

Inter-Mountain Labs Validation Study

For

Polonium 210 in Solids

Prepared by

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1- Scope of the Project

Inter-Mountain Labs was asked to review the feasibility and appropriateness of performing Po210 in soils. This study focused on digesting solids in acids and then performing Po210 analysis on the digestate with an Eichrom standard procedure for Polonium 210 in solutions.

Inter-Mountain Labs validated the procedures using certified solution standards of Polonium 210. Inter-Mountain labs also validated the method with a solid Certified Reference Material, UTS-4. Inter-Mountain labs estimated the detection limits with five different concentration levels of full method detection limit studies using UTS-4.

2- Method Summary

Inter-Mountain Labs performed a wet acid digestion on solid samples. The wet acid digestion consisted of a nitric acid digestion refluxed overnight on a hot plate, see R-DIGSOIL-.1.0 section 6. The samples were then filtered and brought to a volume of 1 liter. A portion of the solution was then prepared for polonium 210 analysis, R-PL210-1.1. The samples were analyzed using procedures described by Eichrom OTW01-rev2, see sections 7 and 8. The heavy metals of the digest solutions were precipitated via an iron hydroxide precipitation procedure. Then the precipitate was separated and re-dissolved. Then the resulting solution was passed through a Eichrom Sr resin column and the polonium was selectively eluted. The elute containing Po210 was chemically plated onto a nickel disk. The disks were then alpha counted using a Gas Proportional Counter.

3- Data Presentation

Four Laboratory Control Samples were analyzed full method. Liquid spike samples were prepared and taken through the entire method. The results are presented in Table 1. An average recovery of 74.6% was found for Po210 with this study.

Table 1

Polonium 210 Recovery Study EZ-1556-86 (LCS Study 1)			
Sample	Expected pCi	Observed pCi	Recoveries
EZ-1556-86-1	12.29	11.09	90.2%
EZ-1556-86-2	12.29	9.48	77.1%
EZ-1556-86-3	12.29	7.32	59.6%
EZ-1556-86-4	12.29	8.79	71.5%
Average		9.17	74.6%
Po210 Solution Standard Eckert and Ziegler Lot 1556-86			

Five solid Laboratory Control Samples were analyzed full method. Solid material identified as Standard Reference Material UTS-4 were prepared and taken through the entire method. The results are presented in Table 2. The results are acceptable and recoveries closely match the liquid sample study. The average recovery is 80.75%. A discussion on the UTS-4 true value appears in section 5.

Table 2

Polonium 210 Recovery Study UTS-4 (LCS Study 2)			
Sample	*Expected pCi/g	Observed pCi/g	Recoveries %
UTS4-A	983.78	800.71	81.39
UTS4-B	983.78	706.31	71.80
UTS4-C	983.78	1025.98	104.29
UTS4-D	983.78	770.09	78.28
UTS4-E	983.78	668.83	67.99
Average			80.75
Po210 Solid Standard CANMET UTS-4			
*Expected based on ingrowth with decay series			

Method detection limit studies were undertaken performing full method analysis using different amounts of UTS-4 in order to estimate the lower limit of detection. The studies are presented in Tables 3, 4, 5, 6, and 7 and are presented with lowest to highest. MDL study findings range from a level of 0.6 pCi to 3.94 pCi. The two highest level studies fall into EPA recommended levels for MDL spike values and are assumed to be the most accurate. Based on these studies, the MDL is estimated at 2.5 pCi and with a recommended reporting level of 5 pCi.

Table 3

Polonium 210 UTS-4 (MDL Study 1)			
Sample	*Expected pCi	Observed pCi	Recoveries %
UTS4-MDL-1	0.49189	0.0855	17.38
UTS4-MDL-2	0.49189	0.6288	127.83
UTS4-MDL-3	0.49189	0.6126	124.54
UTS4-MDL-4	0.49189	0.4801	97.60
UTS4-MDL-5	0.49189	0.2557	51.98
UTS4-MDL-6	0.49189	0.6493	132.00
UTS4-MDL-7	0.49189	0.328	66.68
Average			88.29
Standard Deviation		0.22	
Estimated MDL in pCi/g		0.68	
*Expected based on ingrowth with decay series			

Table 4

Polonium 210 UTS-4 (MDL Study 2)			
Sample	*Expected pCi	Observed pCi	Recoveries %
UTS4-MDL-1	0.98378	1.06	107.75
UTS4-MDL-2	0.98378	0.4997	50.79
UTS4-MDL-3	0.98378	1.253	127.37
UTS4-MDL-4	0.98378	1.091	110.90
UTS4-MDL-5	0.98378	0.5504	55.95
UTS4-MDL-6	0.98378	1.0797	109.75
UTS4-MDL-7	0.98378	0.8523	86.64
Average			92.73
Standard Deviation		0.29	
Estimated MDL in pCi/g		0.91	
*Expected based on ingrowth with decay series			

Table 5

Polonium 210 UTS-4 (MDL Study 3)			
Sample	*Expected pCi	Observed pCi	Recoveries %
UTS4-MDL-1	1.4757	1.186	80.37
UTS4-MDL-2	1.4757	1.4776	100.13
UTS4-MDL-3	1.4757	1.1437	77.50
UTS4-MDL-4	1.4757	4.3659	295.85
UTS4-MDL-5	1.4757	1.4468	98.04
UTS4-MDL-6	1.4757	0.7087	48.02
UTS4-MDL-7	1.4757	2.6193	177.50
Average			125.34
Standard Deviation		1.96	
Estimated MDL in pCi/g		3.94	
*Expected based on ingrowth with decay series			

Table 6

Polonium 210 UTS-4 (MDL Study 4)			
Sample	*Expected pCi	Observed pCi	Recoveries %
UTS4-MDL-1	5	3.53	70.60
UTS4-MDL-2	5	4.31	86.20
UTS4-MDL-3	5	2.52	50.40
UTS4-MDL-4	5	5.24	104.80
UTS4-MDL-5	5	3.46	69.20
UTS4-MDL-6	5	3.41	68.20
UTS4-MDL-7	5	3.88	77.60
Average			75.29
Standard Deviation		0.85	
Estimated MDL in pCi/g		2.66	
*Expected based on ingrowth with decay series			

Table 7

Polonium 210 UTS-4 (MDL Study 5)			
Sample	*Expected pCi	Observed pCi	Recoveries %
UTS4-MDL-1	10	8.56	85.60
UTS4-MDL-2	10	8.67	86.70
UTS4-MDL-3	10	7.92	79.20
UTS4-MDL-4	10	6.66	66.60
UTS4-MDL-5	10	8.06	80.60
UTS4-MDL-6	10	7.02	70.20
UTS4-MDL-7	10	7.73	77.30
Average			78.03
Standard Deviation		0.74	
Estimated MDL in pCi/g		2.34	
*Expected based on ingrowth with decay series			

4- Conclusions

This data validates these proposed procedures for Polonium 210 in solid materials. This study shows that these procedures are effective at measuring polonium 210 in a solid matrix, where polonium is expected to be soluble in a nitric acid digestion. The study does not address sample requirements such as particle size, potential interferences, and sample homogeneity. Since acid digestions have been shown to digest metals when processed appropriately, it is assumed the samples require processing and should be processed to -60 mesh. Expected recoveries will be in the range of 75% with quantifiable measurements at 5 pCi. If the required detection limit is below 5 pCi/g then the analyst will need to increase the amount of sample digested and validate MDL's at that level.

5- UTS-4 Discussion

The standard used in this study was UTS-4. UTS-4 is a Canadian Certified Reference Material with Ra226, Pb210, and Po210 values. UTS-4 was prepared and analyzed in 1980, the exact dates are unknown. The reference material report on UTS-4 is included as an attachment to this document.

The important certified values are Ra226 = 38.6Bq/g, Pb210 = 32.4Bq/g, and Po210 = 30.8Bq/g. The values of each constituent were measured independently in 1980 prior to the production of the standard report. This study assumed the values were correct at the time of analysis in 1980. Po210 was assumed to be in secular equilibrium with Pb210 today. This study assumed that Pb210 is approaching secular equilibrium with Ra226 and that there is no significant disassociation of radon gas from the sample. The UTS-4 material is finely ground and stored in a sealed glass jar with a headspace approximately equal to the volume of sample. These assumptions lead to an "estimated true value" of Po210 = 36.4Bq/g in UTS-4. This corresponds to the values that appear in the tables as "expected based on ingrowth with decay series". This "estimated true value" translates into an increase of the originally reported value of 18 percent

Inter-Mountain Labs believes that the "estimated true value" of Po210 must be close to true based on the average recovery data being similar to the liquid standards and for the purposes of validation it was not necessary to have an exact value.

