LEAD-210 AND POLONIUM-210 IN WATER

1. SCOPE

1.1. This is a method for the separation and measurement of lead-210 and polonium-210 in water.

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. Lead and polonium are concentrated from up to 1.5L samples by iron hydroxide precipitation. Pb and Po are separated from the other elements with Eichrom Sr Resin. The purified lead fraction is prepared for analysis evaporation onto a stainless steel counting planchet or by liquid scintillation counting. The polonium fraction is prepared for alpha spectrometry by autodeposition onto a metal planchet or by bismuth phosphate precipitation onto an Eichrom Resolve® Filter.

3. SIGNIFICANCE OF USE

3.1. This is a rapid, reliable method for measurement of lead and polonium in water samples that is efficient and reduces interferences to analysis.

4. INTERFERENCE

4.1. Any beta emitter can cause an interference with the measurement of the ^{210}Bi daughter of ^{210}Pb.

4.2. Polonium auto deposition on silver, copper, or nickel planchet can be reduced by high concentrations of Fe, Te, Au, Pt and Hg.

4.3. This method effectively eliminates these possible interferences.

5. APPARATUS

- Alpha Spectrometry system (For measurement of Po)
- Aluminum foil – 0.003 inch thickness, if counting ^{210}Bi and ^{210}Pb via gas flow proportional counter.
- Beakers, glass
- Centrifuge
- Centrifuge tubes, plastic, 50mL
- Detection System for measurement of ^{210}Pb via ^{210}Bi daughter:
    - Option 1: Low background proportional counter
        - Stainless steel planchets, cupped flat bottom, compatible with sample holders for proportional counter
    - Option 2: Liquid Scintillation Counter (LSC)
        - Liquid scintillation cocktail
        - Liquid scintillation vials, 20mL
- Fume hood
- Hot plate
- Planchets, Silver, copper or nickel, flat, 1 inch diameter, polished on one side and coated on the back side with an acid resistant acrylic paint.
- 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, Eichrom Part: AR-BOX-12 or AR-BOX-24
- Inner support tubes, Eichrom Part: AR-1000-TUBE-PE
- Vacuum pump, dry pump, 115V, 60 Hz, Fisher Part: 01-092-25 or equivalent
- Water bath, shaking or ultrasonic
- Yellow outer tips, Eichrom Part: AR-1000-OT

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.

Ammonium citrate, $(NH_4)_3C_6H_5O_8$
Ammonium hydroxide (57%), concentrated NH_4OH
Ammonium hydrogen phosphate, $(NH_4)_2HPO_4$
Bismuth Chloride, $BiCl_3$
Sodium Hydroxide, NaOH
Ascorbic acid, $C_6H_8O_6$
Deionized water, All reagents are prepared with deionized water
Ethanol denatured, C_2H_5OH
Ferric nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$
Hydrochloric acid (37%), concentrated HCl
Isopropyl alcohol – C_3H_7OH
Lead nitrate, $Pb(NO_3)_2$
Nitric acid (70%), concentrated HNO_3
Phenolphthalein pH indicator
Po yield tracer, ^{208}Po or ^{209}Po
Sr® resin, 2mL prepacked column, 100-150µm, Eichrom Part SR-C50-A
Sulfuric acid (98%), concentrated H_2SO_4

6.1. *Ammonium Citrate (0.05M)* – Add 11.3g of ammonium citrate and 700mL water to a 1L volumetric flask. Mix to dissolve. Dilute to 1L with water.

6.2. *Ammonium Hydrogen Phosphate (3.*2M) – Dissolve 211g $(NH_4)_2HPO_4$ in 400mL water. Dilute to 500mL with water.

6.3. *Ascorbic Acid (1M)* – Dissolve 17.6g of ascorbic acid in 90mL of water. Dilute to 100mL with water. **Prepare fresh weekly.**

6.4. *Hydrochloric Acid (0.5M)* - Add 41mL concentrated HCl to 800mL water. Dilute to 1L with water.

6.5. *Hydrochloric Acid (2.0M)*- Add 165 mL concentrated HCl to 700 mL water. Dilute to 1L with water.

6.6. *Iron carrier (20 mg/mL)* – Dissolve 14.5g of $Fe(NO_3)_3 \cdot 9H_2O$ in 70mL water. Dilute to 100mL with water.

6.7. *Lead carrier (10 mg/mL)* - Dissolve 1.6 grams of $Pb(NO_3)_2$ in water and dilute to 100mL with water (Check batches for ^{210}Pb and ^{210}Po levels).

6.8. *Bismuth carrier (1mg/mL)* - Dissolve 0.75g $BiCl_3$ and 42mL 37% HCl in 200mL of water. Dilute to 500mL with water.

