

AP8

RADIUM-228 IN WATER

PART A

PRINCIPLE

Radium in water is concentrated by co-precipitation with barium sulfate. The barium sulfate is metastasized to barium carbonate. The carbonate is dissolved and passed through a chromatographic column to separate radium/barium from actinium. The radium/barium fraction is eluted and barium-133 is counted by gamma spectrometry to quantify the chemical yield. Actinium is eluted and co-precipitated with cerium fluoride for beta counting.

REFERENCES

1. Sill C. W. (1987). Determination of Radium-226 by high-resolution alpha spectrometry.
2. Burnett, H. B. & Cable, P. Radium-228 in natural waters via extraction chromatography. 38th Annual Conference on Bioassay, Analytical, and Environmental Radiochemistry.
3. Eichrom Technologies, Inc., Analytical Procedure RAW03, Rev. 0.5, 2001.

Certification Record for

AP8

RADIUM-228 IN WATER

CHECKPOINTS

- 1. **JOB HAZARD ANALYSIS (JHA)** _____
- 2. **MSDS/HAZARDS DISCUSSED** _____
- 3. **TRACER ADDED** _____
- 4. **BARIUM SULFATE PRECIPITATE** _____
- 5. **ACTINIUM SEPARATION** _____
- 7. **ACTINIUM DEPOSITION** _____
- 8. **FINAL CALCULATIONS** _____

ANALYST'S SIGNATURE: _____

CERTIFIED BY: _____

DATE: _____

ANALYSIS VALUE: _____

KNOWN VALUE: _____

MEASURED/KNOWN: _____

See Task _____, Batch _____ for the original data.

COMMENTS: _____

PART B

1.0 PURPOSE AND SCOPE

This procedure provides the analytical method for determination of radium-228 in water.

2.0 REAGENTS

All chemicals are hazardous. See MSDS for specific precautions. **See step 2.0 of AP8 JHA.** Unless otherwise indicated, all references to water should be understood to mean reagent grade water.

Barium carrier, 30 mg/mL: Dissolve 13.3 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 mL of water. Filter the solution through a DM-450, 47mm filter (or equivalent) and dilute to 250 mL with water.

Barium chloride dihydrate, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$: crystalline.

Ba-133, NIST traceable standardized solution, approximately 300-600 pCi for each sample.

Cerium carrier, 1 mg/mL: AA quality Ce solution of 1000 $\mu\text{g}/\text{mL}$.

Ethanol, 95%: Dilute 475 mL ethyl alcohol to 500 mL with water.

Hydrochloric acid, HCl, concentrated, 12 M

Hydrochloric acid, HCl, 2 M, slowly add 83 mL of 12 M HCl to 300 mL of water. Dilute to 500 mL with water and mix.

Hydrochloric acid, HCl, 5 M, slowly add 207 mL of 12 M HCl to 200 mL of water. Dilute to 500 mL with water and mix.

Hydrofluoric acid, HF, concentrated, 28 M: CAUTION: Skin contact with HF causes very severe burns.

DGA resin, 2 mL cartridges, 50-100 mm particle size.

Potassium carbonate, 50% (w/v) K_2CO_3 : Add 500 g of K_2CO_3 in 950 mL of water. Dilute to 1 L with water and filter through a DM-450, 47 mm filter (or equivalent).

Ra-228, NIST traceable standardized solution.

Sulfuric acid, H_2SO_4 , concentrated, 18 M.

3.0 APPARATUS AND MATERIALS

Analytical balance
Beakers, appropriate for sample volume
Centrifuge
Centrifuge tube, 50 mL
Column rack
DM-450 filter, 47 mm or equivalent
Extension funnels
Metricol polypropylene filter, 0.1 μm , 25 mm or equivalent
Gamma spectrometry system
Gas-flow proportional counting system
Glass filter setup
Hot plate
Polysulfone filter apparatus
Stainless steel disks
Vortex mixer

4.0 PROCEDURE

4.1 General Requirements

Before proceeding, you must be certified, as indicated in QCP1 of this manual, and Section 3 of the Quality Program (QP) Manual. See page 2 of this section for a copy of the certification record.

