Processing Sediment Samples for determination of $^{210}Po/^{210}Pb$

Based on the McKee Lab Method (version Feb 7, 2021)
Revised: December 15, 2023

Reagents

- ^{209}Po in 4N HCl tracer solution
  - Made from spike. Stored in Wilkinson 231 in the locked cabinet.
- Conc. Hydrochloric Acid [HCl] (~35% w/w)
  - Stored under fume hood.
- 8N Nitric Acid [HNO_3]
  - Stored under fume hood.
- Conc. Ammonium Hydroxide [NH_4OH]
  - Stored in 268. Buy from Fisher (A669-212, 2.5 L)
- 30% Hydrogen Peroxide [H_2O_2]
  - Stored under fume hood in 274B. Buy from Fisher (5155-01, 450mL).
- Milli-q water
  - Dispenser in lab. (Note: DI and milli-q are used interchangeably.)
- L-Ascorbic Acid
  - Stored under fume hood in 274B. Buy from Fisher or Chem Stores (0143-100G)

Equipment

- Squeeze Bottles (in Wilk 231)
- Pipette, 1mL, 5 mL, 10 mL (in 274B)
- Pipette Tips, 1mL, 5 mL, 10 mL (in 274B)
- pH paper (in 274B)
- Planchets (in Wilk 231)
- 24 x Microwave vessels (in 274B)
- 24 x 100ml Teflon beakers (in Wilk 231) – NOTE: There are 3 “fat” beakers that evaporate slowly. Use these for dispensing acid/base, not for samples.
- 3x multi-position stir plate (in 274B)
- 24x small stir bars (in 274B, spares in Wilk 231)
- 50ml Falcon centrifuge tubes (in 274B, spares in Wilk 231). Replace tubes if they look worn or brittle.
- Centrifuge (in 274B)
- 2x centrifuge inserts (in Wilk 231)
- Hotplate (in 274B – stays in fume hood)
- Temperature gun (in 274B)
- Scooptula (in 274B)
- Empty rad waste bottle (request from EHS)
- Gloves and eye protection (in Wilk 231)
- Lab coat with cinched wrists (vending machine in Linus Pauling Center)

Recommended schedule:

Week Before:

- Dry/weigh samples for analysis.
- Book Lab and check supplies.

Day 1:

- 0700–0800: Load microwave. Complete paperwork and prep during 25 min heating stage (everything in Part 1).
- 0800–0900: Eat breakfast and finish prep.
- 0900–1100: Everything in Part 2. Take a break to eat lunch while samples are heating to 85C.
- 1100–1300: Monitor samples while finishing cleaning tasks. This is a time to answer emails in between temperature checks.
- 1300–1500: Finish Steps 2 and 3.

Day 2:

- 1100: Change out beakers in acid wash and rinse centrifuge tubes.
- 1200–1300: Complete Step 4

Day 3/4/5:

- Run samples on alpha detector.

0. Preliminary preparation:

0.1. Prepare and weigh samples in advance. This can be done months in advance and you can prepare many samples at once. Samples can be run in sets of 8, 16, or 24.

- Dry ~5 g of sediment in the oven at 60 C. Record wet and dry weights to calculate porosity.
- Crush the dried sediment with the mortar and pestle. No clumps larger than a few mm should be left.
- Weigh 1.4-1.6 g of the dried and crushed sediment into a scint vial. Record the weight.

0.2. Book the Microwave and Microwave Fume Hood.

0.3. Check chemical supplies (Nitric Acid, Hydrochloric Acid, Hydrogen Peroxide, Ascorbic Acid, Ammonium Hydroxide, pH strips

1. Microwave sediment:

1.1. Dump sediment into microwave vessel, and add 1.0 ml of calibrated ^{209}Po tracer (~XX dpm) and 15ml of 8M HNO_3 to each vessel.

1.2. Let the vessels vent for 15 mins after the addition of acid to allow organic reactions to vent.

1.3. Place stoppers and caps on the vessels, secure with the cap clamp until it clicks, and swirl or vortex to combine contents.

