AP14

DETERMINATION OF SULFUR-35 IN SOLID ENVIRONMENTAL SAMPLES

PART A

PRINCIPLE

Sulfur in solid environmental samples is oxidized to the sulfate anion using perchloric and nitric acids. Potassium and ammonium ions are removed from the samples as perchlorate salts. The sulfate is precipitated as barium sulfate. The insoluble barium sulfate is suspended in scintillation cocktail and counted in a liquid scintillation analyzer.

REFERENCE

1. Willis, C. P., Olson, D. G., and Sill, C. W., Radiological Determination of Sulfur-35 in Large Samples of Vegetation, *Anal. Chem.*, **1970**, *42(1)*, 124.

CERTIFICATION RECORD FOR

AP14
DETERMINATION OF SULFUR-35 IN SOLID ENVIRONMENTAL SAMPLES

CHECKPOINTS

1.	**JOB HAZARD ANALYSIS (JHA)**	**____**
2.	**MSDS/HAZARDS DISCUSSED**	**____**
3.	**SAMPLE PREPARATION**	**____**
4.	**SAMPLE DISSOLUTION**	**____**
5.	**BARIUM SULFATE PRECIPITATION**	**____**
6.	**LSC PREPARATION**	**____**
7.	**CALCULATIONS**	**____**

ANALYST SIGNATURE: _____

CERTIFIED BY: _____

DATE: _____

ANALYSIS VALUE: _____

KNOWN VALUE: _____

MEAS/KNOWN: _____

See Task _____, Batch_____ for the original data.

COMMENTS:_____
_____
_____
_____
_____
_____

PART B

1.0 PURPOSE AND SCOPE

This is a radiochemical procedure for the determination of sulfur-35 in solid materials.

2.0 REAGENTS

All chemicals are hazardous. See MSDS for specific precautions. Unless otherwise indicated, all references to water should be understood to mean reagent grade water.
See STEP 2.0 of AP14 JHA.

Barium chloride dihydrate, $BaCl_2 \cdot 2H_2O$, crystalline.

Barium chloride solution, 20% (w/v): Dissolve 20 g $BaCl_2 \cdot 2H_2O$ in 80 mL water. Dilute to 100 mL with water.

Hydrogen peroxide, H_2O_2, 30-35% (w/v).

Insta-Gel scintillation cocktail or equivalent.

Nitric acid, HNO_3, concentrated, 16 M.

Perchloric acid, $HClO_4$, concentrated, 11.7 M.

Sodium sulfate, Na_2SO_4, crystalline.

Sulfuric acid, H_2SO_4, concentrated, 18 M.

3.0 APPARATUS

Balance
Beakers, various sizes
Centrifuge
Centrifuge tubes
Erlenmeyer flasks
Filtering apparatus
Filters, 0.45 µm
Fume Hood
Hot plates
Liquid Scintillation Analyzer (LSA)
Scintillation vials

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 for a copy of the certification record.

A batch yield sample must be run with each batch to determine chemical recovery for the batch (see calculations). This is not a QC sample; two QC samples must be run with each batch.

4.2 Sample Preparation

4.2.1 Weigh approximately 2-3 g sample and transfer to a 250 mL Erlenmeyer flask. To each sample along with the blank and Laboratory Control Standard (LCS), add 1 drop 18 M H_2SO_4. **See step 4.2.1 of AP14 JHA.**

4.2.2 Add 20 mL 16 M HNO_3 and 20 mL 11.7 M $HClO_4$ to each Erlenmeyer flask. Place flask on medium temperature hot plate. Continue slow boil ~45 minutes. (Sulfur is volatile at high temperatures and prolonged heating.) **See step 4.2.2 of AP14 JHA.**

4.2.3 Swirl sample periodically, as it is heated. Carefully add 1 mL H_2O_2 dropwise to each sample. Repeat H_2O_2 additions until brown fumes of nitrogen oxides no longer evolve. The solution should then turn yellow-green. **See step 4.2.3 of AP14 JHA.**

4.2.4 Heat sample an additional 15 minutes to eliminate all HNO_3. Remove Erlenmeyer from hot plate and allow solution to cool. **See step 4.2.4 of AP14 JHA.**

4.2.5 Transfer sample to 50 mL centrifuge tube, using a minimum of water. Cool the solution in cold water bath to precipitate potassium and ammonium perchlorates. The precipitate may or may not be visible. Centrifuge 2000 RPM for 5 minutes. Decant supernate into a 50 mL centrifuge tube. Discard precipitate. If visible solid material remains, filter sample through a 0.45 micron filter. Discard filter. Put the supernate into a centrifuge tube. **See step 4.2.5 of AP14 JHA.**

4.2.6 Place open centrifuge tube into slow boiling water bath. Boil solution, using low heat. **See step 4.2.6 of AP14 JHA.**

4.2.7 Add 10 mL 20% (w/v) $BaCl_2$ and continue boiling solution for 5 minutes. **See step 4.2.7 of AP14 JHA.**

4.2.8 Centrifuge 2000 RPM for 5 minutes. Decant supernate. Dispose of $HClO_4$ is the $HClO_4$ waste stream. **See step 4.2.8 of AP14 JHA.**

4.2.9 Transfer precipitate with reagent water to a counting vial and bring final volume to 7 mL. **See step 4.2.9 of AP14 JHA.**

4.2.10 Vortex to suspend the barium sulfate precipitate. **See step 4.2.10 of AP14 JHA.**

4.2.11 Add 13 mL Insta-Gel scintillation suspension to the vial. Shake vigorously to mix. Solution will be cloudy, and will form a thick gel. **See step 4.2.11 of AP14 JHA.**

4.2.12 Centrifuge at 500 RPM for 1 minute to remove air bubbles from the scintillation gel. **See step 4.2.12 of AP14 JHA.**

4.2.13 Store samples in the dark for 1 hour, to allow any initial fluorescence to decay. Count for 60 minutes in the LSA.