4.2 Sample Preparation

4.2.1 Measure sample in a volumetric flask and transfer to an appropriate size beaker. Use water for the blank and Laboratory Control Standard (LCS).
See step 4.2.1 of AP8 JHA.

4.2.2 Add a known amount of Ba-133 tracer to all samples, blank, and LCS. **See step 4.2.2 of AP8 JHA.**

NOTE: If HF was initially added as a preservative to the sample to prevent Pu hydrolysis, transfer the sample to a platinum crucible, evaporate to dryness on a hot plate, and proceed to step 4.2.30.

4.2.3 Add approximately 30 pCi of Ra-228 to the LCS. **See step 4.2.3 of AP8 JHA.**

4.2.4 While stirring, *carefully* add 10 mL of 18 M H_2SO_4 . Heat sample to boiling.
See step 4.2.4 of AP8 JHA.

4.2.5 Add 1 mL Ba carrier to all samples, blank, and LCS. **See step 4.2.5 of AP8 JHA.**

4.2.6 Filter the precipitate through a DM-450 filter. Pour the supernate in the

dilute waste acid stream. **See step 4.2.6 of AP8 JHA.**

- 4.2.7 Transfer the filter paper to a centrifuge tube.
- 4.2.8 Add 10 mL of water and vortex to remove the precipitate from the filter paper. Discard the filter paper. Centrifuge the precipitate at 2000 RPM for 5 minutes and discard the supernate. **See step 4.2.8 of AP8 JHA.**
- 4.2.9 Add 10 mL of water and vortex to rinse the precipitate. Centrifuge at 2000 RPM for 5 minutes and discard supernate. **See step 4.2.9 of AP8 JHA.**
- 4.2.10 Repeat step 4.2.9.
- 4.2.11 Add 20 mL 50% K_2CO_3 to the precipitate. Vortex. Heat for at least 30 minutes in boiling water, with occasional stirring, to metastasize the precipitate to $BaCO_3$. **See step 4.2.11 of AP8 JHA.**
- 4.2.12 Centrifuge the samples at 2000 RPM for 5 minutes and discard the supernate. **See step 4.2.12 of AP8 JHA.**
- 4.2.13 Add 10 mL of water and vortex to rinse the precipitate. Centrifuge at 2000 RPM for 5 minutes and discard the supernate. **See step 4.2.13 of AP8 JHA.**
- 4.2.14 Repeat step 4.2.13 two more times.
- 4.2.15 Allow the Ac-228 to grow in at least 24 hours before proceeding to step 4.2.16.

Note: Confirm that low background proportional detectors will be available. Proceed with 2 samples at a time. The detector is the limiting factor, but the samples must be counted within 2 hours.

Note: Use DGA Resin Cartridges Only

- 4.2.16 Attach a syringe barrel to a DGA cartridge and affix to an Eichrom vacuum box.
- 4.2.17 Add 10 mL of 5 M HCl to each column and collect in a waste centrifuge tube for disposal into the dilute acid waste. **See step 4.2.17 of AP8 JHA.**
- 4.2.18 Prepare load solution by adding 10 mL 5 M HCl to the precipitate from step 4.2.13 and vortex to dissolve the precipitate. **See step 4.2.18 of AP8 JHA.**
- 4.2.19 Place labeled centrifuge tubes under each cartridge for Ba-133 and Ra-228.
- 4.2.20 Pour the load solution into each cartridge and collect. (Do not allow the flow rate to exceed 1mL/min.) **See step 4.2.20 of AP8 JHA.**

4.2.21 Rinse each centrifuge tube with 5 mL of 5 M HCl and pour into each column and save in the same centrifuge tube as from step 4.2.19. **See step 4.2.21 of AP8 JHA.**

Note: Record Ac-228 Separation Time.

