# Determination of Polonium-210 in Drinking Water by Alpha Particle Counting

Method 912.0

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1. Scope and Application
   - 1.1 This method is applicable to the determination of polonium-210 (Po-210) in drinking water samples.
   - 1.2 The method detection limit as defined by the National Interim Primary Drinking Water Regulations is 0.1 pCi/L based on an instrumental alpha particle background of 0.1 count/minute and a 100-minute counting period.
   - 1.3 This method may be applied to surface and ground water samples provided these samples are immediately filtered upon collection.

2. Summary of Method
   - 2.1 Lead is added as a nonisotopic carrier and the polonium-210 is concentrated by coprecipitation on lead sulfide from an acetic acid solution using hydrogen sulfide gas. The lead sulfide is collected by filtration and dissolved in concentrated nitric acid. Nitrates are removed by fuming with a small quantity of perchloric acid. The solution is treated with diluted hydrochloric acid and the polonium-210 is spontaneously electroplated onto a nickel disk. The nickel disk is washed, dried, and alpha counted.

3. Safety
   - 3.1 Hydrogen sulfide gas is not only toxic but also highly flammable. Its use should be restricted to well ventilated hood facilities and away from all open flames.
   - 3.2 Perchloric acid is used in a very limited amount. Adequate precautions should be taken to insure that the acid fumes are purged through a water trap when not used in hoods specifically designed for perchloric acid usage.

4. Apparatus
   - 4.1 Concentric ring water bath.
   - 4.2 Plating cell, 8 ounce plastic nursing bottle (See Fig. 13.1).
   - 4.3 Stirring motor with glass stirrer.
   - 4.4 Internal proportional counter.
   - 4.5 Membrane filtering assembly, 300 mL.

5. Reagents
   - 5.1 Acetic acid, glacial, CAS Reg 64-19-7, 99.7% w/w.
   - 5.2 Acetone, CAS Reg 67-64-1.
   - 5.3 Ammonium hydroxide, CAS Reg 1336-21-6 ($NH_4OH$) 6N. Dilute 400 mL of concentrated ammonium hydroxide to 1000 mL using distilled water.
   - 5.4 Hydrochloric acid, CAS Reg 7647-01-0. (HCl) 0.5N. Dilute 42 mL 36-38% HCl to 1000 mL using distilled water.
   - 5.5 Hydrogen sulfide gas ($H_2S$). Lecture bottle 99.5%.
   - 5.6 Lead nitrate carrier solution, CAS Reg 10099-74-8, ($Pb(NO_3)_2$) 0.1N. Dissolve 16.5g lead nitrate ($Pb(NO_3)_2$) in 500 mL of 0.1N nitric acid. 1 mL = 10.4 mg lead ion.

5.7 Methyl red, CAS Reg 493-52-7. 0.1% w/v. Dissolve 0.1 g methyl red in 100 mL water.
5.8 Nickel disk — 1.5-inch diameter by 0.020-inch in thickness. Highly polished on one side.
5.9 Nitric acid, CAS Reg 7697-37-2. ($HNO_3$) 69-71% w/w.
5.10 Perchloric acid, CAS Reg 7601-90-3, ($HClO_4$) 70-72% w/w.

6. Sample Collection, Preservation and Storage
6.1 Sample Collection
6.1.1 Sampling should conform to ASTM D3370-76, "Standard Practices for Sampling Water."
6.2 Preservation and Storage
6.2.1 Sample should be preserved by the addition of nitric acid to a strength of 0.1N (6 mL 69-72% per liter of sample).
6.2.2 Preserved samples need not be refrigerated for storage. However, analysis should be performed as soon as possible and before 60 days after collection.
6.2.3 All samples shall be collected and stored in plastic containers.

7. Calibration and Standardization
7.1 Internal proportional counter efficiency
7.1.1 Transfer an aliquot containing 200-500 d/m of polonium 210 to a 150-mL beaker.
7.1.2 Add 1 mL of the lead nitrate solution, 20 mL concentrated nitric acid and 1 mL of perchloric acid.
7.1.3 Cover with a watch glass and evaporate to dense fumes of perchloric acid.
7.1.4 Remove from hot plate, cool, and dissolve residue in 20 mL of 0.5N hydrochloric acid.
7.1.5 Assemble plating cell and fill with water to check for leaks. Discard water if no leaks are present.
7.1.6 Transfer solution to plating cell and rinse the beaker four more times with 20 mL of 0.5N HCl.
7.1.7 Place plating cell in boiling water bath, immerse the glass stirrer, stir and plate for 4 hours.
7.1.8 Remove stirrer, discard solution, and rinse disk with water.
7.1.9 Disassemble cell, remove disk, rinse with water and acetone, dry and count for a period of time to accumulate at least 10,000 counts.
7.1.10 Calculate counter efficiency, c/m/d/m.
7.2. Recovery Factor
7.2.1 Spike triplicate 1-L aliquots of tap water with a known quantity of Po-210 tracer (1000 d/m).
7.2.2 Analyze these aliquots as prescribed in Section 9.0, Procedure.
7.2.3 Determine recovery factor (RF) as shown in Section 10.0, Calculation.

