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Determination of Radium in Water

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Lockheed
Idaho Technologies Company

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DETERMINATION OF RADIUM IN WATER

APPLICABILITY

These detailed work instructions (DWIs) are tailored for the analysis of radium-226 and radium-228 in drinking water supplies from ground water and surface water sources and composites derived from them. The instructions have been adapted from several sources, including a draft EPA method (Cf. References). One objective was to minimize the generation of mixed wastes.

Quantitative determinations of actinium-228 are made at 911 kEv. The minimum detection level (MDL) for the gamma spectrometric measurements at this energy vary with matrix, volume, geometry, detector, background, and counting statistics. The range of MDL's for current detectors is 0.07 to 0.5 Bq/sample.

Quantitative determinations of radium-226 are made by counting the high energy alpha particles which radium-226 progeny emit using liquid scintillation counting (LSC). The minimum detectable activity (MDA) is 3.8 E-3 Bq/sample. The maximum concentration which may be counted on available instruments without dilution is about 2 E+5 Bq/sample.

Typically, this determination of radium in a 2 L sample has a yield of 80%. If radium-228 is determined using a 16 h count after 50 h grow-in, the typical MDL is 1 E-9 to 8 E-9 μCi/mL (1 to 8 pCi/L). If radium-226 is determined using a 2.5 h count after 150 h grow-in, the typical MDA is about 1 E-10 μCi/mL (0.1 pCi/L).

PRINCIPLE

Radium is a naturally occurring radioactive element whose radioisotopes ultimately decay to isotopes of lead and bismuth. Radium-226 first decays to radon-222 with a half life of 5.75 years. Radium-228 first decays to actinium-228 with a half life of 6.13 hours. The progeny of both radioisotopes undergo further decay emitting a variety of alpha, beta, and gamma radiation.

Barium-133 tracer is added and equilibrated with an aliquot of sample. Strontium carrier is then added and equilibrated. Strontium, barium, radium are precipitated as the sulfate. The precipitate is washed, metathesized to the carbonate, converted to the chloride, dissolved in dilute acid, and placed in a glass liquid scintillation counting (LSC) vial under a layer of immiscible LSC cocktail.

Radon, a noble gas formed by radioactive decay of radium, diffuses from the aqueous phase into the LSC cocktail for which it has a greater affinity than for water. After a 2 day grow-in period, the sample is gamma scanned to determine barium-133 and actinium-228. These data are used to calculate the chemical yield for radium and the concentration of radium-228, respectively.

The sample is then equilibrated for 2 additional days (or longer) and counted in a liquid scintillation counter using energy discrimination to measure alpha particles from radon progeny.

There are no known chemical interferences from species found in drinking water nor from the dilute concentration of acid which may be present in the standards. Calcium may cause problems at high concentrations because its sulfate is slightly soluble. Uranium is removed as the carbonate complex. Radium-224 ($t_{½} = 3.62$ d) is carried along with other radium isotopes if it is present; it diminishes as a result of decay when separated from its parent, thorium-228. Other radioactive elements may cause positive bias if present in significant quantities.

QUALITY ASSURANCE REQUIREMENTS

The electronic balances used in weighings must be serviced and calibrated once a year. Proof of service must be posted on the balance. Balances with internal calibration features may have their performance checked at the beginning of each use period.

Duplicate aliquots from at least one sample in the set are analyzed as described in this DWI if sufficient sample is available.

Quality assurance for chemical yield and ^{228}Ra determinations (i.e., gamma counting) rely on counting room QA requirements reported in INEL-94/051. Gamma scanning of each sample for ^{228}Ra detects unanticipated gamma emitting radionuclides which may interfere.

A minimum of one ^{226}Ra bench standard (or control), prepared as described in RP-Std, must be analyzed with each set of ten samples in the exact same manner that the samples were analyzed. A minimum of one blank must be analyzed with each set of ten samples in the exact same manner that the samples were analyzed. If more than ten samples are analyzed in a set, at least two ^{226}Ra bench standards (or controls) and two blanks, prepared as described in the DWI, must be analyzed with each set.

The bench standards and controls verify the response of ^{226}Ra and its progeny; they are acceptable if they agree with the known value within two standard deviations. Blanks verify the absence of interfering radioactivity in the equipment and reagents; they are acceptable if they contain no activity except background quantities of natural radioactivity.

Precision and bias of the method is affected by the background in the energy window used for analysis. A method is provided for selection of the analytical window which minimizes the contribution of background to the measurement.

The samples are counted for ^{226}Ra on either a Beckman Liquid Scintillation System, Model 6500, or a Wallac Instruments, Model 1411 DSA. These instruments are checked to verify proper performance with a ^{3}H source whenever samples are to be counted. Discriminator settings minimize crossover of alpha particles into beta particle accumulations and vice versa. Additional discriminator settings minimize carryover of low energy photons into the region where photons from ^{222}Rn and its progeny are recorded.