4.2.22 Rinse the column two times with 5 mL of 5 M HCl and collect in the same centrifuge tube as in Step 4.2.19. **See step 4.2.22 of AP8 JHA.**

4.2.23 Pour the solution from step 4.2.21 into a counting container and submit to the counting room for gamma analysis for the Ba-133 yield determination.

4.2.24 Place a new, labeled centrifuge tube under each column to collect the Ac-228 fraction.

4.2.25 Elute the Ac-228 from the column with 10 mL of 2 M HCl. **See step 4.2.25 of AP8 JHA.**

4.2.26 Add 200 μ L Ce carrier and 2 mL 28 M HF to each sample, mix, and wait 20 minutes. **See step 4.2.26 of AP8 JHA.**

4.2.27 Assemble polysulfone filtering apparatus for each sample. Wet the filter paper with 5 mL 95% ethanol.

4.2.28 Filter each sample onto a 0.1 μ m filter paper. **See step 4.2.28 of AP8 JHA.**

4.2.29 Count the CeF_3 from step 4.2.27 immediately on a low background proportional counter long enough to achieve the desired statistics.

Note: Steps 4.2.30 through 4.2.41 are only used if HF was used a preservative.

4.2.30 Add 3 to 5 g of KHF_2 to the crucible. **See step 4.3.3 of AP7 JHA.**

4.2.31 Place the platinum dish on a ring stand using a nichrome triangle.

4.2.32 Start heating the sample over a blast burner with low flame. Heat until the KHF_2 has completely dried. **See step 4.3.5 of AP7 JHA.**

4.2.33 Use as much heat as possible, with limited splattering, to bring the temperature to about 900°C (the color of the platinum dish will turn cherry red). Continue heating until total dissolution occurs. Swirl the hot melt to ensure removal of sample clinging to the sides of the dish. **See step 4.3.6 of AP7 JHA.**

4.2.34 Remove the melt from the burner and swirl gently around the dish to form a thin layer upon cooling. (Never set hot platinum on iron). Wait 45 seconds before proceeding to step 4.2.35. **See step 4.3.7 of AP7 JHA.**

NOTE: IT IS CRITICAL FOR THE FLUORIDE CAKE TO BE SOMEWHAT COOLER BEFORE THE ADDITION OF H₂SO₄ TO PREVENT SPLATTERING.

- 4.2.35 Add 3 to 5 mL of 18 M H₂SO₄ to dissolve the fluoride cake. The acid should be added to the edge of the dish and allowed to run to the bottom of the dish. **See step 4.3.8 of AP7 JHA.**
- 4.2.36 After the addition of the H₂SO₄, heat as much as frothing will allow until the fluoride cake is totally dissolved. **See step 4.3.9 of AP7 JHA.**
- 4.2.37 Remove from heat and add ~2 g of anhydrous Na₂SO₄ to the slurry. Place sample over the blast burner with small flame and heat until the slurry begins to turn a golden brown. Slowly increase the temperature until the slurry is completely melted and maintain this temperature for approximately 1 minute. **See step 4.3.10 of AP7 JHA.**
- 4.2.38 Remove the melt from the burner and swirl gently around the dish to form a thin layer upon cooling. **See step 4.3.11 of AP7 JHA.**
- 4.2.39 Transfer the pyrosulfate cake to a 150 mL beaker. **See step 4.3.12 of AP7 JHA.**
- 4.2.40 Add 35 mL of water and 1 mL of 12 M HCl to the crucible to dissolve the residual pyrosulfate cake. Heat if necessary. Transfer the solution to the 150 mL beaker. **See step 4.3.13 of AP7 JHA.**
- 4.2.41 Rinse the platinum dish with water and add rinse to 150 mL beaker containing the pyrosulfate cake.
- 4.2.42 Add a stir bar and heat to boiling to dissolve the pyrosulfate cake. If the pyrosulfate cake does not dissolve, see the Laboratory Manager, or designee. Allow the solution to cool and proceed to step 4.2.4. Continue through step 4.2.29.