6- Attachment: Solids Digestion Procedures, Lab SOP

Standard Operating Procedure for Digestion of Soil for Use in Radiochemical Analyses

Document Title: Standard Operating Procedure for Digestion of Soil for Use in Radiochemical Analyses

Document Control Number: R-DIGSOIL-1.0

Location: Sheridan Lab

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Plan Coverage:

Standard Operating Procedure for Digestion of Soil for Use in Radiochemical Analyses.

Original:

Lab Representative: _____

Lab Supervisor: _____

Standard Operating Procedure for Digestion of Soil for Use in Radiochemical Analyses

1.0 Scope and Application

- 1.1 This method is applicable to digestion of soil for analysis of Radium-226, Radium-228, Thorium-230, Lead-210/Polonium-210, and naturally occurring Uranium.

2.0 Summary of Method.

- 2.1 This method is for the collection of radionuclides through the digestion of soil in nitric acid solutions. The soil is heated in a nitric acid solution just below the boiling point for a period of eight hours, then cooled. The extracted solution is then filtered and split into separate aliquots for each analysis.

3.0 Interferences, Considerations.

- 3.1 The coarser the soil material is, the more difficult it will be to leach the target analytes into solution. This requires the soil to be processed to a fine powder (most likely 60 mesh) before it can be digested.
- 3.2 Glassware and other equipment can become radioactively contaminated from continued use.
- 3.2.1 All glassware and other equipment will be thoroughly cleaned with a detergent designed to remove radioactive contaminants, followed by a rinse with 1:4 hydrochloric or nitric acid, and a final rinse with de-ionized water.
- 3.2.2 Glassware may also be put through a glassware washer. A heavy cycle with detergent, followed by a light cycle with a rinsing agent but no detergent should be used to make sure all contamination is removed from glassware. See glassware washing procedure for further details.
- 3.2.3 Use of a method blank will monitor the condition of the glassware and equipment.

4.0 Sample Collection, Preservation, and Handling.

- 4.1 Samples should be collected in plastic or glass bottles of sufficient quantity to do a complete analysis and requisite quality control samples.

5.0 Safety.

- 5.1 Concentrated hydrochloric acid and nitric acid should be handled under a fume hood. Standard laboratory protective clothing and safety glasses should be worn.

6.0 Apparatus and Materials.

- 6.1 Thermolyne Cimarec 3 hot plate or equivalent hot plate/surface
- 6.2 GraLab interval timer/outlet or equivalent
- 6.3 Analytical balance
- 6.4 250 mL glass beakers (Griffin, low form) and 9 cm watch glasses
- 6.5 Metal spatulas or measuring spoons

- 6.6 1-L class A volumetric flasks
- 6.7 Plastic funnels
- 6.8 Ahlstrom 24 cm filter paper or equivalent
- 6.9 250 mL, 100 mL, and 50 mL class A graduated cylinders
- 6.10 Parafilm
- 6.11 2-L, 500 mL, and 250 mL pre-cleaned plastic sample bottles.

7.0 Reagents.

- 7.1 Reagent water: De-ionized water (DI-water), free of radioactive materials.
- 7.2 Nitric acid, Concentrated HNO₃: Reagent grade nitric acid.
- 7.3 Nitric acid, 1:1: dilute 500 mL of concentrated nitric acid with 500 mL of DI-water.
- 7.4 Standard in soil, Uranium tailings for naturally occurring isotopes: Natural Resources Canada, Uranium Tailings Samples UTS-4. To be used as a check source for Natural uranium and Radium-226.

8.0 Calibration and Standardization.

- 8.1 Balance should be monitored with traceable, calibrated weights before use each day. See Balance Calibration Procedure 1.0.

9.0 Quality Control.

- 9.1 Batch Requirements
 - 9.1.1 Each batch will contain no more than 18 samples, not including quality control samples.
 - 9.1.2 Each batch will contain a Method Blank (MB), a Laboratory Control Sample (LCS), and a Uranium Tailing Sample (UTS). The LCS is prepared in the digest, but the actual spike is added during the analysis of each individual analyte.
 - 9.1.3 The duplicate (DUP) quality control is taken from the aliquot generated from the extra gram digested. However, a client may request a DUP be processed from the raw soil sample. In this case, the DUP will be digested as a separated sample and analyzed as the DUP.

10.0 Procedure.

- 10.1 Soil preparation
 - 10.1.1 Soil must be processed to 60 mesh before being digested. The Soil Department at Inter-Mountain Labs will accomplish this process from the raw sample and deliver the prepared samples to the RadChem Department. This should homogenize the sample, but if the sample looks uneven the sample should be stirred before weighing out the sample.
 - 10.1.1.1 For the actual processing procedure see Standard Operating Procedure S-SAMPPROC-3.0 from September 19, 2008.

10.2 Digestion

10.2.1 Place a clean, glass 250 mL beaker on the analytical balance, zero the balance.

10.2.2 Using a metal spatula or spoon, measure out the appropriate amount of sample into the beaker. Refer to Table 1 in Section 10.7.

10.2.3 Add 200 mL of 1:1 HNO₃ and cover sample with watch glass.

10.2.4 Turn hot plate to 250° F. Heat samples for 8 hours.

10.2.4.1 **Note:** Do not allow acid to evaporate completely from the beaker. After 4 hours the heat can be reduced to 200°F, or additional acid can be added to the beaker.

10.2.5 Remove samples from heat.

10.3 Set up 1-L volumetric flasks and plastic funnels, one for each sample.

10.4 Using Ahlstrom filter papers in the plastic funnels, pour the sample including the soil into the funnel. Rinse the beaker with DI-water a couple of times with DI-water and pour this into the funnel. Allow the sample to filter completely then rinse the soil and Ahlstrom filter with DI-water to ensure all of sample has been collected in the volumetric flask. Bring sample to volume of 1-L using DI-water.

10.5 Cover volumetric flask with parafilm and invert the flask 8-10 times. The sample must be well homogenized before the aliquots are split, to ensure accurate analytical results.

10.6 Split sample according to sample amount used from Table 1.

Table 1

	Pb/Po	Ra-226	Th-230	U	Extra/Ra-228
5 grams digested	200 mL	200 mL	200 mL	200 mL	1 x 200 mL
8 grams digested	125 mL	125 mL	125 mL	125 mL	4 x 125 mL
20 grams digested					1 x 1-L

10.6.1 Note: The split for analysis of Uranium by ICP or ICP-MS needs to be taken from the 200/125 mL aliquot to a final volume of 1-L.

11.0 References.

ATTACHMENT #1
STANDARD OPERATING PROCEDURE
METHOD TRAINING RECORD

Document Title: **Standard Operating Procedure for Digestion of Soil for Use in Radiochemical Analyses**

Document Control Number: R-DIGSOIL-1.0

Location: Inter-Mountain Laboratories, Inc.

I have read the preceding document and understand all sections.

I have been trained in the performance of the methods and any recent revisions to this procedure.

<u>ANALYST</u>	<u>SIGNATURE</u>	<u>DATE</u>	<u>TRAINER</u>
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7- Attachment: Pb210 and Po210, Lab SOP



Standard Operating Procedure for Analysis of Lead 210 and Polonium 210

Document Title: Standard Operating Procedure for Lead 210 and Polonium 210

Document Control Number: R-PL210-1.0

Location: Sheridan Lab

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Plan Coverage: Standard Operating Procedure for Analysis of Lead 210 and Polonium 210

Original 4/27/2012

Lab Representative: _____

Lab Supervisor: _____

Standard Operating Procedure for Lead 210 and Polonium 210

1.0 Scope and Application.

- 1.1. This method is applicable to the determination of dissolved lead (Pb-210) and polonium (Po-210) in water and wastewater. Suspended solids in water can be evaluated if the solids are put into a water matrix by acid digestion. This digestion process can also be applied to soil, air, and organic samples to place lead and polonium into a dissolved state for analysis.

2.0 Summary of Method.

- 2.1. Lead and polonium are concentrated from a 1.0 L sample by an iron oxide [Fe(OH)₃] scavenge. Pb and Po are separated from other elements with Eichrom Sr Resin™. The purified Pb and Po fractions are collected separately and prepared for analysis. Bismuth-210 (Bi-210) is allowed to in-grow to secular equilibrium with Pb-210, and is measured by low-background gas flow proportional counting. Lead carrier and a Po-210 NIST traceable standard are used to monitor yields and to adjust results in order to improve accuracy and precision.
- 2.2. Significance of use – significantly eliminates contamination from other beta emitters.

