RADIUM IN WATER

(CATION EXCHANGE AND LN 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 ^{228}Ac (^{228}Ra) 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. This test method is based on the utilization of solid phase extraction of radium from water samples. The detection of the ^{226}Ra is by alpha spectrometry and ^{228}Ra via ^{228}Ac by gas flow proportional beta counter.

2.2. An aliquot of the sample is measured into a beaker, and barium carrier and ^{133}Ba are added. Radium and barium are sorbed on a cation exchange column, eluted, evaporated to dryness, and dissolved in 0.095M HNO_3. ^{228}Ac is selectively retained on a column of LN resin. ^{228}Ac is eluted with 0.35M HNO_3, precipitated with rare earth fluoride, and collected on a resolve filter for measurement by gas flow proportional counting. ^{226}Ra and ^{133}Ba are collected from the LN load solution, precipitated with barium sulfate, and collected on a resolve filter. ^{133}Ba is counted using a gamma spectrometry while ^{226}Ra is counted via alpha spectrometry.

3. SIGNIFICANCE OF USE

3.1. This is a rapid, reliable method for measurement of ^{226}Ra and ^{228}Ra in water samples that is more cost-effective and efficient than traditional ion exchange, solvent extraction and precipitation techniques.

4. INTERFERENCES

4.1. Potential beta emitters such as bismuth, yttrium and thorium would be retained on the solid phase extraction resin column, while eluting actinium from the resin.

4.2. Interferences from other radioactive rare earth elements are eliminated under the stripping conditions of 0.35M HNO_3.

4.3. High levels of calcium can interfere with Ra sorption on the ion exchange resin column and can cause excessive quantities of precipitate in the final barium sulfate micro precipitation step. For samples containing less than 200 ppm, use 500 mL to 1 liter. Sample size is limited to 100mL if the Ca content is greater than 200 ppm but less than or equal to 500 ppm. The method has not been tested on samples containing greater than 500 ppm calcium.

4.4. This method is suitable for the measurement of alpha emitting radium isotopes and ^{228}Ra (via ^{228}Ac) from water samples. The measurement of ^{228}Ac may be biased high if samples contain high levels of ^{227}Ac (from ^{235}U decay chain) or fission products, such as ^{140}Ba, ^{140}La, and Ce radionuclides. If measuring ^{228}Ra from samples potentially containing these interfering radionuclides, a method isolating radium and then allowing for ^{228}Ac in-growth would be more effective (Eichrom Method RAW01).

5. APPARATUS

- Analytical balance, 0.0001 g sensitivity
- Centrifuge tubes, 50mL
- Column rack, Eichrom Part: AC-103
- Extension funnels, 25 mL, Eichrom Part: AC-120
- Flame burner
- Fume hood
- Gamma spectrometry system
- Hotplate
- Ion exchange column, 1 to 1.5cm diameter column with 10mL of cation exchange resin, Eichrom Part: AC-20E-20M (column), Eichrom Part: AC-20X-20M (funnel)
- Low background gas flow proportional counter with appropriate sample carriers and planchets
- Petri dishes, plastic, 5-1/2 x 1 cm
- Stir rods, glass
- Vortex mixer

6. REAGENTS

Note: Analytical grade or ACS grade reagents recommended.

Ammonium sulfate,$(NH_4)_2SO_4$
^{133}*Ba tracer* (~3000 dpm/mL)
Barium chloride dihydrate, $BaCl_2 \cdot 2H_2O$
Cation exchange resin, hydrogen form, 100-200 mesh, Eichrom Part C8-B500-M-H
Deionized water, all reagents are prepared with deionized water
*Hydrogen peroxide (30%), c*oncentrated H_2O_2
LN® resin, 2mL prepacked column, 100-150µm, Eichrom Part LN-C50-A
Nitric acid (70%), concentrated HNO_3

6.1. *Barium carrier (0.75 mg/mL)*- Dissolve 0.34g $BaCl_2 \cdot 2H_2O$, in water. Dilute to 250mL with water.

6.2. *Cerium carrier*- Dissolve 0.155g cerium nitrate hexahydrate in 50mL water. Dilute to 100 mL with water.

6.3. *Ethanol, 80%*- Add 80 mL denatured ethanol to 20 mL water.

6.4. *Nitric acid solution (0.095M)*- Add 5.9 mL of concentrated HNO_3 to 900mL of water. Dilute to 1L with water.

6.5. *Nitric acid solution (0.35M)*- Add 22mL of concentrated HNO_3 to 800mL of water. Dilute to 1L with water.

6.6. *Nitric acid solution (0.1M)*- Add 6.3 mL of concentrated HNO_3 to 800 mL of water. Dilute to 1L with water.

6.7. *Nitric acid solution (8M)*- Add 500 mL of concentrated HNO_3 to 400 mL of water. Dilute to 1L with water.

7. PROCEDURE

7.1. Water Sample Preparation:

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

7.1.2. Aliquot 500 to 1000mL of the sample (or enough to meet required detection limit) into an appropriate size beaker. Add an appropriate amount of ^{133}Ba tracer.

7.1.3. Acidify sample with nitric acid to pH 2, if necessary.

7.1.4. Prepare a cation exchange column containing 10 mL of cation exchange resin.

7.1.5. Precondition the column with 50mL of 0.1M HNO_3.

7.1.6. Pass the sample through the column at the rate of not more than 5 mL/min.

7.1.7. Rinse the column with 25mL of 0.1M HNO_3.

7.1.8. Properly dispose of the feed and rinse.

7.1.9. Elute radium, barium, and ^{228}Ac (and other cations) with 100mL of 8M HNO_3 into a 250mL beaker.

7.1.10. Evaporate the eluate completely to dryness on a hot plate in a fume hood.

Note: The effectiveness of the subsequent radium/^{228}Ac separation on LN resin is dependent on the concentration of HNO_3 in the solution prepared in step 7.1.10. Traces of HNO_3 remaining from the evaporation step 7.1.10. can prevent the uptake of ^{228}Ac by LN resin. Ensure complete evaporation of all HNO_3 in step 7.1.10.

