Lead

Environmental Measurements Laboratory
U.S. Department of Energy

Pb-01-RC

LEAD-210 IN BONE, FOOD, URINE, FECES, BLOOD, AIR, AND WATER

Contact Person(s) : Isabel M. Fisenne

APPLICATION

This procedure is applicable to samples of bone, food, urine, feces, blood, air, and water and is based on the solvent extraction of a lead bromide complex into Aliquat-336 (Petrow and Cover, 1965; Morse and Welford, 1971).

Lead-210 is isolated from most interferences. Its progeny ^{210}Bi is separated from ^{210}Pb, and the β activity is measured radiometrically after ingrowth.

SPECIAL APPARATUS

1. Atomic absorption (AA) spectrometer.
2. Aluminum foil - 7.2 mg cm^{-2}.
3. Rings and discs - see Specification 7.2.
4. Mylar film - see Specification 7.3.
5. Teflon filter holder.
6. Combination magnetic stirrer and hot plate.
7. Plastic scintillation phosphors - see Specification 7.9.

SPECIAL REAGENTS

1. Aliquat-336, methyltricapryl-ammonium chloride (Henkel Corporation, 2430 N. Huachuca Dr., Tucson, AZ 85745-1273), 3:7 in toluene and washed twice with an equal volume of 1.5$\underline{M}$ hydrobromic acid.

2. Hydrobromic acid 48%.

3. Hydrobromic acid 3.0$\underline{M}$ - 340 mL of 48% HBr L^{-1} of water.

4. Hydrobromic acid 1.5$\underline{M}$ - 170 mL of 48% HBr L^{-1} of water.

5. Hydrobromic acid 0.1$\underline{M}$ - 10 mL of 48% HBr L^{-1} of water.

6. Toluene.

7. Standard Pb solution - 1000 $\mu g\ mL^{-1}$.

8. Lead carrier: 20 mg Pb mL^{-1} - 32 g $Pb(NO_3)_2$ L^{-1} in 1:19 HNO_3.

9. Bismuth carrier: 10 mg Bi mL^{-1} - 23.2 g $Bi(NO_3)_3 \cdot 5\ H_2O$ L^{-1} in 1:19 HNO_3.

SAMPLE PREPARATION

A. Water.

1. To daily collections of 20 L of tap water add 100 mL of HNO_3 and evaporate to about 100 mL (see **Note 1**).

2. Add 100 mL of HNO_3 and transfer to a 400-mL beaker. Complete the destruction of organic material and evaporate to near dryness.

3. Add 50 mL of 10% HNO_3 to the beaker and warm to affect dissolution of any residue.

4. Cool the solution to room temperature and transfer the sample solution to a 100-mL volumetric flask. Bring the solution to volume with 10% HNO_3.

5. Pipette 1 mL of sample solution into a 10-mL volumetric flask. Bring the solution to volume with 10% HNO_3. Reserve this solution to determine the stable Pb content of the sample by AA spectrometry (see **Note 2**).

6. Return the sample solution in the 100-mL volumetric flask (Step 4) to the 400-mL beaker. Add 1 mL of Pb carrier and evaporate the solution to dryness.

7. Add 100 mL of 3M HBr to the sample beaker and warm the solution. Cool the solution to room temperature and proceed with the **Determination.**

B. Urine, blood, feces and air filters.

1. Measure 2-L of urine and transfer to a 3-L beaker. Place a measured volume of blood or 24 h fecal sample in a 1-L beaker. Place the air filter in a 600-mL beaker (see **Note 1**).

2. Destroy most of the organic material by carefully heating with HNO_3. Hydrogen peroxide can be used to complete the oxidation of organic material (see **Note 3**).

3. Add 50-mL of 10% HNO_3 to the beaker and warm to affect dissolution of any residue.

4. Cool the solution to room temperature and transfer the sample solution to a 100-mL volumetric flask. Bring the solution to volume with 10% HNO_3.

