

## RiO5 METHOD (21)

COE-XMU

Min Chen

College of Ocean and Earth Sciences, Xiamen University

mchen@xmu.edu.cn

Contributors: Renmin Jia (1012941342@qq.com)

### **$^{226}\text{Ra}$ and $^{228}\text{Ra}$ —Manganese-oxide Impregnated Acrylic Fiber— Seawater sample**

Seawater sample preparation for radium isotopes ( $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ )

#### **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.

*Insert here links to other complementary documents to this method available in the RIO web page:*

## Table of Contents

|          |   |          |
|----------|---|----------|
| <b>1</b> | <b>SCOPE</b>                                      | <b>1</b> |
| <b>2</b> | <b>EQUIPMENT CHEMICAL REAGENTS</b>                | <b>1</b> |
| 2.1      | EQUIPMENT   | 1        |
| 2.2      | TRACERS   | 1        |
| 2.3      | CHEMICAL REAGENTS                                 | 1        |
| 2.4      | SOLUTIONS   | 2        |
| <b>3</b> | <b>PROCEDURE</b>                                  | <b>2</b> |
| 3.1      | PRE-CONCENTRATION OF RADIUM ISOTOPES              | 2        |
| 3.2      | MEASUREMENT OF $^{226}\text{Ra}$                  | 3        |
| 3.3      | SEPARATION AND PURIFICATION OF $^{228}\text{Ra}$  | 3        |
| 3.4      | SEPARATION AND PURIFICATION OF $^{228}\text{Ac}$  | 3        |
| 3.5      | MEASUREMENT OF $^{228}\text{Ac}$                  | 4        |
| 3.6      | CHEMICAL YIELD DETERMINATION OF $^{228}\text{Ac}$ | 4        |
| <b>4</b> | <b>REFERENCES</b>                                 | <b>5</b> |
| <b>5</b> | <b>FLOW CHART</b>                                 | <b>5</b> |

## 1 SCOPE

This method specifies the minimum requirements and laboratory methods for measuring  $^{226}\text{Ra}$  in seawater samples using alpha-spectrometry via its daughter  $^{222}\text{Rn}$ , and  $^{228}\text{Ra}$  using beta-counter via its daughter  $^{228}\text{Ac}$ .

Samples are concentrated by  $\text{MnO}_2$ -fibers with flow rate less than 0.5 L/min. Then the  $\text{MnO}_2$ -fibers are sealed in valve bag and stored for the determination of  $^{226}\text{Ra}$ . After the analysis of  $^{226}\text{Ra}$ , Ra isotopes on  $\text{MnO}_2$ -fibers are eluted by 2 M HCl solution and co-precipitated for the determination of  $^{228}\text{Ra}$ .

## 2 EQUIPMENT CHEMICAL REAGENTS

### 2.1 Equipment

- $\text{MnO}_2$ -fiber

Add ~50 g acrylic fibre and 30 mL concentrated sulfuric acid in 3 L 0.5 M  $\text{KMnO}_4$  solution, heat to boiling and keep 1-2 h. During the boiling period, stir to keep a sufficient contact of fibre with  $\text{KMnO}_4$ . After the reaction, the fibre should be totally atropurpureus. Cool down and wash it with ultrapure water till the leaner is colourless (almost 10 times). After washing, the loose  $\text{MnO}_2$  particle on fibre is removed. The colour of  $\text{MnO}_2$ -fiber should be dark.

### 2.2 Tracers

- Standard tracer:  $^{232}\text{Th}$  standard solution,  $31.48 \pm 0.62$  dpm/g activity. Used for the determination of recovery.

