

## AP16

### DETERMINATION OF IRON-55 IN SOIL AND OTHER SOLID MATRICES

#### PART A

#### PRINCIPLE

Iron-55 (Fe-55) in soil and other miscellaneous solid samples is separated from other isotopes by using a combination of iron hydroxide coprecipitations and anion exchange chromatography. The samples are completely dissolved by a combination of potassium hydrogen fluoride and pyrosulfate fusions. The fusion cake is dissolved and the iron is preconcentrated using an iron hydroxide precipitation. The iron hydroxide is dissolved and the iron is separated from other elements using anion exchange chromatography. The Fe-55 activity is determined via liquid scintillation counting. A batch yield is used to determine chemical recovery.

#### REFERENCES

1. Backstrom, G., personal communications, **2005**.
2. Sill, Claude, W., *Anal. Chem.* **1974**, *46*, 1426.
3. DOE RESL CHEM-TP-FE.1, modified

**Certification Record for**

**AP16**

**DETERMINATION OF IRON-55 IN SOIL  
AND OTHER SOLID MATRICES**

**CHECKPOINTS**

- 1. **JOB HAZARD ANALYSIS (JHA)** \_\_\_\_\_
- 2. **MSDS/HAZARDS DISCUSSED** \_\_\_\_\_
- 3. **SAMPLE DIGESTION** \_\_\_\_\_
- 4. **COLUMN SEPARATION** \_\_\_\_\_
- 5. **COUNTING PREPARATION** \_\_\_\_\_
- 6. **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 Fe-55 in soil and other solid matrices.

### 2.0 REAGENTS

All chemicals are hazardous. See MSDS for specific precautions. **See step 2.0 of AP16 JHA.** Unless otherwise indicated, all references to water should be understood to mean reagent grade water.

Ammonium hydroxide,  $\text{NH}_4\text{OH}$ , concentrated, reagent grade.

Anion exchange resin, BioRad 1 X 8, chloride form, 100-200 mesh, or equivalent.

Fe-55, NIST traceable standardized solution.

Iron carrier, 1 mg/mL, AA quality.

Liquid scintillation cocktail - Packard Instrument Ultima Gold LLT, or equivalent.

Hydrochloric acid, HCl, concentrated, 12 M.

Hydrochloric acid, HCl, 10 M: Add 416 mL of concentrated HCl to 50 mL water and dilute to 500 mL with water and mix.

Hydrochloric acid, 6 M: Add 500 mL 12 M HCl to 400 mL reagent water. Dilute to 1 L with water and mix.

Hydrochloric acid, 4 M: Add 334 mL 12 M HCl to 500 mL water. Dilute to 1 L with water and mix.

Hydrochloric acid, 0.5 M: Add 62.5 mL 4 M HCl to 400 mL water. Dilute to 500 mL with water and mix.

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

Potassium hydrogen fluoride,  $\text{KHF}_2$ , anhydrous crystal.

Sodium sulfate,  $\text{Na}_2\text{SO}_4$ , anhydrous crystal.

Sulfuric acid,  $\text{H}_2\text{SO}_4$ , concentrated, 18 M.

### 3.0 APPARATUS

Analytical balance  
Anion exchange column  
Beakers, various sizes  
Blast Burner  
Centrifuge tubes  
Column rack  
Fume hood  
Hot plate  
Liquid scintillation analyzer (LSA)  
Liquid scintillation vials  
Specimen cups  
Stir bar  
Transfer pipette  
Vortex

### 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 two for an example certification record.

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

#### 4.2 Sample Preparation

4.2.1 Measure the sample in a platinum dish and record the mass. Typical soil sample size is 1-2 grams. Use a NIST traceable soil for the laboratory control sample and blank soil for the blank. **See step 4.2.1 of AP16 JHA.**

4.2.2 Add an appropriate amount of Fe-55 solution to the batch yield sample to reach desired counting statistics. **See step 4.2.2 of AP16 JHA.**

4.2.3 Place the batch yield sample on a hot plate to dry the Fe-55 solution. Proceed to Sample Decomposition for Solid Samples, section 4.3.

