Add 100 μL concentrated HNO_3 to Th vials
19. Heat down to 50 μL
20. Add 50 μL MQ to Th vials
21. Add 2 mL 8M HNO_3 to Th vials
22. Condition columns for Th cleanup
   a. After finishing Pa cleanup column, pass two full reservoirs of MQ through columns, to waste
   b. Add 3 mL concentrated HCl, to waste
   c. Add full reservoir MQ, to waste
   d. Add 2x2 mL 8M HNO_3, to waste
23. Load Th samples in 8M HNO_3 on column, to waste
24. Rinse Th vials 2x1 mL 8M HNO_3, to waste
25. Add 1 mL 8M HNO_3 to Th vials, cap, heat for 30 minutes at 130º to reflux acid and clean vials
26. Add 3x1 mL 8M HNO_3 on column, to waste

27. Remove Th vials from hot plate, dump acid in them to waste, and rinse well with MQ
28. Place Th vials under columns
29. Add 200 μL concentrated HCl on column, collect Th
30. Add 3x2 mL concentrated HCl on column, collect Th
31. Remove Th vials from under columns
32. Clean columns with 2x full reservoirs of MQ, cap, and set aside
33. Add 0.5 mL 8M HNO_3 + 2 drops concentrated $HClO_4$ to Th and Pa vials, heat overnight at 100º

Day 8: Final Drydown

1. Samples should be in a drop of $HClO_4$
2. Add 100 μL concentrated HNO_3 to Th and Pa vials
3. Heat until there the final drop of $HClO_4$ vanishes, tapping down walls to ensure dryness
4. Take up samples in 500 μL of ICP-MS run solution (0.16M HNO_3/0.028M HF) – take up mix Pa sample in 1.5 mL of run solution
5. Transfer samples to labeled 2 mL microcentrifuge tubes to run on ICP-MS.

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