RADIUM-226/228 IN WATER

(MnO_2 RESIN AND DGA RESIN)

1. SCOPE

1.1. This is a method for the separation and measurement of radium-226 and radium-228 in water. This method is meant to be used in conjunction with Eichrom Method SPA01 for the rare earth fluoride micro precipitation preparation of sources for Ac-228(Ra-228) analysis by gas flow proportional counting.

1.2. This method does not address all aspects of safety, quality control, calibration or instrument set-up. However, enough detail is given for a trained radiochemist to achieve accurate and precise results for the analysis of the analyte(s) from the appropriate matrix, when incorporating the appropriate agency or laboratory safety, quality and laboratory control standards.

2. SUMMARY OF METHOD

2.1. An aliquot of the sample is measured into a beaker and the pH of solution is adjusted to 6-7.

2.2. The sample solution is passed through a MnO_2 Resin column. Radium and barium are retained by the MnO_2 resin column. Ra and Ba are eluted by dissolving the MnO_2 with 5M HCl/1.5% H_2O_2.

2.3. The Ra/Ba solution is held for >30 hours for ^{228}Ac ingrowth.

2.4. The Ra/Ba solution with ingrown ^{228}Ac is loaded onto a DGA cartridge. ^{228}Ac is retained by the DGA Resin, while Ra and Ba pass through.

2.5. ^{228}Ac is eluted with 2M HCl and is prepared for measurement by gas flow proportional counting using rare earth fluoride precipitation onto Eichrom Resolve® Filters (Eichrom Method SPA01).

2.6. The Ra/Ba fraction is prepared for alpha spectrometry (^{226}Ra) and gamma counting (^{133}Ba) using a barium sulfate precipitation onto an Eichrom Resolve® filter.

2.7. ^{133}Ba is counted using by gamma spectrometry, while ^{226}Ra 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

3.1. This method for measurement of ^{226}Ra and ^{228}Ra in water samples uses MnO_2 Resin to preconcentrate radium from the sample. MnO_2 Resin can better handle matrices with high levels of calcium than standard cation exchange resin.

3.2. The DGA Resin can be loaded from higher concentration acid solutions and allows for a better separation of ^{228}Ac from other actinide elements than Eichrom's Ln Resin.

4. INTERFERENCES

4.1. Potential beta emitters such as bismuth, yttrium, thorium and other actinides would be retained on the DGA resin, while eluting actinium from the resin.

4.2. Interferences from most other radioactive rare earth elements are eliminated by separating Ra, waiting for ^{228}Ac ingrowth, and stripping ^{228}Ac from the DGA resin with 2M HCl acid.

5. APPARATUS

- Alpha spectrometry system
- Analytical balance- 0.0001 g sensitivity
- Cartridge reservoirs-10mL, Eichrom Part: AR-25-RV10 or 20mL, Eichrom Part: AR-25-RV20
- Centrifuge tubes, 50mL
- Centrifuge, with rotor and carriers for 50mL and 250mL tubes
- Column, 20 mL column, Eichrom Part: AR-20E-20M
- Fume hood
- Funnel, 250 mL funnel, Eichrom Part: AR-20X-20M
- Gamma Spectrometry System (for ^{133}Ba measurement)
- Hotplate
- Low background gas flow proportional counter
- pH meter
- Stir rods, glass
- Vacuum box inner support tubes, Eichrom Part: AR-1000-TUBE-PE
- Vacuum box liner- Eichrom Part: AR-24-LINER or AR-12-LINER
- Vacuum box system- Eichrom Part: AR-24-BOX or AR-12-BOX

- Vacuum box yellow outer tips, Eichrom Part: AR-1000-OT
- Vortex mixer

6. REAGENTS

Note: Analytical grade or ACS grade reagents are recommended.

Ammonium sulfate, $(NH_4)_2SO_4$
^{133}*Ba tracer* (~3000 dpm/mL)
Barium chloride dihydrate, $BaCl_2 \cdot 2H_2O$
Deionized water, all reagents are prepared with deionized water
DGA® resin, normal, 2mL prepacked cartridge, 50-100µm, Eichrom Part DN-R50-S
Hydrochloric acid (37%), concentrated HCl
Hydrofluoric acid (49%), concentrated HF
*Hydrogen peroxide (30%), c*oncentrated H_2O_2
MnO_2® *resin,* 75-150 µm, Eichrom Part MN-B100-A
Sodium hydroxide, NaOH

6.1. *Barium carrier (0.75 mg/ml)*- Dissolve 338mg reagent grade barium chloride, dihydrate in water and dilute to 250 mL with water.