Method Performance

This method has been developed and evaluated utilizing intra-laboratory radium-226 controls prepared by dilution of NIST SRM 4965. It has also been evaluated utilizing blind water samples containing radium-226 and radium-228 sent out by Environmental Protection Agency, National Exposure Research Laboratory, Characterization Research Division, Las Vegas, NV, as part of their Uranium-Radium in Water Performance Evaluation Study whose results are routinely published. Concurrent determination of radium-228 on EPA samples are presented. These data for two analysts are reported in Table 1 and in Table 2.

Based on barium-133 recoveries in these limited evaluations, yields have averaged 80%; the higher recovery in EPA samples is attributed to higher dissolved solids. Recoveries for laboratory blanks, trip blanks, and samples have been comparable to those obtained for controls. The precision of duplicate samples has been within 20%. Although the data in Tables 1 and 2 are suggestive, they are insufficient data to support definitive global statements regarding accuracy, precision, and bias of the method.

TABLE 1

Method Performance with Radium-226

Sample Source	Analyst	n	Barium-133 Yield [a] (%)	Accuracy [a,b] (normalized)
NIST	1	10	75.6 ± 6.2	0.940 ± 0.078
NIST	2	12	76.0 ± 13.6	0.976 ± 0.051
EPA	1	3	92.0 ± 2.8	0.958 ± 0.036
EPA	2	3	96.5 ± 5.4	0.882 ± 0.184
ALL		28	79.8 ± 12.3	0.951 ± 0.081

---

[a] Uncertainties are standard deviations, s.
[b] Data for each determination has been normalized <u>via</u> division by the accepted value for radium-226. Samples contained from 16 to 37 pCi.

TABLE 2

Method Performance with Radium-228

Sample Source	Analyst	n	Barium-133 Yield [a] (%)	Accuracy [a,b] (normalized)
EPA	1	3	92.0 ± 2.8	0.963 ± 0.077
EPA	2	3	96.5 ± 5.4	0.920 ± 0.042
ALL		6	94.3 ± 4.6	0.942 ± 0.060

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[a] Uncertainties are standard deviations, s.
[b] Data for each determination have been normalized <u>via</u> division by the accepted value for radium-228. Samples contained from 14 to 20 pCi.

SAFETY REQUIREMENTS

The analyst performing the procedure must be familiar with standard operating procedures and practices for the IRC and INEL-94/052 (formerly WIN-186) detailed working instructions regarding waste disposal and the handling of hazardous materials.

Eye protection meeting ANSI Standard Z87.1 for splash protection should be worn when handling more than 100 mL of carcinogens, corrosives, or oxidizers. Face shields and safety glasses must be worn when transferring solutions of 1) hazardous materials from or to containers 4-L or larger; 2) concentrated (>8M) acids or bases from or to containers 2.5-L or larger; 3) or solutions of > 1M sulfuric acid or >1% HF to containers 500-mL or larger.

Laboratory coats should be worn when handling corrosives, carcinogens, or oxidizers. Laboratory aprons must be worn when pouring concentrated acids from containers greater than 1-L.

Plastic or rubber gloves must be worn when handling organics, corrosives and oxidizers. Neoprene gloves must be used when pouring concentrated acids from bottles larger than 1-L or when handling HF.

If an exposure to a strong acid occurs, rinse the affected area with water for at least 15 minutes. Notify supervision and contact Medical for treatment. Other safety precautions for hazardous chemicals handled in this procedure are described in Detailed Working Instruction SC-F "Chemical Handling, Storage and Labeling". A summary of applicable precautions for this detailed working instruction is as follows:

> Hydrochloric acid: Handle solutions more concentrated than 4M HCl in an exhaust hood or in a manner to avoid inhalation of HCl vapors. The odor of HCl provides adequate warning for a prompt voluntary withdrawal from excessive exposure. Contact with skin results in a burning sensation at the location of the contact.
>
> Sodium carbonate: Solutions are slippery to the touch and may result in a burning sensation at the location of the contact. Addition of solutions more concentrated than 0.1M NaOH to acidic solutions should be done slowly to avoid rapid evolution of heat and carbon dioxide which may cause splattering of the solution.
>
> Sulfuric acid: Handle solutions more concentrated than 1M H_2SO_4 in an exhaust hood

or in a manner to avoid inhalation of SO_x vapors. Vapors from sulfuric acid generally appear as white aerosol clouds. Contact with the skin results in a burning sensation and a black/brown discoloration of the skin at the location of the contact. Sulfuric acid is hygroscopic and absorbs water quickly, so any drops of solution in the vicinity of work with sulfuric acid may be an indication of a sulfuric acid spill.

Consult MSDS sheets before using any materials. Consult DWI SC-F for further safety related information. Report all accidents to managers or their designated alternates.

APPARATUS AND EQUIPMENT

1. Beakers, borosilicate glass, 250 mL.
2. Liquid scintillation counter - A system permitting spectral analysis as well as particle differentiation is recommended.
3. Mixer, vortex, variable speed.
4. pH paper - Range 1 to 12.
5. Pipets - 1 mL and 5 mL mechanical pipetters.
6. Scintillation cocktail dispenser - Adjustable to deliver 10 mL.
7. Scintillation vials - 20 mL glass vials with Teflon® lined caps.
8. Thermometer - Range 0 to 100°C, metal, factory calibration is adequate.
9. Tubes, centrifuge, borosilicate glass, 50 mL.
10. Tubes, centrifuge, plastic, 50 mL.
11. Wash bottles, 500 mL, or equivalent.

