RiO5 METHOD (45)

ERL-ECU/LM/0002Contact person
School of Science. Edith Cowan University (Australia)
Viena PUIGCORBE LACUEVA <v.puigcorbelacueva@ecu.edu.au>
Contributors:
Muntsa Roca Martí <muntsa.roca.marti@gmail.com>

^{234}**Th** — MnO_2 precipitation — seawater samples

Determination of ^{234}Th in 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

^{234}Th is a naturally occurring beta emitter and exists in the environment as a result of the ^{238}U decay. Its biogeochemical behavior (particle reactive) and half-live (24.1 d) make it suitable to be used as particle tracer in the ocean.

The Environmental Radiochemistry Laboratory at the School of Science uses data on the concentration profiles of ^{234}Th along the water column in the ocean for the determination of export fluxes of carbon and other key elements of biogeochemical interest in the marine environment.

The procedure involves the following major steps:

- Acidification and tracer addition
- Precipitation of manganese oxides
- Filtration
- Measurement of filter by beta counting
- Second measurement by beta counting >6 months later
- Digestion of the filters and preparation for ICP-MS measurements

2 EQUIPMENT and CHEMICAL REAGENTS

Insert a bullet list of the necessary material in each of the sections (or those that apply)

2.1 Equipment and consumables

- Standard laboratory equipment
- 25 mm QMA filters
- Eyela
- Th-filtration rack and filter supports
- Dehumidifier/Oven
- Analytical balance with an accuracy of ± 0.1 mg
- Hot plate
- Acrodisc syringe filters
- Sonicator
- ICP-MS vials
- Ar 99% + Isobutene 1%
- RISO beta counter and beta holders

2.2 Tracers

- ^{230}Th (~0.2 Bq mL^{-1})
- ^{229}Th (~2.0 Bq mL^{-1})

2.3 Chemical reagents

- Th-230 and Th-229 solutions
- Nitric acid (HNO_3 65 % QP)
- Potassium permanganate ($KMnO_4$ 7.5 mg/mL)
- Manganese (II) chloride ($MnCl_2$ 30.5 mg/mL)
- Ammonia (NH_3)
- Nitric acid (HNO_3 70 % trace metal grade)
- Hydrofluoric acid (HF 49 % trace metal grade)
- Hydrogen peroxide (H_2O_2 30% trace metal grade)

2.4 Solutions

2.4.1 Preparation of solutions for digestion and ICP-MS analysis

The volumes have been calculated considering the use of the following conc. acids and H_2O_2:

HNO_3 70%

H_2O_2 30%

HF 49% (47-51%)

In case of using concentrated acids with different %, the volumes required must be recalculated.

8M HNO_3 / 10% H_2O_2 (To make 1L)

503 mL HNO_3

333.3 mL H_2O_2

Dilute them with DIW in a volumetric flask

Note: This solution has to be relatively "fresh" in order to dissolve the precipitate, otherwise the H_2O_2 gets old and it is not as effective.

8M HNO3 (To make 1L)

Dilute 503 ml of conc. HNO_3 with DIW in a volumetric flask.

5% HNO_3 / 0.08% HF (To make 500 mL)

0.816 mL HF

35.7 mL HNO_3

Dilute them with DIW in a volumetric flask

2.2% HNO3 (To make 500 mL)

Dilute 15.7 mL of conc. HNO_3 with DIW in a volumetric flask.

3 PROCEDURE

3.1 Sampling and processing at sea

Seawater samples

1. Four-liter seawater samples are collected, acidified with concentrated nitric acid (5 mL) to pH<2 and spiked with a known amount of ^{230}Th. Shake vigorously and allow equilibration (8h).
2. After equilibration, raise the pH to 8.5 with concentrated ammonia (5-6 mL). Add $KMnO_4$ and $MnCl_2$ (50 µL each). Shake vigorously and let the sample rest for at least 8h prior filtering.
3. Filter the precipitates and dry the filters overnight at 50°C prior preparation for beta counting. Filters are placed in beta holders and covered by 1 layer of plastic film and 2 layers of common aluminum foil.
4. Count the samples until the counting uncertainty is <3% if a beta counter is available, otherwise store the samples for counting at home laboratory.