6.9. *Nitric acid solution (8M)* - Add 500 mL of concentrated HNO_3 to 400mL of water. Dilute to 1L with water.

6.10. *Nitric Acid (1M)* - Add 62.5 mL of concentrated HNO_3 to 800mL water. Dilute to 1L with water.

6.11. *Nitric Acid (0.1M)* - Add 6.3 mL of concentrated HNO_3 to 800mL water. Dilute to 1L with water.

6.12. *Phenolphthalein solution* - Dissolve 1g phenolphthalein in 100mL 95% isopropyl alcohol. Dilute with 100mL of water.

6.13. *Sodium Hydroxide (1M)* - Dissolve 40g of NaOH in 800mL of water. Dilute to 1L with water.

7. PROCEDURE

7.1. Water Sample Preparation:

7.1.1. If required, filter the sample through a 0.45 micron filter.

7.1.2. Aliquot 500 to 1,500 mL of the sample (or enough to meet required detection limit) into an appropriate size beaker.

7.1.3. Acidify the sample to pH 2, with concentrated HNO_3.

7.1.4. Add 1 mL of stable Pb carrier or an appropriate amount of Po tracer.

7.1.5. If samples larger than 1L are analyzed, evaporate the sample to approximately 1L.

7.1.6. *Iron hydroxide precipitation*

7.1.6.1. Add 1mL of iron carrier to each sample. Cover beaker with a watch glass and heat at near boiling for an hour.

7.1.6.2. Remove watch glass. Add 1mL of phenolphthalein solution. While stirring, slowly add enough concentrated NH4OH to reach the phenolphthalein pink endpoint (pH

8-9). An iron hydroxide precipitate should form. Allow the beakers to heat for another 30 minutes.

7.1.6.3. Let the precipitate settle for 1-2 hours or centrifuge. Decant the supernate. Transfer the precipitate into a 50 mL plastic centrifuge tube with deionized water.

7.1.6.4. Centrifuge and discard the supernate.

7.1.6.5. Wash the precipitate with 10mL water. Centrifuge and discard the supernate.

7.1.6.6. Add 10mL 2M HCl to dissolve the precipitate.

7.1.6.7. Add 1mL of 1M ascorbic acid to each solution, swirling to mix. Wait for 2-3 minutes.

Note: Any yellow color should disappear which indicates the reduction of Fe(III) to Fe(II). If the color persists add ascorbic acid should drop-wise with mixing until the color disappears. Add 0.5mL excess ascorbic acid to maintain Fe reduction.

7.2. Pb and Po Separation using Sr Resin

7.2.1. For each sample solution, place a Sr 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. Condition Sr Resin with 10mL 2M HCl. Allow solution to drain.

7.2.4. Load the sample from step 7.1.6.7. onto the Sr resin column. Allow solution to drain.

7.2.5. Rinse each sample tube with 5mL 2M HCl. Add the rinse to the Sr Resin column. Allow solution to drain.

7.2.6. Rinse Sr Resin column with 5mL 2M HCl. Record the time and date of this addition. This will be used to calculate the ingrowth of ^{210}Bi. Allow solution to drain. Discard the eluent.

Note: This will remove bismuth and yttrium if present.

7.2.7. Place a clean and labeled centrifuge tube under each Sr Resin column to collect Polonium fractions.

7.2.8. Add 5mL 1.0M HNO_3 to the Sr Resin. Allow solution to drain.

7.2.9. Add 15mL 0.1M HNO_3 to the Sr Resin. Allow solution to drain.

7.2.10. Remove tubes and set aside for Po auto-deposition in Section 7.3.

7.2.11. Place a clean, labeled centrifuge tube under each the Sr Resin column to collect the Pb fraction.

7.2.12. Add 20mL of 0.05M ammonium citrate to the Sr Resin to strip Pb. Allow solution to drain. Set Pb samples aside for Pb source preparation.

7.3. *Sample preparation for Po analysis:* Auto Deposition on Ag, Cu or Ni planchet.

7.3.1. Rinse polished planchets with water, ethanol and acetone. Let air dry.

7.3.2. Place the planchets, polished side facing out, in the cap of a 50mL polypropylene centrifuge tube.

Note: The planchet should just fit inside the centrifuge tube cap and remain in place while fastening the cap to the centrifuge tube. If the planchet does not stay in place by friction alone, it can be affixed to the centrifuge tube cap using a hot glue gun.

7.3.3. Add 1mL of 1M ascorbic acid to each Po fraction. The ascorbic acid will reduce any Fe(III) in the solution and improve reduction of polonium and adhesion to the planchet.

