



Standard Test Method for Plutonium in Water¹

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1. Scope

1.1 This test method covers the determination of alpha-particle-emitting isotopes of plutonium concentrations over 0.01 Bq/L (3 pCi/L) in water by means of chemical separations and alpha pulse-height analysis (alpha-particle spectrometry). The isotopes, plutonium-239, 240, and plutonium-238, are chemically separated from a 1-L water sample by coprecipitation with ferric hydroxide, anion exchange and electrodeposition. The test method applies to soluble plutonium and to suspended particulate matter containing plutonium. In the latter situation, an acid dissolution step is required to assure that all of the plutonium dissolves.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazards are given in Section 9

2. Referenced Documents

2.1 ASTM Standards:

- C 859 Terminology Relating to Nuclear Materials²
- D 1129 Terminology Relating to Water³
- D 1193 Specification for Reagent Water³
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water³
- D 3084 Practice for Alpha Spectrometry of Water⁴
- D 3370 Practices for Sampling Water³
- D 3648 Practices for the Measurement of Radioactivity⁴

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology D 1129, and C 859.

4. Summary of Test Method

4.1 The water sample is acidified and plutonium-242 is added as a tracer before any chemical separations are per-

formed. Iron is added to the water as iron (III), and the plutonium is coprecipitated with the iron as ferric hydroxide. After decantation and centrifugation, the ferric hydroxide precipitate containing the coprecipitated plutonium is dissolved, and the solution is adjusted to 8 M in HNO₃ for anion exchange separation. When the sample fails to dissolve because of the presence of insoluble residue, the residue is treated by a rigorous acid dissolution using concentrated nitric and hydrofluoric acids.

4.2 After an anion exchange separation, the plutonium is electrodeposited onto a stainless steel disk for counting by alpha pulse-height analysis using a silicon surface barrier or ion-implanted detector. Table 1 shows the alpha energies of the isotopes of interest in this test method. From the recovery of the plutonium-242 tracer, the absolute activities of plutonium-238 and plutonium-239, 240 can be calculated.

5. Significance and Use

5.1 This test method was developed to measure plutonium in environmental waters or waters released to the environment, and to determine whether or not the plutonium concentration exceeds the maximum amount allowable by regulatory statutes.

6. Interferences

6.1 Thorium-228 when present at concentrations 100 times or greater than plutonium-238 has been found to interfere with the determination of plutonium-238. Some thorium-228 comes through the chemical separation procedure and is electrodeposited with the plutonium. If the disk is poorly plated and if the resolution of the sample as determined by the alpha spectrometer is not better than 60 keV, the plutonium-238 and the thorium-228 may appear as one peak; the principal alpha energy of plutonium-238 is 5.50 MeV while that of thorium-228 is 5.42 MeV.

7. Apparatus

7.1 *Alpha Pulse—Height Analysis System*, consisting of a silicon surface barrier, or ion-implanted detector, supporting electronics, and pulse-height analyzer capable of giving a resolution of 50 keV WHM or better with a sample electrodeposited on a flat, mirror-finished stainless steel disk. The counting efficiency of the system should be greater than 15 % and the background in the energy region of each peak should be less than ten counts in 60 000 s.

7.2 *Electrodeposition Apparatus*, consisting of a 0 to 12 V, (0 to 2 A power supply (preferably constant current) and a

¹ This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

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² *Annual Book of ASTM Standards*, Vol 12.01.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 11.02

TABLE 1 Radioactive Decay Characteristics of Isotopes of Interest in the Determination of Plutonium in Water^A

Isotope	Half Life Years	Principal Alpha Energies in MeV (Abundance)
Pu-236	2.858	5.767 (69.14) 5.730 (30.70)
Pu-238	87.7	5.499 (71.4) 5.456 (28.6)
Pu-239	2.4110×10^4	5.158 (73.3) 5.144 (15.1) 5.105 (11.5)
Pu-240	6563	5.168 (73.51) 5.123 (26.39)
Pu-242	3.733×10^5	4.902 (79) 4.858 (21)
Am-241 ^B	432.2	5.544 (0.36) 5.485 (85.1) 5.442 (13.3)
Th-228 ^B	1.9131	5.423 (73.4) 5.340 (26.6)

^ATable of Isotopes, Eighth Edition, Vol. 11, Richard B. Firestone, Lawrence Berkeley National Laboratory, University of California, 1996.