Particulate samples

Particulate samples are collected on a 25 mm combusted QMA and dried overnight at 50°C prior preparation for beta counting. Carbon contamination is easy to occur, always use gloves and clean surfaces when preparing the filters for beta counting. If other elements are to be measured on the filters, such as trace metals, take the necessary precautions to avoid contamination. The counting is conducted as done for seawater samples.

3.2 Preparation for the ICP-MS measurements

After counting, the determination of the chemical recovery of ^{230}Th (only for seawater samples) is done via ICP-MS measurements. Prior these analyses, filters need to be digested and reconstructed to have a matrix appropriated for the measurement by ICP-MS.

1. Dismount the filters and place them in 50 ml beakers, avoiding the lost of sample on the transfer.
2. Add ^{229}Th solution to each sample (gravimetric addition) to obtain a 1:1 atom ratio (^{230}Th:^{229}Th) and note the amount added.
3. Add 10 ml of 8M HNO_3/ 10% H_2O_2 solution. The precipitate will dissolve.
4. Cover the beakers with parafilm and sonicate the samples for 20 minutes
5. Allow the samples to stand covered for 6 hours.
6. Transfer the solution to a new 50 ml beaker (keep the filter in the other beaker)

7. Rinse the beaker that contains the filter 3 times with 4 ml of 8 M HNO_3 and transfer the rinse to the beaker that contains de sample.
8. Evaporate the samples to dryness. Be careful because, due to the H_2O_2, samples will "boil" and they can splash and "contaminate" other samples.
9. Rinse the sample from the walls of the beaker with 1 ml of conc. HNO_3
10. Repeat step 9 once more.
11. Rinse the beaker with 4 ml of 8M HNO_3; evaporate to <0.5 ml, and let cool.
12. Bring up sample with 2 ml of 5%HNO_3 and 0.08 %HF.
13. Filter the final solution using Acrodisc 0.2 µm HT Tuffryn membrane syringe filters (Gelman Laboratory) into 1-2ml screw cap vials.
14. Pipette 120ul of sample into an ICPMS vial.
15. Add 880ul of 2.2% HNO_3 to get to 1ml. The final concentration of the sample that is to be run on the ICPMS is now: **2.5% HNO_3/ 0.01% HF**.
16. Store remaining sample in the sealed vials for archive.

❖ Note: Run some (at least 3) standards with the same amount of Th-229 and Th-230 as control.

4 REFERENCES

Benitez-Nelson, C., Buesseler, K.O., Rutgers van der Loeff, M., Andrews, J., Ball, L., Crossin, G., Charette, M.A., 2001. Testing a new small-volume technique for determining ^{234}Th in seawater. J. Radioanal. Nucl. Chem. 248, 795–799. doi:10.1023/A:1010621618652

Pike, S.M., Buesseler, K.O., Andrews, J., Savoye, N., 2005. Quantification of Th-234 recovery in small volume seawater samples by inductively coupled plasma-mass spectrometry. J. Radioanal. Nucl. Chem. 263, 355–360.

Puigcorbé, V., Roca-Martí, M., Masqué, P., Benitez-Nelson, C.R., Rutgers v. d. Loeff, M., Laglera, L.M., Bracher, A., Cheah, W., Strass, V.H., Hoppema, M., Santos-Echeandía, J., Hunt, B.P. V, Pakhomov, E.A., Klaas, C., 2017. Particulate organic carbon export across the Antarctic Circumpolar Current at 10°E: Differences between north and south of the Antarctic Polar Front. Deep Sea Res. Part II Top. Stud. Oceanogr. 138, 86–101. doi:https://doi.org/10.1016/j.dsr2.2016.05.016

5 FLOW CHART

SAMPLE PROCESSING AT SEA
4 L of seawater

Acid nitric (5 mL) and ^{230}Th addition

- ❖ Shake vigorously

Equilibration

- ❖ Allow to equilibrate for at least 8h

Ammonia addition (5-6 mL)

- ❖ Check pH to be 8.5

Addition of $KMnO_4$ and $MnCl_2$ (50 µL each)

- ❖ Shake vigorously
- ❖ Wait at least 8h prior filtration

FILTRATION:
Using 25 mm diameter QMA filters and Th-filtration system with Eyela
Dry filters overnight at 50°C

