AP7

DETERMINATION OF RADIUM-226 IN WATER AND SOIL SAMPLES USING ALPHA SPECTROSCOPY

PART A

PRINCIPLE

Radium-226 (Ra-226) in water and soil is concentrated by a lead sulfate co-precipitation. The precipitate is dissolved in DTPA and Ra-226 is separated from possible interfering radionuclides using a micro barium sulfate precipitation. The barium precipitate is filtered and the Ra-226 is counted by alpha spectroscopy. Barium-133 (Ba-133) is used to quantify the yield by gamma spectroscopy.

REFERENCES

Sill, C. W., Determination of Radium-226 in Ores, Nuclear Wastes and Environmental Samples by High Resolution Alpha Spectrometry. Nuclear Chemical Waste Management, 7(3-4), pp. 239-256 (1987).

Certification Record for

AP7

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CHECKPOINTS

1. **JOB HAZARD ANALYSIS (JHA)** ____
2. **MSDS/HAZARDS DISCUSSED** ____
3. **LEAD SULFATE PPT** ____
4. **DTPA DISSOLUTION OF PPT** ____
5. **BARIUM MICRO PPT** ____
6. **FILTER FOR COUNTING** ____
7. **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 Ra-226 in water and soil.

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.

Acetic acid, CH_3COOH, 17.4 M: concentrated reagent.

Acetic acid, CH_3COOH, 50% (v/v): To 250 mL water, add 250 mL of 17.4 M CH_3COOH and mix well.

Ba-133 tracer: NIST traceable standard.

Barium carrier, 0.75 mg/mL (as Ba^{2+}): Dissolve 338 mg of $BaCl_2 \bullet 2H_2O$ in 100 mL of water. Filter the solution through Supor-450, 47mm filter (or equivalent) and dilute to 250 mL with water.

Barium chloride dihydrate, $BaCl_2 \bullet 2H_2O$: crystalline.

DTPA, 0.1 M: Dissolve 19.7 g of DTPA (Diethylenetriaminepentaacetic acid), in 460 mL of water. Dissolve 9.5 g of sodium hydroxide in 25 mL water, cool and add to the DTPA solution. Filter the solution through Supor-450, 47 mm filter (or equivalent) and adjust pH to 10.6 with 10 M NaOH using a pH meter.

DTPA, 0.5 M: Dissolve 19.7 g of DTPA (Diethylenetriaminepentaacetic acid), in 60 mL of water. Dissolve 2.5 g of sodium hydroxide in 10 mL water, cool and add to the DTPA solution. Filter the solution through Supor-450, 47 mm filter (or equivalent) and adjust pH to 10.6 with 10 M NaOH using a pH meter.

Ethanol, CH_3CH_2OH, 95%.

Hydrochloric acid, HCl, 12 M: concentrated reagent.

Lead metal, Pb, granulated: ACS reagent.

Lead perchlorate, $Pb(ClO_4)_2$, 10 mg/mL (as Pb^{2+}): Carefully dissolve 1 g of granulated Pb metal by boiling in 2 mL of 11.7 M $HClO_4$ in a covered 50 mL beaker. Filter the solution through Supor-450, 47 mm filter (or equivalent). Dilute to 100 mL with water.

Perchloric acid, $HClO_4$, 11.7 M, concentrated: reagent grade.
Potassium hydrogen fluoride, KHF_2: crystalline.

Potassium sulfate, K_2SO_4: crystalline.

Potassium wash, 5% K_2SO_4 - 0.4% H_2SO_4: Dissolve 25 g of K_2SO_4 and 2 mL of 18 M of H_2SO_4 in 250 mL water. Filter through a Supor-450, 47 mm filter (or equivalent) and dilute to 500 mL with water.

Ra-226: NIST Traceable Standard.

Seeding Suspension, 0.125 mg/mL (as Ba^{2+}): Place 2.5 mL of 0.45% $BaCl_2$, 10 mL of 70% $NaHSO_4$, and one drop of 11.7 M $HClO_4$ into a 250 mL Erlenmeyer flask. Evaporate the solution carefully using a hot plate. Increase heating, until most of the excess H_2SO_4 has been expelled, and a pyrosulfate fusion forms. Swirl flask to deposit melt evenly, and cool. Add 25 mL of 40% Na_2SO_4 and 25 mL of water, swirl continuously to dissolve cake, and form a fine suspension of $BaSO_4$. Shake vigorously before using.

Sodium hydrogen sulfate, $NaHSO_4$, 70% (w/v): Dissolve 70 g of $NaHSO_4$ in 50 mL of water. Filter through a Supor-450, 47 mm filter (or equivalent) and dilute to 100 mL with water.