3.0 Definitions

- 3.1. Secular equilibrium – when the half-life of the progeny is much less than the half-life of the parent (for a single progeny, the total activity reaches a maximum of about twice the initial activity, and then displays the characteristic half-life of the parent—usually no change over normal measurement intervals.)
- 3.2. Daughter product – the progeny of a parent radioisotope.
- 3.3. Ingrowth – a period of daughter product production.

4.0 Interferences, Considerations.

- 4.1. By traditional methods, any beta emitter can potentially cause interference with the measurement of the Bi-210 daughter of Pb-210. This method effectively eliminates these possible interferences.
- 4.2. Significant amounts of dissolved metals, detergents, or organic material in a sample can compete with the target analytes for load sites on the Sr Resin™. It may be necessary to deal with these either during the precipitation or before loading the resin to ensure that the target analytes are completely extracted.
- 4.3. Glassware and other equipment can become radioactively contaminated from continued use.
 - 4.3.1. All glassware and other equipment will be thoroughly cleaned with a detergent designed to remove radioactive contaminants, followed by a rinse with (1:4) hydrochloric or (1:2) nitric acid, and a final rinse with de-ionized water.
 - 4.3.2. Glassware may also be put through a glassware washer. Either a heavy cycle with detergent and rinse cycle using an acid rinsing agent, or a heavy cycle followed by a light cycle using an acid rinsing agent should be used. See Glassware Washing Procedure for further details.

- 4.3.3. For plating glassware, soaking with 3-5% Contrad overnight and magnetic stir bars; soaking with 20-50% hydrochloric acid over-night will be necessary to ensure complete radioactive decontamination.
- 4.3.4. Taking a method blank through the entire process will monitor the condition of glassware and equipment.

5.0 Sample Collection, Preservation, and Handling.

- 5.1. Samples should be collected in plastic or glass bottles of sufficient quantity to do a complete analysis and requisite quality control samples.
- 5.2. Samples should be filtered with a 0.45 μm filter and preserved with nitric acid to pH=2. All samples will be preserved in the RadChem laboratory, because the nitric acid preservative must be analyzed to screen for radioactive contaminants.
 - 5.2.1. If samples arrive at the laboratory unfiltered, the laboratory will filter them prior to analysis. Samples may be analyzed without preserving if sample preparation immediately follows filtration. In the case where an analysis will be delayed after filtration, the laboratory will preserve the samples, and delay proceeding to analysis for 16 hours.
 - 5.2.1.1. If the suspended particle portion of the sample is to be analyzed in conjunction with the dissolved, the 0.45 μm filters are saved from this process and digested.

6.0 Safety.

- 6.1. Radionuclide sources will be kept in a cabinet in the RadChem sample room with at least ¼ inch carbonaceous material for shielding. Low level and low activity sources are considered safe to handle; however, all sources shall be handled with appropriate personal protective equipment employed.
- 6.2. The laboratory will monitor background radiation in strategic locations with a radiation badge program through an off-site, independent company. The monitoring will include gamma in all sites, and radon in select sites.
- 6.3. The laboratory will perform monthly radiation scans with 47 mm paper filters to determine the removable alpha radiation present on surfaces. Lower levels should be kept at background, however maximum levels should not exceed 200 dpm/100 cm^2 .
- 6.4. The RadChem laboratory will maintain detergents and other agents that remove radioactive substances from clothes, hair, and skin, as well as laboratory equipment.
- 6.5. See MSDS sheets for information on all chemicals. See the Chemical Hygiene Plan for further safety information.

7.0 Apparatus and materials

- 7.1. Tennelec LB 4110 Gas flow proportional counter with 2 inch detectors
- 7.2. Vacuum pumps, high suction and low suction capable
- 7.3. Centrifuge, International Equipment Co.
- 7.4. Analytical balance, 0.0001 g capacity

- 7.5. Eichrom vacuum box (24 position) with yellow and white tips with plugs
- 7.6. Torrey Pines Scientific stirring hot plate with 9 positions, or equivalent
- 7.7. Fisher Vortex Genie 2 test tube mixer or equivalent
- 7.8. Muffle furnace or oven capable of maintaining temperatures of 300°C
- 7.9. Filtration apparatus for 47 mm filter
- 7.10. 0.45 µm mixed cellulose ester 47 mm filters
- 7.11. Whatman GF/C 47 mm glass microfibre filters or equivalent
- 7.12. 1500 mL glass beakers (Griffin, low form) and 15 cm watch glasses
- 7.13. 250 mL Erlenmeyer flasks with yellow plastic caps
- 7.14. 2 liter, 1 liter, and 500 mL vacuum flasks
- 7.15. 1 liter, 500 mL, 250 mL, and 100 mL graduated cylinders
- 7.16. 500 mL plastic squirt bottles
- 7.17. Glass stirring rods and rubber policemen
- 7.18. Stir bars, Teflon coated
- 7.19. 50 mL centrifuge tubes with caps and trays
- 7.20. Eichrom Sr Resin™ 2 mL cartridge, 50-100 µm particle size
- 7.21. Eichrom pre-filter material, 2 mL cartridge
- 7.22. 20 mL syringe
- 7.23. Eppendorf repipettor with Combitips and adaptors for 25 and 50 mL
- 7.24. Eppendorf pipettors and tips, 0.1-1.0 mL adjustable
- 7.25. pH strips 5-10 and 0-14 range
- 7.26. Transfer pipettes, plastic, 3 mL
- 7.27. Metal tweezers
- 7.28. Acrylic spray paint, clear (acid resistant paint)
- 7.29. Aluminum foil and double sided tape
- 7.30. Pall filter apparatus for 25 mm membrane filters with stainless steel support screen
- 7.31. Plastic coated phone cable wire
- 7.32. Eichrom Resolve™ Filter, 0.1 µm 25 mm filter

7.33. Nickel disc, 1 inch diameter with hanging hole approx. 2 mm from edge

7.34. Stainless steel planchets, 2 in

8.0 Reagents

8.1. Reagent water: Nano water[®] or De-ionized water (DI-water), free of radioactive materials

8.2. Ammonium citrate, 0.05M: dissolve 6.08g of ammonium citrate in 0.5-L of water.

8.3. Ammonium hydroxide, 15N: Concentrated Ammonium hydroxide reagent grade.

8.4. Ammonium Thiocyanate indicator

8.5. Ascorbic acid, 1M, dissolve 176.13g ascorbic acid in 500 mL of water and dilute to 1-L. **NOTE:**
This solution must be made fresh at least every week.

8.6. Ethanol, 80%

8.6.1. Dilute 80 mL ethyl alcohol, 100%, to 100 mL with DI-water.

8.6.2. Dilute 84.2 mL ethyl alcohol, 95% to 100 mL with DI-water.

8.7. Ethyl alcohol, USP, 100%, Absolute alcohol

8.8. Ethyl alcohol, USP, 95 %, can be substituted for 100% ethyl alcohol

8.9. Hydrochloric acid (HCl), concentrated hydrochloric acid

8.10. Hydrochloric acid, 2M: add 167 mL of concentrated HCl to 100 mL of DI-water and dilute to 1-L.

8.11. Hydrochloric acid, 0.5M: add 41.6 mL of concentrated HCl to 100 mL of DI-water and dilute to 1-L.

8.12. Iron carrier, 20 mg Fe¹³/mL: dissolve 96.8g of ferric chloride (FeCl₃•6H₂O) in 1-L of 0.5M HCl (See 8.11).

8.13. Lead carrier (Pb(NO₃)₂), 10 mg/mL Pb: dissolve 15.985g lead nitrate in 900 mL DI-water then dilute to 1-L.

8.13.1. To standardize the carrier – In four centrifuge tubes add 10 mL DI water and 1 mL of the newly prepared lead carrier. Prepare samples as per instructions in Sections 11.2.4.4. - 11.2.4.11., except filters do not need to be mounted on planchets to be counted.

8.13.2. Record recoveries and average; this becomes the chemical yield in Section 12.4.

8.14. Nitric acid (HNO₃), concentrated nitric acid, 15.7M

8.15. Nitric acid, 1M: add 63 mL of concentrated nitric acid to 400 mL DI-water and dilute to 1-L.

8.16. Nitric acid, 0.1M: add 6.3 mL of concentrated nitric acid to 400 mL DI-water and dilute to 1-L.

8.17. Sulfuric acid (H₂SO₄), 18.8M, concentrated sulfuric acid

8.18. P-10 gas for instrument

9.0 Calibration and Standardization

9.1. Determination of instrument efficiency – the instrument undergoes a full calibration once a year with alpha and beta sources of similar geometries to those of the method samples. This will establish efficiencies, plateaus, and a 'dead band' between the alpha and beta ranges.