5.0 CALIBRATIONS

5.1 Low Background Alpha/Beta Counter Efficiency Calibration

- 5.1.1 Add enough Ra-228 and Ba-133 to achieve desired statistics into a centrifuge tube. Ensure that the solution is 10 mL in volume and 5M HCL.
- 5.1.2 Attach a syringe barrel to a DGA cartridge and affix to an Eichrom vacuum box.
- 5.1.3 Add 10 mL of 5M HCL and collect in a centrifuge tube for disposal into the dilute acid waste. **See step 4.2.21 of AP8 JHA.**

5.1.4 Pour the solution into the DGA cartridge and allow to drain into a centrifuge tube for Ba-133 and Ra-228. (Do not allow the flow rate to exceed 1 mL/min.) **See step 4.2.21 of AP8 JHA.**

5.1.5 Rinse the centrifuge tube with 5 mL 5M HCL and pour into each cartridge and allow the solution to drain into the centrifuge tube. **See step 4.2.21 of AP8 JHA.**

Note the time for Ac-228 separation.

5.1.6 Rinse the DGA cartridge twice more with 5 mL 5M HCL and allow the solution to drain into the centrifuge tube. Transfer the solution into a counting container and submit to the counting room for Ba-133 yield. **See step 4.2.21 of AP8 JHA.**

5.1.7 Go to step 4.2.24 and continue through step 4.2.29.

5.1.8 Calculate the Ac-228 counting efficiency using the efficiency equation in section 6.

5.1.9 The Laboratory Manager or designee must review and approve the Ac-228 counting efficiency.

5.2 Ba-133 Calibration for Yield Determination

5.2.1 Add an appropriate amount of a Ba-133 standard to a specimen cup and bring the volume to 25 mL with 5M HCL. **See step 4.2.21 of AP8 JHA.**

5.2.2 Submit to the counting room to establish the counting efficiency of Ba-133 in the specimen cup geometry.

5.2.3 The Laboratory Manager must review and approve the Ba-133 counting efficiency.

6.0 CALCULATIONS

Critical data values will be documented on standard forms maintained as critical records. The following equations define the critical data values. All data will be recorded and reduced according to these calculations. TPU has not been evaluated for this non-routine procedure.

$$\text{Concentration} = \frac{G - B}{T_2 \cdot E \cdot Y \cdot Q \cdot e^{-\lambda_{Ac}T_1}} \cdot \frac{\lambda_{Ac}T_2}{1 - e^{-\lambda_{Ac}T_2}} = pCi / unit$$

$$2\sigma \text{ Error} = \frac{1.96\sqrt{G + B}}{T_2 \cdot E \cdot Y \cdot Q \cdot e^{-\lambda_{Ac}T_1}} \cdot \frac{\lambda_{Ac}T_2}{1 - e^{-\lambda_{Ac}T_2}} = pCi / unit$$

In the event of G=0 and B=0, 1 will be substituted for G+B to prevent a division by or into zero error in this uncertainty calculation.

$$2\sigma \text{ TPU} = C \cdot 1.96 \sqrt{\frac{G+B}{(G-B)^2} + RE^2 + RY^2 + RQ^2 + RHL^2} = \text{pCi / unit}$$

In the event of G=0 and B=0, 1 will be substituted for G+B/(G-B)² to prevent a division by or into zero error in this uncertainty calculation.

$$\text{MDC} = \frac{3 + 4.65\sqrt{B}}{T_2 \cdot E \cdot Y \cdot Q \cdot e^{-\lambda_{Ac}T_1}} \cdot \frac{\lambda_{Ac}T_2}{1 - e^{-\lambda_{Ac}T_2}} = \text{pCi / unit}$$

