

RiO5 METHOD (30)

OCG-MEL-XMU

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^{224}Ra and ^{228}Th — MnO_2 co-precipitation—RaDeCC counting—Sediment sample and pore water samples

Disclaimer

It is the responsibility of each analyst to follow established practices when handling and examining the samples referenced in this Rio5 Cookbook. Although the methods may have been tested by each laboratory identified as the source, each user must perform a validation procedure to ensure the validity of their results. Woods Hole Oceanographic Institution, its officers, directors and employees are not responsible for any of the data or the results that may be achieved from using the information in the Rio5 Cookbook and disclaim all liability for the same.

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1 SCOPE

This method specifies the minimum requirements and laboratory methods for measuring ^{224}Ra and ^{228}Th in sediment core and pore water samples via MnO_2 co-precipitation–RaDeCC counting.

Sediment cores are collected with polycarbonate columns and sectioned based on the research. Pre-treatment on each sediment slice must be completed as soon as possible on board or at laboratory. The sediment slurry is filtrated using a special filtration unit and the sediment plate is finally measured by RaDeCCs within 12 h after sampling. The second measurement should be done in the same RaDeCCs after 8~10 days. Isotope ingrowth and decay corrections are applied to calculate the ^{224}Ra and ^{228}Th activities (see Cai et al., 2012).

2 EQUIPMENT CHEMICAL REAGENTS

2.1 Equipment

- 250 ml Teflon beaker
- 142 mm GF/F filter (nominal pore size: 0.7 μm)
- Vacuum pump
- 142 mm membrane filtration unit
- 1 ml pipette
- 1 ml pipette tips
- 150 mm petri-dish
- Scale or balance
- Waterproof marker
- Sample chamber for RaDeCC counting
- High-pure Helium
- Radium decayed coincidence counting system (the RaDeCC system)
- Rhizon samplers for porewater

2.2 Tracers

- ^{232}U - ^{228}Th solute (in secular equilibrium) or ^{232}Th solute (<50 dpm ml^{-1} in Th activity)

2.3 Chemical reagents

- KMnO_4 solution (3.0 g l^{-1})

- MnCl_2 solution (8.0 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ l⁻¹)
- Concentrated $\text{NH}_3 \cdot \text{H}_2\text{O}$

2.4 Solutions

Ra-free water.

3 PROCEDURE

3.1 Preparation and measurement of sediment

1. Take sediment core from a box corer. Record date and time.
2. Slice the sediment core into 1-cm thick slabs immediately after sample collection.
3. Place the sediment into a pre-labelled 250 ml Teflon beaker, and add 150 ml Milli-Q water to the sediment slabs to form a slurry.
4. Add 5–10 drops of concentrated $\text{NH}_3 \cdot \text{H}_2\text{O}$ to the slurry to adjust the pH to 8.0–9.0.
5. Add 1.0 ml of KMnO_4 solution (3.0 g l⁻¹) and 1.0 ml of MnCl_2 solution (8.0 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ l⁻¹) to form a suspension of MnO_2 . (The suspension of MnO_2 serves to absorb dissolved ²²⁴Ra in interstitial water).
6. Sediment slurry together with the MnO_2 precipitate is filtered onto a pre-weighed 142-mm GFF filter. Note that while filtering, the slurry is vigorously stirred to ensure that sediment particles are evenly distributed onto the filter.
7. The filtration is terminated when droplets of water cease to issue from the filter.
8. Place the sample into the sample chamber for RaDeCC counting and dry the sample for using an air stream.
9. Adjust the weight ratio of water/sediment to 0.4–0.5, and record the weight of the sample.
10. Connect the sample chamber to RaDeCC system.
11. Circulated Helium through the sediment sample and the counting cell at a rate of 12–15 L/min for 1 min.
12. Count the sample for 4–6 h or until > 2000 counts in the 220 channel.
13. After measurement, remove the sample from the sample chamber and store in the 150 mm Petri-dish at 4 °C until the second and the third measurement. During storage, the water content of the sample should be maintained in the vicinity of the in-situ level by periodically spraying Milli-Q water onto the sediment surfaces.
14. Re-measure the sample for two times 8–10 days later, and ~25 days later. (Note that these two measurements are performed to check the consistency of ²²⁸Th measurement.) For these two measurements, the measurement parameters (like water content, counting time, etc.) should be controlled to be consistent with the first measurement.

15. The final ^{224}Ra and ^{228}Th activities at the sampling time are calculated from the first and the second measurements or from the first and third time. Chance coincidence and contributions from the 219 channel should be corrected for the calculation of the final activities.

Note: 1. The measurement should be performed within 12 h after sampling.

2. The overall efficiency is determined by measuring a set of standards in which known activities of ^{224}Ra and ^{228}Th are absorbed onto an unknown sediment sample.