9.1.1. Efficiency of the system is calculated by dividing the counts per minute by the disintegrations per minute of a known source (Section 12.1.) This is calculated automatically by the instrument software, which is graphed, printed, and archived.

9.2. Determination of method efficiency

9.2.1. Lead-210: Efficiency is established through a curve with Lead-210 standard of a known value, and increasing values of lead carrier. A range of lead carrier recoveries which will reflect those possible from samples are placed on filters and allowed to ingrow for 5 days. These are then counted and the standard recovery is graphed against the lead recovery.

9.2.2. Polonium-210: Polonium-210 is the isotope that is used for both the annual calibration and for the daily calibration of the instrument. The efficiency that is determined in the annual calibration will be used as the efficiency for polonium in all calculations.

9.3. Background determination:

9.3.1. Lead-210: An initial mock up of the planchet, filter, double-sided tape, and aluminum foil cover will be counted for the standard lead-210 counting time, to demonstrate they do not contribute any beta counts to a sample. If this mock up rises above background, the individual elements will be assessed to determine the source of the contamination.

9.3.1.1. Subsequent mock ups can be done if materials significantly change and a background needs to be re-established or re-checked.

9.3.1.2. The method blank also serves as a check for contamination of the materials.

9.3.2. Polonium-210: Each newly purchased batch of nickel planchets (when it has been painted on one side) will be counted for the standard polonium-210 counting time, to demonstrate they do not contribute any alpha counts to a sample. A subset can be counted to represent the entire batch.

9.4. Daily calibration of the instrument

9.4.1. Background of the instrument

9.4.1.1. Each day of use, the instrument shall have a background run of at least 2 hours, or run time equivalent to sample count time of the method being counted.

9.4.1.1.1. Alpha backgrounds should be below 0.15 CPM and beta backgrounds should be below 1.4 CPM.

10.0 Quality Control (See Table 1)

10.1. Batch requirements

10.1.1. Each batch will contain a method blank (MB), a laboratory control sample (LCS) for both the lead-210 and polonium-210 spikes, a duplicate sample (DUP), and matrix spike (MS) of two samples. The matrix spike will be spiked with the lead-210 standard; because it

contains polonium-210 in secular equilibrium both can be recovered without having to do separate matrix spikes for each standard.

- 10.1.2. Since the laboratory must protect the client samples, enough volume of sample must be saved to repeat the analysis. If there is not enough to run a duplicate and a matrix spike, and protect the client sample, a 'sample' using tap water will be used for either the duplicate or the matrix spike.
- 10.2. The method blank results should be below the reporting limit or minimum detectable amount (MDA). If the method blank is above the reporting limit, the data may be reported if qualified appropriately.
- 10.3. Laboratory control sample (LCS)
 - 10.3.1. Working limits – The laboratory control sample (LCS) shall be within 3 standard deviations of the average of a minimum of 20 spike recoveries.
 - 10.3.1.1. If the LCS is out of limits, the samples may be repeated. This applies to both LCSs, however, so if one passes and the other does not, the data will be accepted.
 - 10.3.1.2. The working limits shall be 50-150 percent recovery until actual limits are established.
 - 10.3.1.3. Laboratory control samples will be spiked near any action limits defined by regulatory agencies and delineated in methodology, as possible.
- 10.4. Duplicates shall be within a relative percent difference of $\pm 20\%$ (See Section 13.1).
 - 10.4.1. If a duplicate is greater than the 20 percent window and less than 5 times the MDA, the duplicate will be evaluated using the replicate error ratio (RER, See Section 13.2.) If this is less than 2, the duplicate data will be accepted.
 - 10.4.2. If a sample exceeds these 2 criteria it will be re-counted. If the sample is still out of these criteria, it may be re-analyzed; however, the batch may still be reported if the remaining quality control samples all meet acceptance criteria.
- 10.5. Matrix spike (MS)
 - 10.5.1. Working limits – Sample/matrix spike recoveries will be within 3 times the standard deviation of the average of a minimum of 20 spike recoveries, as is the criteria for LCS.
 - 10.5.1.1. If a sample falls outside this criteria, and all other criteria are acceptable, the data can be accepted and poor spike recovery attributed to sample matrix. This information will be placed in the case narrative of the report package.
 - 10.5.1.2. The control limits will be 50-150 percent recovery until actual limits can be established.
 - 10.5.1.3. Spike concentrations shall be the same as that for the LCS.

11.0 Procedure.

- 11.1. Water sample preparation
 - 11.1.1. Filtration:

- 11.1.1.1. Samples to be stored for future processing: Filter 1000 mL per sample—or however many liters required, if it is part of the quality control—through a 0.45 µm cellulose ester filter using a vacuum flask and filter apparatus. Sample is stored in a plastic bottle and preserved to pH<2 with nitric acid.
- 11.1.1.2. If the samples are to be processed immediately, filter through a 0.45 µm cellulose ester filter, but the sample is not preserved and is poured into a 1500 mL glass beaker and covered with a 15 cm watch glass.

11.1.2. Precipitation

- 11.1.2.1. Once samples are poured into 1500 mL beakers, add 1-5 mL concentrated nitric acid to pH<2; some samples may need more acid to reach pH<2. **NOTE:** Suspended waters, soils, vegetation, meat, and air samples should be checked but will probably not need additional nitric acid, as they are digested in nitric acid and already below a pH of 2.
- 11.1.2.2. Add 1 mL of lead carrier (10 mg/mL), 1 mL of iron carrier (20mg/mL), and appropriate amount of lead-210 or polonium-210 spike to LCS and MS.
- 11.1.2.3. Heat the sample on stirring hot plate at near boiling for 1 hour.
- 11.1.2.4. Very carefully, while stirring, add NH₄OH until a reddish-brown precipitate of Fe₂O₃ forms. Adjust the final pH of the solution to 8.5 ± 0.5. **NOTE:** Digested samples may need a final pH of 10 to complete the precipitation.
- 11.1.2.5. Stir the solution with a glass rod if necessary, and continue heating and stirring for another 30 minutes. Remove the sample from the hotplate and allow the precipitate to settle for at least 2 hours, preferably overnight.
- 11.1.2.6. After decanting as much supernate as possible, transfer the remainder of the sample to a 50 mL centrifuge tube. Centrifuge and decant the supernate. Repeat until all precipitate is collected in centrifuge tube.
- 11.1.2.7. Wash the precipitate with 10 mL of DI-water by vortexing. Centrifuge and discard supernate.
 - 11.1.2.7.1. If precipitate dissolves in the DI-water, the sample will need to be re-precipitated.
 - 11.1.2.7.1.1. Return sample to 1500 mL beaker, take to 1-L volume with DI-water, adjust to pH<2 with nitric acid, then start again at Section 11.1.2.3.
 - 11.1.2.7.1.2. This process will allow the sample to remain included with the initial set.
 - 11.1.2.7.2. If supernate is not clear, but particulate free, label and save the supernate in case further analysis is needed.
- 11.1.2.8. Add 10 mL 2M HCl and vortex to dissolve precipitate. If precipitate does not dissolve, heat the sample and vortex again. If the precipitate still does not go into solution, add 10 mL additional HCl, heat and vortex. The solution should have a yellow hue when dissolved completely.
- 11.1.2.9. Add 5 mL of 1M ascorbic acid to the solution, swirling to mix. Wait 2-3 minutes for the solution to clear. **NOTE:** Any yellow or red color should disappear, which

indicates the reduction of Fe(III) to Fe(II). If the color persists, then additional ascorbic acid should be added drop-wise with mixing until the color disappears. Ammonium thiocyanate can be used to indicate if all the iron in the solution has been reduced.

11.2. Lead-210 and Polonium-210 Separation Using Eichrom Sr Resin™

11.2.1. In the following steps, every sample needs an Eichrom Sr Resin™ cartridge set up. (This includes a white tip, yellow tip, the cartridge, and a 20 mL syringe.) All holes of the box not used for samples need to be covered with a plugged tip assembly, or a plug directly over the hole in the lid.

11.2.1.1. The Sr Resin™ is used in conjunction with a Vacuum box system. Conditioning and rinsing steps have a maximum flow rate of 3 mL/min (22-24 drops = 1 mL.) Loading and eluting samples step have a maximum flow rate of 1 mL/min. [See Eichrom procedure number VBS01, "Setup and Operation Instructions for Eichrom's Vacuum Box System (VBS)].

11.2.1.2. For rinsing the resins, the box liner is used to collect the acid rinse, but for loading and rinsing of samples, the centrifuge tray and tubes are used to collect waste.

11.2.2. Loading samples on Sr Resin™

11.2.2.1. Set up the vacuum box with the necessary number of assemblies for the batch. Condition/rinse the Sr Resin™ with 10 mL 2M HCl. Each solution of dissolved precipitate is emptied into its own setup on the vacuum box.