5. Pipette 1 mL of sample solution into a 10-mL volumetric flask. Bring the solution to volume with 10% HNO_3. Reserve this solution to determine the stable Pb content of the sample by AA spectrometry (see **Note 2**).

6. Transfer the sample solution in the 100-mL volumetric flask (Step 4) to the 400-mL beaker. Add 1 mL of Pb carrier and evaporate the solution to dryness.

7. Add 100 mL of 3M HBr to the sample beaker and warm the solution. Cool the solution to room temperature and proceed with the **Determination.**

C. **Bone** (see **Note 4**)

1. Weigh 20 g of bone ash and transfer to a 400-mL beaker.

2. Dissolve the ash in about 80 mL of 3$\underline{M}$ HBr and warm to complete the dissolution.

3. Cool the solution to room temperature and transfer the sample solution to a 100-mL volumetric flask. Bring the solution to volume with 3$\underline{M}$ HBr.

4. Pipette 1 mL of sample solution into a 10-mL volumetric flask. Bring the solution to volume with 10% HNO_3. Reserve this solution to determine the stable Pb content of the sample by AA spectrometry (see **Note 2**).

5. Transfer the sample solution in the 100-mL volumetric flask (Step 3) to the 400-mL beaker and add 1 mL of Pb carrier.

6. Proceed with the **Determination.**

D. Food.

1. Depending upon food type, freeze drying should be used to remove excess water prior to wet ashing the sample (see **Note 1**).

2. Destroy most of the organic material by carefully heating with HNO_3. Hydrogen peroxide can be used to complete the oxidation of organic material (see **Note 3**).

3. Add 50 mL of 10% HNO_3 to the beaker and warm to affect dissolution of any residue.

4. Cool the solution to room temperature and transfer the sample solution to a 100-mL volumetric flask. Bring the solution to volume with 10% HNO_3.

5. Pipette 1 mL of sample solution into a 10-mL volumetric flask. Bring the solution to volume with 10% HNO_3. Reserve this solution to determine the stable Pb content of the sample by AA spectrometry (see **Note 2**).

6. Transfer the sample solution in the 100-mL volumetric flask (Step 3) to the 400-mL beaker. Add 1 mL of Pb carrier and evaporate the solution to dryness.

7. Add 100-mL of 3<u>M</u> HBr to the same beaker and warm the solution. Cool the solution to room temperature and proceed with the **Determination.**

Notes:

1. It is necessary to analyze reagent blanks with each batch of samples to correct the ^{210}Pb results.

2. The stable Pb content of some samples may be high enough to contribute a significant fraction to the total stable Pb measured by AA. This would result in an inflated estimate of the Pb carrier yield.

3. Hydrogen peroxide contains measurable and variable amounts of stable Pb and should be used sparingly.

4. It has been shown at this Laboratory that no ^{210}Pb loss occurs from bone dry ashed below 700°C (Fisenne, 1994). The absence of ^{210}Pb loss was determined for three bone types — ribs, vertebrae, and femur. It is the practice at EML to dry ash bones for ^{210}Pb analyses at 550°C.

DETERMINATION

1. Transfer the 3<u>M</u> HBr solution to a 250-mL separatory funnel containing 75 mL of Aliquat-336.

2. Shake for 30 sec. Let the phases separate and discard the aqueous (lower) phase.

3. Wash the organic phase three times with 50-mL portions of 0.1<u>M</u> HBr and discard all washes (lower phases).

4. Wash the organic phase twice with an equal volume of water. Transfer the washed organic phase to a suitable disposal container.

5. Combine the strip solutions in a 400-mL beaker and add 100 mL of HNO_3.

6. Wait for any reaction to subside and heat gently until the organic residue is destroyed. Evaporate the solution to ~ 10 mL.