Sodium hydroxide, NaOH: ACS reagent.

Sodium hydroxide, NaOH, 10 M: **Slowly** add 200 g of NaOH to 400 mL water with stirring. Dilute to 500 mL with water.

Sodium sulfate, Na_2SO_4: crystalline

Sodium sulfate, Na_2SO_4, 40% (w/v): Dissolve 12 g of Na_2SO_4 in 30 mL water. Make fresh daily before use. Use heat and vortex to dissolve. Filter through a Supor-450, 47 mm filter (or equivalent) prior to use.

Sulfuric acid, H_2SO_4, 18 M: concentrated reagent.

Sulfuric acid, H_2SO_4, 9 M: **Slowly** add 250 mL of 18 M H_2SO_4 to 200 mL water with stirring. Dilute to 500 mL with reagent water.

3.0 APPARATUS AND SUPPLIES

Alpha spectrometer(s)
Analytical balance
Beaker, appropriate sizes needed for the analysis
Blast burner
Centrifuge
Centrifuge tube, 50 mL
Supor-450 filter, 47 mm, or equivalent
Gamma spectrometer(s)
Hot plate
Ice water bath
0.1 µm polypropylene filter, 25 mm

pH meter
Polysulfone filter apparatus
Stainless steel disk
Stir bars
Volumetric flaks, appropriate sizes needed for the analysis
Vortex mixer
Watch glass

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. Quality control requirements for this procedure are defined in QCP5. These requirements may be augmented by requirements in a client's statement of work. See page 2 for a copy of the certification record.

4.2 Water Samples

4.2.1 Measure the sample in a volumetric flask and quantitatively transfer into an appropriate size beaker. Add enough activity of the Ba-133 tracer so that reasonable counting statistics can be achieved in a 30 minute gamma count. Add a stir bar to each sample and cover with watch glass. **See step 4.2.1 of AP7 JHA.**

NOTE: If HF was initially added as a preservative to the sample to prevent Pu hydrolysis, then transfer the sample to a platinum crucible, evaporate to dryness on a hot plate, and proceed to step 4.3.3.

4.2.2 Evaporate the solution to approximately 30-35 mL using a hot plate.

4.2.3 Add 1 mL of 12 M HCl, 3 mL of 9 M H_2SO_4, 2 g of Na_2SO_4, and 5 g of K_2SO_4. Dissolve the salts with stirring and low heat if needed. **See step 4.2.3 of AP7 JHA.**

4.2.4 If necessary, allow the sample to cool to room temperature.

4.2.5 Add three 1 mL portions of the Pb^{2+} carrier with five minutes of stirring between each addition. **See step 4.2.5 of AP7 JHA.**

4.2.6 Remove the stir bar, and allow the precipitate to settle.

4.2.7 Swirl the solution to suspend the precipitate and transfer the precipitate to 50 mL centrifuge tube using potassium wash. **See step 4.2.7 of AP7 JHA.**

4.2.8 Centrifuge at 2000 RPM for 5 minutes. Discard supernate in dilute acid waste container. **See step 4.2.8 of AP7 JHA.**

4.2.9 Add 10 mL of potassium wash and vortex to wash the precipitate. Centrifuge at 2000 RPM for 5 minutes and decant supernate into the dilute acid waste container. **See step 4.2.9 of AP7 JHA.**

4.2.10 Loosen the pellet with a vortex mixer. Add 3 mL of 0.1 M DTPA. Place in hot water bath to dissolve precipitate. If the precipitate does not completely dissolve, add 50 µL of 0.5 M DTPA and re-heat. Continue adding 50 µL increments of 0.5 M DTPA until the precipitate completely dissolves. **See step 4.2.10 of AP7 JHA.**

4.2.11 Cool to below room temperature in an ice bath. Add 100 µL of the Ba^{2+} carrier (0.75 mg/mL).

4.2.12 Add 3 mL of freshly prepared and filtered 40% Na_2SO_4. **See step 4.2.12 of AP7 JHA.**

4.2.13 Add 3 drops of 50% acetic acid. Swirl to mix. **See step 4.2.13 of AP7 JHA.**

4.2.14 Immediately add 200 µL of the seeding suspension. Swirl to mix.

4.2.15 Place centrifuge tubes in ice water bath for 30 minutes.

4.2.16 Deposit slowly onto a 25 µm polypropylene filter in a polysulfone filter apparatus:

- Rinse filter with 95% ethanol
- Rinse filter with H_2O
- Add sample to filter
- Wash centrifuge tube with H_2O, add to filter
- Rinse filter with 95% ethanol