11.2.2.2. Vacuum is applied slowly. As drops begin, the fastest sample is counted to establish the flow rate for the batch, which should not be greater than 1 mL/min.

11.2.2.3. Rinse each centrifuge tube with 10 mL 2M HCl and add to samples. Record time and date of this addition. This is the start of ingrowth (SOI) for Bismuth-210 and is used in the final calculation. Discard the eluent. **NOTE:** The HCl rinse will remove bismuth and yttrium, if present.

11.2.3. Stripping Polonium-210 off the Sr Resin™

11.2.3.1. This step must be performed even if Lead-210 is the only analyte of interest.

11.2.3.2. Place a clean and labeled centrifuge tube in rack under each cartridge.

11.2.3.3. Pipet 5 mL 1M Nitric acid into the cartridge assembly; pass through cartridge at 1 mL/min flow rate, and collect eluent.

11.2.3.4. Pipet 15 mL 0.1M Nitric acid and repeat as per Section 11.2.3.3., collecting eluent.

11.2.3.5. Remove tubes and set aside for Po-210 auto-deposition in Section 11.2.5.

11.2.4. Stripping Lead-210 off the Sr Resin™ and sample preparation

11.2.4.1. Samples should be precipitated within an hour after eluting from resin since bismuth-210 may not co-precipitate with lead-210.

11.2.4.2. Place a clean and labeled centrifuge tube in rack under each cartridge.

- 11.2.4.3. Pipet 13 mL of 0.05M Ammonium citrate into the cartridge assembly, pass through the cartridge at 1 mL/min. flow rate, and collect eluent.
 - 11.2.4.4. Very carefully add 4 mL of concentrated sulfuric acid to each lead eluent and allow the solution to cool for 10-15 minutes. **NOTE:** Addition of sulfuric acid to a water matrix is an exothermic reaction. Caution should be taken to avoid burns and spattering.
 - 11.2.4.5. Weigh Resolve 0.1 μm filters on 4-place balance and record weight. Place them on 2 in. stainless steel planchets, one for each sample.
 - 11.2.4.6. Cap centrifuge tubes and vortex the solution gently. A white precipitate should form.
 - 11.2.4.7. Set up Pall filter apparatus for 25 mm Resolve 0.1 μm filter. Place first filter in apparatus. Turn on vacuum.
 - 11.2.4.8. Add 3-5 mL 80% Ethanol to filter and check apparatus for leaks. Rinse filter with 2-3 mL DI-water.
 - 11.2.4.9. Filter sample onto Resolve filter and rinse centrifuge tube with 5 mL DI-water, adding rinse to filter. Wash filter with 3-5 mL 100% Ethanol. Remove filter and place back on corresponding planchet and allow to dry.
 - 11.2.4.10. Clean filter apparatus and wipe down with Kim wipe, then set up for next sample. Continue until all samples are on filters.
 - 11.2.4.11. Weigh back filters on 4 place balance, then mount filters on planchets using double-sided tape and cover with aluminum foil. **NOTE:** Extend enough tape on the planchet to hold the aluminum foil edges down.
 - 11.2.4.12. Place planchets in tray and wait at least 5 days for Bi-210 ingrowth.
 - 11.2.4.13. Count beta particles in gas flow proportional counter. For calculation of results, see Section 12.
- 11.2.5. Sample preparation for Polonium and Auto-deposition on nickel discs
- 11.2.5.1. Rinse nickel discs with DI-water and ethanol. Let air dry. Label discs with a permanent marker "1-24" or enough to fill the batch. Spray paint one side with clear acrylic paint or spray paint and allow to completely dry before starting deposition process. String the discs with approximately 5-6 inches of plastic coated wire to suspend the discs into a 250 mL Erlenmeyer.
 - 11.2.5.2. For each sample set up a 250 mL glass Erlenmeyer and weigh out 0.1 g of ascorbic acid. Add 185 mL of 0.5M HCl acid. **NOTE:** The ascorbic acid will reduce any Fe(III) in the solution to Fe(II) and ease the reduction of polonium.
 - 11.2.5.3. Transfer the solution from Section 11.2.3.5 into appropriately numbered beaker, to a final volume of 200 mL.
 - 11.2.5.4. Place the sample on a stirring hot plate and add magnetic stirrer.
 - 11.2.5.5. Suspend the discs on coated wire into beakers. Cover beaker with a yellow plastic cap.

- 11.2.5.6. Heat the beakers to 70°C and constantly stir. Plating should continue for 6 hours. **NOTE:** If volume reduces, continue to add 0.5M HCl back to the 200 mL.
- 11.2.5.7. Once plated, remove discs from solution and rinse with DI-water and ethanol. Air dry on 2 inch stainless steel planchet.
- 11.2.5.8. Count alpha particles in gas flow proportional counter. For calculation of results see Section 12.

12.0 Calculations.

- 12.1. Standardization: calculation of the efficiency (E) of the system.

$$E = \text{CPM/DPM}$$

Where:

CPM = Counts per minute

DPM = Disintegrations per minute

- 12.2. Polonium matrix spike yield: Polonium-210

$$\text{Po}_Y \text{ (matrix spike yield)} = \frac{\text{Spike (pCi/unit)} - \text{Sample (pCi/unit)}}{\text{Nominal Concentration (pCi/unit)}} \times 100$$

Calculate average matrix spike yield by adding the 2 matrix spike yields and divide by 2.

- 12.3. Calculation of initial Po-210 activity:

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

Where:

S = sample activity, CPM

B = background, CPM

2.22 = conversion factor for DPM to pCi

E = counting efficiency, measured CPM/DPM of isotopic standard

Po_Y = Po matrix spike yield

λ = 0.005008 day⁻¹ (decay constant for polonium-210)

t₀ = time of initial sampling

t₀₁ = time of mid-point of sample count

V = sample volume in liters, L

- 12.4. Gravimetric yield: Lead carrier

$$\text{Pb}_Y \text{ (carrier yield)} = \frac{R_W - T_W}{C_W}$$

Where:

R_W = Lead recovery plus filter, g

T_W = tare weight of Resolve filter, g

C_W = Standardized lead sulfate added, g (See Section 8.13.)

12.5. Calculation of initial Lead-210 recovery based on Bismuth-210 ingrowth

$$\text{Pb-210 (pCi/L)} = \frac{S - B}{2.22 * E * \text{Pb}_Y * (1 - e^{-\lambda_1(t_{01} - t_{B1})}) * V * (e^{-\lambda_2(t_0 - t_{01})})}$$

Where:

S = sample activity, CPM

B = background, CPM

E = counting efficiency, measured CPM/DPM of isotopic Pb-210 standard

Pb_Y = Carrier yield

λ₁ = 0.138 day⁻¹ (decay constant for Bismuth-210)

λ₂ = 0.0000855 day⁻¹ (decay constant for Lead-210)

t₀ = time of initial sampling

t_{B1} = time of Bi-210 start of ingrowth, recorded in Section 11.2.2.3.

t₀₁ = time of mid-point of sample count

V = sample volume in liters, L

12.6. Calculate the laboratory control sample (LCS) recovery:

$$\text{LCS recovery (\%)} = \frac{\text{LCS Result (pCi/unit)}}{\text{Nominal LCS Conc. (pCi/unit)}} \times 100$$

12.7. Calculation of error at the 95% confidence level:

$$\text{Error} = \frac{1.96 \sqrt{\frac{R_o}{t_1} + \frac{B}{t_2}}}{2.22 * E * V * R_Y}$$

Where:

R_o = gross count rate, CPM

t₁ = counting time for sample count, minutes

B = background count rate, CPM

t₂ = counting time for background count, minutes

E = efficiency of the isotopic standard, CPM/DPM

V = volume of sample in liters, L

R_Y = recovery yield, Po_Y or Pb_Y

12.8. Calculation of the Minimum Detectable Activity (MDA):

$$\text{MDA} = \frac{3.29 * \sqrt{\frac{B}{t_1} + \frac{B}{t_2}}}{K} + \frac{3}{K * t_2}$$

and

$$K = 2.22 * E * V * R_Y$$

Where:

B = background count rate, CPM

t₁ = counting time for sample, minutes

t₂ = counting time for background, minutes

E = efficiency of isotopic standard

R_Y = recovery yield, Po_Y or Pb_Y

13.0 Precision and Accuracy.

13.1. Relative percent difference, RPD:

$$\text{RPD} = \left| \frac{(A - B)}{\frac{(A + B)}{2}} \right|$$

Where:

A = Net activity of the first measurement

B = Net activity of the second measurement

13.2. Replicate error ratio, RER:

$$\text{RER} = \frac{|A - B|}{\sqrt{s_a^2 + s_b^2}}$$

Where:

A = Net activity of the first measurement

B = Net activity of the second measurement

s_a^2 = uncertainty of the first measurement

s_b^2 = uncertainty of the second measurement

14.0 References

- 14.1. Lead-210 and Po-210 in Water (OTW01), Rev. 2.0, Eichrom Technologies, LLC., July 28, 2009.
- 14.2. Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP), NUREG-1576, EPA 402-B-04-001A, NTIS PB2004-105421, July 2004.

