LEAD-210 IN SOIL

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}Bi daughter of ^{210}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.
- Centrifuge, with rotor and carriers for 50mL and 250mL tubes
- Centrifuge tubes, 50mL and 250mL
- Column rack, Eichrom Part: AC-103
- Extension funnels, 25 mL, Eichrom Part: AC-120

- 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
- Watch glasses

6. REAGENTS

Note: Analytical grade or ACS grade reagents are recommended. Evaluation of key reagents for contribution to method background levels from naturally occurring radioactive materials is recommended.

Ammonium citrate, $(NH_4)_3C_6H_5O_8$
Deionized water, All reagents are prepared with deionized water
Lead nitrate, $Pb(NO_3)_2$
Nitric acid (70%), concentrated HNO_3
Pb® resin, 2mL prepacked column, 100-150µm, Eichrom Part PB-C50-A
Sulfuric acid (98%), concentrated H_2SO_4

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_3 to 800 mL water. Dilute to 1 liter with water.

6.3. *Nitric Acid (1M)* - Add 63 mL of concentrated HNO_3 to 800 mL water. Dilute to 1 liter with water.

6.4. *Pb carrier (10 mg/mL)* - Dissolve 1.6 grams of $Pb(NO_3)_2$ 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 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 HNO_3.

7.2. Pb separation using Pb Resin column:

7.2.1. For each sample solution, place a Pb Resin column (with extension funnel) in the column rack.

7.2.2. Place a waste tray below the columns, remove the bottom plugs from each column, push the top frit down to the top of the resin bed, and allow to drain.

7.2.3. Add 5mL of 1M HNO_3 to each Pb Resin column reservoir to condition the resin. Allow solution to drain.

7.2.4. Load the solution from step 7.2.6 onto the column. Allow solution to drain.

7.2.5. Add 10mL 1M HNO_3 to rinse the column. Allow solution to drain.

Note: This will remove bismuth and iron if present.

7.2.6. Add 20 mL 0.1M HNO3 to rinse the column. Allow solution to drain.

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

7.2.7. Record the time and date when the 0.1M HNO_3 has completely passed through the Pb resin column. This will be used to calculate the in-growth of bismuth-210. Discard eluate to this point as waste.

7.2.8. Place a clean and labeled centrifuge tube under each column. Add 20mL of 0.05M ammonium citrate to the column to elute lead. Allow solution to drain.

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

7.2.9. Very carefully add 4mL of concentrated sulfuric acid to each Pb eluent.

7.2.10. Cap the tubes and mix the solution well. A white precipitate of $PbSO_4$ is formed. Allow 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 solution from step 7.2.10.. and discard the supernate.

7.3.1.5. Add 10mL of water to the precipitate 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 precipitate and mix well to slurry.

7.3.1.8. Transfer the slurry to a planchet in 2-3 mL aliquots. 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 tube with 2-3 mL of water to recover any remaining 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 0.1μm 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. Filter the sample. Rinse 50mL centrifuge tube with 5mL water, transferring this rinse to the filter apparatus.

7.3.2.4. Allow liquid to completely pass through all filters.

7.3.2.5. Wash each filter with 3-5mL of anhydrous ethanol.

7.3.2.6. Remove filters from the filter apparatus and mount filters in the center of the 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

$$\text{Y (carrier yield)} = \frac{Rw - Tw - Bw}{Cw}$$

where:

R_w =residue + planchet or filter, mg
T_w =tare weight of planchet or filter, mg
B_w =blank weight, mg
C_w =$PbSO_4$ added, mg

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

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

where:

S = sample counts per minute
B = background counts per minute
E = efficiency of counter
λ = 0.138 day^{-1} (decay constant for ^{210}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. PERFORMANCE 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).

1) Weigh 2-3g of soil into a 200mL glass beaker.
2) Heat sample at 110ºC for 12 hrs or unitl dry.
3) Cool sample and weigh. Record dry weight.
4) Add 50mL of concentrated HNO_3 and 1mL of lead carrier.
5) Cover beakers with watch glass and heat at medium heat for 3-4 hours.
6) Cool samples. Transfer leachate and residue to 250mL centrifuge tubes. Centrifuge at 2000rpm for 10-15 minutes.
7) Decant Supernate into a clean labeled beaker.
8) Wash the residue in centrifuge tube with 50mL DI water.
9) Centrifuge at 2000rpm for 10-15 minutes. Decant supernate into the same beaker as step 7.
10) Evaporate the combined solution from 7 and 9 to dryness.
11) Dissolve residue in 25mL of 1M HNO_3.
Soil in 200 mL Glass Beaker. Dry. Record dry weight. Leach with HNO_3.
Centrifuge
Evaporate to dryness. Redissolve in 50mL 1M HNO_3.
Sample in 50mL 1M HNO_3
12) Precondition Pb Resin column with 5mL 1M HNO_3.
13) Load sample on to column. Allow liquid to drain to waste. Pb is retained.
14) Rinse column with 10mL 1M HNO_3. Allow liquid to drain to waste.
15) Rinse column with 20mL 0.1M HNO_3. Allow liquid to drain to waste.
16) Record Pb-210 separation time.
17) Strip Pb with 20mL 0.05M ammonium citrate.
2mL Pb Resin Column with 25mL extension funnel
(12) (13) (14) (15)
Waste
(17)
Pb sample to source preparation