RiO5 METHOD (14)

ERL-ECU/LM/0004

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^{210}Po and ^{210}Pb — Iron hydroxide co-precipitation — Seawater samples

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 specifies the minimum requirements and laboratory methods for the analysis of total ^{210}Pb and ^{210}Po in seawater samples.

Samples are collected in acid-cleaned containers and pretreated on board, by acidifying and co-precipitating the samples. Post processing will take place at the home laboratory by auto-plating of Po isotopes onto silver disks on a 1 M HCl solution. Po isotopes emissions are measured by alpha spectrometry. Isotope ingrowth and decay corrections are applied to calculate the ^{210}Po and ^{210}Pb activities (see Rigaud et al., 2013).

2 EQUIPMENT AND CHEMICAL REAGENTS

2.1 Equipment

- Plastic containers
- Standard laboratory equipment
- Plastic columns (BioRad)
- Glass beakers
- Analytical balance with an accuracy of ± 0.1 mg
- Hot plate
- Hot plate with magnetic stirrer
- Alpha spectrometry system
- Urethane seal coat
- Plastic vials for ICP-OES

2.2 Tracers

- ^{209}Po (0.4 Bq mL^{-1})
- Stable Pb (free of ^{210}Pb) (20 mg mL^{-1})

2.3 Chemical reagents

- Hydrochloric acid (HCl)
- Ammonia (NH_3)
- Ascorbic acid ($C_6H_8O_6$, powder form)
- Anion exchange resin (DOWEX-1-X8 or AG 1-X8)

2.4 Solutions

- 30 mg mL^{-1} $Fe(OH)_3$
  Use $FeCl_3 \cdot 6H_2O$ to prepare the solution using Milli-Q water

- 1 M, 9 M HCl

3 PROCEDURE

1. Collect 5-10 L seawater samples. Weight them or use calibrated containers.
2. Add concentrated HCl until pH < 2 (1 mL HCl per 1 L of sample).
3. Shake vigorously to homogenize.
4. Spike the samples with a known amount of ^{209}Po (with a 0.4 Bq mL^{-1} ^{209}Po solution we add 75 µL) using a calibrated micropipette.
5. Add a known amount of stable Pb (ideally use old lead to minimize contamination; with a 20 mg mL^{-1} solution of stable Pb we add 200 µL) using a calibrated micropipette.
6. Add the iron carrier (5-8 mL of a 30 mg Fe mL^{-1}; do not add more than 10 mL, not even for larger samples; 10 mL of the $Fe(OH)_3$ solution are enough to precipitate samples up to 120 L).
7. Shake vigorously to facilitate equilibration. Allow equilibration for ~12 h.
8. Add conc. NH_3 (usually 1 mL more than the amount of acid added in step 2; it can also be done adding NaOH 0.5 kg L^{-1}) to raise the pH to 8.0–8.5. A precipitate of $Fe(OH)_3$, with a characteristic orange-red-brown color, is formed which will co-precipitate Po and Pb.
9. Allow the precipitate to settle for a few hours. The precipitate will settle to the bottom of the bottle or container.
10. Carefully siphon off the supernatant, keeping the precipitate.
11. Transfer the precipitate into a smaller bottle (i.e. 250 mL) and rinse the original container with Milli-Q water at pH ~8.0 to ensure minimal losses.
12. Siphon off the supernatant again to reduce the volume and weight of the sample for comfortable transportation.

This first part usually takes place at sea, the following steps are usually done at the home laboratory.

13. Centrifuge the samples at 2000 rpm for 5 minutes.
14. Siphon off the supernatant to remove as much salty water as possible.
15. Add a few mL of Milli-Q water at pH ~8.0 to help dissolve salts. Repeat steps 13 and 14 to avoid salt crusts to form in the following steps.
16. Dissolve the precipitate by adding ~4 mL of concentrated HCl into the bottle.
17. Transfer the sample into a glass beaker, previously weighted, and rinse the bottle 3 times with 1M HCl, pouring the rinses into the beaker to ensure minimal losses.