REAGENTS

1. Barium Tracer - a solution containing 1000 to 3000 dpm of barium-133 per gram of

solution.

2. Cocktail - A high efficiency, commercially available, non-hazardous, ready-to-use mineral oil cocktail containing scintillators which is immiscible in water.

3. Hydrochloric acid, 12 M - ACS Reagent grade.

4. Hydrochloric acid, 1 M.

5. Hydrochloric acid, 0.1 M.

6. Radium Solutions - Bench standards and controls are required for calibration and check standards. These solutions are prepared per RP-Std. The ^{226}Ra content or the ^{228}Ra content or both must be traceable to NIST.

7. Sodium Carbonate - ACS Reagent grade.

8. Sodium Carbonate - Saturated solution in water prepared by adding 25 g to 100 ml water; decant solution as it is needed.

9. Strontium Carrier, 1 M, (87.6 mg Sr^{2+}/mL) prepared by dissolving 15.85 g $SrCl_2$, 19.46 g $SrCl_2 \cdot 2\,H_2O$, or 26.66 g $SrCl_2 \cdot 6\,H_2O$ in water to make 100.0 mL of solution.
NOTE: An 18 mg/mL barium carrier may be substituted for strontium carrier with the approval of the manager or designated alternate.

10. Sulfuric acid, 6.0 M.

11. Water - Demineralized or deionized water or the equivalent.

DETAILED WORK INSTRUCTIONS

General Instructions

1. Record data for each sample on an individual "Determination of Radium, Work Sheet" which is illustrated in Figure 1.	Photocopy these forms as necessary.

2. Record the total original sample size, the total concentrate volume, and the aliquot volume being analyzed if the sample is a concentrate.

3. Choose appropriate actions from the list below:

Action	For
Proceed to Step 4.	Normal Samples
Proceed to Step 4.	Dilute Samples.
Proceed to Step 13.	Solutions from DWI SP-SW-Main.
Proceed to Step 13.	High Nitrate Samples.
Proceed to Step 21.	Sulfate Precipitation.
Proceed to Step 35.	Concentrating the Precipitate.
Proceed to Step 43.	Metathesis to Carbonate.
Proceed to Step 58.	Conversion to Chloride
Proceed to Step 66.	Preparation for Counting.
Proceed to Step 74.	Submission for Counting.
Proceed to Step 81.	Blanks.
Proceed to Step 86.	Controls and Bench Standards.
Proceed to Step 93.	Calibration Solutions.
Proceed to Step 101.	Selecting Optimal Window.
Proceed to Step 104.	Barium Tracer Preparation.
Proceed to Step 111.	Cleanup.

Sample Concentration

4. Consult your manager or designated alternate regarding non-routine samples.

A usual aliquot will have a volume of 1-2 L. The aliquot size of non-routine samples may vary.

5. Measure out a suitable sample aliquot into a beaker.

6. Record the aliquot size.

7. Acidify using 10 ± 1 mL of 12 M HCl.

The resultant pH should be ≤ 1 and may be checked with pH paper.

8. Add ≈1 mL Barium Tracer.

9. Record the mass added to the nearest 0.2 mg.

10. Evaporate to reduce the volume to 200 mL or less, if necessary.

11. Transfer the sample to a 250 mL beaker, if necessary.

12. Proceed to Step 21.

Removal of Nitrate

13. Measure out a suitable aliquot into a 250 mL beaker.

    Purer crystal formation and better separation are achieved in a low nitrate matrix.

14. Record the aliquot size.

15. Add 15 ± 2 mL 12 M HCl.

16. Add ≈1 mL Barium Tracer.

17. Record the mass added to the nearest 0.2 mg.

18. Evaporate to dryness on a hotplate.

    Reduce the heating rate near the end of the evaporation to minimize spattering.

19. Repeat Steps 15 & 18 twice more.

20. Add 10 mL 12 M HCl.

Sulfate Precipitation

21.	Dilute the aqueous solution to 200 ± 10 mL with water.	The actions described should result in a solution containing (0.6 ± 0.1) M HCl in which precipitate formation will be excellent.
22.	Heat to 60-90 °C on a hot plate.	The temperature may be checked using the thermometer.
23.	Add 1.00 ± 0.05 mL Strontium Carrier.	Non-routine samples may require changes in volume or type of carrier.
24.	Record the volume added.	
25.	Heat at 60-90°C for ≈30 min.	
26.	Add 5 ± 1 mL 6M H_2SO_4.	The actions described should result in a solution containing (0.15 ± 0.02) M H_2SO_4 in which precipitate formation will be excellent.
27.	Record the time on the worksheet.	This time may be needed if an estimate of ^{224}Ra concentration becomes necessary.
28.	Heat at least 60 min at 60-90°C.	
29.	Turn off heat.	Use of an electrically timed switch for remote shutoff followed by cooling overnight is acceptable.
30.	Do not disturb until cool.	Radium (as well as barium and strontium) is in the precipitate as the sulfate: $Ra^{2+} + SO_4^{2-} \rightarrow RaSO_4\downarrow$
31.	Skip to Step 35 if a precipitate is visible in the bottom of the beaker.	A dense precipitate should be present in the bottom of the beaker. The presence of some anions may increase the solubility of $SrSO_4$ so that no precipitate is visible.
32.	Heat to 60-90 °C on a hot plate.	

