

## LEAD-210 IN SOIL

(WITH VACUUM BOX SYSTEM)

### 1. SCOPE

- 1.1. This is a method for separation and measurement of Lead-210 in soil.
- 1.2. This method does not address all aspects of safety, quality control, calibration or instrument set-up. However, enough detail is given for a trained radiochemist to achieve accurate and precise results for the analysis of the analyte(s) from the appropriate matrix, when incorporating the appropriate agency or laboratory safety, quality and laboratory control standards.

### 2. SUMMARY OF METHOD

- 2.1. This method enables separation of lead from soil prior to measurement by gas flow proportional counting.

### 3. SIGNIFICANCE OF USE

- 3.1. This is a rapid, reliable method for measurement of Lead-210 in soil samples that is more cost-effective and efficient than traditional ion exchange, solvent extraction and precipitation techniques.

### 4. INTERFERENCES

- 4.1. Any beta emitter can cause an interference with the measurement of the  $^{210}\text{Bi}$  daughter of  $^{210}\text{Pb}$ . This method effectively eliminates these possible interferences.

### 5. APPARATUS

- Aluminum foil, 0.003 inch thickness
- Beakers, glass
- Beta detector, low background gas flow proportional, liquid scintillation or Cerenkov counter and appropriate sample holders, planchets or vials
- Cartridge reservoirs, 10mL (Eichrom Part: AR-200-RV10) or 20mL (Eichrom Part: AR-200-RV20)
- Centrifuge and carriers, 250mL tube holders

- Centrifuge tubes, 250mL disposable, polyethylene, conical bottomed centrifuge tubes or 50 mL centrifuge tubes
- Fume hood
- Hot plate
- Resolve™ filter- 0.1 micron 25 mm polypropylene, Eichrom Part: RF-100-25PP01 and filter apparatus- Pall 25mm polysulfone filter apparatus with polycarbonate base, metal screen and 50 mL reservoir (Pall Part: 4203) -or-
- Resolve™ filter- 0.1 micron 25 mm polypropylene in disposable funnel, Eichrom Part: RF-DF-25-25PP01
- Stir rods, glass
- Vacuum box system, Eichrom Part: AR-12-BOX or AR-24-BOX
- Vacuum box white inner support tube-PE- Eichrom Part: AR-1000-TUBE-PE
- Vacuum box yellow outer tips- Eichrom Part: AR-1000-OT
- Vacuum pump, 115 V, 60 Hz Fisher Part: 01-092-25 (or equivalent) or house vacuum
- Watch glasses
- Optional: vacuum box inner liner - For collection of load and rinse fractions, Eichrom Part: AR-12-LINER or AR-24-LINER

## 6. REAGENTS

**Note: Analytical grade or ACS grade reagents are recommended. Evaluation of key reagents, such as aluminum nitrate and ammonium hydrogen phosphate, for contribution to method background levels from naturally occurring radioactive materials is recommended.**

<i>Ammonium citrate</i> , (NH <sub>4</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>8</sub>
<i>Deionized water</i> , All reagents are prepared with deionized water
<i>Lead nitrate</i> , Pb(NO <sub>3</sub> ) <sub>2</sub>
<i>Nitric acid (70%)</i> , concentrated HNO <sub>3</sub>
<i>Pb® resin</i> , 2mL prepacked cartridge, 50-100µm, Eichrom Part PB-R50-S
<i>Sulfuric acid (98%)</i> , concentrated H <sub>2</sub> SO <sub>4</sub>

- 6.1. *Ammonium citrate solution (0.05M)*. Dissolve 12.2g of ammonium citrate in 700mL of water. Dilute to 1liter with water.
- 6.2. *Nitric Acid (0.1M)* - Add 6.3mL of concentrated HNO<sub>3</sub> to 800 mL water. Dilute to 1 liter with water.

- 6.3. *Nitric Acid (1M)* - Add 63 mL of concentrated  $\text{HNO}_3$  to 800 mL water. Dilute to 1 liter with water.
- 6.4. *Pb carrier (10 mg/mL)* - Dissolve 1.6 grams of  $\text{Pb}(\text{NO}_3)_2$  in 70mL of water. Dilute to 100mL with water.