Table 1		
Ground water and monitoring samples/Clean Water Act		
Instrument calibration-plateaus, efficiencies		Yearly
System background		Yearly
Stability check-efficiencies	90-110%	Day of use
Stability check-background	Less than method detection limit	Day of use
Method blank	Less than method detection limit	Every batch
LCS-Laboratory control sample	Ongoing QC charts at 3 sigma	Every batch
LCSD-Laboratory control sample duplicate	Ongoing QC charts at 3 sigma AND $\pm 20\%$ RPD or RER < 2	If requested
Matrix spike	Ongoing QC charts at 3 sigma	Every batch
Matrix spike duplicate	Ongoing QC charts at 3 sigma AND $\pm 20\%$ RPD or RER < 2	Every batch
MDL-Method detection limit	7 fortified blanks spiked between MCL and required detection limit	Yearly

**ATTACHMENT #1
STANDARD OPERATING PROCEDURE
METHOD TRAINING RECORD**

Document Title: **Standard Operating Procedure for Analysis of Lead 210 and Polonium 210**

Document Control Number: R-PL210-1.1

Location: Inter-Mountain Laboratories, Inc.

*I have read the preceding document and understand all sections.
I have been trained in the performance of the methods and any recent revisions to this procedure.*

<u>ANALYST</u>	<u>SIGNATURE</u>	<u>DATE</u>	<u>TRAINER</u>
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8- Eichrom - OTW01



Lead-210 and Polonium-210 in Water

1. Scope

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

2. Summary of Method

- 2.1. Lead and polonium are concentrated from a 500 mL to 1,500 mL sample by iron hydroxide scavenge or cation exchange column. Pb and Po are separated from the other elements with Eichrom Sr Resin. The purified lead and polonium fractions are collected and prepared for analysis. Pb Resin can be used, however Po yields will be lower by approximately 25%.

3. Significance of Use

- 3.1. This method 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 Ag disk can be reduced by high concentrations of Fe, Te, Au, Pt and Hg.
- 4.3. This method effectively eliminates these possible interferences.

5. Apparatus

- 5.1. *Aluminum foil* – if counting ^{210}Bi and ^{210}Pb via gas flow proportional counter
- 5.2. *Alpha Spectroscopy system* – if determining radioactive ^{210}Po with Po tracers.
- 5.3. *Centrifuge*
- 5.4. *Centrifuge tubes (50 mL, plastic)*
- 5.5. *Column reservoirs, 25 mL available from Eichrom*
- 5.6. *Fume hood*
- 5.7. *Filter- 0.45 micron*
- 5.8. *Filter apparatus- Gelman apparatus with polycarbonate base and metal screen, 25 mm polysulfone funnels*
- 5.9. *Glass beakers*
- 5.10. *Glass stir rods*
- 5.11. *Hot plate*

- 5.12. *Ion exchange columns* - 1 to 1.5 cm diameter, 10 ml resin volume
- 5.13. *Low Background proportional counter*- For measurement of ^{210}Bi daughter of ^{210}Pb .
- 5.14. *Liquid Scintillation Counter (LSC)* – For measurement of ^{210}Bi daughter of ^{210}Pb .
- 5.15. *Low Background Scintillation Vials* – for sample measurement via LSC
- 5.16. *Resolve™ Filter* – 0.1 micron 25 mm polypropylene, Eichrom part number RF-100-25PP01
- 5.17. *Stainless steel planchets*- 50.8 mm diameter, 6.4 mm deep flat bottom, cupped planchet.
- 5.18. *Silver planchets, flat (Recommended)* – 25 mm diameter, polished on one side with jewelers' polish and coated on the back side with an acid resistant acrylic paint. Drill a small hole near the edge before polishing.
 - 5.18.1. *Nickel planchets, flat (Lower Po Recoveries)* – 25 mm diameter, polished on one side and coated on the back side with an acid resistant acrylic paint. Drill a small hole near the edge before polishing.

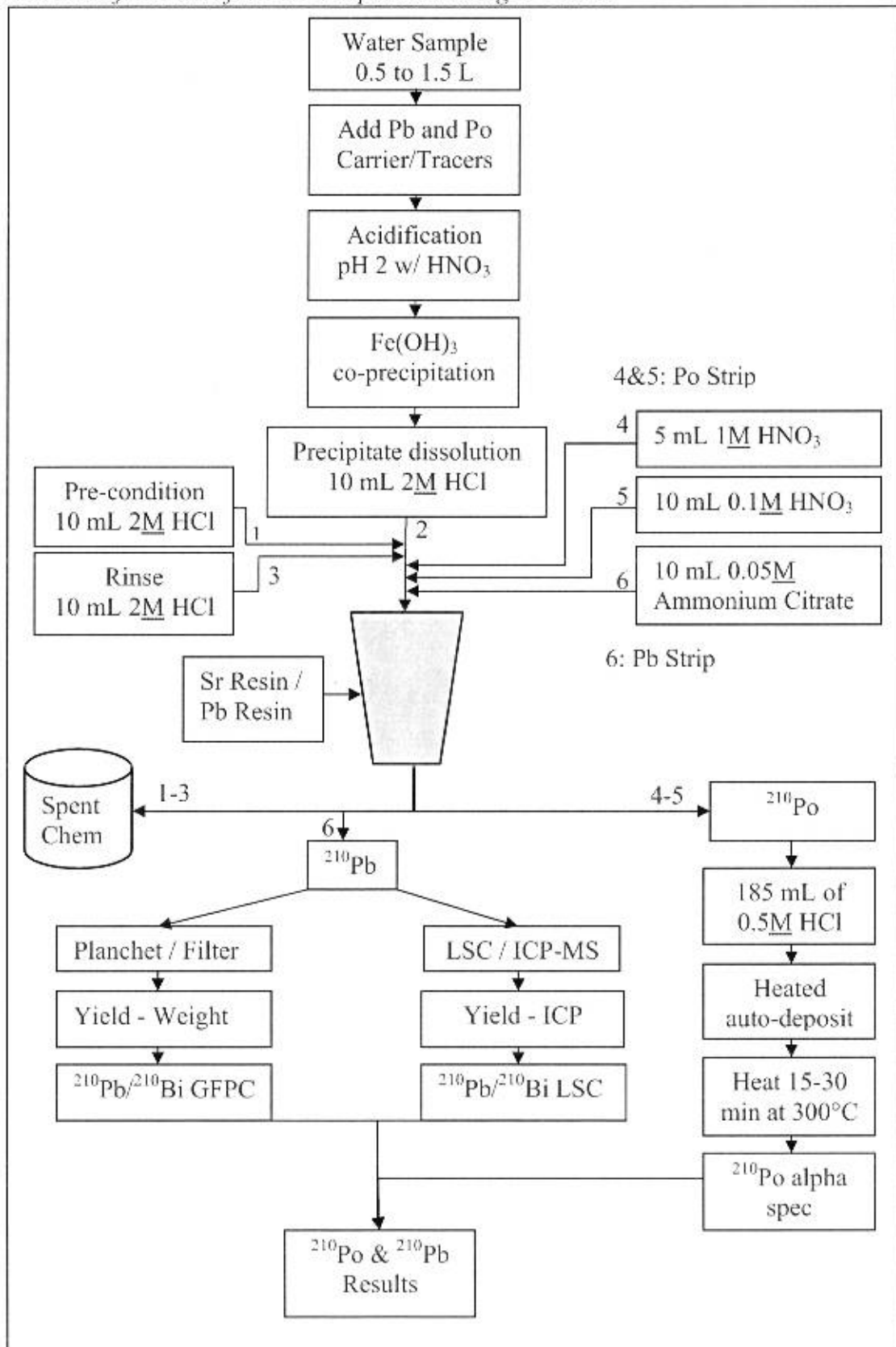
6. Reagents

- 6.1. Unless otherwise indicated, all references to water should be understood to mean deionized distilled water.
- 6.2. *Ammonium hydroxide*, concentrated.
- 6.3. *Ammonium Citrate (0.05M)* – (Recommended Pb eluent) in a 1L volumetric flask add 11.3 g of ammonium citrate to 700 mL water. Cap and shake flask until ammonium citrate has dissolved. Dilute to 1L with water.
- 6.4. *Ammonium Tartrate (0.05M)* – (Optional Pb eluent) in a 1L volumetric flask add 9.2g of ammonium tartrate to 700 mL water. Cap and shake flask until ammonium citrate has dissolved. Dilute to 1L with water.
- 6.5. *Ascorbic Acid (1M)* – Dissolve 17.6g of ascorbic acid in 90 mL of water and dilute to 100 mL with water. Prepare weekly.
- 6.6. *Cation exchange resin* - C8-B500-M-H, hydrogen form, 100 to 200 mesh. Available from Eichrom.
- 6.7. *Citric Acid (0.1M)* – (Pb elution option) - In a 1L volumetric flask add 19.2 g of citric acid to 700 mL water. Cap and shake flask until Citric Acid is dissolved. After citric acid has dissolved dilute to 1 liter with water.
- 6.8. *Ethanol*, USP, 100%
- 6.9. *Hydrochloric Acid (12M)* – concentrated HCl