#### 4.3 Sample Decomposition for Solid Samples

4.3.1 Add ~12-15 g of  $\text{KHF}_2$  to the sample. **See step 4.3.1 of AP16 JHA.**

- 4.3.2 Place the platinum dish on a ring stand using a nichrome triangle. **See step 4.3.2 of AP16 JHA.**
- 4.3.3 Start heating the sample over a blast burner with low flame. Heat until the  $\text{KHF}_2$  has completely dried. **See step 4.3.3 of AP16 JHA.**
- 4.3.4 Use as much heat as possible with limited splattering. Bring the temperature to about  $900^\circ\text{C}$  (the color of the Pt 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 4.3.4 of AP16 JHA.**
- 4.3.5 Remove the melt from the burner and swirl the melt gently around the dish to form a thin layer upon cooling. Wait 45 seconds before proceeding to step 4.3.6. (Never set hot platinum on iron). **See step 4.3.5 of AP16 JHA.**

**NOTE: IT IS CRITICAL FOR THE FLUORIDE CAKE TO BE SOMEWHAT COOL BEFORE THE ADDITION OF  $\text{H}_2\text{SO}_4$  TO PREVENT SPLATTERING. WAIT 45 SECONDS BEFORE PROCEEDING.**

- 4.3.6 Add  $\sim 8$  mL of concentrated  $\text{H}_2\text{SO}_4$  to the fluoride cake. Add another  $\sim 8$  mL. The acid should be added to the edge of the dish and allowed to run to the bottom of the dish. **See step 4.3.6 of AP16 JHA.**
- 4.3.7 After the addition of  $\text{H}_2\text{SO}_4$ , heat as much as frothing will allow until the fluoride cake is totally dissolved. **See step 4.3.7 of AP16 JHA.**
- 4.3.8 Remove from heat and add  $\sim 3$  g of anhydrous  $\text{Na}_2\text{SO}_4$  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; maintain this temperature for approximately 1 minute. **See step 4.3.8 of AP16 JHA.**
- 4.3.9 Remove the platinum dish from the burner and swirl the melt gently around the dish to form a thin layer upon cooling. **See step 4.3.9 of AP16 JHA.**
- 4.3.10 Transfer the hardened pyrosulfate cake to a specimen cup by gently bending the dish to crack and loosen the cake. Proceed to Iron Hydroxide Preconcentration, section 4.4. **See step 4.3.10 of AP16 JHA.**

#### 4.4 Iron Hydroxide Preconcentration

- 4.4.1 To a clean 150 mL beaker, add 50 mL of water and 5 mL of concentrated HCl. Add a stir bar and begin stirring the sample. Heat the solution to boiling on a hot plate. **See step 4.4.1 of AP16 JHA.**