4.2.17 Remove the filter from the funnel. Mount on a stainless steel disk.

4.2.18 Submit to counting room for both an alpha spec count and 30 minute gamma spec count for Ba-133 yield.

4.3 Soil Samples

4.3.1 Weigh 0.1 to 0.25 g of dried soil into a platinum crucible. Do not use more than 0.25 g or the resolution of the alpha spectrum will be degraded. **See step 4.3.1 of AP7 JHA.**

4.3.2 Add enough activity of the Ba-133 tracer so that reasonable counting statistics can be achieved in a 30 minute gamma count. **See step 4.3.2 of AP7 JHA.**

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

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

4.3.5 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.**

4.3.6 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.**

4.3.7 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 4.3.8. **See step 4.3.7 of AP7 JHA.**

NOTE: IT IS CRITICAL FOR THE FLUORIDE CAKE TO BE SOMEWHAT COOLER BEFORE THE ADDITION OF H_2SO_4 TO PREVENT SPLATTERING.

4.3.8 Add 3 to 5 mL of 18 M H_2SO_4 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.**

4.3.9 After the addition of H_2SO_4, heat as much as frothing will allow until the fluoride cake is totally dissolved. **See step 4.3.9 of AP7 JHA.**

4.3.10 Remove from heat and add ~2 g of anhydrous Na_2SO_4 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.**

4.3.11 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.**

4.3.12 Transfer the pyrosulfate cake to a 150 mL beaker. **See step 4.3.12 of AP7 JHA.**

4.3.13 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.**

4.3.14 Rinse the platinum dish with water and add rinse to 150 mL beaker containing the pyrosulfate cake.

4.3.15 Add a stir bar and heat to boiling. If the pyrosulfate cake does not dissolve, see the Laboratory Manager, or designee. Add 3 mL of 9 M H_2SO_4, 2 g of Na_2SO_4, and 5 g of K_2SO_4. Evaporate the solution to 35 or 40 mL. Allow

the sample to cool to room temperature. **See step 4.3.15 of AP7 JHA.**

4.3.16 Add three 1 mL portions of the Pb^{2+} carrier, while stirring. Wait 5 minutes between each addition. **See step 4.3.16 of AP7 JHA.**

4.3.17 Transfer to a 50 mL centrifuge tube using the potassium wash. **See step 4.3.17 of AP7 JHA.**

4.3.18 Centrifuge at 2000 RPM for 5 minutes. Decant and discard supernate into the dilute acid waste container. **See step 4.3.18 of AP7 JHA.**

4.3.19 Add 10 mL of the potassium wash and vortex to wash the precipitate. Centrifuge at 2000 RPM for 5 minutes and discard supernate into the dilute acid waste container. Repeat. **See step 4.3.19 of AP7 JHA.**

4.3.20 Add 3 mL of 0.1 M DTPA solution to dissolve the precipitate. Heat in a hot water bath, if necessary. If the precipitate does not completely dissolve, add 50 µL of 0.5 M DTPA and re-heat. Continue adding 50 µL increments of 0.5 M DTPA until the precipitate completely dissolves. **See step 4.3.20 of AP7 JHA.**

4.3.21 Cool to below room temperature in an ice bath.

4.3.22 **To blanks and liquid Laboratory Control Standard (LCS) only**, add 100 µL of the Ba^{2+} carrier (0.75 mg/mL).

4.3.23 Continue the procedure with step 4.2.11.

5.0 INTERFERENCES

High levels of natural barium will add mass to the final sample causing self attenuation and degradation of the alpha spectrum. If this can be predetermined, it may be possible to adjust sample size and not add the Ba^{2+} carrier (0.75 mg/mL) in step 4.2.11. Contamination with Ba-133 will interfere with the yield determination. This may be corrected by gamma counting before analysis and adjusting the barium yield accordingly.

6.0 CALIBRATIONS

6.1 The alpha spectrometers and detectors used to quantify Ra-226 have been calibrated according the calibration section of CP2.

6.2 The gamma spectroscopy detectors have been calibrated using a Ba-133 disk prepared by the following steps.

6.2.1 Add a known amount of Ba-133 to a 25 µm polypropylene filter and dry under a heat lamp. **See step 4.2.1 of AP7 JHA.**

NOTE: This may take several additions of the Ba-133. Do not allow the Ba-133 to spill over the edge of the filter.

6.2.2 Submit to counting room for a 30 minute gamma spec count for Ba-133 counting efficiency.

6.2.3 The Laboratory Manager must review and approve the counting efficiency.

7.0 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.

$$Concentration = \frac{G - B}{T \cdot E \cdot A \cdot Y \cdot Q \cdot 2.22} = pCi / unit$$

$$2\sigma\ Error = \frac{1.96\sqrt{G + B}}{T \cdot E \cdot A \cdot Y \cdot Q \cdot 2.22} = pCi / unit$$

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.