### 2.3 Chemical reagents

The crystal water of chemical reagents are not shown in the chemical formula

- Hydrochloric acid, HCl, analytically pure
- Nitric acid,  $\text{HNO}_3$ , analytically pure
- Sulfuric acid,  $\text{H}_2\text{SO}_4$ , analytically pure
- Acetic acid,  $\text{CH}_3\text{COOH}$ , analytically pure
- Chloroacetic acid,  $\text{CH}_2\text{ClCOOH}$ , analytically pure
- Barium nitrate,  $\text{Ba}(\text{NO}_3)_2$ , analytically pure
- Lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ , analytically pure
- Sodium sulfate,  $\text{Na}_2\text{SO}_4$ , analytically pure
- Cerium chloride,  $\text{CeCl}_3$ , analytically pure
- Sodium acetate,  $\text{CH}_3\text{COONa}$ , analytically pure
- Ammonium oxalate,  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , analytically pure

- Hydroxylamine hydrochloride,  $\text{HONH}_3\text{Cl}$ , analytically pure
- Sodium hydroxide,  $\text{NaOH}$ , analytically pure
- EDTA-2Na,  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8$ , analytically pure
- DTPA,  $\text{C}_{14}\text{H}_{23}\text{N}_3\text{O}_{10}$ , analytically pure
- D2EHPA ( $\text{P}_{204}$ ),  $\text{C}_{16}\text{H}_{35}\text{O}_4\text{P}$ , analytically pure
- n-Heptane,  $\text{C}_7\text{H}_{16}$ , analytically pure
- Ammonium citrate dibasic,  $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_7$ , analytically pure

## 2.4 Solutions

The solutions below are made with Milli-Q water matrix if not special mentioned

- HCl solution, 2 M/L
- $\text{HONH}_3\text{Cl}$  saturated solution in indoor temperature
- $\text{Ba}(\text{NO}_3)_2$  solution, 12 mg Ba/mL
- $\text{Pb}(\text{NO}_3)_2$  solution, 80 mg Pb/mL
- 1:1  $\text{H}_2\text{SO}_4$  solution
- EDTA-2Na solution, 150 g EDTA-2Na with 45g NaOH in 1000 mL
- DTPA solution, 134 g DTPA with 64 g NaOH in 1000 mL
- $\text{Na}_2\text{SO}_4$  solution, 200 g  $\text{Na}_2\text{SO}_4$  in 1000 mL
- 36%  $\text{CH}_3\text{COOH}$  solution
- $\text{CH}_2\text{ClCOOH}$  solution, 2 M /L
- $\text{P}_{204}$  solution, 150 mL  $\text{P}_{204}$  with 850 mL n-Heptane, washed by the mix solution of 2 M /L ammonium citrate dibasic solution and 0.90 g/mL ammonium hydroxide (volume 1:1) twice, 200 mL each time, and then washed by 4 M /L  $\text{HNO}_3$  twice, 200 mL each time, finally washed by 200 mL Milli-Q water.
- Mix solution for actinium cleaning, 100 g  $\text{CH}_2\text{ClCOOH}$ , 10 g DTPA and 33 g NaOH in 1000 mL (pH should be 3.0)
- $\text{CH}_3\text{COONa}$  solution, 300 g  $\text{CH}_3\text{COONa}$  in 1000 mL
- $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution, 28.4 g  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  in 1000 mL
- $\text{CeCl}_3$  solution, 5 mg Ce/mL

## 3 PROCEDURE

### 3.1 Pre-concentration of radium isotopes

120 L seawater flows through a column (3×20 cm) packed with ~12 g manganese-oxide impregnated acrylic fiber (i.e.  $\text{MnO}_2$ -fiber), the flow rate is less than 0.5 L/min to assure quantitative adsorption of Ra on fiber.

### 3.2 Measurement of $^{226}\text{Ra}$

$^{226}\text{Ra}$  activity is measured by its daughter  $^{222}\text{Rn}$  emanation method.

1.  $\text{MnO}_2$ -fiber is taken out from the column, and the residual water is removed.
2. The fiber is filled into a diffusion tube, sealed and vacuumized.
3. After 5-7 days,  $^{222}\text{Rn}$  reaches a high level; a vacuumed scintillation counting cell was sequentially connected to the diffusion tube.
4.  $^{222}\text{Rn}$  is emanated from  $\text{MnO}_2$ -fiber in the ZnS counting cell, and the cell is sealed for 3 hours,  $^{222}\text{Rn}$  will be equilibrium with its daughters.
5. Activity of  $^{222}\text{Rn}$  is measured by an Rn-Th analyzer.