8. Quality Control
8.1 General Requirements
8.1.1 All analysts using this method are required to demonstrate their ability to use the method and to define their respective accuracy and precision criteria.

8.1.2 The minimum requirements for the establishment of accuracy and precision criteria is four replicate analyses of an externally prepared performance evaluation sample.

8.1.3 Application of this method to samples of different matrix composition requires the analyst to demonstrate its successful use by the addition of a standardized spike solution and evaluation of the spike recovery.

8.2 Requirements in support of National Interim Primary Drinking Water Regulations (NIPDWR) regulations.

8.2.1 The laboratory must be certified.

8.2.2 The laboratory must participate once each year in an unknown performance study for polonium-210 administered by EPA.

8.2.3 The laboratory must participate at least twice each year in EPA laboratory intercomparison studies for polonium-210.

8.2.4 To verify internal laboratory precision for polonium-210, a minimum of 10 percent duplicate analyses must be performed.

8.2.5 When 20 or more polonium-210 analyses are performed in a day, a performance standard and a background sample must be measured with each 20 samples. If less than 20 samples are performed in a day, a performance sample and a background sample, must be measured along with the samples.

8.2.6. Quality control performance charts, or performance records, must be maintained.

8.3 Requirements for Non-Regulated Activities

8.3.1 It is recommended that the requirements criteria specified for the NIPDWR be adopted for all study activities.

8.4 Acceptance Criteria

8.4.1 Support of NIPDWR

8.4.1.1 Analytical results must conform to control limits established by EPA as described in "Environmental Radioactivity Laboratory Intercomparison Studies Program - FY 1977," (EPA-600/4-77-001) or in subsequent revisions.

8.4.1.2 Duplicate measurements are considered acceptable when the difference between them is less than two standard deviations as described in EPA 600/4-77-001 or subsequent revisions.

8.4.1.3 The performance standard measurement will be considered acceptable when the difference between the observed or measured value and the true value is less than two standard deviations as described in EPA-600/4-77-001 or subsequent revisions.

8.4.2 Support of Non-Regulated Activities

8.4.2.1 It is recommended that the following hierarchy be used for the setting of accuracy and precision statements.

8.4.2.1.1 Defined by Purpose of Study

8.4.2.1.2 Defined by Interlaboratory Collaborative Study

8.4.2.1.3 Defined by Intralaboratory - Multi-operator Study

8.4.2.1.4 Defined by Single Operator Study

8.4.2.2 Duplicate measurements are considered acceptable when the difference between them is less than two standard deviations as described in Section 8.4.2.1.1 through 8.4.2.1.3. Duplicate measurements are considered acceptable when the difference between them is less than three standard deviations as described in Section 8.4.2.1.4.

8.4.2.3 The performance standard measurement is considered acceptable when the difference between the observed and true value is less than two standard deviations as described in Sections 8.4.2.1.1 through 8.4.2.1.3. The performance standard measurement is considered aceptable when the difference between the observed and true value is less than three standard deviations as described in Section 8.4.2.1.4.

9. Procedure

9.1 Neutralize a 1-L aliquot of the acid preserved sample to the basic side of methyl red using 6N $NH_4OH$.

9.2 Add 25 mL glacial acetic acid and 1 mL of the lead nitrate carrier solution. Mix thoroughly.

9.3 Heat to near boiling on a hot plate and precipitate the lead by bubbling a slow stream of hydrogen sulfide gas into the solution for 3 minutes.

9.4 Remove the hydrogen sulfide source, and continue boiling for 1 minute. Remove from hot plate and allow to cool until cool enough to safely handle.

9.5 Filter the solution through a 47 mm 0.45 micron cellulose triacetate membrane filter. Discard the filtrate.

9.6 Transfer the filter to a 100-mL beaker and add 20 mL concentrated nitric acid and 1 mL perchloric acid.

9.7 Evaporate to the first signs of dense fumes of perchloric acid. Remove from hot plate.

9.8 Assemble the plating cell and fill with water to check for leaks. Discard water if cell is watertight, or reassemble and test if found to leak.

9.9 Add 20 mL 0.5N HCl to the perchloric acid residue and dissolve. Heat, if necessary.

9.10 Transfer solution to plating cell.

9.11 Rinse beaker four more times using 20 mL 0.5N HCl each time and adding each rinse to the plating cell.

9.12 Immerse plating cell in a boiling water bath, position the electric stirring motor, and stir without cavitation for 4 hours.