33. Add 2.00 ± 0.10 mL Strontium Carrier.

NOTE: Consult your manager or designated alternate if no precipitate forms in the solution after one repeat of Steps 27-31 as directed in Step 34.

34. Go once to Step 27 and procede stepwise through to Step 34.

Concentrating the Precipitate

35. Decant most of the supernate slowly and reserve it as potentially radioactive waste.

36. Transfer the precipitate to a 50 mL centrifuge tube with a stream of water.

37. Wash the precipitate with ≈10 mL water.

Use of a vortex mixer facilitates washing the precipitate. Washing removes residual sulfate which could otherwise form a precipitate upon dissolution of the precipitate.

38. Centrifuge.

39. Decant the liquid and reserve it as potentially radioactive waste.

40. Repeat Steps 37-39 twice more.

41. Test pH of last wash with pH paper.

42. Repeat Steps 37-39 until pH > 4.

Metatheses to Carbonate

43.	Add 5 ± 1 mL saturated Na_2CO_3 solution to the precipitate.	
44.	Add 0.5 ± 0.2 g Na_2CO_3 with mixing.	A total of ≈2 g Na_2CO_3 will be added of the course of 1 h.
45.	Heat to 60-90°C for ≈20 min in a water bath, swirling occasionally.	Use of a vortex mixer facilitates swirling the precipitate.
46.	Add 0.5 ± 0.2 g Na_2CO_3.	
47.	Repeat Steps 45-46 two more times.	
48.	Heat for 30 min after the last addition.	Solid Na_2CO_3 should be visible at the end of this heating step.
49.	Cool.	
50.	Centrifuge for 10 ± 5 min at 2000 ± 400 rpm.	Radium, barium, and strontium are in the precipitate as carbonates.
51.	Decant the liquid and reserve it as potentially radioactive waste.	
52.	Wash the precipitate with ≈10 mL H_2O.	Use of a vortex mixer facilitates washing the precipitate. Washing removes excess sulfate which could otherwise form a precipitate upon acidification.
53.	Centrifuge for 10 ± 5 min at 2000 ± 400 rpm.	
54.	Decant the liquid and reserve it as potentially radioactive waste.	
55.	Repeat Steps 52-54 twice more.	
56.	Test the pH of last wash solution with pH paper.	

57. Repeat Steps 52-54 until pH < 8.

Conversion to Chloride

58. Add (1.0 ± 0.1) mL 1 M HCl.

59. Add 12 M HCl dropwise if solids remain until bubbling ceases.

The acid dissolves radium (as well as Ba and Sr):

$$RaCO_3 + 2\ HCl \rightarrow RaCl_2 + H_2O + CO_2\uparrow$$

60. Skip to Step 64 if the solution is transparent.

The solution should be transparent; translucence or opacity indicates undissolved sulfates are present.

61. Add 4 mL H_2O.

62. Add solid Na_2CO_3 until bubbling ceases.

NOTE: Consult your manager or designated alternate if the solution is not transparent after one repeat of Steps 43-60.

63. Go once to Step 43 and procede stepwise through to Step 60.

64. Evaporate to dryness.

65. Record the time.

This is the backup time for grow-in calculation. No ^{222}Ra is present at this time.

Preparation for Counting

66. Dissolve solids in 5.00 ±0.05 mL 0.1 M HCl.

67.	Transfer solution to an LSC vial.	
68.	Rinse all surfaces of the centrifuge tube using 5.00 ± 0.05 mL 0.1 M HCl.	
69.	Transfer rinse solution to the same LSC vial.	All Ra^{2+}, Ba^{2+}, and Sr^{2+} is now present as chloride in 10.0 mL 0.1 M HCl in the LSC vial.
70.	Add 10 mL LSC cocktail to the LSC vial.	
71.	Cap tightly with a Teflon™ lined lid.	A drop of glue may be applied to the outside of the cap to assure that the cap remains tight.
72.	Do not shake the mixture.	Shaking disturbs the equilibria.
73.	Record the time on the worksheet.	This is the time used in calculating the start of the grow-in period for ^{226}Ra progeny.

Submission for Counting

74.	Set the LSC vials aside for grow-in of radium daughters.	Negligible correction will be necessary for ^{228}Ac after 48 h or ^{222}Rn after 28 d grow-in.
75.	Delay counting the LSC vials for an additional 6 hours if they have been shaken or otherwise disturbed.	Shaking disturbs the equilibria.
76.	Compute the volume of each sample aliquot and furnish that information to the counting room.	Direct that results be as μCi per unit volume of sample unless other units are required.