18. Evaporate the sample to dryness (avoid boiling the sample).
19. Add 2 mL conc. HCl and evaporate to dryness again (avoid boiling the sample).
20. Repeat the previous step 2 times more.
21. If salt crust is present some concentrated acid may still remain underneath the crust. In this case add 1–2 mL of 1 M HCl (or Milli-Q water) and evaporate again to get rid of the concentrated acid and evaporate to dryness.
22. Reconstruct the sample by adding ~80 mL of 1 M HCl.
23. Weight the beaker with the sample and annotate the weight to obtain the weight of the sample.
24. Add a stirring magnet and cover the beaker with a glass watch. Stir the sample on a stirring plate.
25. When the sample is well homogenized extract an aliquot of 0.4 g on a vial and add Milli-Q until the total weight of the sample is ~10 g. This aliquot will be used to obtain the Pb recovery (expected Pb concentration is ~2 ppm, considering amount of stable Pb added in step 5). The sample is then analyzed by ICP-OES.
26. Heat the sample to 80°C and stir it continuously.
27. When the sample is hot, add ascorbic acid ($C_6H_8O_6$, powder form) in small amounts until the solution turns from bright yellow to transparent, uncolored. If the sample is cold the ascorbic acid will take longer to dissolve. If too much ascorbic acid is added, the solution will turn black when heated.
28. Place a silver disc, with only one of the sides available for auto-deposition[1], in the sample using a nylon string. Auto-deposition of polonium onto silver discs is used to separate ^{210}Po and ^{210}Pb.
29. Keep the beaker with a glass watch and heat it to 80°C while stirring it. Leave it for 4-6 h to allow auto-deposition.
30. Get the silver disc, rinse it with Milli-Q water and let it dry before measuring it for alpha spectrometry.
31. Solutions are re-plated. This time the silver disc does not need to be lacquered, thereby providing as much active surface area as possible for auto-deposition of the remaining polonium.
32. Pass solution through an anion exchange resin (DOWEX-1-X8 or AG 1-X8) (see steps 39-45) to ensure complete elimination of polonium from samples. Collect the sample on a bottle that can be properly sealed and will resist strong acid (9 M HCl).
33. Re-spike samples with ^{209}Po (same volume and concentration), using a micropipette

[1] Add urethane seal coat on one side of the silver disc so that polonium can only be deposited onto the other side, optimizing the counting statistics of the sample given that the alpha detector can only measure one side of the disc at a time.

and weight the amount added on a precision scale.

34. Store for 6-9 months for later determination of ^{210}Pb via ^{210}Po in-growth.
35. After allowing ^{210}Po in-growth, samples are transferred to a glass beaker (pre-weighted) and evaporated to dryness (avoid boiling the sample).
36. Repeat steps 22-30. Samples are plated again using a lacquered silver disc, which later on is counted on an alpha spectrometry detector. Step 27 (ascorbic acid addition) can be skipped.
37. ^{210}Pb and ^{210}Po activities at the sampling time can then be calculated applying in-growth, decay and recovery corrections following Rigaud et al., (2013).

Column Chemistry to separate Pb and Po

39. Dry the plated sample solution completely on a hot plate; some residue will be evident.
40. Add 5 mL conc. HCl and dry completely again; much less or no residue should remain.
41. Add 5 mL 9 M HCl to the sample.
42. Prepare a 9 M HCl anion exchange column as follows. Take ~6 mL of anion exchange resin (DOWEX-1-X8 or AG 1-X8) and load a column. Rinse by passing through 20 mL of deionized water. Condition by adding 5 column volumes (= 5 x 6 mL = 30 mL) of 9 M HCl through the column and discard the solution.
43. Transfer the sample solution from (41) to the column. Collect the effluent in a clean beaker or plastic bottle (e.g. 50-100 mL CPE).
44. Rinse the column with 30 mL more of 9M HCl and collect the combined effluents in the same beaker/bottle. Only the Pb passes and Po is retained.
45. Store combined solution for in-growth of ^{210}Po for at least 1-2 half-lives. (Note: Some labs prefer to re-spike the solution at this time with ^{209}Po, and some at the time of the second plating for ingrown ^{210}Po, we recommend to do it at this time).

4 REFERENCES

Nozaki, Y. 1986. ^{226}Ra-^{222}Rn-^{210}Pb systematics in seawater near the bottom of the ocean. Earth Planet. Sci. Lett. 80:36-40.