5.0 CALIBRATIONS

5.1 Add 1 drop of 18 M H_2SO_4 to 5 mL of water in a centrifuge tube. **See step 4.2.1 of AP14 JHA.**

5.2 Add the appropriate amount of a S-35 standard to the centrifuge tube to produce counting statistics of 1 percent or less. **See step 4.2.1 of AP14 JHA.**

5.3 Place open centrifuge tube into slow boiling water bath. Boil solution, using low heat. **See step 4.2.6 of AP14 JHA.**

5.4 Add 10 mL 20% (w/v) $BaCl_2$ and continue boiling solution for 5 minutes. **See step 4.2.7 of AP14 JHA.**

5.5 Centrifuge 2000 RPM for 5 minutes. Decant supernate. Dispose of $HClO_4$ is the $HClO_4$ waste stream. **See step 4.2.8 of AP14 JHA.**

5.6 Transfer the precipitate with reagent water to a counting vial and bring final volume to 7 mL. **See step 4.2.9 of AP14 JHA.**

5.7 Vortex to suspend the barium sulfate precipitate. **See step 4.2.10 of AP14 JHA.**

5.8 Add 13 mL Insta-Gel scintillation suspension to the vial. Shake vigorously to mix. Solution will be cloudy, and will form a thick gel. **See step 4.2.11 of AP14 JHA.**

5.9 Centrifuge at 500 RPM for 1 minute to remove air bubbles from the scintillation gel. **See step 4.2.12 of AP14 JHA.**

5.10 Submit the standard to the count room for counting.

5.11 After counting the standard, the efficiency is calculated.

5.12 The Laboratory Manager must review and approve the efficiency. The approval may occur with the review of data from an analytical batch.

6.0 CALCULATIONS

All necessary data is recorded and reduced using the following calculations.

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

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

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

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

To calculate efficiency:

$$E = \frac{G_E - B}{A} = cpm / pCi$$

To calculate chemical yield:

$$Y = \frac{G_{BY} - G}{E \cdot A_Y} = no\ units$$

where: A = activity in pCi for efficiency determination
A_Y = activity in pCi for yield determination
B = background cpm beta
C = concentration in pCi/unit

E	=	counting efficiency (cpm/pCi)
G	=	sample gross cpm beta
G_E	=	efficiency gross cpm beta
G_{BY}	=	batch yield gross cpm beta
MDC	=	minimum detectable concentration
Q	=	quantity
RE	=	1σ relative uncertainty of the efficiency
RY	=	1σ relative uncertainty of the yield
RQ	=	1σ relative uncertainty of the quantity
T	=	time in minutes
TPU	=	total propagated uncertainty
Y	=	chemical yield

7.0 RECORDS

7.1 Reference QP Manual for record requirements.

7.2 The raw count data is saved during the weekly backup of the Liquid Scintillation Analyzer to the ORISE network disks.

7.3 Hard copies of assignment and calculation sheets are maintained in the archived task 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:

- S-35 Analysis Assignment Form
- S-35 Lab Data Sheet
- S-35 Concentration and Uncertainty Report (This report may be generated using approved Excel spreadsheets or from the database, if available.)

AP14 (Rev 7) - S-35 ANALYSIS ASSIGNMENT FORM

Assigned To: _____ Date: _____ Batch: _____

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

Sample #s: _____

_____

_____

Analysis Required:

Batch Yield ☐ Sample # _____
Initial below sample

S-35 STD # _____ Quantity: _____
Units: _____

Eff. Spike ☐ S-35 STD _____ Quantity: _____
(see Special Instructions, if any) Units: _____

QC Required:

Blank ☐

LCS ☐ S-35 STD # _____ Quantity: _____ Initials ☐
Units: _____

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

Replicate ☐ Sample # _____ Replicates: _____

Matrix Spike ☐ Sample # _____ Quantity: _____ Initials ☐
S-35 STD # _____ Units: _____

SPECIAL INSTRUCTIONS: _____

_____

_____

_____

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

COMMENTS: _____

_____

_____

_____

AP14 (Rev 7) - S-35 LAB DATA SHEET

BATCH YIELD SAMPLE

Sample #							
Quantity							
Units							

Sample #							
Quantity							
Units							

Sample #							
Quantity							
Units							

Sample #			
Quantity			
Units			

AP14 (Rev 7) S-35 (by batch yield) CONCENTRATION and UNCERTAINTY REPORT

INPUT BY:
DATE:
SITE#
BATCH#

Yield Calculation	
Batch Yield (BY) sample cpm	
BY sample quantity	
BY sample quantity error	
Sample cpm	
Sample quantity	
Sample quantity error	
BY pCi added	
BY pCi added error	
BY	
BY Error	
BY Relative Error	

Efficiency (EFF) Calculation	
EFF spike cpm	
Background cpm	
pCi added	
pCi added error	
EFF (cpm/pCi)	
EFF Error (cpm/pCi)	
EFF Relative Error	

Counting time for EFF and BY calculations (min)	

Position #	SAMPLE ID	GROSS cpm	QUANTITY	QUANTITY ERROR	UNITS	TIME (min)	CONCENTRATION	TPU	4.65 sigma MDC
1									
2									
3									
4									
Matrix Spk									
Matrix Spk Sample									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									

S-35 Known	Unc.	Meas/ Known	Unc

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:_____
QC ENTERED BY:_____ DATE:_____