6.2. *Hydrochloric acid solution (5M)*- Add 417 mL of concentrated HCl to 400mL of water. Dilute to 1L with water.

6.3. *Hydrochloric acid solution (5M)-1.5% hydrogen peroxide*- Add 417 mL of concentrated HCl and 15mL of 30% hydrogen peroxide to 400mL of water. Dilute to 1L with water.

6.4. *Hydrochloric acid solution (2M)*- Add 167mL of concentrated HCl to 800mL of water. Dilute to 1L with water.

6.5. *Sodium hydroxide (1M)* - Dissolve 4g of sodium hydroxide in 50mL of water and dilute the solution to 100mL

7. PROCEDURE

7.1. Preconcentration of Ra and Ba on MnO_2 Resin:

7.1.1. Adjust pH of sample to pH 6-7 with 2 M HCl acid or 1 M NaOH, if necessary.

7.1.2. If required, filter the sample through a 0.45 micron filter.

7.1.3. Aliquot up to 1L of sample into an appropriate size beaker. Add an appropriate amount of ^{133}Ba tracer.

7.1.4. Slurry 1g of MnO_2 Resin with water and pour the resin into a 20mL column.

7.1.5. Precondition the column with 25mL of water.

7.1.6. Pass the sample through the column using gravity flow or vacuum assistance. Flow rates up to 15 mL/min have been evaluated successfully.

7.1.7. Rinse the sample beaker with 10mL of water. Add rinse to the column.

7.1.8. Properly dispose of the feed and rinse.

7.1.9. Place a clean, labeled 50mL centrifuge tube below each column. Elute radium and barium with from the MnO_2 column with 10mL of 5M HCl/1.5% H_2O_2.

Note: The resin beads start turning white as the MnO2 is dissolved.

7.1.10. Loosely cap sample tubes and hold the radium/barium fraction for >30 hours.

Note: Some chlorine gas will be generated from the HCl/H_2O_2 solution, which can cause a slight pressure build-up in the sealed tubes.

7.2. ^{228}Ac Separation Using DGA Resin:

7.2.1. Insert the vacuum box liner into the vacuum box and fit the lid onto the vacuum box.

7.2.2. Place the yellow outer tips into all openings of the lid of the vacuum box. Fit an inner support tube into each yellow tip.

7.2.3. For each sample solution, place a DGA cartridge onto the inner white tip.

7.2.4. Attach syringe barrels (funnels/reservoirs) to the top end of the DGA cartridge.

7.2.5. Connect the vacuum pump to the vacuum box. Turn the vacuum pump on and ensure proper fitting of the lid.

Note: The unused openings on the vacuum box should be sealed. The yellow manifold plugs supplied with the vacuum box system can be used to plug unused white tips to achieve good seal during the separation. Alternatively, scotch tape affixed to the lid of the vacuum box can be used to seal any unused openings.

7.2.6. Add 5mL of 5M HCl to each cartridge reservoir and allow the solution drain. Turn off vacuum.

7.2.7. Insert the tube rack into the vacuum box with clean labeled tubes beneath each cartridge. Fit the lid onto the vacuum box.

Note: ^{228}Ac has a 6.13 hour half-life. The following steps for the determination of ^{228}Ac must be performed quickly.

7.2.8. Carefully transfer the sample solution from step 7.1.10 to the reservoir of each cartridge. Turn on the vacuum and adjust the flow rate to 1mL/min. Radium and barium will elute from the cartridge, while ^{228}Ac and actinides will be retained on DGA.

7.2.9. Rinse the sample tubes with 5mL of 5M HCl. Add the rinse to the appropriate cartridge reservoir. **Record the time and date of this rinse**. This will be the separation of ^{228}Ac from ^{228}Ra. Collect the eluate for ^{226}Ra and barium. Turn off vacuum.

7.2.10. Set tubes aside for preparation of radium samples for alpha spectrometry.

7.2.11. Place the vacuum box liner in the vacuum box.

7.2.12. Add 5mL of 5M HCl to each cartridge reservoir. Allow the rinse to drain at 1-2mL/min. Turn off vacuum. Remove vacuum box liner and dispose of liquid as waste.

7.2.13. Place the vacuum box rack with a clean, labeled tube under each cartridge into the vacuum box.

7.2.14. Add 15mL of 2M HCl into each cartridge reservoir. Elute ^{228}Ac at 1-2mL/min.

7.2.15. Prepare sources for the measurement of ^{228}Ac by rare earth fluoride micro precipitation using Eichrom Method SPA-01.