Rigaud et al., (2013), A methods assessment and recommendations for improving calculations and reducing uncertainties in the determination of 210Po and 210Pb activities in seawater. Limnology and Oceanography: Methods 11, pp. 561-571.

5 FLOW CHART

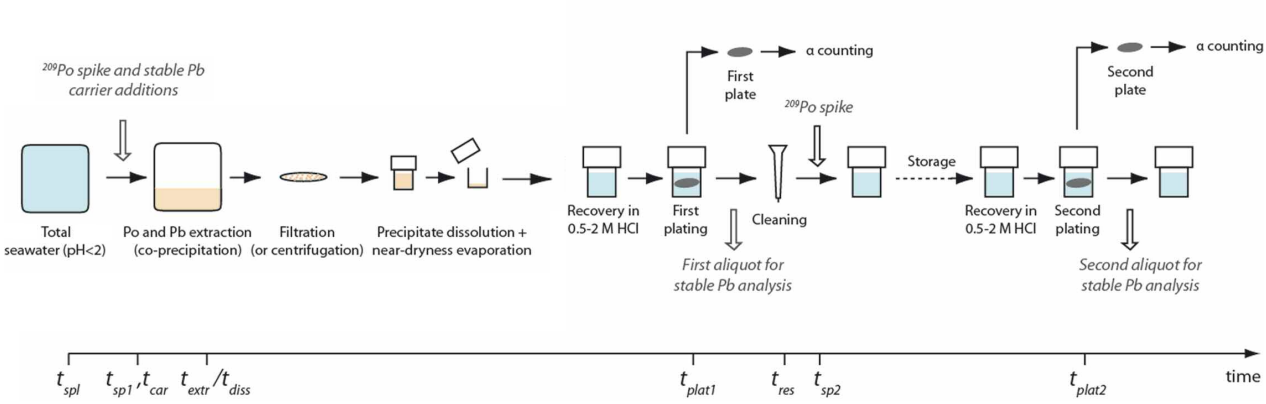


Figure 1: Sample processing scheme for the determination of total ^{210}Po and ^{210}Pb activities. The times term (t) required for each step used in the calculation are provided (see Rigaud et al. 2013). Figure adapted from Rigaud et al. (2013).

6 IMAGES

Image 1: Samples containing the $Fe(OH)_3$ precipitate (see the reddish color of the samples).

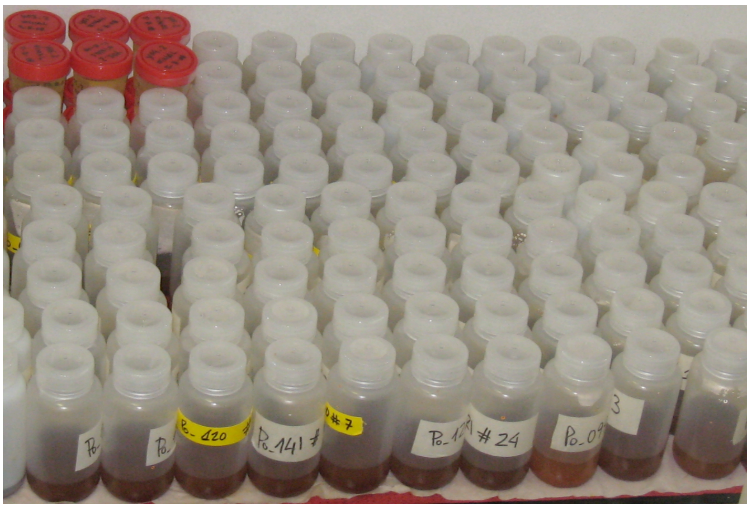
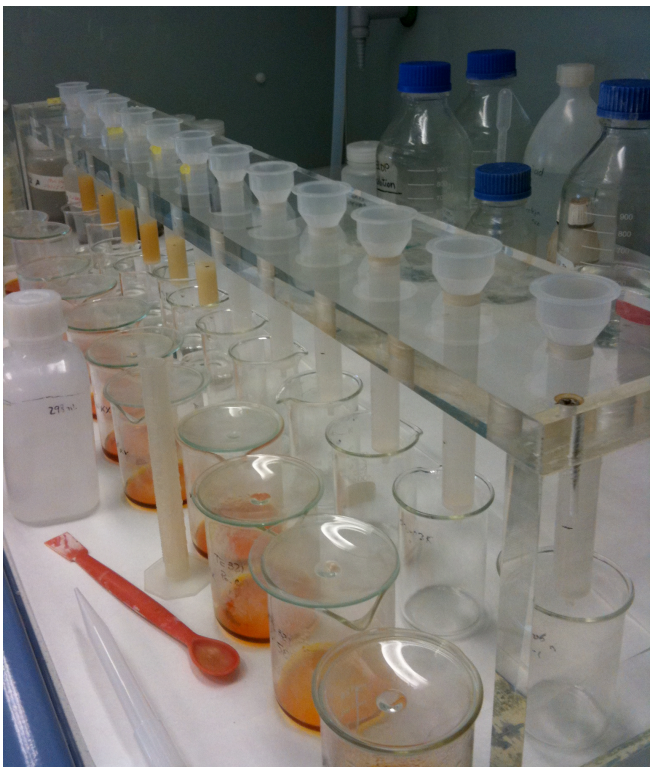