^BThese two isotopes are listed, especially in Am-241, since they could interfere in the determination of Pu-238.

preferably disposable) electrodeposition cell. The cathode is an approximately 20-mm diameter stainless steel disk prepolished to a mirror finish. The anode is an approximately 1-mm diameter platinum wire with an approximately 8-mm diameter loop at the end of the wire parallel to the cathode disk. Cooling of the cell during electrodeposition to at least 50°C is recommended.

7.3 *Centrifuge*, capable of handling a 100-mL centrifuge bottle.

7.4 *Ion Exchange Column*, approximately 13-mm inside diameter and 150 mm long with a 100-mL reservoir, and either a fritted glass or Borosilicate glass-wool plug at the bottom.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without reducing the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specifications D 1193, Type III.

8.3 *Radioactive Purity*—Radioactive purity shall be such that the measured radioactivity of blank samples does not exceed the calculated probable error of the measurement.

⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*. U.S. Pharmaceutical Convention, Inc. (USPC).

8.4 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH₄OH).

8.5 *Ammonium Hydroxide Solution* (1+9)—Mix 1 volume of concentrated NH₄OH (sp gr 0.90) with 9 volumes of water.

8.6 *Ammonium Hydroxide Solution* (1+99)—Mix 1 volume of concentrated NH₄OH (sp gr 0.90) with 99 volumes of water.

8.7 *Ammonium Iodide Solution* (145 g/L)—Dissolve 14.5 g of NH₄I in water and dilute to 100 mL. This solution must be prepared fresh weekly.

8.8 *Anion Exchange Resin*—Strongly basic, styrene, quaternary ammonium salt, 4 % crosslinked, 100 to 200 mesh, chloride form.

8.9 *Boric Acid* (H₃BO₃)—Powdered or crystalline.

8.10 *Electrolyte, Preadjusted*—Dissolve 132 g of ammonium sulfate in water and dilute to 1 L. Add concentrated NH₄OH or concentrated H₂SO₄ while stirring to adjust the pH of the solution to 3.5. The solution is 1 M (NH₄)₂SO₄.

8.11 *Ethyl Alcohol* (C₂H₅OH)—Make slightly basic with a few drops of concentrated NH₄OH per 100 mL of alcohol.

8.12 *Ferric Chloride Carrier Solution* (50 mg Fe/mL)—Dissolve 24 g of FeCl₃·6H₂O in a mixture of 4.4 mL of concentrated hydrochloric acid (sp gr 1.19) and 95.6 mL of water.

8.13 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

8.14 *Hydrochloric Acid Solution* (3+1)—Mix 3 volumes of concentrated HCl (sp gr 1.19) with 1 volume of water.

8.15 *Hydrofluoric Acid* (sp gr 1.15)—Concentrated hydrofluoric acid (HF).

8.16 *Hydrogen Peroxide Solution* (1+2)—Standard 30 %. Commercially available reagent grade.

8.17 *Nitric Acid* sp gr. 1.42)—Concentrated nitric acid (HNO₃).

8.18 *Nitric Acid Solution* (1+1)—Mix 1 volume of concentrated nitric acid (sp gr 1.42) with 1 volume of water.

8.19 *Nitric Acid Solution* (1+8)—Mix 1 volume of concentrated nitric acid (sp gr 1.42) with 8 volumes of water.

8.20 *Plutonium-242 Solutions, Standard (Approximately 0.2 Bq/mL)*.

NOTE 1—Standard plutonium-242 solutions usually are available from the National Institute of Standards and Technology; dilution to the required concentration may be necessary.

8.21 *Sodium Hydrogen Sulfate—Sulfuric Acid Solution*—Dissolve 10 g of sodium hydrogen sulfate in 100 mL of water and then carefully add 100 mL of concentrated H₂SO₄ (sp gr 1.84) while stirring. This solution contains approximately 5 g of NaHSO₄ per 100 mL of 9 M H₂SO₄.

8.22 *Sodium Nitrite* (NaNO₂).

8.23 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H₂SO₄).

8.24 *Sulfuric Acid Solution* (1+9)—Carefully mix 1 volume of concentrated sulfuric acid (sp gr 1.84) with 9 volumes of water.

8.25 *Thymol Blue Indicator Solution*—Dissolve 0.04 g of sodium salt of thymol blue in 100 mL of water.

9. Hazards

NOTE 2—**Warning:** Hydrofluoric acid is extremely hazardous. Wear

rubber gloves, safety glasses or goggles and a laboratory coat. Avoid breathing any HF fumes. Clean up all spills and wash thoroughly after using HF.