7.3.4. Carefully place a cap, containing a planchet, on each sample tube. Seal the cap tightly and invert the sample tube so that the planchet is submerged below the solution containing polonium.

Note: Heating the samples in the following step can lead to some pressure buildup in the centrifuge tubes. A pressure release hole can be melted into the centrifuge tube with a soldering tool.

7.3.5. Place the samples in a stirring water bath or ultrasonic water bath. Heat to a temperature of 80-90°C and stir for at least 2 hours.

7.3.6. Remove tubes from water bath and carefully drain solution to waste.

7.3.7. Remove each planchet from the centrifuge tube cap and rinse it with water, ethanol and then acetone. Let planchets air dry.

7.3.8. Planchets may be heated on a 200-300°C hotplate for 15-30 minutes to convert Po to Po oxide to minimize the risk of detector contamination. However, care must be taken not to overheat planchets and lose polonium to volatilization.

7.3.9. Count in an alpha spectrometry system.

7.4. *Sample preparation for Po analysis:* Bismuth phosphate precipitation onto Resolve® filter.

7.4.1. Add 125µL of bismuth carrier, 0.75mL of 3.2M (NH4)2HPO4, and 50µL 30% H_2O_2 to each polonium sample.

7.4.2. Mix well.

7.4.3. Add 0.6mL of concentrated NH4OH to each polonium sample.

7.4.4. Mix well.

7.4.5. Wait 20-30 minutes.

7.4.6. Collection bismuth phosphate precipitate, containing the polonium, on an Eichrom Resolve Filter as described in steps 5.4 to 5.15 of Eichrom Method SPA01.

7.5. Sample preparation and analysis option for Pb determination

7.5.1. Planchet option

7.5.1.1. Samples should be precipitated within an hour after eluting from resin as Bi may not fully co-precipitate with Pb.

7.5.1.2. 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.

7.5.1.3. Weigh the dried counting planchet on an analytical balance and record the weight to 0.0001 gram.

7.5.1.4. Place each planchet in a fume hood, either under a heat lamp or on a hot plate with low heat.

7.5.1.5. Very carefully add 4mL of concentrated sulfuric acid to each Pb fraction.

7.5.1.6. Cap the tubes and mix the solution well. A white precipitate is formed. Mix periodically for 15-30 minutes to re-suspend the precipitate.

7.5.1.7. When the sample has cooled to room temperature, centrifuge and discard the supernate.

7.5.1.8. Add 10mL of water to the precipitate and mix well. Centrifuge the solution and discard the supernate. Repeat once.

7.5.1.9. Add 5mL of DI water to the precipitate and mix well to slurry.

7.5.1.10. Transfer the slurry to dried, weighed 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.

7.5.1.11. Rinse the empty sample tubes with 2-3 mL of water to recover any additional residue. Transfer the rinse to the planchet.

7.5.1.12. After all the solution has evaporated to dryness, cool each planchet.

7.5.1.13. Weigh each planchet, and record the weight to 0.0001 gram.

7.5.1.14. Cover planchet with aluminum foil and wait at least three days for ^{210}Bi ingrowth.

7.5.1.15. Count on a gas flow proportional counter.

Note: Samples should be counted with the aluminum foil covering the planchet. The aluminum foil will absorb the low energy beta emission from ^{210}Pb (60 keV). The same thickness of aluminum absorber (~0.03 inches) should be used for all samples and detector calibrations.

7.5.2. LSC/ICP-MS option.

7.5.2.1. For LSC ^{210}Pb determination

7.5.2.1.1. Add 7mL of the lead fraction from into a clean, labeled LSC vial.

7.5.2.1.2. Add 15mL of appropriate scintillation cocktail to the vial. Shake to mix and ensure that cocktail does not from separate layers.

7.5.2.1.3. Count on LSC after ^{210}Bi in-growth of at least 3 days. Take care to ensure that the measurement window is set to count the ^{210}Bi emission (~15-1200 keV) and not the entire beta spectrum.

7.5.2.2. Analyze remaining Pb sample fraction and initial sample aliquot by AA/ICP/ICP-MS for Pb yield determination.

7.5.2.3. The Pb sample fraction can also be used to directly determine ^{210}Pb mass concentration via ICP-MS. (See reference 2).