A. First milking.

1. Transfer the sample to a 40-mL centrifuge tube with water. Add 1 mL of Bi carrier.

2. Adjust the pH of the sample to 8 with NH_4OH.

3. Stir the sample and heat in a hot water bath.

4. Cool and centrifuge the tube for 10 min. Decant and discard the supernate.

5. Dissolve the precipitate with five drops of HCl.

6. Add 40 mL of water and heat with constant stirring.

7. Cool and centrifuge for 10 min. Decant and reserve the supernate in a 250-mL beaker.

8. Repeat Steps 5-7 twice more, combining the supernates. Discard the precipitate. Record the time and date for ingrowth of ^{210}Bi.

9. Add 1 mL of Bi carrier and 3-5 mL of HCl to the combined supernates. Reduce the volume to <100 mL.

10. Cool, transfer to a 100-mL volumetric flask and bring to volume with 0.5N HCl.

11. Pipette 1 mL of sample into a 10-mL volumetric flask. Bring to volume with 0.5N HCl.

12. Measure the quantity of Pb in both the sample and the separated Pb fraction in the 10-mL volumetric flasks on an AA spectrometer at 283 µm. (The calibration curve should have a working range of 0-50 µg mL^{-1}.)

13. Subtract the Pb content of the dissolved sample and the reagent blank from the total Pb content determined in Step 12 to obtain the Pb carrier yield.

14. Allow 2-3 weeks for ingrowth of ^{210}Bi into the main portion of the sample (Step 10).

B. Second milking.

1. Transfer the solution from the 100-mL volumetric flask to a 250-mL beaker and evaporate to about 15 mL.
2. Transfer the sample to a 40-mL centrifuge tube and adjust the pH to 8 with NH_4OH. Centrifuge the tube for 10 min. Decant and discard the supernate.
3. Dissolve the precipitate with five drops of HCl and bring volume of sample to 30 mL with H_2O. (Record the time and date for decay of ^{210}Bi.)
4. Heat with constant stirring in a hot water bath. Cool and centrifuge the tube for 10 min. Reserve the supernate for additional ^{210}Pb analysis in a 150-mL beaker.
5. Dissolve the precipitate with five drops of HCl and dilute to 30 mL with water.
6. Heat in a hot water bath with constant stirring. Cool and centrifuge the tube for 10 min. Combine the supernate with that from Step 4.
7. Dissolve the precipitate with five drops of HCl. Stir and dilute to 30 mL with water.
8. Heat the tube in a hot water bath with constant stirring. Cool, filter with suction on a preweighed 2.4 cm Whatman No. 42 filter paper using a Teflon filter holder.
9. Wash the tube and the precipitate with water and alcohol. Dry the paper and precipitate for 30 min at 110ºC in a drying oven.
10. Cool and reweigh the filter to determine weight of BiOCl precipitate.
11. Mount the filtered sample on a nylon ring and disc, covering the sample with aluminum foil (7.2 mg cm^{-2}), a plastic scintillation phosphor and Mylar film.
12. Measure the ^{210}Bi on a low-level β-scintillation counter. (Record the time and date for decay of ^{210}Bi.)

13. Standardize the counter with a known amount of ^{210}Pb from which ^{210}Bi has been separated and prepared in the same way as the sample.

DATA PROCESSING AND ANALYSES

The ^{210}Pb activity of the sample is calculated using the following formula:

$$\text{Bq of }^{210}\text{Pb} = \frac{R_s Y_1 Y_2 E}{GD}$$

where

R_s = net counting rate of the sample,
Y_1 = yield factor for Pb carrier,
Y_2 = yield factor for Bi carrier,
E = counter efficiency factor,
G = growth factor (growth of ^{210}Bi from first milking to final milking), and
D = decay factor (decay of ^{210}Bi from final milking to time of counting).

LOWER LIMIT OF DETECTION (LLD)

		A	B
Counter efficiency	(%)	35	-
Counter background	(cps)	0.005	-
Yield	(%)	80	80
LLD (400 min)	(Bq)	0.01	0.007
LLD (1000 min)	(Bq)	0.005	0.005

A = ^{210}Pb separation, ^{210}Bi ingrowth, ^{210}Bi separation.
B = ^{210}Bi separation only.