10. Sampling

10.1 Collect the sample in accordance with Practices D 3370. Preserve the sample by adjusting the acidity to $\text{pH} < 1$ with HNO_3 (1+8) if the sample is not to be analyzed within 24 h. Record the volume of the sample and the volume of acid added.

11. Calibration and Standardization

11.1 If National Institute of Standards and Technology plutonium-242 is not used as a tracer, standardize the plutonium-242; for guidance refer to practices D 3084 and D 3648. These references may also be consulted in regard to energy calibration and counting efficiency determination of the counting system.

12. Procedure

12.1 Coprecipitation:

12.1.1 Measure a known volume approximately 1 L of the water sample to be analyzed plus the volume of acid added, if any.

12.1.2 If the sample has not been acidified, add 150 mL of concentrated HNO_3 per litre of sample.

12.1.3 Mix the sample completely, and add an accurately known amount of the plutonium-242 standard solution to give about 0.2 Bq of plutonium-242. If the plutonium-238 or plutonium-239 content of the sample is known to be high plutonium-236 tracer is recommended.

12.1.4 Heat the sample to about 60°C and stir at this temperature for about 1 h.

12.1.5 Add 1 mL of ferric chloride carrier solution and stir about 10 min.

12.1.6 Add concentrated NH_4OH while stirring to precipitate the iron. Add a slight excess of the concentrated NH_4OH to raise the pH to 9 to 10 as indicated with pH paper.

12.1.7 Continue to stir the sample for about 30 min before allowing the precipitate to settle.

12.1.8 After the sample has settled sufficiently, decant the supernate, being careful not to remove any precipitate. (If the analyst wishes to continue immediately, the iron hydroxide may be filtered out at this time.)

12.1.9 Slurry the precipitate and remaining supernate and transfer to a centrifuge bottle.

12.1.10 Centrifuge the sample and pour off the remaining supernate.

12.1.11 Dissolve the ferric hydroxide with a minimum of concentrated HNO_3 . If organic matter is believed to be present, transfer to 250 mL TFE beaker; add 2 mL 30% H_2O_2 , 2 mL concentrated HNO_3 and heat to near dryness. Repeat as necessary. Then add 2 mL concentrated HNO_3 and proceed.

12.1.12 If the precipitate dissolves completely, add a volume of concentrated HNO_3 equal to the volume of the sample solution, dilute to 100 to 150 mL with 8 M HNO_3 , and then proceed to 12.3. If the precipitate does not dissolve in HNO_3 , proceed to 12.2.

12.2 Acid Dissolution of Insoluble Residue:

12.2.1 If the precipitate fails to dissolve in HNO_3 , add more concentrated HNO_3 to a total volume of about 75 mL, transfer the entire sample to a TFE-fluorocarbon beaker, and add 75 mL of concentrated HF. (**Warning**—See Section 9.)

12.2.2 Stir and heat on a magnetic stirrer hot plate for about 4 h at a temperature near boiling. Add equal amounts of concentrated HNO_3 and concentrated HF to keep the volume at about 150 mL.

12.2.3 Allow the mixture to cool, and decant the solution into another TFE-fluorocarbon beaker.

12.2.4 Evaporate this solution to dryness.

12.2.5 While this solution is drying, add 75 mL of concentrated HCl and 2 g of H_3BO_3 to the undissolved residue. Stir and let stand until the solution from the previous step has evaporated to dryness.

12.2.6 Transfer the HCl- H_3BO_3 mixture from the last step to the dried sample, leaving any residue behind. Rinse the residue once with water and transfer this water to the sample.

12.2.7 Evaporate the sample in the TFE-fluorocarbon beaker to about 10 mL.

12.2.8 Add 100 mL of concentrated HNO_3 and boil to remove the HCl.

12.2.9 Evaporate the sample to a volume of about 50 mL.

12.2.10 Remove from the hot plate, and add a volume of water equal to the volume of the sample.

12.2.11 Add HNO_3 (1+1) to a volume of 150 mL, add 1 g of H_3BO_3 , and allow the solution to cool.

12.2.12 Filter the solution through a glass fiber filter and wash the filter a few times with HNO_3 (1+1). Discard any residue in the filter paper and proceed with the analysis of the filtrate in accordance with 12.3.1.

12.3 Column Preparation:

12.3.1 Slurry about 10 mL of the anion exchange resin with water.

12.3.2 Pour it into a column of about 13-mm inside diameter to a resin depth of about 80 mm. Use more resin when analyzing samples which were treated for suspended matter.

