# RADIUM-228 IN WATER

## (WITH VACUUM BOX SYSTEM)

## 1. SCOPE

1.1. This is a method for the separation and measurement of $^{228}$Ra in water via its beta emitting $^{228}$Ac daughter.

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. A barium sulfate precipitation technique is used to concentrate radium from water samples. $^{133}$Ba is used to monitor chemical recovery and correct results to improve precision and accuracy. After ingrowth, $^{228}$Ac, a daughter of $^{228}$Ra, is separated by Ln Resin, prior to measurement by low background gas flow proportional counter.

## 3. SIGNIFICANCE OF USE

3.1. This is a rapid, reliable method for measurement of $^{228}$Ra in water samples that is based on chemistry similar to EPA procedure RA-05.

## 4. INTERFERENCES

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

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

## 5. APPARATUS

- Analytical balance- 0.0001 g sensitivity
- Beakers, glass

- Bunsen burner
- Cartridge reservoirs, 10mL (Eichrom Part: AR-200-RV10) or 20mL (Eichrom Part: AR-200-RV20)
- Centrifuge, with rotor and carriers for 15mL tubes
- Centrifuge tubes, 50mL
- Fume hood
- Gamma spectrometry system (for determination of $^{133}$Ba recovery)
- Hotplate
- Liquid scintillation vials
- Low background gas flow proportional counter with appropriate sample carriers and planchets.
- Stir rods, glass
- Test tubes, Pyrex glass, 15mL
- Vacuum box system, Eichrom Part: AR-12-BOX or AR-24-BOX
- Vacuum box white inner support tube-PE- Eichrom Part: AR-1000-TUBE-PE
- Vacuum box yellow outer tips- Eichrom Part: AR-1000-OT
- Vacuum pump, 115 V, 60 Hz Fisher Part: 01-092-25 (or equivalent) or house vacuum
- Vortex mixer
- Watch glasses
- Optional: vacuum box inner liner - For collection of load and rinse fractions, Eichrom Part: AR-12-LINER or AR-24-LINER

## 6. REAGENTS

***Note: Analytical grade or ACS grade reagents are recommended.***

| |
|---|
| *$^{133}$Ba tracer* (~3000 dpm/mL) |
| *Barium chloride dihydrate*, $BaCl_2 \cdot 2H_2O$ |
| *Deionized water*, all reagents are prepared with deionized water |
| *Hydrogen peroxide (30%),* concentrated $H_2O_2$ |
| *LN® resin,* 2mL prepacked cartridge, 50-100µm, Eichrom Part LN-R50-S |
| *Nitric acid (70%),* concentrated $HNO_3$ |
| *Potassium carbonate*, $K_2CO_3$ |
| *Sulfuric acid (96%),* concentrated $H_2SO_4$ |

6.1. *Barium carrier (30 mg/ml)*- Dissolve 13.3g $BaCl_2 \cdot 2H2O$ in 200mL deionized water. Dilute 250mL with water.

6.2. *Nitric acid solution (0.095 M)*- Add 5.9mL of concentrated $HNO_3$ to 900mL of water. Dilute to 1L with water. Check that pH of solution is ~1.

6.3. *Nitric acid solution (0.35 M)*- Add 21.9mL of concentrated $HNO_3$ to 800mL of water. Dilute to 1L with water.

6.4. *Potassium carbonate (50wt%)*- Dissolve 50g $K_2CO_3$ in 50mL of 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 $^{133}$Ba tracer and 1mL of barium chloride carrier.

7.1.3. Add 10mL of concentrated $H_2SO_4$ to sample. Place each beaker on a hot plate.

7.1.4. Cover each beaker with a watch glass. Heat samples at about 90°C for 2 hours.

7.1.5. Allow samples to cool. A fine white precipitate is formed. Allow precipitate to settle until solution can be decanted or centrifuge.

7.1.6. Decant supernate and discard to waste.

7.1.7. Transfer the precipitate to a 15mL Pyrex glass centrifuge tube using water. Centrifuge for 10 minutes at 2000 rpm.

7.1.8. Decant supernate and discard to waste.

7.1.9. Wash the precipitate with 4-5 mL of water. Mix well and centrifuge for 5-10 minutes. Check the pH of the supernate. The pH should be about 6, if necessary decant supernate and repeat wash/centrifuge steps.