### 3.3 Separation and purification of $^{228}\text{Ra}$

1. After measurement of  $^{226}\text{Ra}$ ,  $\text{MnO}_2$ -fiber containing Ra isotopes is unwound and heated in 300 mL 2 M HCl plus 2 mL concentrated  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution until the color of the fiber turned whitish, and collect the solution.
2. Repeating the above step and combining the solution.
3. Adding 1 mL  $\text{Ba}(\text{NO}_3)_2$  (12 mg  $\text{Ba}^{2+}/\text{mL}$ ) and 5 mL  $\text{Pb}(\text{NO}_3)_2$  (80 mg  $\text{Pb}^{2+}/\text{mL}$ ) carriers with stirring.
4. Adding 15 mL 9 M  $\text{H}_2\text{SO}_4$  with stirring to form  $\text{Ba}(\text{Pb})\text{SO}_4$  precipitate, and leave for more than 12 hours.
5. Siphoning the overlying solution and leave the bottom precipitate.
6. Centrifuging the precipitate at 2500 r/min for 2 min and decanting the solution.
7. Adding Milli-Q water to wash the precipitate, and separating it again by centrifugation.
8. Adding 8 mL EDTA and 10-15 mL Milli-Q water, then warm the solution to dissolve the precipitate.
9. Adding 9 M  $\text{H}_2\text{SO}_4$  drop by drop to reach the pH value of 3.0-3.5, and  $\text{BaSO}_4$  precipitates. Recording the time of  $^{228}\text{Ac}$  production.
10. The precipitate is heated at  $100^\circ\text{C}$  for 5 min to form large-size particles, and then separate the precipitate by centrifugation (2500 r/min for 2 min).
11. Washing the precipitate using Milli-Q water again, and separate the purified precipitate.

### 3.4 Separation and purification of $^{228}\text{Ac}$

1. Adding 10 mL DTPA to the purified  $\text{BaSO}_4$  precipitate and heated at  $100^\circ\text{C}$  to dissolve the precipitate, and then leave it for more than 48 hours to let  $^{228}\text{Ac}$  reach an equilibrium status with  $^{228}\text{Ra}$ .

2. Adding Milli-Q water to a volume of 30 mL, and then add 1 mL Na<sub>2</sub>SO<sub>4</sub> (20%) and 2.2 mL HAc (36%), recording the time of BaSO<sub>4</sub> formation, i.e. the time of separation of <sup>228</sup>Ac from <sup>228</sup>Ra. Separating the precipitate by centrifugation.
3. Adding 10 mL P<sub>204</sub> solution and 10 mL actinium-washing solution into a separating funnel (75 mL), shocking for 2 min to clean P<sub>204</sub> solution, and then discard the actinium-washing solution.
4. Putting the solution containing <sup>228</sup>Ac after the separation of <sup>228</sup>Ac from <sup>228</sup>Ra into the prepared separating funnel.
5. Using 10 mL Milli-Q water to wash the BaSO<sub>4</sub> precipitate and transfer the water into the above separating funnel.
6. Adding 5 mL monochloroacetic acid (2 M) to the separating funnel and shocking for 2 min, and then putting the water solution (i.e. the lower solution) into the other prepared separating funnel with 5 mL cleaned P<sub>204</sub> solution.
7. Shocking the second separating funnel for 2 min, and then discard the water solution, combining the organic phase (i.e. P<sub>204</sub> solution) with that in the first separating funnel.
8. Adding 10 mL actinium-washing solution into the separating funnel, shocking for 2 min, and discard the water phase (i.e. actinium-washing solution).
9. Adding 10 mL HNO<sub>3</sub> (3 M) into the separating funnel, shocking for 2 min, and collecting the HNO<sub>3</sub> phase into a 50 mL beaker.
10. Using 5 mL HNO<sub>3</sub> (3 M) to extract <sup>228</sup>Ac resided in P<sub>204</sub> solution again, and combining the HNO<sub>3</sub> phase with the first collected HNO<sub>3</sub>.
11. Adding 6 mL NaAc (30%) and 1 mL Ce(NO<sub>3</sub>)<sub>3</sub> (5 mg/mL) to the HNO<sub>3</sub> solution, warm the solution, and then drop by drop add 5 mL (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> to form Ce<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> precipitate, quickly cool the solution down in ice-water.
12. Filtering the precipitate onto a piece of ashless filter with very slow flow velocity (i.e. drop by drop), and wash the precipitate with a little Milli-Q water.
13. Drying the filter and precipitate using an infrared lamp, and store it for measuring.

