DETERMINATION OF PLUTONIUM IN DRINKING WATER

METHOD 911

by

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1. Scope and Application

1.1 This method covers the measurement of total plutonium alpha particle activity in water samples.

2. Summary of Method

2.1 An acidified aliquot of the sample is treated with bismuth carrier and the plutonium is oxidized to the tetravalent state using sodium nitrite. Bismuth phosphate carrying the plutonium is precipitated from a heated solution and filtered. After treatment with 8N HCl, the plutonium is extracted into tri-iso-octylamine (TIOA). The plutonium is reduced with hydriodic acid, and separated from the TIOA. The acid solution is taken to dryness and the plutonium is dissolved in dilute HCl. Lanthanum fluoride carrying the plutonium is precipitated and counted.

3. Sample Handling and Preservation

3.1 Tetravalent plutonium in weakly acidic or neutral solutions may hydrolyze to form colloids. Samples should be acidified as soon as possible after collection to maintain the plutonium in an ionic form.

3.2 Since polymeric plutonium is slowly dissolved in slightly acidic solutions, it is recommended that samples be stored for several days prior to analysis.

4. Interferences

4.1 Alpha activity is present to various degrees in the lanthanum carrier. If the activity associated with the lanthanum carrier is not determined, it will interfere in the determination. Lanthanum reagent equivalent to < 0.2 cpm/mg lanthanum ion is satisfactory.

5. Apparatus

5.1 Gas-flow internal proportional counting system or alpha scintillation detection system.

5.2 Stirring hot plates.

5.3 Separatory funnels, 125 mL.

5.4 Large Millipore glass filtering apparatus, and 47 mm diameter 0.45µ PVC filters.

5.5 Stainless steel planchet, 2-inch diameter.

6. Reagents

6.1 All chemicals should be of reagent grade or equivalent whenever they are commercially available.

6.2 Alcohol-acetone mixture; mix equal volumes of 95% ethanol and acetone.

6.3 Bismuth carrier, 10 mg/mL; dissolve 5.8 g $Bi(NO_3)_3 \cdot 5H_2O$ in 250 mL of 0.5<u>N</u> HNO_3.

6.4 Ethanol 95%.

6.5 Hydrochloric acid, 12N; concentrated
8N; add 300 mL 12N HCL to 150 mL water.

6.6 Hydrofluoric acid, 48%.

6.7 Hydriodic acid, 47%.

6.8 Lanthanum carrier, 5 mg/mL; dissolve 1.55 g $La(NO_3)_3 \cdot 6H_2O$ in 100 mL of 0.1N HNO_3.

6.9 Nitric acid, concentrated, 16N.

6.10 Phosphoric acid, 11M; dilute 100 mL concentrated phosphoric acid with 300 mL water.

6.11 Sodium bisulfate, 5%; dissolve 10 g $NaHSO_4$ in 100 mL water and carefully add 100 mL of 36N H_2SO_4 while stirring.

6.12 Sodium nitrite, solid.

6.13 Tri-iso-octylamine (TIOA) 10% in xylene; dilute 50 mL TIOA to 500 mL using xylene.

7. Calibration

7.1 Determine the counting efficiency factor (E), by transferring a known amount of standardized plutonium-239 tracer to a beaker containing 50 mL of water and 2 mL of 12N HCl. Add 1 mL of the lanthanum carrier and mix. With constant stirring, add 2 mL of 48% HF, and allow to stand for 30 minutes with occasional stirring. Filter through a 47 mm membrane filter, wash two times with 10 mL each of water and ethanol. Transfer the filter to a 2-inch stainless steel planchet previously coated with rubber cement and containing 5 drops of 1:1 acetone-alcohol mixture. Dry at 80°C for 3-5 minutes. Count for sufficient times (50 minute) to accumulate a total of 10^4 total counts.

Counting efficiency, $E = \frac{A - B}{C}$

where: A = Gross counts per minute of standard
B = Reagent blank
C = dpm of standard used

8. Procedure

8.1 To a liter of water, add sufficient nitric acid to make the solution 0.25N in nitric acid (Note 1).

8.2 Add 5 mL of bismuth carrier and 0.5 grams sodium nitrite.

8.3 Heat to 70°C with slow stirring on a hot plate magnetic stirrer.

8.4 Add 5 mL of 11M phosphoric acid and mix vigorously for 30 seconds.

8.5 Turn off heat and stir slowly for 30 minutes. Remove from stirrer, retrieve magnetic stirring bar and allow the precipitate to settle for 20-30 minutes. (Note 2).