## 7. PROCEDURE

### 7.1. Soil Sample Preparation

- 7.1.1. Weigh 2-3 grams of soil in a 200mL glass beaker on an analytical balance.
- 7.1.2. Dry the sample at 110°C until a constant weight is achieved. Record Dry weight.
- 7.1.3. Place the dried soil sample in muffle furnace and ash at 500°C for 8-12 hours.
- 7.1.4. Allow the sample to cool. Add 50mL of concentrated  $\text{HNO}_3$  and 1mL of lead carrier to each beaker.
- 7.1.5. Place a watch glass on each beaker and heat on a hot plate, in a fume hood, at medium heat for 3-4 hours.
- 7.1.6. Remove beakers from hotplate and cool samples.
- 7.1.7. Transfer the leachate and the residue from the beaker into a centrifuge tube. Centrifuge at 2000rpm for 10-15 minutes.
- 7.1.8. Decant the supernate into a clean, labeled beaker.
- 7.1.9. Wash the residue in centrifuge tube with 50mL of DI water. (Vortex may be used to wash the residue). Centrifuge at 2000rpm for 10minutes.
- 7.1.10. Add the rinse solution to the beaker from 7.1.8.
- 7.1.11. Evaporate the solution to near dryness.
- 7.1.12. Prepare the lead resin load solution by dissolving the residue with 25mL of 1M  $\text{HNO}_3$ .
- 7.2. Pb separation using Pb Resin cartridge:
- 7.2.1. Place the inner tube rack (supplied with vacuum box system) into the vacuum box. Place centrifuge tubes in the rack. Fit the lid to the vacuum system box. Alternatively, a vacuum box inner liner may be used.

- 7.2.2. Place yellow outer tips into all 12 or 24 openings in the lid of the vacuum box. Fit a white inner support tube into each yellow tip.
- 7.2.3. For each sample solution, fit a Pb Resin cartridge on to the inner support tube.
- 7.2.4. Add syringe barrels (funnels/reservoirs) to the top end of each Pb Resin cartridge.
- 7.2.5. Connect the vacuum pump to the box. Turn the vacuum pump on and ensure proper fitting of the lid.

**Note: The unused openings on the vacuum box should be sealed. Vacuum manifold plugs can be used to plug unused white tips to achieve good seal during the separation. Alternatively, unused vacuum box holes can be sealed with scotch tape.**

- 7.2.6. Add 5mL 1M HNO<sub>3</sub> to condition the Pb resin cartridge. Adjust vacuum to achieve a flow rate of 1-2mL/min. Allow solution to completely pass through each cartridge.
- 7.2.7. Add the load solution from step 7.1.12. to the Pb resin cartridge reservoir. Allow solution to completely pass through each Pb Resin cartridge at 1-2mL/min.
- 7.2.8. Add 10mL 1M HNO<sub>3</sub> to the Pb cartridge reservoir. Allow solution to completely pass through each cartridge at 1-2mL/min.

**Note: This will remove bismuth and iron if present.**

- 7.2.9. Disengage vacuum. Empty solution from centrifuge tubes to waste or place fresh centrifuge tubes below each Pb Resin cartridge. Place clean reservoirs above each Pb Resin cartridge.
- 7.2.10. Add 20 mL 0.1M HNO<sub>3</sub> to the Pb Resin cartridge reservoir. Engage vacuum. Allow solution to completely pass through each cartridge at 1-2mL/min.

**Note: This will remove any Sr and Po isotopes, if present in the sample.**

- 7.2.11. Record the time and date when the 0.1M HNO<sub>3</sub> has completely passed through the Pb resin cartridge. This will be used to calculate the in-growth of bismuth-210.
- 7.2.12. Disengage vacuum and place a clean, labeled centrifuge tube under each Pb resin cartridge. Replacing the yellow outer tips

and inner tube supports at this point can help ensure clean Pb fractions in the following steps.

- 7.2.13. Add 20mL of 0.05M ammonium citrate to the Pb Resin cartridge reservoir to elute lead. Engage vacuum and strip Pb at 1-2mL/min.

**Note: Previous versions of this method used water to strip Pb from the lead resin. Ammonium citrate allows for more complete recovery of Pb.**

- 7.2.14. Very carefully add 4mL of concentrated sulfuric acid to each Pb eluent.
- 7.2.15. Cap the tubes and mix the solution well. A white precipitate of  $\text{PbSO}_4$  is formed. Allow the solution to cool to room temperature.

### 7.3. Sample preparation for counting

#### 7.3.1. Planchet option

- 7.3.1.1. For each sample analyzed, clean a 2 inch diameter counting planchet by moistening a paper towel with ethanol, wiping the dish and letting it dry.

**Note: Planchets can also be annealed in an oven at 450°C for 1.5 hours. Properly annealed planchets will appear bronze/brown in color. Do not overheat planchets or they could become more susceptible to acid degradation.**

- 7.3.1.2. Weigh the counting planchet on an analytical balance and record the weight to 0.1mg.
- 7.3.1.3. Place each planchet under a heat lamp in a hood or on a hot plate with low heat.
- 7.3.1.4. Centrifuge the Pb sample tubes and discard the supernate.
- 7.3.1.5. Add 10mL of water to the Pb sample precipitates and mix well. Centrifuge the solution and discard the supernate.
- 7.3.1.6. Repeat step 7.3.1.5.
- 7.3.1.7. Add 5mL of DI water to the Pb sample precipitates and mix well to slurry.
- 7.3.1.8. Transfer the slurry to planchets in 2-3 mL aliquots and evaporate to near dryness between additions.