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

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.

$$MDC = \frac{3 + 4.65\sqrt{B}}{T \cdot E \cdot A \cdot Y \cdot Q \cdot 2.22} = pCi / unit$$

To calculate efficiency: $$E = \frac{C_{STD} - B}{STD\alpha}$$

To calculate chemical yield:

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

where:
A = alpha abundance in α/d
B = background counts (alpha)
$Ba\text{-}133_{MA}$ = Ba-133 measured activity by gamma spec
$Ba\text{-}133_{KA}$ = Ba-133 known activity

C	=	concentration pCi/unit
C_{STD}	=	gross counts of standard
E	=	detector efficiency, counts/α
G	=	gross counts (alpha)
MDC	=	minimum detectable concentration
Q	=	sample quantity
RE	=	1σ relative uncertainty of the efficiency
RY	=	1σ relative uncertainty of the yield
RQ	=	1σ relative uncertainty of the quantity
STDα	=	emission rate of the standard
T	=	length of count, minutes
TPU	=	total propagated uncertainty
Y	=	radiochemical yield
2.22	=	dpm to pCi conversion

8.0 RECORDS

8.1 Reference QP Manual for general record requirements.

8.2 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.

8.3 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-226 Analysis Assignment Form
- Ra-226 Data Sheet
- Ra-226 Concentration and Uncertainty Report (This report may be generated using approved Excel spreadsheets or from the database, if available.)

(AP 7, Rev 19) - Ra-226 ANALYSIS ASSIGNMENT FORM

Assigned To: _____ Date: _____ Batch: _____

Task #: _____ LWR #: _____ Activity Level*: _____

Sample #s: _____

_____

_____

QC REQUIRED:

Blank ☐

LCS ☐ Ra-226 STD # _____ Quantity: _____ Initials ☐

Units: _____

Pipette # _____ Volume (mL) _____ Weight (g) _____

Replicate ☐ Sample # _____ # Replicates: _____

Matrix Spike ☐ Sample # _____ Initials

Ra-226 STD # _____ Quantity: _____ ☐

Units: _____

Initials

Ba-133 STD # _____ Quantity: _____ ☐

Units: _____

SPECIAL INSTRUCTIONS: _____

_____

_____

_____

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

COMMENTS: _____

_____

_____

_____

(AP 7, Rev 19) - Ra-226 DATA SHEET

Sample #							
Quantity							
Units							
Ba-133 meas.							
Ba-133 known							
Ba-133 yield							

Sample #							
Quantity							
Units							
Ba-133 meas.							
Ba-133 known							
Ba-133 yield							

Sample #							
Quantity							
Units							
Ba-133 meas.							
Ba-133 known							
Ba-133 yield							

Sample #			
Quantity			
Units			
Ba-133 meas.			
Ba-133 known			
Ba-133 yield			

Procedure AP7 - Revision 19
Radium-226 Concentration & Uncertainty Report
For Task #:

Batch #: **Acq Date:**

AVERAGE EFFICIENCY:		YIELD:		CORRECTED TRACER:		SAMPLE QUANTITY	
DETECTOR #:							
SAMPLE ID	ISOTOPE	Conc. (pCi/g)	TPU (pCi/g)	MDC (pCi/g)	ENERGY (KEV)	SAMPLE COUNTS	DETECTOR BKG

AVERAGE EFFICIENCY:		YIELD:		CORRECTED TRACER:		SAMPLE QUANTITY	
DETECTOR #:							
SAMPLE ID	ISOTOPE	Conc. (pCi/g)	TPU (pCi/g)	MDC (pCi/g)	ENERGY (KEV)	SAMPLE COUNTS	DETECTOR BKG

AVERAGE EFFICIENCY:		YIELD:		CORRECTED TRACER:		SAMPLE QUANTITY	
DETECTOR #: A5							
SAMPLE ID	ISOTOPE	Conc. (pCi/g)	TPU (pCi/g)	MDC (pCi/g)	ENERGY (KEV)	SAMPLE COUNTS	DETECTOR BKG

LCS	LCS Known Activity (pCi)	LCS Known Uncertainty	Meas./Known Activity Ratio	Meas./Known Uncertainty Ratio
Ra-226				

BLK CORRECT? YES[ ] NO[ ]
LCS CORRECT? YES[ ] NO[ ]
YIELDS CORRECT? YES[ ] NO[ ]
IF NO, SPECIFY REASON:

QC Review: _____
(Initials/Date)

_____ Analyst Review _____ Date

_____ Reviewed By _____ Date

_____ Given To: _____ Date

_____ QC Entered By _____ Date