- 4.4.2 Add the fusion cake and allow the solution to boil for 10 minutes. Turn heat off and allow the solution to cool to room temperature.
- 4.4.3 While stirring, add concentrated  $\text{NH}_4(\text{OH})$  dropwise until  $\text{Fe}(\text{OH})_3$  forms. Add an additional 5 mL of concentrated  $\text{NH}_4(\text{OH})$  to ensure complete precipitation. Remove the stir bar and allow the precipitate to settle for about 30 minutes. **See step 4.4.3 of AP16 JHA.**
- 4.4.4 Quantitatively transfer the precipitate into a labeled centrifuge tube with water. Centrifuge for 5 minutes at 2000 rpm.
- 4.4.5 Decant the supernate and add 15 mL of water to the centrifuge tube. Vortex and centrifuge for 5 minutes at 2000 rpm. Decant supernate.
- 4.4.6 Add 10 mL of 10 M HCl and vortex to dissolve the precipitate. **See step 4.4.6 of AP16 JHA.** Proceed to Anion Exchange Separation, section 4.5.
- 4.5 Anion Exchange Separation
- 4.5.1 Make a slurry of the anion exchange resin using 10 M HCl and allow to equilibrate for at least 30 minutes. Approximately 8-9 grams of dry resin is used per column. Use an equal amount in each column to ensure consistent conditions across all the samples. **See step 4.5.1 of AP16 JHA.**
- 4.5.2 Pour enough of the slurry into an empty column to give a 5 cm resin bed. Allow the resin to settle and place a frit on top of the resin.
- 4.5.3 Pour 25 mL of 10 M HCl through the column and collect as waste. **See step 4.5.3 of AP16 JHA.**
- 4.5.4 Pour the sample through the column and collect as waste.
- 4.5.5 Rinse the centrifuge tube with 5 mL of 10 M HCl and pour through the column and collect as waste. **See step 4.5.5 of AP16 JHA.**
- 4.5.6 Rinse the column with 3 additions of 15 mL of 10 M HCl and collect as waste. Allow each addition to drain before adding the subsequent additions. **See step 4.5.6 of AP16 JHA.**
- 4.5.7 Rinse the column with 3 additions of 15 mL of 6 M HCl and collect as waste. Allow each addition to drain before adding the subsequent additions. **See step 4.5.7 of AP16 JHA.**
- 4.5.8 Rinse the column with 15 mL of 4 M HCl. Watch the drops as they flow through the column. Start collecting this rinse as waste. Continue to watch the drops. If the drops are colorless, continue collecting them as waste. If the

drops begin to take on a yellow color, quickly start collecting the rinse in a labeled 250 mL beaker. If the drops do not turn to a yellow color, that is fine, just collect them as waste. **See step 4.5.8 of AP16 JHA.**

**NOTE: Dispose of all acid waste in the appropriate waste container.**

4.5.9 Strip the iron from the column by adding 100 mL of 0.5M HCl and collect in a labeled 250 mL beaker. Proceed to Sample Preparation for Liquid Scintillation Counting, section 4.6. **See step 4.5.9 of AP16 JHA.**

#### 4.6 Sample Preparation for Liquid Scintillation Counting

4.6.1 Add a stir bar to the 250 mL beaker and start stirring the sample on a stir plate.

4.6.2 Slowly add concentrated  $\text{NH}_4(\text{OH})$  dropwise until  $\text{Fe}(\text{OH})_3$  precipitates. Add 5 more mL of concentrated  $\text{NH}_4(\text{OH})$  to ensure complete precipitation. **See step 4.6.2 of AP16 JHA.**

4.6.3 Quantitatively transfer the precipitate into a labeled centrifuge tube with water. Centrifuge for 5 minutes at 2000 rpm.

4.6.4 Decant the supernate and add 15 mL of water to the centrifuge tube. Vortex and centrifuge for 5 minutes at 2000 rpm. Decant supernate.

4.6.5 Add 28M HF in 2-drop increments to each sample to dissolve the  $\text{Fe}(\text{OH})_3$ . Gently swirl and heat in a water bath for 10 minutes between HF additions. Use the minimum amount of HF required to dissolve the product. Normally this will be approximately 3-5 drops. **See step 4.6.5 of AP16 JHA.**

4.6.6 Carefully transfer the solution to a tared plastic scintillation vial. Use a very small amount of D.I. water to rinse the centrifuge tube, adding this to the tared scintillation vial. Add D.I. water to the scintillation vial until the weight is 3.0g and add 10 mL of scintillation cocktail. Mix the solution with vigorous shaking. **See step 4.6.6 of AP16 JHA.**

4.6.7 Submit samples to the counting room.

### 5.0 CALIBRATIONS

#### 5.1 Instrument Background Preparation

5.1.1 Add 2.0 mL of Fe carrier and 10 mL of water to a centrifuge tube. **See step 5.1.1 of AP16 JHA.**

5.1.2 Add concentrated  $\text{NH}_4(\text{OH})$  dropwise to precipitate  $\text{Fe}(\text{OH})_3$ . Add 5 more drops to ensure complete precipitation. **See step 5.1.2 of AP16 JHA.**