1.4. Load the vessels symmetrically into the carousel, place the carousel in the microwave and make sure the turntable can rotate. Run Classic Method "pb210_v2"

- The Procedure includes a 25-minute ramp-up followed by a 40-minute hold at 190ºC (400 watts of power). Cool down takes another 20 mins.
- You must stay in the lab and watch 25-minute ramp-up in case there are any issues. The most common issue is a sudden spike in temperature of one of the vessels, which will cause the program to auto-exit. Once the vessels are cool you should check the seal on all the vessels and try to re-run the program.

1.5. Prepare and label the planchets. Sort out planchets that have no knicks or wrinkles. Soak the planchets in a minimum amount of [HNO3] and swirl for 2-3 mins then rinse with DI. Allow the planchets to dry, and label the coated side.

1.6. Complete a sheet for the Microwave Log (blue binder). Add an entry to the RAD Waste Log (green binder).

2. Prepare and reduce acid solution:

2.1. Once microwave procedure is finished, and vessels have cooled remove carousel and place under fume hood. Gases vent when opening caps – use caution!

2.2. Turn hot plate on (instructions are posted above the unit). Set hot plate temperature to 190 ºC to 205 ºC and use laser thermometer to check temperatures in beakers as they heat up. Some places of the hot plate maybe hotter than others.

2.3. Transfer contents of vessels to appropriately labeled 50 ml centrifuge tubes, rinse vessels with DI H_2O to recover all contents then level off with DI H_2O to balance mass. Use only as little DI H_2O as possible.

2.4. Centrifuge at 3500 rpm for 8 minutes; pour supernate into appropriately labeled Teflon beakers and place on the warmed hotplate.
2.5. Add 5ml of 8M HNO_3 to centrifuge tubes, Vortex tube, and centrifuge at 3500 rpm, and pour supernate into appropriate Teflon beakers on hotplate.
2.6. Monitor the temperature of the liquid using the temperature gun. Best Po-209 tracer recovery if temperature is kept around 85 ºC. Occasionally swirling solution slightly also helps to break temperature stratification that may be volatizing Polonium in parts of solution. Make sure temperature is warmed to between 85- 90 °C not to exceed 95 °C.
2.7. When the solution in the beakers has warmed up add 1-2ml of H_2O_2 to each beaker and let effervesce. Add more if samples have lots of tannin.
2.8. Take samples to near dryness on hotplate. The residual should look like honey. ***Avoid allowing samples to dry and bake to beaker. Temperatures should not exceed 95 °C to avoid volatilizing the polonium-209.*** This is a critical step that will take ~2 h, check the temperature at least every 10 minutes. If samples get too warm, remove the beaker and let it sit in the hood for 30 s.
2.9. During the "cooking", discard sediment into radioactive waste. Then thoroughly rinse tubes with DI H_2O for later use. Clean the Teflon tubes and put them into acid steam cleaner.
- Pre-rinse the vessels with water and 1% micro-90 detergent to remove any bathtub rings in vessels. Cap and shake vessels then let soak for ~10-minutes. The tubes must be loaded on the taller stands and the stoppers go in a funnel. The caps do not get acid washed.

3. Fe scavenge and plating

3.1. Dilute the reduced samples with DI H_2O to ~15ml, then swirl beaker to suspend dried material.
- *(If samples are iron limited, add permanganate/ manganese chloride procedure here before Step 2.1. – Titration step).* → *We're not set up to do this step.*