12.3.3 Wash the resin with 10 column volumes of HNO_3 (1+1) to convert the resin to the nitrate form.

12.4 Anion Exchange Separation:

12.4.1 To the solution from the coprecipitation procedure or from the acid dissolution that should be 7 to 9 M in HNO_3 , add 1 g of NaNO_2 , heat to boiling and cool.

12.4.2 Pass the sample solution through the prepared anion exchange resin column at a flow rate no greater than 5 mL/min.

12.4.3 After the sample has passed through the column, rinse the column with six column volumes of HNO_3 (1+1) again at a flow rate no greater than 5 mL/min.

12.4.4 Rinse the ion exchange resin column with six column volumes of HCl (3+1) at a flow rate no greater than 2 mL/min.

NOTE 3—The purpose of this step is to remove any thorium present in the sample. Experience with soil and other samples containing relatively large amounts of thorium has shown that additional rinsing of the column with 9 M HCl at a low-flow rates is required to remove the thorium. Normally water samples will not contain large amounts of thorium, but if they do, additional rinsings at this step may be required.

12.4.5 Into a clean container elute the plutonium at a flow rate no greater than 2 mL/min with four column volumes of a

freshly prepared $\text{NH}_4\text{I-HCl}$ mixture containing 1 mL of 1 M NH_4I per 30 mL of concentrated HCl.

12.4.6 Rinse the column at maximum flow rate with two portions of concentrated HCl equal to the volume of the column of resin. Allow this rinse to flow into the effluent from the last step.

12.4.7 Evaporate the sample containing the plutonium to about 20 mL and add 5 mL of concentrated HNO_3 .

12.4.8 Evaporate the sample to near dryness.

12.4.9 Add 20 mL of concentrated HNO_3 and evaporate to near dryness.

12.5 Electrodeposition:

12.5.1 Add 2 mL of a 5 % solution of $\text{NaHSO}_4\cdot\text{H}_2\text{O}$ in 9 M H_2SO_4 to the sample.

12.5.2 Add 5 mL of concentrated HNO_3 , mix well and evaporate to dryness, but do not bake.

12.5.3 Dissolve the sample in 5 mL of the preadjusted electrolyte warming to hasten the dissolution.

12.5.4 Transfer the solution to the electrodeposition cell using an additional 5 to 10 mL of the electrolyte in small increments to rinse the sample container.

12.5.5 Add three or four drops of thymol blue indicator solution. If the color is not salmon pink, add NH_4OH (1+9) until a salmon pink color is obtained. If too much is added, pH may be readjusted with 1.8 M H_2SO_4 .

12.5.6 Place the platinum anode into the solution about 10 mm above the stainless steel disk that serves as the cathode.

12.5.7 Connect the electrodes to the source of current, turn the power on, and adjust the proper supply to give a current of 1.2 A. (Constant current power supplies will require no further adjustment, but others may require further voltage adjustments to keep the current constant at 1.2 A during the electrodeposition.)

12.5.8 Continue the electrodeposition for a total of 1.5 to 2.0 h.

12.5.9 When the electrodeposition is to be terminated add 1 mL of concentrated NH_4OH and continue the electrodeposition for 1 min.

12.5.10 Turn off the power and then remove the anode from the cell.

12.5.11 Discard the solution in the cell and rinse cell a few times with NH_4OH (1+99).

12.5.12 Disassemble the cell and wash the disk with ethyl alcohol.

12.5.13 Touch the edge of the disk to a tissue to absorb the alcohol from the disk.

12.5.14 Dry the disk, place it in a suitable closed container and label for counting.

12.6 Alpha Pulse Height Analysis:

12.6.1 Count the sample with the alpha pulse height analysis system. See Practice D 3084 for guidance.

12.6.2 Determine the total counts in the plutonium-238, plutonium-239, and plutonium-242 energy regions and make background, blank, and tailing corrections as necessary.

13. Calculation

13.1 Calculate the concentrations of plutonium-239, plutonium-238 in the aliquot of water taken for analysis as follows:

$$A_i = N_i A_t V_t / N_t V_s \quad (1)$$

where:

A_i = concentration of plutonium-239, or plutonium-238 in the water, Bq/L

N_i = net sample counts in the plutonium-239 or plutonium-238 energy region of the alpha spectrum,

A_t = the concentration of the plutonium-242 tracer, Bq/mL

V_t = the plutonium-242 tracer added, mL,

N_t = net sample counts in the plutonium-242 tracer energy region of the alpha spectrum, and

V_s = the water sample taken for analysis (this does not include the volume of acid added in 10.1), L.