- ❖ Particulate samples processing starts at this step

COUNTING:
Prepare filters for beta counting with 1 layer of plastic film and two layers or common aluminum foil
Count samples until uncertainty is <3% on 60 min cycles
Recount the samples >6months later

PREPARATION FOR RECOVERY MEASURMENTS:
Digest the filter after addition of ^{229}Th
Evaporate and reconstruct solution following procedure (see section 7)

- ❖ This does not apply to particulate samples

6 IMAGES

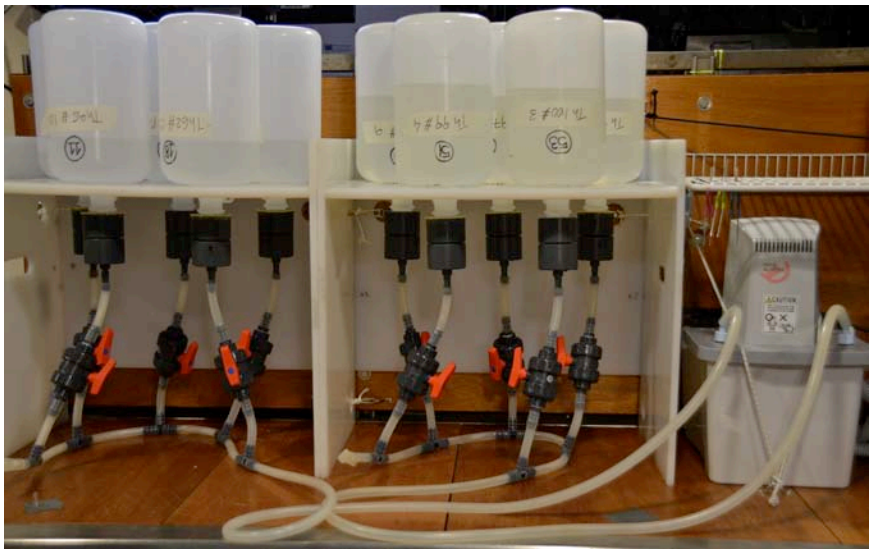

Image 1: Filtration system, with the 4 L bottles containing the sample after being precipitated with MnO_2

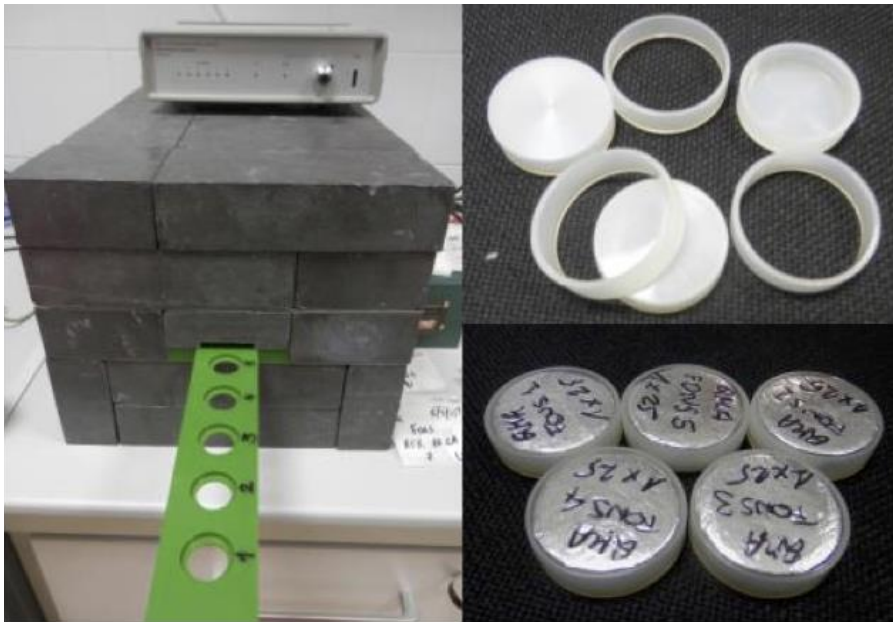

Image 2: Riso beta counter with a led shield and the sample support (green) (left image). Beta holders to place the samples in the detector (top right image) and samples prepared to be measured in the beta counter (low right image)