**Note: If the samples evaporate completely between additions, allow the planchets to cool slightly before adding more sample. This will minimize splattering and losses of the sample.**

- 7.3.1.9. Rinse the empty Pb sample tubes with 2-3 mL of water to recover any additional residue. Transfer to the planchet.
- 7.3.1.10. After all the solution has evaporated to dryness, cool each planchet.
- 7.3.1.11. Reweigh each planchet, and record the weight to 0.0001 gram.

**Note: If  $PbSO_4$  recovery is over 100%, water may still be present. Heat the planchet further and repeat 7.4.1.11.**

- 7.3.1.12. Cover planchet with aluminum foil and wait at least three days for bismuth-210 ingrowth.
- 7.3.1.13. Count on a gas flow proportional counter.

#### 7.3.2. Filter option

- 7.3.2.1. Set up a 0.1  $\mu$ m 25mm resolve filter, on a Gelman or Pall filter apparatus with stainless steel screen, 50mL polysulfone funnel and 100mL polypropylene Erlenmeyer flask.

**Note: Alternatively, a resolve filter in disposable funnel can be used (Eichrom Part: RF-DF25-25PP01).**

- 7.3.2.2. Add 3-5mL of 80% ethanol to each filter, applying vacuum and ensuring there are no leaks along the sides. Add 2-3mL of water to each filter.
- 7.3.2.3. Add the Pb sample to the filter and allow the solution to completely pass through the filter.
- 7.3.2.4. Rinse the 50mL centrifuge tube with 5mL water, transferring this rinse to the filter apparatus. Allow the solution to completely pass through the filter.
- 7.3.2.5. Wash each filter with 3-5mL of anhydrous ethanol.
- 7.3.2.6. Remove filters from the filtration apparatus and mount filters in the center of planchets, using double-sided tape or glue stick.

- 7.3.2.7. Place filter planchets in plastic Petri dishes, and dry under heating (IR) lamps for a few minutes.
- 7.3.2.8. Cover planchet with aluminum foil and wait for at least 3 days for Bi-210 ingrowth.
- 7.3.2.9. Count on a gas-flow proportional counter.

## 8. CALCULATIONS

Gravimetric: Pb carrier

$$Y \text{ (carrier yield)} = \frac{R_w - T_w - B_w}{C_w}$$

where:

- $R_w$  = residue + planchet or filter, mg  
 $T_w$  = tare weight of planchet or filter, mg  
 $B_w$  = blank weight, mg  
 $C_w$  =  $\text{PbSO}_4$  added, mg

Calculate Pb-210 activity based on Bi-210 in-growth

$${}^{210}\text{Pb} \text{ (pCi / L)} = \frac{S - B}{2.22 \times E \times Y \times (1 - e^{-\lambda(t_0 - t_1)}) \times V}$$

where:

- $S$  = sample counts per minute  
 $B$  = background counts per minute  
 $E$  = efficiency of counter  
 $\lambda$  =  $0.138 \text{ day}^{-1}$  (decay constant for  ${}^{210}\text{Bi}$ )  
 $t_0$  = time of Bi-210 separation, recorded in step 7.2.3  
 $t_1$  = time of midpoint of sample count  
 $V$  = volume of sample in liters  
 $Y$  = Pb carrier yield

## 9. VALIDATION DATA

- 9.1. A Tailings Reference Material (TRM-2, see reference 2), which contained a reference value of 49.06dpm Pb-210/g was analyzed in 0.5 gram and 1.0 gram samples.

Sample Size	# Replicates	Chemical Recovery	Pb-210 found, % of Ref. Value
0.5 gram	2	76%	87%
1.0 gram	7	85 ± 7%	89 ± 13%

- 9.2. An EML QAP sample containing no Pb-210 as analyzed. Five 2.0 gram aliquots were spiked with 200.5 dpm Pb-210; two blanks were also analyzed.

Chemical Recovery	Spike Recovery
92.5 ± 6%	99.9 ± 11%
n = 7	n = 5

## 10. REFERENCES

- 1) Horwitz, E. P., et al. "A lead-selective extraction chromatographic resin and its application to the isolation of lead from geological samples," *Analytica Chimica Acta*. 292, 263-273 (1994).
- 2) ASTM Method D7535-09, "Standard Test Method for Lead-210 in water."
- 3) Determination of Lead-210 in Water Using Extraction Chromatography, DOE Methods Compendium RP280, (1997).