REFERENCES

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Pb-02-RC

DETERMINATION OF ^{210}Pb in BONE ASH BY MEASUREMENT OF ^{210}Po

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APPLICATION

The procedure has been tested for sample weights of up to 15 g of bone ash.

Lead-210 may be determined in bone samples which have been dry ashed at temperatures up to 700°C. The dry ashed bone samples should be stored for at least 2 y to allow build-up of ^{210}Po (Fisenne, 1994).

Lead, bismuth, polonium and calcium are separated from phosphate and radium as the oxalates. Lead, bismuth and polonium are separated from calcium as the sulfides. Polonium and bismuth are spontaneously deposited on a nickel disc from a weakly acid solution. The ^{210}Po is measured by alpha spectrometry and the chemical yield is determined with the alpha emitting tracer ^{209}Po.

Radium-226 is separated from the reserved oxalate supernate as the sulfate. The Ra.BaSO$_4$ is dissolved in alkaline EDTA and the chemical yield is determined with the gamma-emitting tracer ^{133}Ba. The ^{226}Ra is determined by the radon emanation method (see Procedure Ra-03-RC).

The total and unsupported ^{210}Pb activities are calculated from the ^{210}Po and ^{226}Ra measurements by application of the Bateman equations for the decay of this subseries of the Uranium Series (see Procedure 5.6).

SPECIAL APPARATUS

1. Nickel discs - 1.74 cm diameter by 0.06 cm thick, "commercial" pure nickel. Prior to use, degrease the disc. [**Note**: Silver or platinum discs may be used but must be cleaned and recycled. The nickel discs are discarded after measurement of the sample.]

2. Deposition cells - see Specification 7.16.

3. Mechanical stirrers.

4. Teflon stirring rods.

5. Alpha spectrometry system.

6. Radon bubblers - see Specification 7.7.

7. Polyethylene transfer pipettes - see Specification 7.11.

SPECIAL REAGENTS

1. Polonium-209 tracer solution - 1 Bq g^{-1} of 1$\underline{N}$ HNO_3 solution.

2. Lead carrier: 20 mg Pb mL^{-1} - 32 g $Pb(NO_3)_2$ L^{-1} of 1$\underline{N}$ HNO_3.

3. Calcium carrier - solid calcium propionate. [**Note**: Calcium carrier is added only to the reagent blank. The ^{210}Po and ^{226}Ra blank value must be established for each lot of calcium propionate salt prior to its use.]

4. Thioacetamide solution - 100 g CH_3CSNH_2 L^{-1} of water.

5. Barium-133 tracer solution - 1×10^4 Bq g^{-1} of 1$\underline{N}$ HCl.

6. Barium carrier: 20 mg mL^{-1} - 30.4 g $BaCl_2$ L^{-1} of 1$\underline{N}$ HCl.

7. Ammonium acetate solution - 15 g NH_4OAc L^{-1} of water.

8. Acetic acid solution - 20 mL glacial HOAc L^{-1} of water.

9. Ammonium sulfate solution - 100 g $(NH_4)_2SO_4$ L^{-1} of water.

10. Aerosol OT solution - 0.1%.

11. EDTA solution - 300 g tetrasodium salt L^{-1} of water. Filter the solution through a glass fiber filter prior to use.

12. Monoethanolamine - 1:1 solution with water.

SAMPLE PREPARATION

1. Weigh 5 g of bone ash and transfer to a graduated 1500-mL beaker.

2. Add a weighed aliquot of ^{209}Po (about 0.05 g) and ^{133}Ba (about 0.1 g) tracer solutions and 1 mL of Pb carrier solution to the beaker. [**Note**: Add 2.5 g of calcium propionate to the reagent blank beaker. DO NOT ADD CALCIUM PROPIONATE TO THE BONE ASH SAMPLES.]

LEAD SEPARATION

1. Add 25 mL of HNO_3 and 1 mL of $HClO_4$ to the samples and reagent blank beakers. [**Note**: $HClO_4$ is not required for samples dry ashed at $\geq 500^{o}C$.]