77. Submit the vial for gamma scan for ^{133}Ba and ^{228}Ac as well as any other gamma emitters after 2 days grow-in.

78. Submit for alpha LSC scan for ^{226}Ra progeny after 4 days grow-in.

Longer grow-in is acceptable if customer deadlines can be met.

79. Calculate results as described under "Calculations".

80. Dispose of vial contents as potentially radioactive analysis residue after results have been logged out.

Blanks

81. Add 190 ± 10 mL water to a 250 mL beaker.

82. Add 10 ± 1 mL 12 M HCl.

83. Add ≈1 mL Barium Tracer.

84. Record the mass of Barium Tracer added to ± 0.2 mg

85. Proceed to Step 21.

Controls and Bench Standards

86. Add 190 ± 10 mL water to a 250 mL beaker.

87. Add 10 ± 1 mL 12 M HCl.

88. Add ≈1 mL Barium Tracer.	
89. Record the mass of Barium Tracer added to ± 0.2 mg	
90. Add ≈1 mL of a Control or Bench Standard.	
91. Record the mass of Control or Bench Standard added to ± 0.2 mg	
92. Proceed to Step 21.	

Calibration using Radium-226

93. Obtain a solution of radium-226 in hydrochloric acid which is traceable to NIST.	NIST SRM 4965 is acceptable. This SRM consists of ≈5 g of solution with a nominal concentration of 31 Bq/g.
94. Prepare a sufficient quantity of diluent containing 1.7 mg $BaCl_2$ per mL of 0.1 M HCl	
95. Prepare at least four dilutions by mass of the radium solution per DWI RP-Std so as to obtain a range of solutions from ≈0.01 to ≈10.00 Bq ^{226}Ra in 10 mL diluent in LSC vials.	The concentrations of ^{226}Ra in solutions toward the higher end of the range may be confirmed by direct gamma ray spectrometric analysis.
96. Add 10 ± 0.1 mL LSC cocktail.	
97. Cap with a Teflon® lined lid.	
98. Secure the lids in place.	A drop of glue may be used on the outside of the cap to assure that it remains tightly sealed.

99. Do not shake.

Shaking disturbs the equilibria.

100 Record the time and date on the worksheet.

This information is needed to calculate the grow-in correction.

Selecting Optimal Window

101 Count a radium standard for fifty minutes to generate a sample spectrum.

102 Set the optimal window as follows: the upper limit is located where the activity in the large peaks returns substan-tially to baseline; the lower limit is the same distance below the alpha peak maximum as the upper boundary is above it.

Manufacturer's instructions should be followed. The region of greatest alpha activity will be obvious as evidenced by three large, overlapping peaks at the high end of the energy spectrum. The calibration factor should be at least 6 cpm/pCi with a background not exceeding 10 cpm. A typical width is 200 Kev.

103 This window will be used for subsequent calibration and analysis with the peak maximum identified on a bench standard or control for each set of vials.

Barium Tracer Preparation

104 Obtain an aliquot of ^{133}Ba solution.

105 Submit the solution for gamma analysis if the concentration is not know.

106	Dilute sufficient solution with 1 M HCl to give approximately 50 mL of solution containing 1000 to 3000 dpm/g.	
107	Weigh out ≈ 1 mL of diluted solution into a glass LSC vial.	
108	Record the mass of solution in a laboratory notebook	
109	Dilute with 0.1 M HCl to 10.0 ± 0.1 mL.	This geometry should match that of the samples.
110	Submit for gamma spectrometric determination of the dpm ^{133}Ba per sample.	Results determine the comparitor activity which will be used to calculate radium chemical yields.

Cleanup

111	Dispose of reserved solutions as directed in DWI SC-D or by management or designated alternate.	
112	Wash all glassware using a mild detergent and a non-metallic brush.	Do not scratch beakers used for the sulfate precipitation as crystal formation and growth may be adversely affected.
113	Rinse all glassware with water.	
114	Air dry all glassware protected from dust.	

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METHOD HISTORY

The method was adapted from the above references, especially Reference 2, to INEL sample matrices and sample pretreatments by Frederick A. Hohorst in the first quarter of 1995. Results of the adaptation may be found in corporation correspondence under FAH-03-95, FAH-05-95, and FAH-07-95. Additional information may be found in Special Technologies Controlled Document Copy No. 82, a bound record notebook.

CALCULATIONS

A calculational program is available on several desk top computers within the department. Consult your manager or designated alternate for the location of copies.

Instrument Calculations

The counting results for the samples shows which counting system was used to measure the set of vials. (Cf. Figures 2, 3, and 4.) Based on that entry, proceed to either Section A, B, or C below, then to Section D:

A. Network Alpha and Gamma Acquisition and Analysis System

The Network Alpha and Gamma Acquisition and Analysis System (NETSPEC) provides quantitative determinations of radioisotopes in submitted samples. Important quantities are the year (1), month (2), day (3), hour (4), and minute (5) the analysis began. Also printed are the nuclide (6), the units (7), the activity (8), the total uncertainty (9) and the minimum detectable level, MDL, if determined (10). These ten items are needed to calculate the results of determinations. Consult Figure 2 for a typical printout.