7.2. Conversion of $Ba(Ra)SO_4$ to $Ba(Ra)CO_3$:

7.2.1. Add 1 mL of $K_2CO_3$ solution and 2-3 mL of water, submerging the precipitate completely.

7.2.2. Heat the bottom of the Pyrex tube over a low flame while stirring the tube periodically. Continue heating, mixing until volume is reduced to ~1mL. (This step may also be performed using microwave heating or a water bath.)

7.2.3. Let the tube cool and repeats step 7.2.1 and 7.2.2 two times.

7.2.4. Add 15-20 mL of water. Mix well. Centrifuge and check the pH of the supernate. The pH of at this point should be approximately 12.

7.2.5. Discard the supernate and continue washing with water and centrifuging until a pH of 7 is achieved. Discard supernate.

***Note: The precipitate now should be primarily $BaCO_3$. The water washing of the $BaCO_3$ precipitate removes excess $CO_3^{2-}$ and $SO_4^{2-}$ ions. Any sulfate remaining in the sample can result in incomplete dissolution during the following steps and decreased Ba/Ra yields.***

7.2.6. Once the pH of 7 is achieved add 5 mL of 0.095M $HNO_3$ to the tube and gently heat as necessary to dissolve the residue in the tube.

***Note: If the entire residue does not dissolve in the load solution, then centrifuge the solution and check the supernatant for $_{133}$Ba yield recovery. If acceptable (>80%) recovery is produced then proceed further if not then take the residue (undissolved) and repeat steps 7.2.1 through 7.2.5. Combine the dissolved solutions and check for Ba-133 recovery.***

7.2.7. Transfer the dissolved solution into a 20mL liquid scintillation vial. Rinse the Pyrex tube with an additional 5 mL of 0.095M $HNO_3$ and add the tube rinse to the same vial.

7.2.8. Count the $^{133}$Ba by gamma spectrometry. Record $^{133}$Ba recovery.

7.2.9. Let the solution sit in the vial for at least 30 hours for ingrowth of $^{228}$Ac from $^{228}$Ra.

7.3. $^{228}$Ac Separation Using Ln Resin:

***Note: $^{228}$Ac has a 6.13 hour half-life. The following steps should be performed quickly to achieve the lowest detection limits.***

7.3.1. Place the inner tube rack (supplied with vacuum box system) into the vacuum box with the centrifuge tubes in the rack. Fit the lid to the vacuum system box. Alternatively, a vacuum box inner liner may be used.

7.3.2. Place yellow outer tips into all 12 or 24 openings in the lid of the vacuum box. Fit a white inner support tube into each yellow tip.

7.3.3. For each sample solution, fit an LN Resin cartridge on to the inner support tube.

7.3.4. Add syringe barrels (funnels/reservoirs) to the top end of each LN Resin cartridge.

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

***Note: The unused openings on the vacuum box should be sealed. Vacuum manifold plugs can be used to plug unused white tips to achieve good seal during the separation. Alternatively, unused vacuum box holes can be sealed with scotch tape.***

7.3.6. Add 5mL of 0.095M $HNO_3$ into each LN Resin cartridge reservoir to precondition resin. Adjust vacuum to achieve a flow rate of 1mL/min.

7.3.7. Transfer each sample solution from step 7.2.7. into the appropriate LN Resin cartridge reservoir.

7.3.8. Allow the load solution to completely pass through the cartridge at 1 mL/min.

7.3.9. Add 5mL of 0.095M $HNO_3$ into the sample vial and transfer this rinse to the appropriate LN Resin cartridge reservoir. Allow the solution to completely pass through each cartridge at 1mL/min. Record the date and time at the start of this rinse for decay correction.

7.3.10. Place clean reservoirs above each LN Resin cartridge.

7.3.11. Rinse each LN Resin cartridge with 5mL of 0.095M $HNO_{3.}$ Allow solution to completely pass through each cartridge at 1mL/min.

7.3.12. Repeat step 7.3.10.

7.3.13. Disengage vacuum. Dispose of eluate to this point as waste (or retain in case issues arise with subsequent analysis of $^{228}$Ra via $^{228}$Ac).

7.3.14. Place clean, labeled centrifuge tubes below each LN Resin cartridge. Replacing yellow outer tubes and inner tube supports at this point will help ensure clean $^{228}$Ac fractions in the following steps.

7.3.15. Add 10mL of 0.35M $HNO_3$ to each LN Resin cartridge reservoir to eluate $^{228}$Ac. Engage vacuum. Allow solution to completely pass through each cartridge at 1mL/min.