Image 2: After syphoning the extra seawater, the precipitate has been transferred to smaller bottles.

Image 3: Plating.



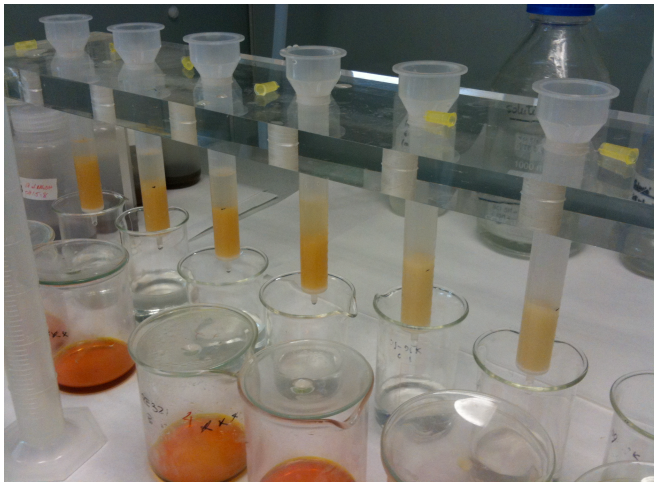


Image 4: Ion exchange columns.

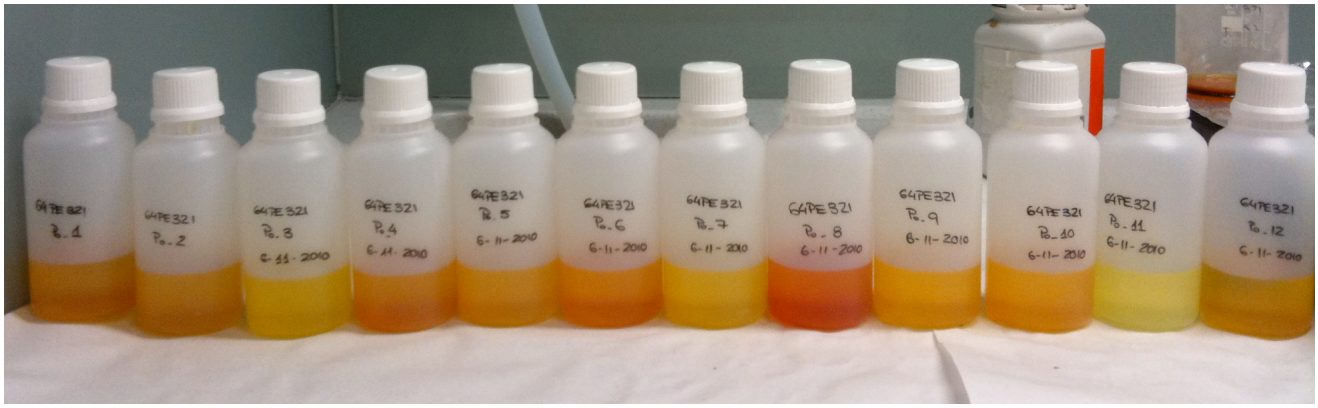


Image 5: Solutions collected after the ion exchange columns that will be stored for at least 6 months prior to re-plating.