B. Wallac NSI, Model 1400 DSA

The liquid scintillation counter is to be set up and operated according to the manufacturer's instruction. Those instructions plus the instructions in this DWI (Steps 74-80 and 101-103) will permit setting of a protocol containing a window to be used for counting the samples, blanks, and controls for radium-226 progeny. The instrument will differentiate the beta counts from the alpha counts so that the selected window will state only the alpha counts (1). The printout also will state the duration of each count (2) and the clock time when the first count of the three counts on each sample began (3). The duration in seconds must be converted to minutes. These three items are needed to calculate the results of the determinations. Consult Figure 3 for a typical printout.

C. Beckman Model LS 6500

The liquid scintillation counter is to be set up and operated according to the manufacturer's instruction. Those instructions plus the instructions in this DWI (Steps 74-80 and 101-103) will permit setting of a protocol containing a window to be used for counting the samples, blanks, and controls for radium-226 progeny. The instrument will differentiate the beta counts from the alpha counts so that the selected window states only the alpha count rate (1). The printout also will state the duration of each count in minutes (2), the clock time when the first sample began counting (3), and the elapsed time since the first count began until the beginning of the first of the three counts of each vial (4). These four items are needed to calculate the results of the determinations. Consult Figure 4 for a typical printout.

D. Personal Calculations:

The quantities defined below are necessary in calculations of the quantity of ^{226}Ra and ^{228}Ra present in the samples and standards:

Use Equation 1 below to calculate the volume, V, of each sample:

$$V_{mL} = \frac{Aliquot\ Analyzed_{mL} * Initial\ Volume}{Reduced\ Volume} \qquad (1)$$

Use Equation 2 below to calculate the chemical yield, CY, for each sample:

$$CY = \frac{Mass\ Tracer_{mg} * Sample\ Activity^{133}Ba}{Mass\ Tracer_{mg} * Comparitor\ Activity^{133}Ba} \qquad (2)$$

The chemical yield for radium calculated above applies to subsequent calculations for both radium-226 and radium-228.

Use Equation 3 below to calculate the concentration of ^{228}Ra in the sample:

$$Conc^{228}Ra = \frac{Activity^{228}Ac_{\mu Ci}}{CY * Volume_{mL}} * \frac{1}{[1 - e^{-\ln 2 * t_{hr} / 6.13}]} \qquad (3)$$

If the sample counting begins more than 48 hours after the vial is sealed, the last term in Equation 3, which corrects for incomplete attainment of secular equilibrium, may be set to 1. Furthermore, if the proper units have been furnished to the counting room, results may be read directly from that printout since ^{228}Ac equals ^{228}Ra. Hence, the only hand calculation needed is division by the yield under these circumstances. See Figures 2 and 3 for examples.

Use Equation 4 below to calculate the concentration of ^{226}Ra in the sample:

$$Conc^{226}Ra = \frac{(G - B) * CF * 60}{Volume_{mL} * CY * t} * \frac{1}{[1 - e^{-\ln 2 * t_{hr} / 91.764}]} \tag{4}$$

Use Equation 5 below to calculate the relative uncertainty of the ^{226}Ra activity in the sample:

$$U_{Ra226\ Total} = \sqrt{U^2_{Ra226} + U^2_B + U^2_{Std} + U^2_{Ba133} + U^2_d + U^2_V + U^2_n} \tag{5}$$

where:

$U_{Ra226\ Total}$ = The relative uncertainty corresponding to one standard deviation of the calculated activity for radium-226.

U_{Ra226} = The relative uncertainty of the counts of the ^{226}Ra sample calculated from the square root of the gross counts divided by the gross counts.

U_B = The relative uncertainty of the counts of the ^{226}Ra blank calculated from the square root of the gross counts divided by the gross counts.

U_{Std} = The relative uncertainty in the standard.

U_{Ba133} = The relative uncertainty in the yield of the ^{133}Ba is set at 11.2%. It is derived from the total error in each determination of ^{133}Ba and each propagated total uncertainty to give an overall uncertainty. The uncertainty of each determination consists of about 1% random uncertainty and 7% systematic uncertainty.

U_d = The relative uncertainty in the decay factors and the ingrowth corrections.

U_V = The relative uncertainty of the initial sample volume measurement and dilutions and transfers. This value is set at 5% due to the number of sample transfer steps.

U_n = The relative uncertainty in the counting statistics as referenced to the current background value. As the sample count rate approaches background, the error increases exponentially. When the sample count rate is approximately three times the one sigma value of the background, this term becomes insignificant. It is calculated using:

$$U_n = \frac{\sqrt{\dfrac{C_{Ra226}}{T^2} + \dfrac{C_B}{T^2}}}{\dfrac{C_{Ra226}}{T} - \dfrac{C_B}{T}} \qquad (6)$$

The absolute uncertainty is calculated by multiplying the relative uncertainty by the calculated activity.