7.3.16. Prepare sources for counting by rare earth micro precipitation using Eichrom Method SPA-01.

## 8. CALCULATIONS

*Calculate $^{228}$Ra in pCi/L:*

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

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)
$\lambda$ = decay constant of $^{228}$Ac ($1.88 \times 10^{-3}$ $\text{min}^{-1}$)

## 9. PERFORMANCE DATA

Reported by Burnett, et al. (1995)

| Sample | Expected Result Ra-228 (pCi/L) | Experimental Result Ra-228 (pCi/L) |
|---|---|---|
| EMSL Ra in Water, 7/17/92 | 16.7 ± 3.3 | 17.6 ± 0.7 |
| EMSL Standard Ra-228 Solution | 59.3 ± 2.1 | 58.0 ± 1.3 |
| Decontamination Experiment[a] | 29.7 ± 1.0 | 31.7 ± 0.5 |
| EMSL Performance Evaluation "A" 4/19/94[b] | 20.1 ± 5.0 | 21.6 ± 1.2 |

a. The decontamination experiment consisted of using approximately 800 mL of EMSL Performance Evaluation “B” (April 20, 1993) which contained the following nuclides: $^{90}$Sr($^{90}$Y) = 397 dpm; $^{60}$Co = 466 dpm; $^{134}$Cs = 438 dpm; $^{137}$Cs = 438 dpm; and $^{226}$Ra 213 dpm. In addition the following were added: approximately 8000 dpm $^{133}$Ba, 900 dpm $^{207}$Bi, 500 dpm $^{210}$Pb, and 65.9 dpm $^{228}$Ra.

b. Ra-226 was analyzed via radon emanation by collection of the sample load and rinse from the Ln Resin column. Their result of 20.1 +/- 1.1 pCi/L compared very well to the expected result of 20.0 +/- 3.0 pCi/L.

## 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).

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

2) Add Ba-133 tracer and 1mL of Ba carrier.

3) Add 10mL of concentrated $H_2SO_4$.

4) Cover with watch glass and heat to 90ºC for 2 hours.

5) Allow samples to cool. Allow fine white $BaSO_4$ precipitate to settle or centrifuge samples to separate more quickly.

6) Decant supernate to waste.

7) Transfer precipitate to 15mL Pyrex glass centrifuge tube.

8) Wash precipitate with 4-5mL water. Centrifuge. Check pH of supernate. Decant supernate and discard as waste. Repeat until pH ~6.

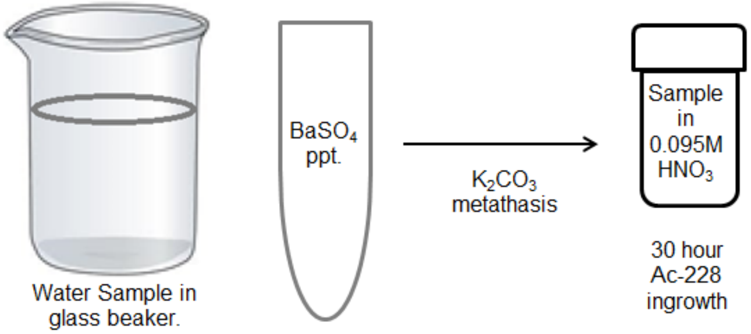
9) Add 1mL 50% $K_2CO_3$ and 2-3mL of water, completely covering precipitate. Heat over flame until dry. Allow tube to cool. Repeat two more times.

10) Add 15-20mL of water. Mix well. Centrifuge. Check pH. Decant supernate to waste. Repeat until supernate pH ~7.

11) Add 5mL of 0.095M $HNO_3$. Gently heat to dissolve residue. If solids remain. Centrifuge. Decant supernate to 20mL LSC vial.

12) Check Ba-133 recovery. If less than 80%, repeat 9-11 on solids from step 11.

13) Allow at least 30 hours for Ac-228 ingrowth.



14) Precondition LN cartridge with 5mL 0.095M $HNO_3$.

15) Load sample on to LN. Allow liquid to drain to waste. Ac-228 is retained.

16) Rinse sample vial with 5mL 0.095M $HNO_3$. Add rinse to LN. Allow liquid to drain to waste.

17) Rinse LN cartridge with 5mL 0.095M $HNO_3$. Allow liquid to drain to waste.

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