3.2. Pour beaker content into appropriately labeled rinsed centrifuge tube. Rinse the beakers well to bring vial volume to ~30 mL.
3.3. Add 2-3 mL of [NH_4OH] slowly to solutions with stirring to bring pH to 8 [range 7 – 8.5]. Fe precipitate will form and turn the solution orange.
3.4. Centrifuge samples at 3500rpm for 8 minutes. If supernate does not appear clear, recheck pH. Additional [NH_4OH] may be needed to fully precipitate Fe.
3.5. Decant supernate in waste container, leaving precipitate in centrifuge tube.
3.6. FIRST RINSE. Rinse precipitates with up to 30ml DI H_2O. Vortex tubes to completely dissolve Fe precipitate and centrifuge at 3500rpm. Decant supernate.
3.7. SECOND RINSE. Rinse precipitates with up to 30ml DI H_2O. Vortex tubes to completely dissolve Fe precipitate and centrifuge at 3500rpm. Decant supernate.
- It is easy to lose track of the sample stages during the 3 centrifuges. Take detailed notes when loading samples into the centrifuge.

3.8. Add 3.75ml of Hydrochloric Acid to each sample to dissolve the precipitate.

3.9. Add 30 ml DI H_2O and ascorbic acid (~50/60 mg weighed out, or 'scoop' on metal spatula). Vortex until fully dissolved. Samples should appear clear and should measure a pH of 1-2. Check before samples plate.

3.10. Set up the 3 stir plates. Add a stir bar to each beaker. Place a labeled planchet in the appropriate beaker, metal side up.

3.11. Add solutions to the beaker, fill the vial with 30 mL of DI water, shake and add the rinse to the beaker. Total volume is then equal to 60ml.

3.12. Set stir plates to ~300 rpm. Continue plating procedure for at least 20 hours and no longer than 40 hours.

3.13. Clean the centrifuge tubes and lids with soap and water and leave them to soak in a 4N HNO3 bath in the fume hood. This bath can be stored and reused for ~3 months.

3.14. Finish running the Teflon microwave tubes in the acid steam cleaner. Leave cleaned tubes to dry in the hood.

4. Final steps:

4.1. Remove plated discs and rinse with DI H_2O. Pat discs dry, then allow airing dry. Allow discs to dry for 24 h before running in the alpha detector.

4.2. Rinse the centrifuge tubes with milli-q and air dry in the hood.

4.3. Wash beakers and stir bars with soap and water and run through the acid steam cleaner.

4.4. Wipe down acid hood after each run, including the doors, bench, hot plates and stir plates.

4.5. If any materials from procedure have run out, make sure to replace before end of run for person running the next day.

4.6. Empty the dry rad waste into the larger container. Place the labelled liquid rad waste in the bin near the door and submit a request for pick-up. You should always request a new container as well. RAD waste pickup can be requested on this webpage https://ehs.oregonstate.edu/rso under the "How do I …?" tab . Allow 1-week for waste container pickup and replacement.

Using the Acid Steam System:

1. Only Teflon materials receive Acid Steam System cleaning.
2. Each spot should be covered with a blank/stopper or a glass stand with a vessel.
3. Place vessels/beakers on glass stands in chamber.
4. Hold down black button and press the lower button on the touch screen until the chamber lid has lowered and created a seal. Make sure none of the vessels catch on the edge of the chamber.
5. Start cleaning cycle (1 hour and 30 minutes at 220 ºC)
6. At end of cleaning cycle, vent the chamber for 20 minutes. When chamber has dropped below 90 ºC, raise the chamber lid until it is cracked.

Fe Limited Samples – $KMnO_4$ / $MnCl_2$ Method Before Titration

1. Add 0.2 mL of each reagent ([$KMnO_4$] and [$MnCl_2$]) to each sample prior to addition of [NH_4OH].
2. How to make reagents:
    - **0.2 mol L-1 $KMnO_4$:** Dissolve 3.161 g of KMnO4 in 100 mL of deionized water. Filter through a dense glass fiber filter (Whatman GF/F) and keep in a dark and cool place.
    - **0.3 mol L-1 $MnCl_2$:** Dissolve 5.938 g of MnCl2·4H2O in 100 mL of deionized water.