To calculate efficiency:

$$E = \frac{G_E - B}{E_{ACT}}$$

To calculate radiochemical yield:

$$Y = \frac{Ba-133_{MA}}{Ba-133_{KA}}$$

To calculate T₁:

$$T_1 = (ECT - ST) * (24 * 60) - \left(\frac{CT}{2}\right)$$

where:

- λ_{Ac} = Ac-228 decay constant, 1.8846 x 10⁻³, min⁻¹
- B = background counts
- Ba-133_{MA} = Ba-133 measured activity by gamma count
- Ba-133_{KA} = Ba-133 known activity added
- C = concentration in pCi/unit
- E = counting efficiency, cpm/pCi
- E_{ACT} = pCi of efficiency standard
- ECT = end of count time and date
- G = gross counts
- G_E = gross counts of efficiency standard
- MDC = minimum detectable concentration
- MT = midpoint of count time
- Q = sample quantity
- RE = relative error of the efficiency
- RHL = relative error of the half-life
- RQ = relative error of the quantity
- RY = relative error of the yield
- ST = Ac-228 separation time and date
- TPU = total propagated uncertainty
- T₁ = Ac-228 decay time, min
- T₂ = count time, min
- Y = chemical yield

7.0 RECORDS

- 7.1 Reference QP Manual for general record requirements.
- 7.2 The raw count data is saved during the weekly backup of the low background alpha/beta counter to the ORISE network disks and during the weekly backups using Tivoli software or the equivalent for data from the Canberra Apex Gamma system.
- 7.3 Hard copies of assignment and calculation sheets are maintained in the archived site file. Electronic copies of assignment and calculation sheets are saved during the daily incremental backup of the network system. The following data sheets should be completed and retained:
- Ra-228 Analysis Assignment Form
 - Ra-228 Data Sheet
 - Ra-228 Concentration and Uncertainty Report (This report may be generated using approved Excel spreadsheets or from the database, if available.)

(AP 8, Rev 5) Ra-228 ANALYSIS ASSIGNMENT FORM

Assigned To: _____ Date: _____ Batch: _____

Task #: _____ LWR #: _____ Activity Lev*: _____

Sample #'s: _____

QC REQUIRED:

BLANK

REPLICATE

Sample # _____ # Replicates: _____

LCS

Ra-228 STD # _____ QUANTITY: _____
UNITS: _____

INITIALS

MATRIX SPK

Sample # _____
Ra-228 STD # _____ QUANTITY: _____
UNITS: _____

MSD

Sample # _____
Ra-228 STD # _____ QUANTITY: _____
UNITS: _____

Pipette # _____ Volume _____ Weight _____

Ba-133 STD # _____ QUANTITY: _____
UNITS: _____

SPECIAL INSTRUCTIONS: _____

* If Activity Level is indicated as Moderate or High, perform area survey.

(AP 8, Rev 5) Ra-228 DATA SHEET

Carrier #							
Sample #							
Quantity							
Units							

Carrier #							
Sample #							
Quantity							
Units							

Carrier #							
Sample #							
Quantity							
Units							

Carrier #			
Sample #			
Quantity			
Units			

NON-ROUTINE (AP8, Rev 5) RADIUM-228 CONCENTRATION & UNCERTAINTY REPORT

OPERATOR
INITIALS

DATE

BATCH #

TASK #

CARRIER #						
SAMPLE NO.						
Ac-228 SEPARATION DATE AND TIME						
END COUNT DATE AND TIME						
Ac-228 DECAY TIME (min)						
COUNT TIME (min)						
SAMPLE COUNTS						
BACKGROUND COUNTS						
EFFICIENCY cpm/pCi						
1 σ EFFICIENCY cpm/pCi						
SAMPLE QUANTITY (L)						
Ba-133 RECOVERED (pCi)						
1 σ ERROR of Ba-133 RECOVERED (pCi)						
Ba-133 ADDED (pCi)						
1 σ ERROR of Ba-133 (pCi)						
Ba YIELD						
1 σ ERROR of Ba Yield						