13.2 The absolute counting efficiency of the alpha spectrometer, E , must be determined if it is desired to calculate the plutonium recovery of the analytical procedure. Calculate this efficiency as follows:

$$E = R_s / R_\alpha \quad (2)$$

where:

R_s = net counting rate of the standard source in the energy region of the calibrated alpha emitting isotope calibrated in counts per second,

R_α = absolute alpha particle emission rate of the calibrated alpha emitting isotope in alphas per second.

13.3 Calculate the plutonium chemical recovery as follows:

$$Y = (N_t/t) / A_t V_t E \quad (3)$$

where:

t = counting time in seconds; the other terms are as defined in 13.1 and 13.2.

13.4 The total propagated uncertainties (1σ) for the individual plutonium isotope concentrations are calculated as follows:

$$\sigma_{A_i} (\text{Bq/L}) = A_i (\text{Bq/L}) * [(\sigma_{N_i}/N_i)^2 + (\sigma_{A_t}/A_t)^2 + (\sigma_{V_t}/V_t)^2 + (\sigma_{N_t}/N_t)^2 + (\sigma_{V_s}/V_s)^2]^{1/2} \quad (4)$$

σ_{N_i} = one sigma uncertainty of the net sample counts in the energy region of interest in the alpha spectrum,

σ_{A_t} = one sigma uncertainty of the concentration of the Pu-242 or Pu-236 tracer, Bq/mL,

σ_{V_t} = one sigma uncertainty in the volume of the Pu tracer added, mL,

σ_{N_t} = one sigma uncertainty of the net sample counts in the Pu-242 or Pu-236 tracer energy region of the alpha spectrum, and

σ_{V_s} = one sigma uncertainty of the volume of the water sample taken for analysis.

The one sigma uncertainties for the net counts in the sample and tracer energy regions of interest are calculated from:

$$\sigma_N = (G + B)^{1/2} \quad (5)$$

where:

G = the gross counts in the region of interest and

B = the expected background counts for the same counting duration in the region of interest.

13.5 The *a priori* minimum detectable concentration (MDC) is calculated as follows:

$$MDC (Bq/L) = \frac{2.71 + 4.65 * B^{1/2}}{t * Y * E * V_s} \quad (6)$$

where:

t = the counting duration, s

Y = the expected fractional plutonium recovery and

E = the absolute counting efficiency of the alpha spectrometer and other terms as defined earlier.

14. Quality Control

14.1 The project leader, as part of the external quality control program, shall submit blind quality control samples to the analyst along with routine samples. These external quality control samples, which usually include duplicate and blank samples, shall test sample collection and preparation as well as sample analysis whenever possible. In addition, analysts are expected to run internal quality control samples that will

TABLE 2 Observed Bias and Precision for Plutonium-238 and Plutonium-239

Plutonium-238			PRECISION	
ADDED, Bq/L	FOUND, Bq/L	BIAS, %	S (o)	S(t)
0.166	0.148	-11	0.0117	0.0205
0.125	0.129	+3.2	0.00629	0.00870
0.0088	0.0084	-4.6	0.00122	0.00125
Plutonium-239			PRECISION	
ADDED, Bq/L	FOUND, Bq/L	BIAS, %	S (o)	S (t)
0.482	0.447	-7.3	0.0207	0.0548
0.074	0.0694	-6.3	0.00362	0.0416
0.016	0.0157	-2.1	0.00149	0.0021

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indicate to them whether the analytical procedures are in control. Both the external and internal quality control samples need to be prepared in such a way as to duplicate the chemical matrix of the routine samples, insofar as this is practical. The quality control samples that are routinely used consist of five basic types: blank samples, replicate samples, reference materials, control samples, and “spiked” samples.

15. Precision and Bias ⁶

15.1 A limited collaborative test of this test method was conducted for the plutonium isotopes of Pu-238 and Pu-239.⁷ Fourteen laboratories participated by processing two replicate samples at three levels. Outlier results from laboratories were rejected as per the statistical tests outlined in Practice D 2777. These collaborative data were obtained on river and substitute ocean waters. It is the user’s responsibility to ensure the validity of this test method for waters of untested matrices.

15.2 The collaborative study of this test method resulted in the observed bias and precision values presented in Table 2.

16. Keywords

16.1 alpha spectrometry; ion exchange chromatography; plutonium; water

⁶ Supporting data are available from ASTM Headquarters, Request RR: D19-1063.

⁷ Bishop, C. T., Glosby, A. A., and Phillips, C.A., “Collaborative Study of an Anion Exchange Method for the Determination of Trace Plutonium in Water,” U.S. Department of Energy Report MLM-2425, June 26, 1978.