9.13 Remove stirrer from cell and remove the plating cell from the water bath.

9.14 Discard plating solution and rinse cell two times using water rinses.

9.15 Disassemble the cell, and rinse both sides of the nickel disk with water and acetone.

9.16 Place in a 60°C drying oven for several minutes to dry. Remove from oven and cool in desiccator.

9.17 Count for 100 minutes in an internal proportional counter.

10. Calculation

10.1 Counter Efficiency (E) (Sec. 7.1)

10.1.1 Compute counter efficiency by calculating the ratio of the observed counts per minute to the added disintegration per minute (c/m/d/m)

$$E = \frac{\text{Observed count rate (c/m)}}{\text{Disintegration rate (d/m)}}$$

10.2 Recovery Factor (RF) (Section 7.2)

10.2.1 Determine recovery factor by calculating the ratio of the observed counts per/minute recovered to the added disintegration rate.

$$RF = \frac{\text{Observed (c/m) recovered}}{\text{Added disintegration rate (d/m)} \times E}$$

10.3 Polonium Concentration

10.3.1 Determine the concentration of the polonium-210 activity by dividing the observed counts per minute by the counter efficiency, recovery factor, sample volume, and the conversion factor 2.22 d/m/pCI

$$\text{Po-210 pCi/L} = \frac{\text{Sample observed count rate}}{E \times RF \times V \times 2.22}$$

where:

E = Counter Efficiency
RF = Recovery Factor
V = Volume in liters
2.22 = Conversion factor (d/m)/(pCi)

11. Precision and Accuracy

11.1 Single operator precision

11.1.1 The precision of the method has been evaluated by the analysis of seven replicate samples at the 10.02 pCi/L concentration level. The precision also includes the counting error which has been determined to be 3% at the 1 S.D. confidence level. The calculated precision has been found to be ± 5.3%.

11.2 Single Operator Accuracy

11.2.1 The average concentration found for the seven replicate analyses was 10.44 pCi/L and ranged from a low of 9.83 to a high of 11.11 pCi/L.

11.2.2 Bias is calculated to be a positive 4.1%.

12. References

Blanchard, R. L., et al., Environmental Science and Technology, 1967, 1, 932-39.

Figgins, P.E., National Academy of Science, National Research Council, 1961. NAS-NS 3037.

13. Appendix

13.1 Plating Cell Assembly (Figure 13.1)

13.1.1 Drill a hole in the bottom of an 8 oz. plastic nursing bottle to accept the glass stirrer.

13.1.2 Using a band saw, cut off a 3/4 to 1-inch section of the bottom to use as a cell cover to prevent excessive evaporation during the plating period.

13.1.3 Using emery cloth, remove the molded seams across the top of the mouth to make a flat seal with the nickel disk.

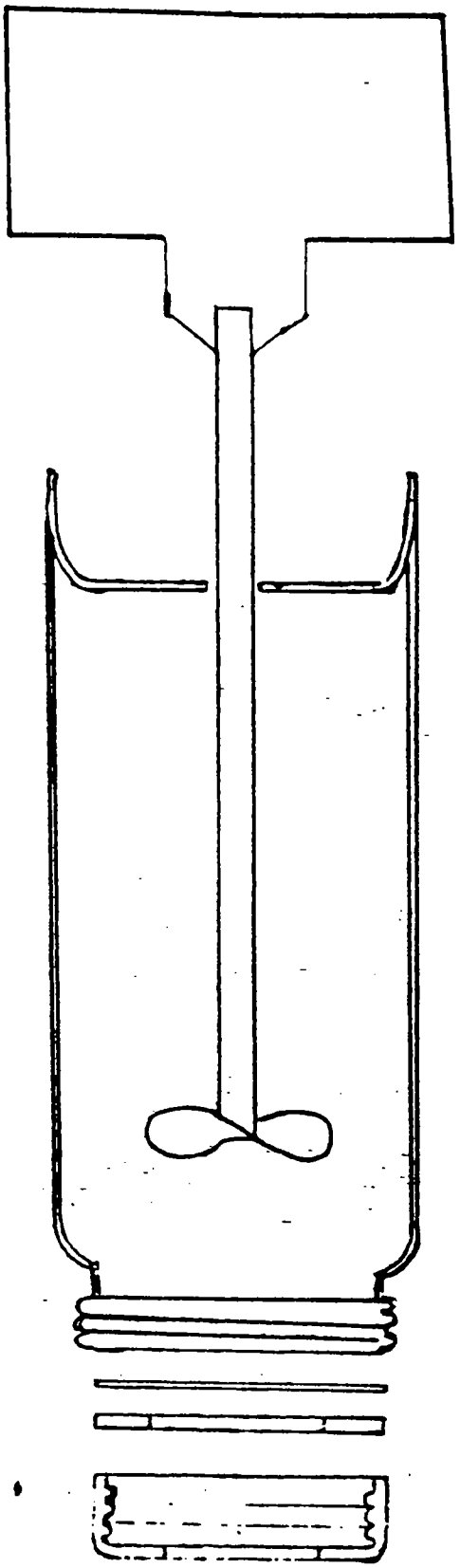
13.1.4 Cut out the rubber nipple and use the flange as the gasket.

13.1.5 Overtightening of the closure tends to cause leakage.

13.1.6 Keeping the water level of the boiling water bath at a higher level than the plating solution prevents any minute leakage out of the cell during plating.

13.1.7 Weight may have to be added to the cover to keep the cell submerged.

13.1.8 It is advantageous to fabricate a plastic or metal concentric ring for the water bath with just a large enough hole to accept and stabilize the plating cell.




PLATING CELL ASSEMBLY

FIGURE 13.1