3.2 Preparation and measurement of pore water

1. Pore water sample is extracted by inserting an array of Rhizon samplers into the sediment.
 2. Approximately 15–20 ml of pore water was retrieved at discrete depths in the sediment.
 3. The pore water sample is transferred into a 250 ml Teflon beaker and 150 ml of Milli-Q water is added.
 4. Adjust the pH to 8.0–9.0 with concentrated $\text{NH}_3\cdot\text{H}_2\text{O}$.
 5. Add 5.0 ml of KMnO_4 solution (3.0 g l^{-1}) and 1.0 ml of MnCl_2 solution ($8.0 \text{ g MnCl}_2\cdot 4\text{H}_2\text{O l}^{-1}$) to form a suspension of MnO_2 .
 6. Filter the MnO_2 suspension onto a 142 mm GFF filter.
 7. Adjust the weight ratio of water/sediment to 0.4–0.5, and record the weight of the sample.
 8. Place the sample into the sample chamber for RaDeCC counting and connect the sample chamber to RaDeCC system.
 9. Circulated Helium through the sediment sample and the counting cell at a rate of 12–15 L/min for 1 min.
 10. Count the sample for >10 h.
 11. About 25 d later, a second measurement is performed to determine the background count rate of the sample due to ^{228}Th .
1. Note: The counting efficiency of ^{224}Ra is calibrated with a ^{232}U – ^{228}Th standard that was prepared in the same manner as the sample.

4 REFERENCES

Cai, P., Shi, X., Moore, W. S. & Dai, M. (2012), Measurement of ^{224}Ra : ^{228}Th disequilibrium in coastal sediments using a delayed coincidence counter. *Mar. Chem.* 138-139, 1–6

5 IMAGES

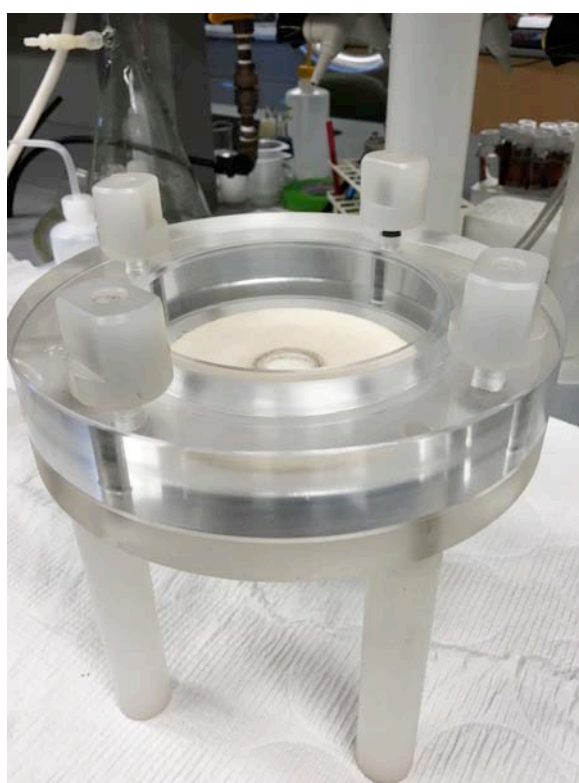
Not mandatory, but recommended. No specific format needed.



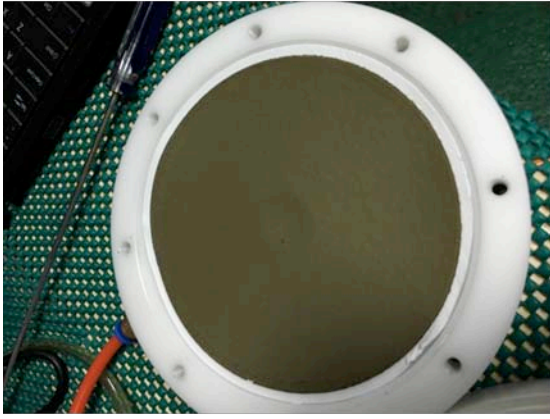
Picture 1 The RaDeCC systems



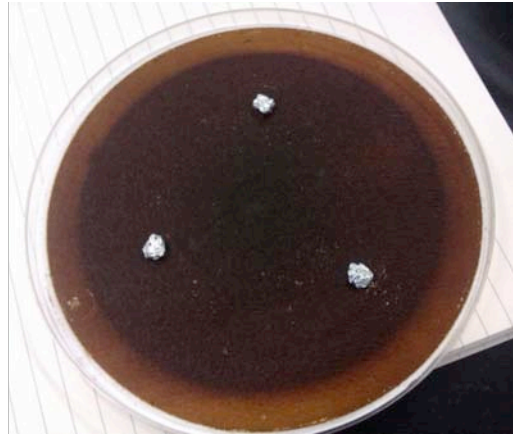
Picture 2 The Rhizon samples



Picture 3 The special filtration unit for sediment



Picture 4 The sediment plate in chamber



Picture 5 Porewater Ra sample in MnO_2 co-precipitation