-
- 6.10. *Hydrochloric Acid (0.5M)* - Add 41 mL concentrated HCl (sp gr 1.19) to 800 mL water and dilute to 1 liter with water.
- 6.11. *Hydrochloric Acid (2.0M)*- Add 165 mL concentrated HCl (sp gr 1.19) to 700 mL water and dilute to 1 liter with water.
- 6.12. *Iron carrier (20 mg/mL)* – (Only for iron hydroxide precipitation) – Dissolve 9.6 grams of ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in 70 mL 0.5M HCl and dilute to 100 mL with 0.5M HCl.
- 6.13. *Lead* – Carrier or Isotopic Tracer
- 6.13.1. *Lead carrier (10 mg/mL)* - Dissolve 1.6 grams of $\text{Pb}(\text{NO}_3)_2$ in water and dilute to 100 mL with water (Check batches for ^{210}Pb and ^{210}Po levels).
- 6.13.2. *Isotopic Tracer* – Pb tracer of known purity and activity
- 6.14. *Liquid Scintillation Cocktail*
- 6.15. *Nitric Acid (15.7M)* - concentrated HNO_3 .
- 6.16. *Nitric acid solution (8M)* - Add 510 mL of concentrated HNO_3 (sp gr 1.42) to 400 mL of water and dilute to 1 liter with water.
- 6.17. *Nitric Acid (1M)* - Add 63.5 mL of concentrated HNO_3 to 800 mL water and dilute to 1 liter with water.
- 6.18. *Nitric Acid (0.1M)* - Add 6.4 mL of concentrated HNO_3 to 800 mL water and dilute to 1 liter with water.
- 6.19. *Pb Resin* – Available from Eichrom technologies prepackaged in 2mL bed volumes: Note: slight losses (15-25%) of Po during initial load and rinse.
- 6.19.1. *Pb Cartridges (2mL)* – 50-100 micron particle size – PB-R50-S
- 6.19.2. *Pb Columns (2mL)* – 100-150 micron particle size – PB-C50-A
- 6.20. *Po tracer* – Either Po-208 ($t_{1/2}$ -2.898 y, 5.115 MeV) or Po-209 ($t_{1/2}$ -102 y, 4.883 MeV) can be used.
- 6.21. *Sr Resin* – (Recommended resin) Available from Eichrom Technologies prepackaged in 2mL bed volumes available in either
- 6.21.1. *Sr Cartridges (2mL)* – 50-100 micron particle size – SR-R50-S
- 6.21.2. *Sr Columns (2mL)* – 100-150 micron particle size – SR-C50-A
- 6.22. *Sulfuric Acid (18M)* - concentrated H_2SO_4

7. Procedure

7.1. Process flow sheet for Pb/Po Separation using Sr Resin:



7.2. Water Sample Preparation:

- 7.2.1. If required, filter the sample through a 0.45 micron filter.
- 7.2.2. Aliquot 500 to 1,500 mL of the sample (or enough to meet required detection limit) into an appropriate size beaker.
- 7.2.3. Add 1 ml of stable Pb carrier or an appropriate amount of Pb tracer.
Note: The use of Pb carrier or tracer is dependent on Pb yield determination technique and final analytical technique. Examples: for Pb yield by weight you will need to use lead carrier and for lead measurements by SC-ICP-MS where the Pb carrier would contaminate the sample use isotopically pure Pb tracers.
- 7.2.4. Add appropriate amount of isotopic Pb spike to Quality Control samples.
- 7.2.5. If performing Po analysis add Po tracer and appropriate amount of Po spike to Quality Control samples as needed.
- 7.2.6. Acidify the sample to pH 2, with concentrated HNO₃ (sp gr 1.42). (typically – 0.6 mL per 1000 mL). If determining Pb recovery by ICP take a small sample to determine initial Pb concentration for carrier recovery calculations.
- 7.2.7. If samples larger than 1 L are analyzed, evaporate the sample to approximately 1 L.
- 7.2.8. Proceed to Po/Pb concentration method – Iron hydroxide Step 7.2.9 or Cation Exchange Step 7.2.10.
- 7.2.9. *Iron hydroxide precipitation: Recommended option*
 - 7.2.9.1. Add 1 mL of iron carrier to sample from step 7.2.7. Cover beaker with a watch glass and heat at near boiling for an hour.
 - 7.2.9.2. Remove watch glass. Add 12 mL concentrated ammonium hydroxide to precipitate iron hydroxide. Stir the solution with a glass rod if necessary. Allow the beakers to heat for another 30 minutes.
 - 7.2.9.3. Let the precipitate settle for at least 2 hours. (preferably overnight) Decant the supernatant. Transfer the precipitate into a 50 mL plastic centrifuge tube.
 - 7.2.9.4. Centrifuge and discard the supernatant.
 - 7.2.9.5. Wash the precipitate with 10 mL water. Centrifuge and discard the supernatant.
 - 7.2.9.6. Repeat step 7.2.9.5 twice.
 - 7.2.9.7. Add 10 mL 2M HCl to dissolve the precipitate.
 - 7.2.9.8. Add 1 mL of 1M ascorbic acid to each solution, swirling to mix. Wait for 2-3 minutes. Go to section 7.3.
Note: Any yellow or red color should disappear which indicates the reduction of

Fe(III) to Fe(II). If the color still persists then additional ascorbic acid should be added drop-wise with mixing until the color disappears.

7.2.10. *Cation Exchange option: (For Pb only separations)*

- 7.2.10.1. Prepare a cation exchange column containing 10 ml (10 g) of C8-B500-M-H, 100-200 mesh for a sample size of 500 mL. A larger resin column may be required for a larger sample size. (20 g resin column for 1.0 L sample)
- 7.2.10.2. Place columns on rack with large volume reservoirs (250 ml to 500 ml).
- 7.2.10.3. Ensure that a suitable container is below each column.
- 7.2.10.4. Add 20 ml of 0.1M HNO₃ to each column to condition columns.
- 7.2.10.5. Load each sample from step 7.2.7 onto the appropriate column and allow to drain.
- 7.2.10.6. Add 25 ml of 0.1M HNO₃ to each column to rinse.
- 7.2.10.7. Discard the feed and rinse the solution collected.
- 7.2.10.8. Ensure that a labeled 150 ml beaker is below each column.
- 7.2.10.9. Add 50 ml of 8M HNO₃ to each column to elute lead.
- 7.2.10.10. Place each beaker on a hot plate in a fume hood and evaporate to dryness.
- 7.2.10.11. Dissolve the residue in 10 mL of 2M HCl then place each beaker on a hot plate in a fume hood and evaporate to dryness.
- 7.2.10.12. Redissolve the residue in 10 mL of 2M HCl.
- 7.2.10.13. Add 1 mL of 1M ascorbic acid to each solution, swirling to mix. Wait for 2-3 minutes. Go to section 7.3.

Note: Any yellow or red color should disappear which indicates the reduction of Fe(III) to Fe(II). If the color still persists then additional ascorbic acid should be added drop-wise with mixing until the color disappears.

7.3. *Pb and Po Separation using Sr Resin or Pb Resin*

- 7.3.1. For each sample will need a Sr Resin cartridge or column.
 - 7.3.1.1. The Sr Resin cartridges are used with the Vacuum Box and flow through the cartridge can be controlled with a vacuum system. For loading and eluting samples we recommend 1 mL/min flow and for rinse steps we recommend 3 mL/min maximum flow rates. See Eichrom procedure number VBS01, "Setup and Operation Instructions for Eichrom's Vacuum Box System (VBS)" available at www.eichrom.com.

