1. Scope

This procedure describes a method for the separation and measurement of Ra-226 and Ra-228 in water. The method is an update of Eichrom method RAW04 V1.0.

2. Summary

An aliquot of the sample is measured into a beaker and the pH of solution is adjusted to 6-7. The sample solution is passed through a MnO_2-PAN Resin column, radium and barium are sorbed on the MnO_2-PAN. Ra and Ba are then eluted with 5M HCl. In case of Ra-228 determination, the solution is held for >30 hours for Ac-228 ingrowth. The solution is loaded on DGA,N cartridge, Ac-228 and other alpha emitters are retained, while Ra and Ba pass through the cartridge. Ac-228 is eluted with 2M HCl and counted by beta spectrometry. Ra-226 and Ba-133 are collected and micro-precipitated with barium sulphate. The precipitate is collected on a Resolve® filter. Ba-133 is counted using a gamma counter while Ra-226 is counted via alpha spectrometry. Other alpha emitting isotopes of radium may be measured using this method, but care must be exercised to account for their short half-lives.

3. Significance of use

This method for measurement of Ra-226 and Ra-228 in water samples uses MnO_2-PAN Resin as a preconcentrate of radium from the sample. MnO_2-PAN Resin can better handle matrices with high levels of calcium than standard cation exchange resin.

The DGA,N Resin can be loaded from higher concentration acid solutions and allows for a better separation of actinium-228 from other actinide elements than LN Resin.

4. Interferences

Other alpha emitter than Ra isotopes are retained on the DGA,N cartridge while Ra passes.

Other beta emitters such as Bi-210, Y-90, Th-234,... are retained on the DGA,N resin, while eluting Ac from the resin.

5. Apparatus

- Alpha spectrometry system
- Low background LSC or gas proportional counter
- Analytical balance - 0.0001 g sensitivity
- Centrifuge
- Centrifuge tubes

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- Cartridge reservoirs-10 mL Cartridge Reservoir, part number AC-25-RV10 or 20 mL Cartridge Reservoir, part number AC-25-RV20
- Column – 20 mL column, part number AC-20E-20M
- Filter – 0.45 micron
- Fume hood
- Funnel- 250 mL funnel, part number AC-20X-20M
- Hotplate
- NaI detector or gamma spectrometer
- pH meter
- LSC vials, PE or glass, e.g. part numbers ME-VIA-PV1 or ME-VIA-GV1
- Resolve® Filter- 0.1 micron 25 mm polypropylene, part number RF-100-25PP01
- Resolve® filter filtration unit - part number RF-DF25-25PP01
- Stirring rods – glass
- Stainless steels discs - part number AC-D100-IN25
- Tips, white inner- part number AC-1000-TUBE-PE
- Tips, yellow outer- part number AC-1000-OT
- Tweezers
- Vacuum Box Liner- part number AC-24-LINER or AC-12-LINER
- Vacuum Box System- part number AC-24-BOX or AC-12-BOX
- Luer-lock two-way valves – part number AC-12-VALVE
- Vortex mixer

6. Reagents

a. Reagents

Unless otherwise indicated, all references to water should be understood to mean deionized distilled water. All reagents should be at least of analytical grade.

- Barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$)
- Ba-133 tracer (~3000 dpm/mL)
- Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$)
- DGA,N Resin - prepacked cartridge, 50-100 µm particle size resin, part number DN-R50-S
- Ethanol pure
- Isopropanol
- Hydrochloric acid (12 M) - concentrated hydrohloric acid
- MnO2-PAN Resin-100 - 300 µm particle size
- Ammonium sulfate - $(NH_4)_2SO_4$
- LSC option only - liquid scintillation cocktail – e.g. part numbers ME-COC-PSHC or ME-COC-GS1

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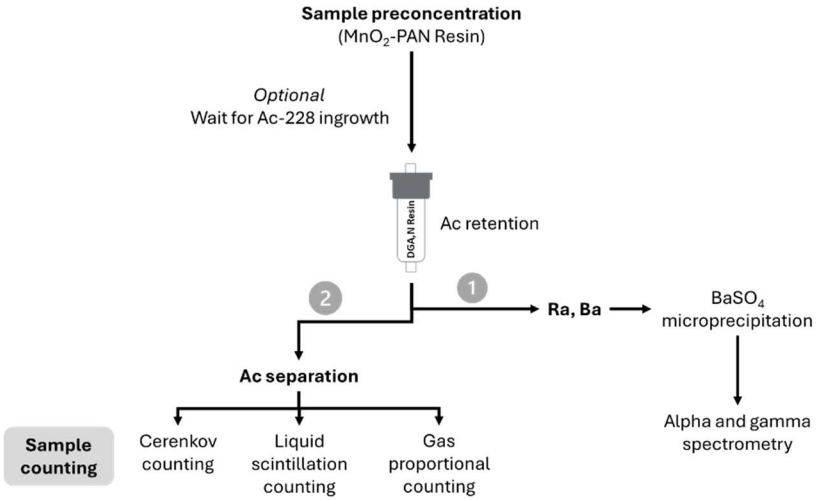
b. Preparation of solutions

- Barium carrier (0.5 mg Ba/mL)- Dissolve 225 mg reagent grade barium chloride dihydrate in water and dilute to 250 mL with water.
- Cerium carrier (1 mg Ce/mL)- Dissolve 310 mg cerium (III) nitrate hexahydrate in 50 mL water and dilute to 100 mL with water.
- Ethanol, 80%- Add 80 mL ethanol to 20 mL water.
- 5 M HCl: Add 417 mL of concentrated hydrochloric acid to 500 mL of water and dilute to 1 liter with water.
- 2 M HCl: Add 167 mL of concentrated hydrochloric acid to 500 mL of water and dilute to 1 liter with water.