2. Place the covered beakers on a medium hotplate. Swirl the beakers to dissolve the bone ash.

3. Evaporate the solution to dense $HClO_4$ fumes. Do not allow the sample to reach dryness.

4. Convert the sample to chloride form with five successive additions of 25 mL of HCl. Evaporate the solution to near dryness between additions.

5. Add 25 mL of HCl and swirl the beaker to dissolve most of the solids. Remove the beaker from the hotplate.

6. Dilute the solution to 1 L with water. Stir the solution with a stirring rod to dissolve any remaining solids.

7. Return the beaker to the hotplate and heat the solution for 10 min.

8. Using NH_4OH in a wash bottle, and stirring constantly, adjust the pH to about 1.5 to 2. At this point no permanent hydroxide flock should be present. Any hydroxide flock is dissolved with the addition of 6N HCL. [**Note**: The pH of the reagent blank is determined with pH paper.]

9. Weigh 5 g of solid oxalic acid and add to the sample with stirring. Continue heating the solution for 10 min.

10. Adjust the pH to 2.0 using NH_4OH and pH paper for both the sample and the reagent blank. Stir continuously.

11. Remove the sample from the hotplate. Remove and rinse the stirring rod with water. Allow the oxalate precipitate to settle overnight.

12. Decant the supernate into a 3-L beaker and reserve for **Radium Separation.**

13. Destroy the oxalates by evaporating with two successive 25-mL portions of HNO_3. Do not allow the sample to reach dryness.

14. Convert the sample to the chloride form with five successive 25-mL portions of HCl.

15. Add 25 mL of HCl and swirl the beaker to dissolve most of the solids. Add a minimum amount of water to reach complete solution.

16. Remove the beaker from the hotplate and cool.
17. Transfer the solution with water to a 250-mL centrifuge bottle. Wash the beaker with water and transfer the washings to the centrifuge bottle. Stir the solution. The solution volume should be about 200 mL.

18. Place the centrifuge bottle in a 90°C hot water bath. Heat for 10 min.

19. Add 5 mL of thioacetamide solution to the sample. Stir and heat in the water bath for 1 or 2 min.

20. Remove the sample from the water bath. While stirring continuously, add NH_4OH to the sample until the black precipitate just persists.

21. Return the sample to the water bath for 1 h.

22. Remove the sample from the water bath. Remove the stirring rod and rinse with water.

23. Dry the outside of the centrifuge bottle. Place the bottle in a centrifuge cup. Tare a pair of samples on a double pan balance.

24. Place the tared samples in the centrifuge. Centrifuge the samples at 1800 rpm for 1 h.

25. Remove the samples from the centrifuge. Add 1 drop of Aerosol OT and decant the sample. Discard the supernate.

26. Add 2 mL of HCl to the sample and stir to break up the PbS precipitate. Place the sample in the water bath. Heat for 5 min.

27. Wash the walls of the bottle with 10 mL of water and heat for an additional 10 min.

28. Gravity filter the sample through a 12.5-cm diameter Whatman No. 42 paper into a prepared deposition cell.

29. Wash the centrifuge bottle with water and add the washing to the filter. Wash the filter with water. Discard the filter.

30. Place a cylindrical metal weight over the deposition cell. [**Note**: A 4-cm diameter by 4-cm height length of galvanized pipe will do.]

31. Place the weighted cell in an 80°C water bath. Lower the stirring motor with the Teflon rod in its chuck so that the rod is within 1 cm of the nickel disc.

32. Turn on the motor and stir for 4 h at maximum agitation without splashing. Add small quantities of 0.5N HCl to the cell, and water to the water bath to replace evaporative losses.

33. Turn off the motor and raise it to clear the stirring rod from the top of the cell. Remove the cell from the water bath.