7.1.11. Dissolve the residue in 10mL of 0.095 M HNO_3. If necessary, cover with a watch glass and heat gently. Check that pH is ~1. Adjust to pH 1 as necessary.

7.2. Ac-228 Separation Using LN Resin:

7.2.1. Prepare an LN Resin column for each sample by removing the bottom plug and the cap. Place each column in the column rack with a waste reservoir below the columns. Press each top frit down snugly to the resin surface using a glass rod (or equivalent) and let the solution drain out.

7.2.2. Add 5mL of 0.095 M HNO_3 to precondition each column. Allow the solution to drain by gravity.

7.2.3. Place a clean, labeled 50mL polypropylene centrifuge tube under each column to collect radium and barium.

7.2.4. Transfer each sample solution to the appropriate column reservoir. Allow the solution to drain by gravity. ^{228}Ac will be retained on the LN column, while radium and barium elute into the centrifuge tube.

7.2.5. Rinse the sample beakers with 5mL of 0.095M HNO_3. Add the rinse to the appropriate column. 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.

7.2.6. Rinse the column with 5 mL of 0.095M HNO_3 and collect the eluate for ^{226}Ra and barium.

7.2.7. Set the combined eluate from steps 7.2.4. to 7.2.6. aside for source preparation for the measurement of radium and barium.

7.2.8. Place a clean, labeled tube under each column. Elute ^{228}Ac with 10 mL of 0.35M HNO_3 into a plastic centrifuge tube.

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

7.2.9. Prepare sources for the determination of ^{228}Ac using rare earth fluoride micro precipitation (Eichrom Method SPA-01).

7.2.10. Measure ^{228}Ac using a low background gas flow proportional counter.

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

7.3.1. Count the eluate from step 7.2.7. for ^{133}Ba on a Gamma counter for tracer recovery.

7.3.2. Add 3.0g of ammonium sulfate to the combined eluate from steps 7.2.7. 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- 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):

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

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 Ra-226 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. PERFORMANCE DATA

9.1. This method has been used to analyze various intercomparison and reference samples supplied by external organizations. Chemical recovery and agreement with reference values was excellent. (To convert pCi/L to Bq/L multiply the value by 0.037, therefore 1.41 pCi/L = 0.052 Bq/L or 2 mBq/L.) Data below was generated from 500 mL samples of drinking water samples supplied as indicated. For more details, contact Eichrom:

	Chemical Yield (^{133}Ba)	Eichrom Result (^{226}Ra - pCi/L)	Reference Value (^{226}Ra - pCi/L)
US EPA (9/18/98)	96%	1.41 ± 0.17	1.7 ± 0.5
New Jersey State Lab	91%	8.64 ± 1	9.1 ± 0.5
Georgia Tech (S8933)	88%	22.6 ± 3.0	18.0 ± 2.0
Georgia Tech (WS14776)	88%	4.14 ± 0.58	3.3 ± 0.3

10. REFERENCES

1) Burnett, W.C., P.H. Cable, and Russ Moser, "Determination of Radium-228 in Natural Waters Using Extraction Chromatographic Resins," *Radioactivity & Radiochemistry*, Vol. 6, No. 3, pp. 36-43 (1995).

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

3) 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 2 with concentrated HNO_3.

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

4) Slurry pack 10mL column of cation exchange resin from 0.1M HNO_3.

5) Precondition cation exchange column with 50mL of 0.1M HNO_3.

6) Load sample on cation exchange column. Do not exceed 5mL/min flow rate. Radium, barium and Ac-228 are retained.

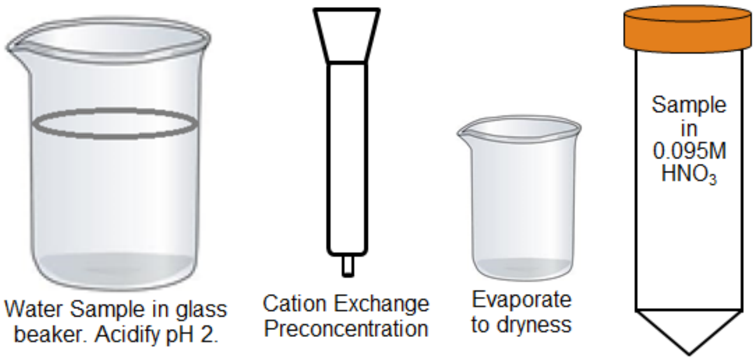
7) Rinse the cation exchange column with 25mL of 0.1M HNO_3.

8) Dispose of load and rinse solutions as waste.

9) Strip radium, barium and Ac-228 with 100mL of 8M HNO_3 in to a 250mL glass beaker.

10) Evaporate the eluate to dryness, ensuring that all HNO_3 is removed.

11) Dissolve residue in 10mL of 0.095M HNO_3.



12) Precondition LN column with 5mL 0.095M HNO_3.

13) Load sample on to column. Allow liquid to drain to waste. Ac-228 is retained.

14) Rinse sample vial with 5mL 0.095M HNO_3. Add rinse to column. Allow liquid to drain to waste.

15) Rinse LN column with 5mL 0.095M HNO_3. Allow liquid to drain to waste.

16) Strip Ac-228 with 10mL of 0.35M HNO_3.