Alpha Detector Procedures

Starting a Count:

1) Turn on the system:
    a. You must open the Apex-Alpha software before turning on detectors.
    b. Turn on detectors – power switch is on back right side.
    c. Turn on vacuum – check the oil level on a regular basis.
    d. Right-Click on chambers and click MCA → "Reconnect"
        i. Chambers should turn from red (offline) to blue (available)
2) Creating Samples to Run
    a. Open the Batches Page
        i. Create a Batch ID (Can just be a running number or a date)
        ii. Sample Matrix = soil
        iii. Sample Type = "planchette"
        iv. Type in # of samples to be run in the batch (1-8)
        v. Add any QA samples (probably won't be using any most of the time)
        vi. Select "ABS – Polonium" Procedure Group
        vii. If all info looks good, hit next
            1. Add in Sample IDs, Description Info, and Update sample Fields
        viii. When all looks good save the batch
    b. Saved Batch should appear in the Sample Assigner Window
3) Place Samples on the slides in the proper chambers. The metal side should be up.
4) Sample Assigner Page
    a. In Left Pane of Sample Assigner, samples to be run should appear in Queued Batches
    b. Drag the sample name to the respective chamber it was placed in → Icon should change cyan (meaning ready to run)
5) When all samples are assigned and icon has turned "cyan" color you can begin counting
    a. Press "Load Samples" in top right hand corner of Sample Assigner Page
    b. Icons should turn green. To check counting, go to Status View page, "counting" should appear next to the icons.
6) If for any reason need to abort, restart, or stop and analyze a run while it is occurring, right click on the chamber on the Main Page go to "Count" and select the desired action.

Reviewing and Saving Data

1) Click on "Data Review" in top banner.
2) Unclick "All Procedures" in the search criteria window and select "ABS – Polonium" or your desired procedure and hit "Search Now".
3) Select batches you would like to review data for.
4) To save data for getting into text file format:
    a. Click Export
    b. In finder window navigate to desired folder (i.e. ABS_Alpha)
    c. Name subsample and save as .CAM file
    d. See "Accessing Channel Data in Text File Format" to see how to save text files.

Shutdown Procedure

1) When all counts are completed, vent the vacuum hose
    a. Open a chamber, pump the chamber with the door open, turn the pump off.
    b. When air stops hissing from chamber door, close the chamber door.
        i. Will remove the vacuum from the line and make sure no vacuum is locked in there and cause potential oil backflow from negative pressure (which can seriously damage the detector).
2) Power-off the detector in the back (icons should change to bright red).
3) Close out software.

Accessing Channel Data in Text File Format

1) Need to open Genie2000
    a. Navigate to Windows Start → Genie2000 → Alpha Acquisition & Analysis
2) Click on File tab and select "Open Datasource"
3) Select subsample .CNF file and open
4) Click on Analyze tab and scroll down to "K Reporting"
5) Click on "Standard"
6) In "Template Name" window scroll down to CSV.TPL
7) Make sure "Section Name" says "CHANNEL_LIST" and hit Execute
    a. Channel data should populate the window
8) Click on Options tab and scroll down to "Report Window"
9) Click on Copy Contents to Clipboard
10) Open Notepad or another text file program
11) Paste in channel data copied to clipboard
12) Save text file to specified folder with sample name.

***Note: If you have a lot of files to save it could be faster to follow procedure to Step 7 then click file "Export Report to PDF" and create a folder of PDF reports. Then use the PDF reader matlab script to go through PDFs and generate text files. Double check which channels are cut off by PDF reader script when doing this though.

Performing QA Checks

1) ** Need to open Apex-Alpha software before turning on detectors
2) Power on Detectors following same procedure as sample runs.
3) Go to Setup → QA Procedures
    a. Check Procedures are setup to desired standars
4) Go to Sample Assigner page
    a. Expand QA list in left pane.
        i. Drag the desired QA Check to the desired chamber or for all chambers
        ii. Make sure all desired chambers turn "cyan".
5) Hit Load Samples to begin QA Check
6) Make sure all chamber icons turn green and status changes to "counting" on Status View