34. Pour off the solution and discard. Rinse the cell successively with 0.5N HCl and water. Discard the rinsing.

35. Dismantle the cell and discard the bottle. Remove the nickel sample disc from the cap and rinse with ethanol.

36. Place the disc on a warm hotplate to dry.

37. Measure the disc in an alpha spectrometry system to determine the ^{209}Po yield and the ^{210}Po content of the sample. [**Note**: Record the deposition date so that decay corrections for the unsupported ^{210}Po can be made from separation date to measurement date.]

RADIUM SEPARATION

1. Evaporate the radium-bearing oxalate solution to dryness on a medium hotplate.

2. Remove the beaker from the hotplate and cool slightly. Add two successive 25-mL portions of HNO_3. Heat to destroy the oxalate.

3. Convert the sample to the chloride form with five successive 25-mL portions of HCl.

4. Add 25 mL of HCl to the beaker and warm to dissolve most of the solids. Add about 50 mL of water and stir to dissolve the remaining solids.

5. Transfer the warm solution to a 250-mL centrifuge bottle. Wash the beaker with water, police and transfer the washing to the centrifuge bottle.

6. Dilute 1 mL of barium carrier to about 5 mL with water. Stir the sample thoroughly and continuously while adding the diluted carrier solution dropwise.

7. Place the centrifuge bottle in a hot water bath and warm the solution for about 5 min.

8. With constant stirring, slowly add NH_4OH until a dense white permanent hydroxide flock forms.

9. Dissolve the flock in a minimum of HCl. [**Note**: For the blank, adjust the pH from 1.5 to 2.0 using pH paper.

10. Add 2 mL of NH_4OAc solution and 1 mL of dilute HOAc solution to the centrifuge bottle. Stir thoroughly and cool the bottle to room temperature in a water bath.

11. Add 1 mL of $(NH_4)_2SO_4$ solution to the bottle. Stir, remove the rod and rinse with water. Let the bottle stand at room temperature for 1 h.

12. Dry the outside of the centrifuge bottle. Place the bottle in a centrifuge cup. Tare a pair of samples on a double pan balance.

13. Place the tared samples in the centrifuge. Centrifuge the samples at 1800 rpm for 1 h.

14. Remove the samples from the centrifuge. Add one drop of Aerosol OT to the bottle. Carefully decant and discard the supernate.

15. Heat 5 mL of EDTA solution (300 g L^{-1}) for each sample in a hot water bath.

16. Break up the $BaSO_4$ precipitate with the stirring rod. Add 5 mL of warm EDTA solution and 1 mL of 1:1 monoethanolamine. Stir and heat for about 5 min.

17. Wash down the sides of the centrifuge bottle with about 10 mL of water. Continue heating the bottle for 15 min, stirring occasionally.

18. Gravity filter the solution through a 12.5-cm diameter Whatman No. 42 filter paper into a 30-mL polyethylene bottle.

19. Wash the centrifuge bottle and the filter paper with water. Discard the filter paper.

20. Dilute the sample to the same liquid level as the ^{133}Ba standard. The standard is prepared by diluting a known aliquot (about 0.1 g) of ^{133}Ba solution to 25 mL in a 30 mL polyethylene bottle.

21. Gamma count the standard and samples to determine the chemical yield of barium.

22. Transfer the solution to a radon bubbler.

23. Proceed with emanation procedure for ^{226}Ra (Ra-03-RC) to determine the radium content of the sample.

LOWER LIMIT OF DETECTION (LLD)*

		^{210}Po	^{226}Ra
Counter efficiency	(%)	30.	56.
Counter background	(cps)	$4x10^{-5}$±$0.7x10^{-5}$	$2.8x10^{-3}$±$0.2x10^{-3}$
Yield	(%)	85.	85.
Blank	(cps)	$3.5x10^{-4}$±$0.6x10^{-4}$	$2.0x10^{-2}$±$0.8x10^{-2}$
LLD (1000 min)	(mBq)	1.3	1.5
LLD (2500 min)	(mBq)	1.0	N/A

*Reagent blanks must be processed with every batch of samples.

REFERENCE

Fisenne, I. M.
"Lead-210 in Animal and Human Bone: A New Analytical Method"
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