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 AP7 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 $BaCl_2 \cdot 2H_2O$ 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, $BaCl_2 \cdot 2H_2O$: 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 μg/mL.

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

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

Ln resin, 2 mL pre-packed columns, 100-150 mm particle size.

Nitric acid, HNO_3, concentrated, 16 M.

Nitric acid, HNO_3, 1 M, slowly add 31.5 mL 16 M HNO_3 to 200 mL of water. Dilute to 500 mL with water and mix.

Nitric acid, 0.35 M: Add 175 mL of 1 M HNO_3 to 500 mL of water. Prepare in a volumetric flask.

Nitric acid, 0.095 M: Add 47.5 mL of 1 M HNO_3 to 500 mL of water. Prepare in a volumetric flask.

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
Metricel 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.**

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 Ln Resin Columns Only

4.2.16 Snap the plastic bottom off each Ln column to be used and allow solution to elute into a waste beaker.

4.2.17 Add 10 mL 0.095 M HNO_3 to each column and collect in a waste beaker 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 0.095 M HNO_3 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 column for Ba-133 and Ra-228.

4.2.20 Pour the load solution into each column and collect. **See step 4.2.20 of AP8 JHA.**

4.2.21 Rinse each centrifuge tube with 5 mL 0.095 M HNO_3 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 0.095 M HNO_3 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 specimen cup 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 0.35 M HNO_3. **See step 4.2.25 of AP8 JHA.**

4.2.26 Add 100 µL Ce carrier and 2 mL 28 M HF to each sample, mix, and wait 10 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 µm 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.

5.0 CALIBRATIONS

5.1 Low Background Alpha/Beta Counter Efficiency Calibration

5.1.1 Add enough Ra-228 to achieve desired statistics into an appropriate size beaker. Carefully take the solution to dryness.

5.1.2 Snap the plastic bottom off each Ln column to be used and allow solution to elute into a waste beaker.

5.1.3 Add 10 mL 0.095 M HNO_3 to each column and collect in a waste beaker for disposal into the dilute acid waste. **See step 4.2.21 of AP8 JHA.**

5.1.4 Add 10 mL 0.095 M HNO_3 to sample from step 5.1.1. Pour solution onto a Ln column and allow to drain into a waste beaker. **See step 4.2.21 of AP8 JHA.**

5.1.5 Rinse the beaker with 5 mL 0.095 M HNO_3 and pour into each column and allow the solution to drain into a waste beaker. **See step 4.2.21 of AP8 JHA.**

5.1.6 Rinse Ln column twice more with 5 mL 0.095 M HNO_3 and pour into each column and allow the solution to drain into a waste beaker. **See step 4.2.21 of AP8 JHA.**

5.1.7 Place a labeled centrifuge tube under each Ln column and add 10 mL of 0.35 M HNO_3. **See step 4.2.24 of AP8 JHA.**

5.1.8 Go to step 4.2.25 and continue through step 4.2.28.

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

5.1.10 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 0.095 M HNO_3. **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.

$$Concentration = \frac{G - B}{T_2 \cdot E \cdot Y \cdot Q \cdot e^{-\lambda_{Ra} T_3} \cdot e^{-\lambda_{Ac} T_1}} \cdot \frac{\lambda_{Ac} T_2}{1 - e^{-\lambda_{Ac} T_2}} = pCi / unit$$

$$2\sigma\ Error = \frac{1.96\sqrt{G + B}}{T_2 \cdot E \cdot Y \cdot Q \cdot e^{-\lambda_{Ra} T_3} \cdot e^{-\lambda_{Ac} T_1}} \cdot \frac{\lambda_{Ac} T_2}{1 - e^{-\lambda_{Ac} T_2}} = pCi / unit$$

$$MDC = \frac{3 + 4.65\sqrt{B}}{T_2 \cdot E \cdot Y \cdot Q \cdot e^{-\lambda_{Ra} T_3} \cdot e^{-\lambda_{Ac} T_1}} \cdot \frac{\lambda_{Ac} T_2}{1 - e^{-\lambda_{Ac} T_2}} = pCi / unit$$

To calculate efficiency:

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

To calculate radiochemical yield:

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

where:

λ_{Ac}	=	Ac-228 decay constant, 1.8846 x 10^{-3}, min^{-1}
λ_{Ra}	=	Ra-228 decay constant, 2.2915 x 10^{-7}, min^{-1}
B	=	background counts
$Ba\text{-}133_{MA}$	=	Ba-133 measured activity by gamma count
$Ba\text{-}133_{KA}$	=	Ba-133 known activity added
C	=	concentration in pCi/unit
E	=	counting efficiency, cpm/pCi
E_{ACT}	=	pCi of efficiency standard
G	=	gross counts
G_E	=	gross counts of efficiency standard
MDC	=	minimum detectable concentration
Q	=	sample quantity
TPU	=	total propagated uncertainty
T_1	=	Ac-228 decay time, min
T_2	=	count time, min
T_3	=	Ra-228 decay time, min, from sample collection to step 4.2.20
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 and monthly backups to a DAT tape or equivalent of the DEC Alpha 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 3) 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:** _____ **INITIALS** ☐
UNITS: _____

MATRIX SPK ☐ **Sample #** _____

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

Pipet # _____ Volume _____ Weight _____

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

SPECIAL INSTRUCTIONS: _____

_____

_____

_____

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

(AP 8, Rev 3) Ra-228 DATA SHEET

Carrier #							
Sample #							
Quantity							
Units							

Carrier #							
Sample #							
Quantity							
Units							

Carrier #							
Sample #							
Quantity							
Units							

Carrier #			
Sample #			
Quantity			
Units			

(AP8, Rev 3) RADIUM-228
CONCENTRATION & UNCERTAINTY REPORT

OPERATOR INITIALS DATE BATCH # TASK #

DETECTOR #						
CARRIER TRAY #						

SAMPLE NO.						
Ac-228 SEPARATION DATE						
Ac-228 SEPARATION TIME						
END COUNT DATE						
Ac-228 DECAY TIME (min)						
LENGTH OF COUNT TIME (min)						
SAMPLE COUNTS						
BACKGROUND COUNTS						
DETECTOR EFFICIENCY cpm/pCi						
SAMPLE QUANTITY (L)						
Ba-133 MEAS. ACTIVITY (pCi)						
Ba-133 KNOWN ACTIVITY (pCi)						
Ba-133 YIELD						

(AP8, Rev 3) RADIUM-228
CONCENTRATION & UNCERTAINTY REPORT

OPERATOR DATE BATCH # TASK #

SAMPLE #						
Concentration, pCi/L						
2-sigma error						
4.65-sigma MDC						

SAMPLE #						
Concentration, pCi/L						
2-sigma error						
4.65-sigma MDC						

Ra-228 Known pCi Meas/Known

Uncertainty Uncertainty

BLANK CORRECT? YES[ ] NO[ ] INIT_____

LCS CORRECT? YES[ ] NO[ ] INIT_____

BATCH YIELD CORRECT? YES[ ] NO[ ] INIT_____

IF NO, SPECIFY REASON:

ANALYST: _____ DATE:_____

REVIEWED BY:_____ DATE:_____

GIVEN TO: _____ DATE:_____