The sample detection limit is calculated from the equation:

$$MDA_{Ra226} = \frac{(\,2.71\ + 4.65\ *\ \sqrt{B}\,)\ *\ Conversion\ Factor}{t\ *\ CF\ *\ V\ *\ Y} \qquad (7)$$

where the conversion factor is that necessary to convert to the desired counting units, and

B = Gross counts of the background

t = gross count time (s, same for sample and background)

CF = Calibration factor,

V = sample volume (mL)

Y = yield as determined by the ratio of ^{133}Ba found to that added.

Assemble and collate results for submission as requested by the manager or designated alternate.

DETERMINATION OF RADIUM WORK SHEET

4820-001 Sample Name: ______________________

Log No.: ______________________

Analyst: ______________________

Date Commenced: ______________________

Type of Sample: ______________________

Preparation Information

Sample Preconcentation: ________ mL concentrated to ________ mL.

Amount of sample or concentrate used for analysis: ________ mL or g.

Interim sample container ID: ________

Mass of Barium Tracer added: ________ g.

Volume of Carrier added: ________ mL.

Time precipitated from solution: ________ on ____/____/____

Time evaporation to dryness: ________ on ____/____/____

Time sealed in LSC vial under Cocktail: ________ on ____/____/____

Unless noted otherwise, calculations will be in microcuries per milliliter.

Additional Notes:

____

____

____

____

____

____

____

Figure 1

```
                 ①          ②   ③    ④ ⑤
Gamma Spectrum 1995-0322-1609.05  Log Number: 95086
Sample: 5
                                                   One Sigma
Nuclide        pC/1   ⑦          Uncrt       %Uncrt  %Rand        %Syst
            *  MDL
-----------------------------------------------------------------------------
                          ⑧               ⑨
⑥ BA133         3.14E+2       2.48E+1        7.9       0.8         7.1

  PB212         8.72E-1       1.36E+0      155.7     150.2         5.5
            *   8.75E-1 ⑩

  PB214         8.75E+0       1.10E+0       12.6       6.7         5.9

  BI212        -1.78E+0       2.33E+0      130.8     125.1         5.6
            *   4.10E+0

  BI214         6.18E+0       1.01E+0       16.4      10.7         5.6

  RA224        -4.99E+1       6.27E+1      125.7     119.7         6.0
            *   8.67E+0

  RA226         2.17E+1       4.37E+0       20.1      15.1         5.1

  AC228         1.81E+1       2.50E+0       13.8       7.6         6.2
```

Figure 2

```
PROTOCOL : 98  Ra-226 Determination
DATE     : 1995/04/19
TIME     : 08:52
FILE     : A:\P98AS038.TXT
FILE     : A:\P98AS038.WKS
ID       : P98AS038

Service Waste Samples

Wallac 1400 DSA ver 2.2  S/N 4110034
Counting mode                    : CPM
Isotope(s)                       : As76
As76                              =     5-1024,1.10 d
Protocol name                    : Ra-226 Determination
Counting time                    : 3000
Repeats                          : 3
Cycles                           : 1
Replicates                       : 1
2 sigma %                        : 0.01
Minimum cpm                      : 0.00 Checking time: 10
Advanced modes                   : PSA
PSA level                        : 180
Output to  Printer               :
  POS,TEXT,TIME,CTIME,SQPE,CPM1,CPMw1,FNCT1,CPMw2,FNCT2,PSALEVEL
Additions to Printer             : Listing,Header
Output to  Display               :
  POS,TEXT,TIME,CTIME,SQPE,CPM1,CPMw1,FNCT1,CPMw2,FNCT2,PSALEVEL
Additions to Display             : Header,Listing
Path of File                     : a:
Output to  File                  :
  POS,TEXT,TIME,CTIME,SQPE,CPM1,CPMw1,FNCT1,CPMw2,FNCT2,PSALEVEL
Additions to File                : Spectrum
Path of WKSfile                  : a:
Output to  WKSfile               :
  POS,TEXT,TIME,CTIME,SQPE,CPM1,CPMw1,FNCT1,CPMw2,FNCT2,PSALEVEL
Header                           : Service Waste Samples
Spectrum                         : Beta,Alpha
Window 1                         :  550- 750 /Beta
Window 2                         :  550- 750 /Alpha
FNCT1 = Gross B                  : (cpmw1*ctime/60)
FNCT2 = Gross A                  : (cpmw2*ctime/60)

                                                                           ①
                                         ②
Unknown samples:              ③
                                                                           ↓
 Pos        Text            Time  CTime↙ SQPE  As76_CPM    CPMw1  Gross B     CPMw2  Gross A  PSA
   1 V1 Blank              →08:53  3000  720.18      53.7     0.5       26       7.3      366  180
   1 V1 Blank               09:44  3000  719.66      53.6     0.3       14       6.9      346  180
   1 V1 Blank               11:48  3000  719.73      51.2     0.4       19       6.3      315  180
                                                                                                  ----- REPEATS
------------------------------------------------------------------------------------------------  = Mean
                                   3000  719.86      52.8     0.4       19       6.8      342     = St.Dev.
                                      0    0.28       1.4     0.1        6       0.5       26

Pos        Text             Time  CTime    SQPE  As76_CPM    CPMw1  Gross B     CPMw2  Gross A  PSA
  7 V7 Control #2          01:28   3000  723.19      66.3      1.0       52      59.9     2994  180
  7 V7 Control #2          02:19   3000  722.68      65.4      1.0       49      61.4     3070  180
  7 V7 Control #2          03:10   3000  722.04      64.1      1.3       63      60.6     3032  180
---------------------------------------------------------------------------------------------------- REPEATS
                                   3000  722.64      65.3      1.1       55      60.6     3032     = Mean
                                      0    0.58       1.1      0.2        8       0.8       38     = St.Dev.

Pos        Text             Time  CTime    SQPE  As76_CPM    CPMw1  Gross B     CPMw2  Gross A  PSA
  8 V8 Control #4          04:02   3000  719.15      83.7      2.1      106     137.0     6851  180
  8 V8 Control #4          04:53   3000  717.93      88.2      1.9       95     137.5     6875  180
  8 V8 Control #4          05:44   3000  717.55      85.0      2.5      124     136.4     6820  180
---------------------------------------------------------------------------------------------------- REPEATS
                                   3000  718.21      85.7      2.2      108     137.0     6849     = Mean
                                      0    0.84       2.3      0.3       15       0.5       27     = St.Dev.
```