- 5.1.3 Centrifuge at 2000 rpm for 5 minutes. Decant supernate.
- 5.1.4 Add 10 mL of water and vortex. Centrifuge at 2000 rpm for 5 minutes and discard the supernate.
- 5.1.5 Add 28M HF in 2-drop increments to each sample to dissolve the  $\text{Fe}(\text{OH})_3$ . Gently swirl and heat in a water bath for 10 minutes between HF additions. Use the minimum amount of HF required to dissolve the product. Normally this will be approximately 3-5 drops. **See step 5.1.5 of AP16 JHA.**
- 5.1.6 Using a transfer pipette, carefully transfer the solution to a tared plastic scintillation vial. Use a very small amount of D.I. water to rinse the centrifuge tube, adding this to the tared scintillation vial. Add D.I. water to the scintillation vial until the weight is 3.0g and add 10 mL of scintillation cocktail. Mix the solution with vigorous shaking. **See step 5.1.6 of AP16 JHA.**
- 5.2 Instrument Efficiency Standard Preparation
- 5.2.1 Add 2.0 mL of Fe carrier and 10 mL of water to a centrifuge tube. **See step 5.2.1 of AP16 JHA.**
- 5.2.2 Add enough Fe-55 standard to the centrifuge tube to give the desired counting statistics. **See step 5.2.2 of AP16 JHA.**
- 5.2.3 Add concentrated  $\text{NH}_4(\text{OH})$  dropwise to precipitate  $\text{Fe}(\text{OH})_3$ . Add 5 more drops to ensure complete precipitation. **See step 5.2.3 of AP16 JHA.**
- 5.2.4 Centrifuge at 2000 rpm for 5 minutes. Decant supernate.
- 5.2.5 Add 10 mL water and vortex. Centrifuge at 2000 rpm for 5 minutes and discard the supernate.
- 5.2.6 Add 28M HF in 2-drop increments to each sample to dissolve the  $\text{Fe}(\text{OH})_3$ . Gently swirl and heat in a water bath for 10 minutes between HF additions. Use the minimum amount of HF required to dissolve the product. Normally this will be approximately 3-5 drops. **See step 5.2.6 of AP16 JHA.**
- 5.2.7 Using a transfer pipette, carefully transfer the solution to a tared plastic scintillation vial. Use a very small amount of D.I. water to rinse the centrifuge tube, adding this to the tared scintillation vial. Add D.I. water to the scintillation vial until the weight is 3.0g and add 10 mL of scintillation

cocktail. Mix the solution with vigorous shaking. See step 5.2.7 of AP16 JHA.

## 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.

$$\text{Concentration } (C) = \frac{(G - B)}{E * Y * Q} = pCi/unit$$

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

$$2\sigma \text{ TPU} = |C| * 1.96 \sqrt{\frac{(G + B) * T}{((G - B) * T)^2} + \left(\frac{\sigma_E}{E}\right)^2 + \left(\frac{\sigma_{BY}}{BY}\right)^2 + \left(\frac{\sigma_Q}{Q}\right)^2} = pCi/unit$$

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

To calculate efficiency:

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

Efficiency Uncertainty:

$$\sigma_E = E \sqrt{\frac{(G_E + B)}{((G_E - B)^2 * T)} + \left(\frac{\sigma_{EACT}}{EACT}\right)^2} = cpm/pCi$$

To calculate batch yield:

$$BY = \frac{G_{BY} - G \left(\frac{Q_{BY}}{Q}\right)}{E * BY_{ACT}}$$

Yield Uncertainty:

$$\sigma_{BY} = BY \sqrt{\left[ \frac{\left( \left( \frac{G_{BY}}{T} \right) * BSQ^2 \right) + \left( \left( \frac{G}{T} \right) * Q^2 \right) + (G^2 * \sigma_Q^2)}{\left( (G * Q) - (G_{BY} * BSQ) \right)^2} \right] + \left[ \frac{\sigma_{BSQ} * G * Q}{\left( BSQ * ((G * Q) - (G_{BY} * BSQ)) \right)^2} \right] + \left( \frac{\sigma_E}{E} \right)^2 + \left( \frac{\sigma_{BYACT}}{BY_{ACT}} \right)^2} = cpm/pCi$$