8. CALCULATIONS

Polonium Tracer yield: ^{208}Po/^{209}Po

$$\mathrm{Po_Y}\ (\text{carrier yield}) = \frac{Po_{AF}}{Po_{AI} \times Po_V}$$

where:

Po_{AF} = Activity of polonium tracer on final filter

Po_{AI} = Activity of polonium tracer spike solution

Po_V = Amount of polonium tracer spiked into initial sample

Calculate initial ^{210}Po activity

$$^{210}Po\ (\text{pCi/L}) = \frac{S - B}{2.22 \times E \times Po_Y \times (e^{-\lambda(t_0 - t_{01})}) \times V}$$

where:

S = sample counts per minute
B = background counts per minute
E = efficiency of alpha counter
Po_Y = Po tracer yield
λ = 0.005008 day-1 (decay constant for ^{210}Po)

t_0 = time of sample collection
t_{01} = time of mid-point of sample count
V = volume of sample in liters

Gravimetric yield: Pb carrier – via planchet or filter

$$\mathrm{Pb_Y\,(carrier\ yield)} = \frac{Rw - Tw - Bw}{Cw}$$

where:

R_w = residue + planchet or filter, mg
T_w = tare weight of planchet or filter, mg
B_w = blank weight, mg
C_w = PbSO4 added, mg

Chemical yield: Pb carrier – via ICP

$$\mathrm{Pb_Y\,(carrier\ yield)} = \frac{C_F \times V_F}{C_I \times V_I}$$

where:

C_I = Pb initial concentration
V_I = Initial Sample Volume at time of aliquot
C_F = Pb final concentration
V_F = Volume of Final Solution at time of final aliquot

Calculate initial ^{210}Pb activity based on ^{210}Bi ingrowth

$$^{210}Pb\ (\mathrm{pCi/L}) = \frac{S - B}{2.22 \times E \times Pb_Y \times (1 - e^{-\lambda_{210Bi}(t_{L1} - t_{BS})}) \times V \times (e^{-\lambda_{210Pb}(t_0 - t_{L1})})}$$

where:

S = sample counts per minute
B = background counts per minute
E = efficiency of ^{210}Bi emissions in beta counter
Pb_Y = Pb carrier yield
λ_{210Bi} = 0.138 day-1 (decay constant for ^{210}Bi)

t_{L1} = time of midpoint of sample count
t_{BS} = time of ^{210}Bi separation, recorded in step 7.2.4
V = volume of sample in liters
λ_{210Pb} = 0.0000855 day-1 (decay constant for ^{210}Pb)
t_0 = time of sample collection

9. 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) “Determination of Pb-210 in water using extraction chromatography,” DOE Methods Compendium, RP280.

3) ASTM Method D7535-09, “Standard Test Method for Lead-210 in water.”

4) Larivière, D., et al “Determination of 210Pb at ultra-trace levels in water by ICP-MS”, *Analytica Chimica Acta*, 549(1-2), 188-196 (2005)

5) Maxwell, S.L., et al., “Rapid Determination of 210Po in Water Samples,” *Radioanalytical and Nuclear Chemistry*, 298(3), 1977-1989, (2013)

1) Aliquot up to 1000mL of water into glass beaker.

2) Acidify to pH 2 with conc. HNO_3.

3) Add Po yield tracer, 1mL of Pb carrier and 1mL of Fe carrier.

4) Cover with a watch glass and heat samples to near boiling for 1 hour.

5) Turn down heat. Remove watch glass. Add 1mL of phenolphthalein indicator.

6) While stirring sample, slowly add conc. NH_4OH until pH8-9.

7) After 30 minutes, turn off heat. Allow precipitate to settle or centrifuge.

8) Decant supernate and discard as waste.

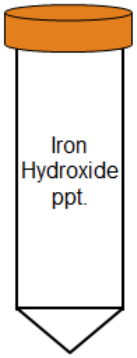
9) Transfer precipitate to centrifuge tube with DI water.

10) Centrifuge ~10minutes at 2000rpm. Decant supernate.

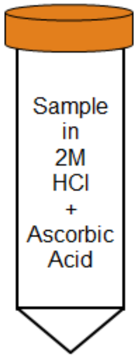
11) Add 10mL DI water to precipitate. Mix well. Centrifuge. Decant supernate.

12) Dissolve precipitate in 10mL 2M HCl. Add 1mL 1M ascorbic acid.


Water Sample in glass beaker. Acidify pH 2.




Centrifuge



13) Precondition Sr Resin with 10mL 2M HCl.

14) Load sample on to column. Allow liquid to drain to waste. Pb and Po are retained.

15) Rinse centrifuge tube with 5mL 2M HCl. Add rinse to Sr Resin. Allow liquid to drain to waste.

16) Rinse Sr Resin with 5mL 2M HCl. Allow liquid to drain to waste.

17) Place clean labeled 50mL centrifuge tube below Sr Resin. Strip Po with 5mL 1M HNO_3. Allow solution to drain. Strip Po with 15mL 0.1M HNO_3. Allow solution to drain.

18) Place clean labeled 50mL centrifuge tube below Sr Resin. Strip Pb with 20mL 0.05M ammonium citrate.