Figure 3.

```
                                                                          PAGE: 1

ID:SW   RA226   FAH                                                20 APR 1995 09:01
USER:20                     COMMENT:FAH 3-29-95                              ③
PRESET TIME   :        50.00
DATA CALC     :          CPM   H#    :YES  SAMPLE REPEATS:   3    PRINTER       :EDIT
COUNT BLANK   :           NO   IC#   : NO  REPLICATES     :  1    RS232         : OFF
TWO PHASE     :           NO   AQC   : NO  CYCLE REPEATS  :  1
SCINTILLATOR:         LIQUID   LUMEX: NO   LOW SAMPLE REJ:   0
LOW LEVEL     :          YES   α HALF LIFE CORRECTION DATE:         none
                               β HALF LIFE CORRECTION DATE:         none

ISOTOPE 1:     226RA*  %ERROR: 0.00  α  FACTOR:    1.000000  BKG. SUB:       0
                                     β  FACTOR:    1.000000  BKG. SUB:       0

ALPHA-BETA DISCRIMINATION: YES          CALIBRATION: 226RA 3-29-95
LEFT RVALUE LIMITS :    1.19 - 500.00   RIGHT RVALUE LIMITS:    1.20 - 500.00
PULSE HEIGHT LIMITS:     0.0 -  683.8   PRIMARY COUNT SOURCE: ALPHA

SAM  POS    TIME      H#          226RA*         LUMEX   ELAPSED
 NO          MIN                 CPM  %ERROR       %       TIME

  1 20-1  ② 50.00 185.9  α  ⑦→ 0.64  -35.36     4.36     51.23
                         β     13.18    7.79
  1 20-1    50.00 187.5  α      0.66   34.82     4.86    102.27
                         β     13.38    7.73
  1 20-1    50.00 189.4  α      1.12   26.73     5.08    153.33
                         β     12.08    8.14                                     #1
          Repeat Average CPM for 226RA*       0.81  COEF. OF VAR:    33.662
                                             12.88  COEF. OF VAR:     5.435

  2 20-2    50.00 184.5  α      0.98   28.57     3.77    204.61
                         β     13.14    7.80
  2 20-2    50.00 186.2  α      0.98   28.57     3.84    255.58
                         β     12.30    8.06
  2 20-2    50.00 185.8  α      1.02   28.01     3.56    306.55
                         β     13.08    7.82
          Repeat Average CPM for 226RA*       0.99  COEF. OF VAR:     2.325 #2
                                             12.84  COEF. OF VAR:     3.650

  7 20-7    50.00 186.6  α     24.34    5.73     0.64    968.99
                         β     54.32    3.84
  7 20-7    50.00 187.1  α     23.10    5.88     0.70   1019.72
                         β     53.90    3.85
  7 20-7    50.00 187.6  α     23.98    5.78     0.72   1070.43 ④
                         β     50.86    3.97
          Repeat Average CPM for 226RA*      23.81  COEF. OF VAR:     2.680 #7
                                             53.03  COEF. OF VAR:     3.561

  8 20-8    50.00 192.7  α     61.28    3.61     0.79   1121.59
                         β    111.50    2.68
  8 20-8    50.00 193.7  α     60.70    3.63     0.87   1172.44
                         β    104.46    2.77
  8 20-8    50.00 192.6  α     63.26    3.56     0.88   1223.47
                         β    103.86    2.78                                     #8
          Repeat Average CPM for 226RA*      61.75  COEF. OF VAR:     2.174
                                            106.61  COEF. OF VAR:     3.985


 INSTRUMENT CALIBRATION:   Mini  21 APR 1995 05:27
 Calibration successful
```

Figure 4.