7.3.1.2. The Sr Resin Columns are used under gravity flow conditions. Samples are loaded in a column reservoir and flow through gravimetrically.

7.3.2. Condition Sr Resin with 10 mL 2M HCl.

7.3.3. Loading samples on Sr Resin

7.3.3.1. Load the dissolved precipitate from step 7.2.9.7 or 7.2.10.12 onto the Sr resin.

7.3.3.2. Rinse each beaker with 10 mL 2M HCl and add to Sr Resin. Record the time and date of this addition. This will be used to calculate the ingrowth of ²¹⁰Bi. Discard the eluent.

Note: This will remove bismuth, yttrium if present.

7.3.4. Strip Po off the Sr Resin.

Note: This step should be performed even if only interested in Pb to remove any Po from the column before stripping the Pb.

7.3.4.1. Place a clean and labeled centrifuge tube under the column.

7.3.4.2. Add 5 mL 1.0M HNO₃ to the column pass through and collect.

7.3.4.3. Add 15 mL 0.1M HNO₃ to the column pass through and collect.

7.3.4.4. Remove tubes and set aside for Po auto-deposition in Section 7.4 if desired.

7.3.5. Strip Pb off the Sr Resin.

7.3.5.1. Place a clean and labeled centrifuge tube under the Sr resin.

7.3.5.2. Pb can be striped with a few different eluents depending on compatibility with final analysis techniques and need to reach higher Pb stripping efficiency.

7.3.5.2.1. Recommended Strip solution: 10 mL – 0.05M Ammonium Citrate

7.3.5.2.2. Optional Stripping solutions:

7.3.5.2.2.1. 10 mL of 0.1M Citric Acid

7.3.5.2.2.2. 10 mL of 0.05M Ammonium Tartrate

7.3.5.2.2.3. 10 mL of 6M HCL

7.3.5.2.2.4. 20 mL of water will only work if using Pb resin and Pb carrier.

7.4. *Sample preparation for Po analysis: Auto Deposition on Ag disk*

7.4.1. Rinse polished auto-deposition discs with water, ethanol and acetone. Let air dry.

- 7.4.2. Transfer the solution from Step 7.3.4.4 to a 250 mL beaker.
 - 7.4.3. Add 185 mL of 0.5M HCL to a final volume of 200 mL.
 - 7.4.4. Add 100 mg of ascorbic acid to the solution. The ascorbic acid will reduce any Fe(III) in the solution and ease the reduction of polonium.
 - 7.4.5. Place the sample on a temperature controlled hot plate and add a magnetic stir bar.
 - 7.4.6. Push a twist tie through the hole on the disc and twist each end to an uncoiled paper clip.
 - 7.4.7. Place the paper clip across the 250 mL beaker and heat to a temperature of 80°C and stir. For Ag discs, samples should be stirred for a minimum of 8 hours to a maximum of 18 hrs. If using Ni discs samples should only be stirred for 4 hrs, due to degradation of alpha spectrum.
 - 7.4.8. Remove the disc from the solution and rinse it with water, ethanol and then acetone. Let disc air dry.
 - 7.4.9. Heat discs on a 300°C hotplate for 15-30 minutes to convert Po to Po oxide to minimize the risk of detector contamination.
 - 7.4.10. Count in an alpha spectrometer system.
- 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 co-precipitate with Pb.
 - 7.5.1.2. Very carefully add 4 mL of concentrated sulfuric acid to each Pb eluent and allow the solution to cool for 10-15 minutes
 - 7.5.1.3. Cap the tubes and mix the solution well. A white precipitate is formed.
 - 7.5.1.4. Centrifuge the solution from step 7.5.1.3 and discard the supernatant.
 - 7.5.1.5. Add 10 mL of water to the precipitate and mix well. Centrifuge the solution and discard the supernatant.
 - 7.5.1.6. Repeat step 7.3.1.2 one more time
 - 7.5.1.7. Add 5 mL of DI water to the precipitate and mix well to slurry (a plastic disposable pipette could be used).
 - 7.5.1.8. 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.
 - 7.5.1.9. Weigh the counting planchet on an analytical balance and record the weight to 0.0001 gram.

- 7.5.1.10. Place each planchet under a heat lamp in a hood or on a hot plate with low heat.
- 7.5.1.11. Transfer the slurry in step 7.3.1.4 to the planchet 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.
- 7.5.1.12. Rinse the tube containing the slurry with 2-3 mL of water and transfer to the planchet.
- 7.5.1.13. After all the solution has evaporated to dryness, cool each planchet.
- 7.5.1.14. Reweigh each planchet, and record the weight to 0.0001 gram.
- 7.5.1.15. Cover planchet with aluminum foil and wait at least three days for ^{210}Bi ingrowth.
- 7.5.1.16. Count on a gas flow proportional counter.

7.5.2. *Filter option*

- 7.5.2.1. Samples should be precipitated within an hour after eluting from resin as Bi may not co-precipitate with Pb.
- 7.5.2.2. Very carefully add 4 mL of concentrated sulfuric acid to each Pb eluent and allow the solution to cool for 10-15 minutes
- 7.5.2.3. Cap the tubes and mix the solution well. A white precipitate is formed.
- 7.5.2.4. Set up a Resolve Filter, 0.1 micron 25 mm filter, on a Gelman filter apparatus with stainless steel screen, 50 mL polysulfide funnel and 100 mL polypropylene Erlenmeyer flask.
- 7.5.2.5. Add 3-5 mL of 80% ethanol to each filter, applying vacuum and ensuring there are no leaks along the sides. Add 2-3 mL of water to each filter.
- 7.5.2.6. Filter the sample from step 7.5.2.3 and rinse the 50 mL centrifuge tube with 5 mL water, transferring this rinse to the filter apparatus.
- 7.5.2.7. Wash each filter with 3-5 mL of 100% ethanol.
- 7.5.2.8. Remove filters and direct mount filters in the center of the planchets, using double-sided tape or glue stick. Let filters air dry for a few minutes.
- 7.5.2.9. Cover planchet with aluminum foil and wait for at least 3 days for ^{210}Bi ingrowth.
- 7.5.2.10. Count on a gas-flow proportional counter.

7.5.3. LSC/ICP-MS option.

7.5.3.1. For LSC ^{210}Pb determination

7.5.3.1.1. Pipette 7 mL of the lead fraction from Step 7.3.5.2 into a clean, labeled LSC vial.

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

7.5.3.1.3. Count on LSC after ^{210}Bi ingrowth of at least 3 days. Take care to ensure that the spectrometer is calibrated to count the ^{210}Bi emissions and not the entire beta spectrum.

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

7.5.3.3. The Pb sample fraction can also be used to directly determine ^{210}Pb mass concentration via ICP-MS. See reference 7)

8. Calculations

8.1. Polonium Tracer yield: Po-208/Po-209

$$\text{Po}_Y \text{ (carrier yield)} = \frac{\text{Po}_{AF}}{\text{Po}_{AI} \times \text{Po}_V}$$

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

8.2. Calculate initial Po-210 activity

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

where:

S = sample counts per minute

B = background counts per minute

E = efficiency of alpha counter

Po_Y = Po tracer yield

$\lambda = 0.005008 \text{ day}^{-1}$ (decay constant for ^{210}Po)

t_i = time of initial sampling

t_0 = time of mid-point of sample count

V = volume of sample in liters

8.3. Gravimetric yield: Pb carrier – via planchet or filter

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

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

8.4. Chemical yield: Pb carrier – via ICP

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

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

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

$$^{210}Pb \text{ (pCi/L)} = \frac{S - B}{2.22 \times E \times Pb_Y \times (1 - e^{-\lambda(t_{1,I} - t_{BS})}) \times V \times (e^{-\lambda(t_0 - t_{1,I})})}$$

where:

S = sample counts per minute
 B = background counts per minute
 E = efficiency of ^{210}Bi emissions in beta counter
 λ = 0.138 day^{-1} (decay constant for ^{210}Bi)
 t_0 = time of initial sampling
 t_{BS} = time of ^{210}Bi separation, recorded in step 7.3.3.2
 $t_{1,I}$ = time of midpoint of sample count
 V = volume of sample in liters
 Pb_Y = Pb carrier yield

References

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- 4) AP15- "Analysis of Polonium-210 in water, soil, air filters, miscellaneous samples and biota", Environmental survey and site assessment program (ESSAP) at the Oak Ridge Institute for Science and Education (ORISE)
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- 7) Larivière, D., et al "Determination of ^{210}Pb at ultra-trace levels in water by ICP-MS", *Analytica Chimica Acta*, Volume 549, Issues 1-2 pp 188-196 (2005)

9- Attachment UTS-4 Reference Material Report

