



Designation: D 3865 – 02

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 (0.3 pCi/L) in water by means of chemical separations and alpha pulse-height analysis (alpha-particle spectrometry). The isotopes, ^{239}Pu , ^{240}Pu , and ^{238}Pu , 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
- C 1192 Test Method for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride³
- C 1284 Practice for Electrodeposition of the Actinides for Alpha Spectrometry²
- D 1129 Terminology Relating to Water⁴
- D 1193 Specification for Reagent Water⁴
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water⁴
- D 3084 Practice for Alpha Spectrometry of Water⁵
- D 3370 Practices for Sampling Water⁴
- D 3648 Practices for the Measurement of Radioactivity⁵

¹ This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.04.

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² Annual Book of ASTM Standards, Vol 12.01.

³ Annual Book of ASTM Standards, Vol 15.02.

⁴ Annual Book of ASTM Standards, Vol 11.01.

⁵ Annual Book of ASTM Standards, Vol 11.02.

- D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water⁴
- D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis⁵

3. Terminology

3.1 Definitions:

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

4. Summary of Test Method

4.1 The water sample is acidified and ^{242}Pu is added as a tracer before any chemical separations are performed. 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 HNO_3 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, hydrofluoric, and hydrochloric 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 ^{242}Pu tracer, the absolute activities of ^{238}Pu and $^{239/240}\text{Pu}$ 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 ^{228}Th when present at concentrations 100 times or greater than ^{238}Pu has been found to interfere with the determination of ^{238}Pu . Some ^{228}Th comes through the chemical separation procedure and is electrodeposited with the

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)
²³⁶ Pu	2.858	5.767 (69.14) 5.730 (30.70)
²³⁸ Pu	87.7	5.499 (71.4) 5.456 (28.6)
²³⁹ Pu	2.4110 × 10 ⁴	5.158 (73.3) 5.144 (15.1) 5.105 (11.5)
²⁴⁰ Pu	6563	5.168 (73.51) 5.123 (26.39)
²⁴² Pu	3.733 × 10 ⁵	4.902 (79) 4.858 (21)
²⁴¹ Am ^B	432.2	5.544 (0.36) 5.485 (85.1) 5.442 (13.3)
²²⁸ Th ^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 ²⁴¹Am, since they could interfere in the determination of ²³⁸Pu.

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 ²³⁸Pu and the ²²⁸Th may appear as one peak; the principal alpha energy of ²³⁸Pu is 5.50 MeV while that of ²²⁸Th 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 FWHM 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 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*, a 100-mL centrifuge bottle is convenient.

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 Commit-

tee on Analytical Reagents of the American Chemical Society.⁶ 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 or better.

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.

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 ²⁴²Pu Solutions, Standard (Approximately 0.2 Bq/mL).

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

⁶ *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).

8.21 *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 pH < 1 with HNO₃ (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 The ²³⁶Pu or ²⁴²Pu tracer used in this method shall be traceable to the National Institute for Standards and Technology. While the laboratory is advised to verify the activity of the received and diluted tracer solution, the results of these verification measurements shall not replace the decay-corrected traceable value. If the verification measurements fail to verify the traceable activity of the as-received ²³⁶Pu or ²⁴²Pu tracer solution the laboratory will resolve this with the supplier.

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 HNO₃ per litre of sample.

12.1.3 Mix the sample completely, and add an accurately known amount of the ²³⁶Pu or ²⁴²Pu standard solution to give about 0.2 Bq of ²³⁶Pu or ²⁴²Pu. If the ²³⁹Pu, ²⁴⁰Pu, or ²³⁸Pu content of the sample is known to be high ²³⁶Pu 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 NH₄OH while stirring to precipitate the iron. Add a slight excess of the concentrated NH₄OH 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 100 mL 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 HNO₃. If organic matter is believed to be present, transfer to a TFE—fluorocarbon beaker, 250 mL being a convenient size; add 2 mL 30 % H₂O₂, 2 mL concentrated HNO₃ and heat to mean dryness. Repeat as necessary. Then add 2 mL concentrated HNO₃ and proceed.

12.1.12 If the precipitate dissolves completely, add a volume of concentrated HNO₃ equal to the volume of the sample solution, dilute to 100 to 150 mL with 8 M HNO₃, and then proceed to 12.3. If the precipitate does not dissolve in HNO₃, proceed to 12.2.

12.2 Acid Dissolution of Insoluble Residue:

12.2.1 If the precipitate fails to dissolve in HNO₃, add more concentrated HNO₃ 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 HNO₃ 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 H₃BO₃ 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-H₃BO₃ 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 HNO₃ 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 HNO₃(1+1) to a volume of 150 mL, add 1 g of H₃BO₃, 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 HNO₃(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.