7. Procedure

a. Synopsis



b. Sample preparation

Water Sample Preparation and Pre-concentration of Ra and Ba on MnO2-PAN Resin

1. Using a pH meter, adjust pH of sample to pH 6-7 with HCl or NaOH, if necessary.
2. If required, filter the sample through a 0.45 micron filter.
3. Aliquot up to 1 liter into an appropriate size beaker. Add an appropriate amount of Ba-133 (approx. 1000 CPM ~ 17 Bq).
4. Slurry 2 g of MnO_2-PAN Resin with water and pour the resin into column.
5. Precondition the column by passing 10 mL of water through the column.
6. Pass the sample through the column using gravity flow or vacuum assistance. Flow rates up to 10 ml/min have been evaluated successfully.
7. Rinse the sample beaker with 10 mL of water. Pour rinse through the column.
8. Properly dispose of the feed and rinse.

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9. Elute Ra and Ba with 15 mL of 5M HCl solution into a centrifuge tube or vial. The elution should be performed at a flow rate of 2 mL/min.
10. Cap sample tubes and hold the radium/barium fraction for >30 hours (only in case Ra-228 needs to be determined).

c. Radiochemical separation

Ac-228 Separation Using DGA,N Resin

1. Insert the vacuum box liner into the vacuum box and fit the lid onto the vacuum box.
2. Place the yellow outer tips into all openings of the lid of the vacuum box. Fit a white inner tip into each yellow tip.
3. For each sample solution, fit in the DGA,N cartridge onto the inner white tip.

⚠ **REMARK: Optionally luer-lock two-way valves can be placed between cartridges and white inner tips allowing for individual flow rate adjustment.**

4. Attach reservoirs to the top end of the DGA,N cartridge.
5. Connect the vacuum pump to the box. Turn the vacuum pump on and ensure proper fitting of the lid.

⚠ **IMPORTANT: The unused openings on the vacuum box should be sealed. The blue manifold plugs supplied with the vacuum box system can be used to plug unused white tips to achieve good seal during the separation.**

6. Add 5 mL of 5M HCl to the reservoir and allow the solution drain.
7. Insert the tube rack into the vacuum box with clean labeled tubes beneath each cartridge. Fit the lid onto the vacuum box. Adjust the vacuum pressure to achieve a flow rate of 1 ml per minute.

⚠ **IMPORTANT: The flow rates for load and strip solutions should be 1 mL/min. For the rinse solutions 3 mL/min can be used, unless specified otherwise in the step.**

8. Add 100 µL of Ce-carrier (Ac-228 yield determination) to the solution from step 10. Shake.
9. Carefully transfer the sample solution to the reservoir of the cartridge. Collect the eluant for Ra-226 and Ba-133.
10. Rinse sample tube with 5 mL of 5M HCl and add to the cartridge after the feed has passed through. Record the time and date of this rinse. This will be the separation of Ac-228 from Ra-228. Collect the eluant for Ra-226 and Ba-133.
11. Rinse the cartridge with 5 mL of 5M HCl and discard the eluant.
12. Rinse the cartridge with an additional 5 mL of 5M HCl and discard the eluant.
13. Place a clean, labelled container under each cartridge. Elute Ac-228 with 15 mL of 2M HCl. Withdraw aliquot for ICP-MS measurement. Set aside for counting sample preparation (d. sample measurement).
14. Evaporate eluants from steps 9 and 10 to about 2 to 3 mL volume.

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15. Transfer the solution to a clean, labeled container, rinse beaker with 7-8 mL of water and transfer to the tube. Count the container for Ba-133 gamma spectrometer.

⚠ **REMARK: Alternatively the gamma spectrometric measurement can be performed on the alpha spectrometry counting sample.**

d. Sample measurement

Ac-228 counting

Cerenkov counting: Count vial in LSC counter without addition of LSC cocktail for a sufficiently long time to obtain requested detection limits.

LSC counting: Evaporate sample to near dryness. Redissolve in 10 mL 0.1M HNO_3 and add liquid scintillation cocktail, cap and shake. Count vial in LSC counter for a sufficiently long time to obtain requested detection limits.

Gas proportional counting. Perform micro-precipitation following method SPA01. Filter micro-precipitated sample through Resolve® Filter filtration unit previously rinsed with 80% EtOH and water. Rinse with water, followed by ethanol. Dry filter, glue on stainless steel disc and count on GPC.

Ra-226 counting: Count sample on alpha spectrometer for sufficiently long time to obtain requested detection limits.

⚠ **REMARK: The alpha spectrometry counting sample can be counted on a gamma spectrometer after the alpha spectrometric measurement to determine the chemical yield via Ba-133.**

8. References

1) Eichrom method RAW04: “Radium-226/228 in Water (MnO2 Resin & DGA Resin Method)”, V 1.0
2) Horwitz, E. P., et al., “Novel Extraction Chromatographic Resins Based on Tetraalkyldiglycolamides: Characterization and Potential Applications”, Solvent Extraction and Ion Exchange., 23, 219 (2005)
3) Moon, D.S., W.C. Burnett, S. Nour, P. Horwitz and A. Bond, “Precontration of radium isotopes from natural waters using MnO2 resin,” Applied Radiation and Isotopes, Vol. 59, pp. 225-262 (2003).
4) S. L. Maxwell, III, “Ra in Water using MnO2 Resin: Update” Presented at Eichrom North American Users’ Group Workshop, Oak Ridge, TN, May 2005, http://www.eichrom.com/radiochem/meetings/2005/oakridge/powerpoint/2 Sherrod Radium.ppt
5) Eichrom method SPA01: “Cerium Fluoride Microprecipitation for Alpha Spectrometry Source Preparation of Actinides”, V1.1

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