- where:
- A = activity in pCi for efficiency determination
  - BY<sub>ACT</sub> = activity in pCi for yield determination
  - B = background cpm beta
  - BSQ = batch yield sample quantity
  - BY = batch yield
  - C = concentration in pCi/unit
  - E = counting efficiency (cpm/pCi)
  - G = sample gross cpm beta
  - G<sub>BY</sub> = batch yield gross cpm beta
  - G<sub>E</sub> = efficiency gross cpm beta
  - MDC = minimum detectable concentration
  - σ<sub>BYACT</sub> = 1σ uncertainty for the batch yield activity
  - σ<sub>BSQ</sub> = 1σ batch yield uncertainty
  - σ<sub>BY</sub> = 1σ batch yield uncertainty
  - σ<sub>E</sub> = 1σ efficiency uncertainty
  - σ<sub>Q</sub> = 1σ efficiency uncertainty
    - = 0.0001 for solids (uncertainty of balance)
    - = 0.000 for filters/smears (no uncertainty for a finite sample)
  - Q = sample quantity
  - T = time minutes
  - TPU = total propagated uncertainty

## 7.0 RECORDS

- 7.1 Reference Quality Program Manual for general record requirements.
- 7.2 The raw count data is saved during the weekly backup of the LSA to the ORISE network disks.
- 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 show the required data and information. These forms or the equivalent should be completed and retained:

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

8.0 REVISION HISTORY

Revision Number	Date	Description of Change
0-1	Various	<a href="#">Fe-55 Past Revisions</a>
2	4/25/12	1. Added Section 8.0 Revision History 2. Step 4.5.1 – Added anion exchange column details. 3. Step 4.5.9 – Revised stripping solution to 0.5M HCl. 4. Updated equations for clarification. 2007 Word Format.

## AP16 (Rev 2) - Fe-55 SOILDS ANALYSIS ASSIGNMENT FORM

Assigned To: \_\_\_\_\_ Date: \_\_\_\_\_ Batch: \_\_\_\_\_

Task #: \_\_\_\_\_ LWR #: \_\_\_\_\_ Activity Level\*: \_\_\_\_\_

Sample #s: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

### QC Required:

Batch Yield  Sample # \_\_\_\_\_ Initials   
 Fe-55 STD # \_\_\_\_\_ Quantity: \_\_\_\_\_  
 Units: \_\_\_\_\_

Eff. Spike  Fe-55 STD # \_\_\_\_\_ Quantity: \_\_\_\_\_ Initials   
 Units: \_\_\_\_\_

Blank

LCS  Fe-55 STD # \_\_\_\_\_ Quantity: \_\_\_\_\_ Initials   
 Units: \_\_\_\_\_

Pipette # \_\_\_\_\_ Volume (mL) \_\_\_\_\_ Weight (g) \_\_\_\_\_

Duplicate  Sample # \_\_\_\_\_ # Replicates: \_\_\_\_\_

Matrix Spike  Sample # \_\_\_\_\_ Initials   
 Fe-55 STD # \_\_\_\_\_ Quantity: \_\_\_\_\_  
 Units: \_\_\_\_\_

Matrix Spike Dup  Sample # \_\_\_\_\_ Initials   
 Fe-55 STD # \_\_\_\_\_ Quantity: \_\_\_\_\_  
 Units: \_\_\_\_\_

SPECIAL INSTRUCTIONS: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

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

COMMENTS: \_\_\_\_\_  
 \_\_\_\_\_

# AP16 (Rev 2) - Fe-55 SOLIDS LAB DATA SHEET

	BATCH YIELD		SAMPLE
<b>Sample #</b>			
<b>Quantity</b>			
<b>Units</b>			

<b>Sample #</b>			
<b>Quantity</b>			
<b>Units</b>			

<b>Sample #</b>			
<b>Quantity</b>			
<b>Units</b>			

<b>Sample #</b>		
<b>Quantity</b>		
<b>Units</b>		