7.3. Barium sulfate micro-precipitation of ^{226}Ra

7.3.1. Count tubes containing Ra/Ba fractions for ^{133}Ba by gamma spectrometry for tracer recovery.

7.3.2. Add 3.0g of ammonium sulfate to the Ra/Ba sample tubes. Mix to dissolve.

7.3.3. Add 100µL of barium carrier to each sample. Swirl to mix.

7.3.4. Add 5mL of isopropanol to each sample. Swirl to mix.

7.3.5. Place tubes in an 'ice-cold' water bath for at least 30 minutes.

7.3.6. Prepare alpha spectrometry sources on resolve filters as outlined in Eichrom Method SPA01, steps 5.4. to 5.15.

7.3.7. Count samples by alpha spectrometry.

8. CALCULATIONS

Calculate ^{228}Ra activity:

(To convert pCi/L to Bq/L, multiply by 0.037):

$$^{228}\text{Ra (pCi/L)} = \frac{A}{2.22 \times \text{E} \times V \times Y \times \text{e}^{-\lambda t_1}} \times \frac{\lambda t_2}{1 - e^{-\lambda t_2}}$$

where:

A = net count rate, cpm
E = counting efficiency expressed as fraction
Y = ^{133}Ba (Ra) yield expressed as fraction
V = Sample volume (liters)
t_1 = decay time of ^{228}Ac, from start of rinse until start of counting (minutes)
t_2 = counting time (minutes)
λ = decay constant of ^{228}Ac ($1.88*10^{-3}$ min^{-1})

Calculation for ^{226}Ra activity

(To convert pCi/L to Bq/L, multiply by 0.037):

$$^{226}\text{Ra (pCi/L)} = \frac{S - B}{2.22. \times E \times Y \times V}$$

where:

S = sample counts per minute
B = background counts per minute
E = efficiency of counter
V = volume of samples in liters
Y=barium-133 yield

9. PRECISION AND BIAS

9.1. *Precision*- A relative standard deviation of 7% at the 10.5 dpm level has been reported for radium-226. A relative standard deviation of 6% at the 135 dpm level has been reported for radium-228.

9.2. *Bias*- Mean chemical recoveries of 83% for barium have been reported. Since results are corrected based on spike recovery, no significant bias exists for the method.

10.REFERENCES

1) Moon, D.S., W.C. Burnett, S. Nour, P. Horwitz and A. Bond, "Preconcentration of radium isotopes from natural waters using MnO2 resin," *Applied Radiation and Isotopes*, Vol. 59, pp. 225-262 (2003).

2) 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

3) Maxwell, S.L., et al., "Rapid method for determination of 228Ra in water samples," *J. Radioanal. Nucl. Chem.* 295, 2181-2188, (2013)

4) Maxwell, S.L., et al., "Rapid method for determination of 226Ra in urine samples," *J. Radioanal. Nucl. Chem*. 300, 1159-1166 (2014)

1) Aliquot up to 1000mL of water into glass beaker.

2) Acidify to pH 6-7 with 2M HCl and/or 1M NaOH

3) Add Ba-133 tracer. Mix sample thoroughly.

4) Slurry pack 1g column of MnO_2 resin from DI water.

5) Precondition MnO_2 column with 25mL of DI water.

6) Load sample on MnO_2 column. Do not exceed 15mL/min flow rate. Radium and barium are retained.

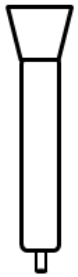
7) Rinse the MnO_2 column with 10mL of DI water.

8) Dispose of load and rinse solutions as waste.

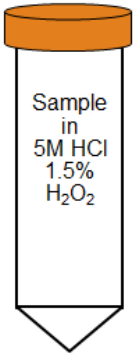
9) Place 50mL polypropylene centrifuge tube below each MnO_2 column. Strip radium and barium from MnO_2 resin with 10mL of 5M HCl-1.5% H_2O_2. (Column will change from dark brown to white)

10) Loosely cap samples and allow Ac-228 ingrowth for at least 30 hours.

Water Sample in glass beaker. Acidify pH 2.



MnO_2 Resin Preconcentration



11) Precondition DGA cartridge with 5mL 5M HCl.

12) Load sample on to DGA cartridge. Allow liquid to drain to waste. Ac-228 is retained.

13) Rinse sample tube with 5mL 5M HCl. Add rinse to DGA cartridge. Allow liquid to drain to waste.

14) Rinse DGA cartridge with 5mL 5M HCl. Allow liquid to drain to waste. Record Ac-228 separation time.

15) Strip Ac-228 with 15mL of 2M HCl.