8.6 Filter through a 47 mm membrane filter, transferring the bulk of the precipitate to the filter near the end of the filtration.

8.7 Wash the remaining precipitate from the beaker using a jet stream of water. Discard filtrate.

8.8 Transfer the filter to a 50 mL beaker and dissolve precipitate in 20 mL of 8N HCl.

8.9 Transfer the solution to a 125 mL separatory funnel containing 25 mL of equilibrated 10% TIOA.

8.10 Wash the filter and beaker twice with 15 mL of 8N HCl, adding the washings to the separatory funnel.

8.11 Cap the separatory funnel and shake vigorously for two minutes.

8.12 Allow the phases to separate for 5-10 minutes and discard the lower acid layer.

8.13 Wash the organic layer two times using 10 mL portions of 8N HCl by shaking for 30 seconds, discarding the lower acid phase after adequate separation.

8.14 Back-extract the plutonium by extracting three times for 1 minute each using 10 mL portions of 8N HCl containing 0.1 mL of 47% HI, combining all separated acid phases in a 50 mL beaker. Discard the organic layer.

8.15 Evaporate the combined extracts to near dryness. Remove from hot plate and cool.

8.16 Add 2 mL of acid $NaHSO_4$ solution and 5 mL of 16N HNO_3.

8.17 Evaporate to complete dryness. If organic material is not completely oxidized, place beaker in a muffle furnace at 400°C and ash until organic material is removed.

8.18 Remove from furnace and cool. Add 2 mL of 12N HCl and rotate beaker slowly to moisten the residue. Dilute to 50 mL with water.

8.19 Add 1 mL of lanthanum carrier and mix.

8.20 With constant stirring, add 2 mL of 48% HF, and allow to stand for 30 minutes, mixing intermittently.

8.21 Filter through a 47 mm membrane filter and wash two times with 10 mL portions of water and two times with 10 mL portions of ethanol.

8.22 Transfer filter to a 2-inch stainless steel planchet previously coated with rubber cement and containing 5 drops of the alcohol-acetone mixture. (Note 3).

8.23 Place in drying oven at 80°C for 3-5 minutes.

8.24 Count for a 100 minute interval in an internal proportional counter or scintillation counter, or store in a desiccator until ready to count.

Notes: 1. If sample has been preserved with nitric acid, ascertain how much acid was used and make the necessary adjustments.

2. While waiting for precipitate to settle, pre-equilibrate the TIOA by shaking 25 mL each of TIOA and 8N HCl for two minutes and allowing the phases to separate. Discard acid.

3. To facilitate the mounting of the filter, it is recommended that the filter be rolled onto the planchet, thereby eliminating entrapped air pockets.

9. Calculation

9.1 Plutonium concentration, pCi/L = $\frac{S - B}{E \times 2.22 \times V}$

where: S = gross counts per minute
B = reagent blank including instrument background
E = detector efficiency, cpm/dpm
2.22 = constant to convert dpm to pCi, pCi/dpm
V = sample volume in liters

10. Precision and Accuracy

10.1 Eight 1-liter aliquots of tap water were spiked with a standard Pu-236 solution to a concentration of 8.5 pCi/L. Single laboratory results of the analyses were 9.1, 7.9, 6.1, 8.4, 7.0, 7.2, 8.1, and 9.4 pCi/L. The precision is calculated to be 1.1 pCi/L and the average concentration 7.9 pCi/L. Relation precision is estimated at 14% and average recovery is estimated at 93%.

11. References

11.1 George Coleman, "The Radiochemistry of Plutonium," NAS-NS 3058, 1965.

11.2 Fletcher L. Moore, "Liquid-Liquid Extraction with High-Molecular Weight Amines," NAS-NS 3101, 1960.

11.3 T. G. Scott, S. A. Reynolds, "Determination of Plutonium in Environmental Samples - Part II Procedures," Radiochem. Radioanal. Letters, 23 (4) 275-281, (1975).