### 3.5 Measurement of <sup>228</sup>Ac

<sup>228</sup>Ac is counted using the low-background beta-counter.

### 3.6 Chemical yield determination of <sup>228</sup>Ac

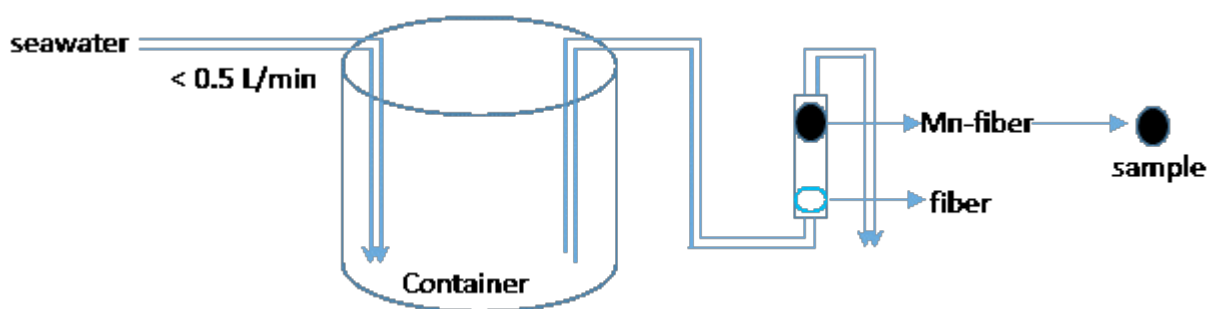
Using the same protocols of separation and purification of <sup>228</sup>Ra and <sup>228</sup>Ac to measure the activity of calibrated <sup>228</sup>Ra sample, and calculate the chemical recovery according to originally added <sup>228</sup>Ra and recovered <sup>228</sup>Ra.

## 4 REFERENCES

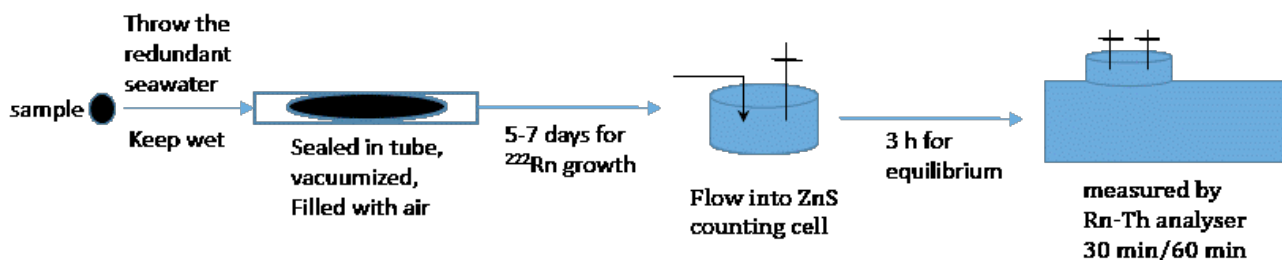
Xie, Y., Huang, Y., Shi, W., Qiu, Y. (1994). Simultaneous concentration and determination of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  in natural waters. *Journal of Xiamen University*, 33(sup.), 86-90.(in Chinese)

## 5 FLOW CHART

Flow chart of sampling.



Flow chart of  $^{226}\text{Ra}$  measurement



Flow chart of  $^{228}\text{Ra}$  measurement.

