



Designation: D3865 – 09

Standard Test Method for Plutonium in Water¹

This standard is issued under the fixed designation D3865; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

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). Due to overlapping alpha-particle energies, this method cannot distinguish ²³⁹Pu from ²⁴⁰Pu. Plutonium is 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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:*²

[C859 Terminology Relating to Nuclear Materials](#)

[C1163 Practice for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride](#)

[C1284 Practice for Electrodeposition of the Actinides for Alpha Spectrometry](#)

[D1129 Terminology Relating to Water](#)

[D1193 Specification for Reagent Water](#)

[D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)

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

Current edition approved Feb. 1, 2009. Published March 2009. Originally approved in 1980. Last previous edition approved in 2002 as D3865 – 02. DOI: 10.1520/D3865-09.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[D3084 Practice for Alpha-Particle Spectrometry of Water](#)
[D3370 Practices for Sampling Water from Closed Conduits](#)
[D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology [D1129](#) and Terminology [C859](#).

4. Summary of Test Method

4.1 The water sample is acidified and a plutonium isotopic tracer, for example ²³⁶Pu or ²⁴²Pu, 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 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, 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. The absolute activities of ²³⁸Pu and ^{239/240}Pu are calculated independent of discrete detector efficiency and chemical yield corrections by directly comparing the number of counts in each peak relative to counts observed from a known activity of ²³⁶Pu or ²⁴²Pu tracer (see [Eq 1](#)).

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 in the original water sample at concentrations 100 times or greater than ²³⁸Pu has been

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.

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

found to interfere with the determination of ²³⁸Pu. Some ²²⁸Th comes through the chemical separation procedure and is electrodeposited with the plutonium. If the disk is poorly plated and if the resolution of peaks in the alpha spectrum 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. After a period of in-growth the presence of ²²⁸Th can be inferred from its decay progeny.

6.2 Unless corrected, the presence of the tracer isotope in the original water sample will bias the yield of that tracer high and bias the results of the analyte plutonium isotopes low. For example, plutonium that originates from high burn-up plutonium may contain a small percentage of ²⁴²Pu, in addition to other plutonium isotopes. The tracer isotope, ²³⁶Pu, is less subject to this problem given that it is not generated in reactors burning plutonium or uranium. However, there is some potential for tailing of the ²³⁶Pu peak into analyte regions. For samples expected to be free of plutonium analyte isotopes ²⁴²Pu may be the preferred tracer isotope.

7. Apparatus

7.1 *Alpha Spectrometry System*, consisting of a silicon surface barrier, or ion-implanted detector, supporting electronics, and multi-channel pulse-height analyzer capable of giving a resolution of 50 keV or better full-width at half-maximum (FWHM) 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 analyte isotope 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 pre-polished 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 Committee on Analytical Reagents of the American Chemical Society.³ 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 **D1193**, 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* (approximately 15 M, 28 %)—Concentrated ammonium hydroxide (NH₄OH). Store in well-sealed container to minimize absorption of carbon dioxide. Do not use if the solution is cloudy or if a precipitate is present.

8.5 *Ammonium Hydroxide Solution* (1.5 M)—Add 100 mL of 15 M NH₄OH to 250 mL of water and dilute to 1 L with water. Store in well-sealed container to minimize absorption of carbon dioxide. Do not use if the solution is cloudy or if a precipitate is present.

8.6 *Ammonium Hydroxide Solution* (0.15 M)—Add 10 mL of 15 M NH₄OH to 250 mL of water and dilute to 1 L with water. Do not use if the solution is cloudy or if a precipitate is present.

8.7 *Ammonium Iodide Solution* (1 M)—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. The 8 % crosslinked form may also be used. The study which generated the precision and bias data referenced in section 15 was performed using only the 4 % crosslinked form. Those using 8 % crosslinked should validate that such a substitution does not impact the performance of the method.

³ *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).

8.9 *Boric Acid* (H_3BO_3)—Powdered or crystalline.

8.10 *Electrolyte, Preadjusted*—The solution is 1 M $(NH_4)_2SO_4$. Dissolve 132 g of ammonium sulfate in water and dilute to 1 L. Add concentrated NH_4OH or concentrated H_2SO_4 while stirring to adjust the pH of the solution to 3.5.

8.11 *Slightly Basic Ethyl Alcohol* (C_2H_5OH) 95 %— Make slightly basic with a few drops of concentrated NH_4OH per 100 mL of alcohol.

8.12 *Ferric Chloride Carrier Solution* (50 mg Fe/mL)— Dissolve 24 g of $FeCl_3 \cdot 6H_2O$ 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* (approximately 12 M, 36 %)— Concentrated hydrochloric acid (HCl).

8.14 *Hydrochloric Acid Solution* (9 M)—Add 750 mL of 12 M hydrochloric acid to 150 mL of water and dilute to 1 L with water.

8.15 *Hydrofluoric Acid* (~ 29 M, 49 %)—Concentrated hydrofluoric acid (HF).

8.16 *Hydrogen Peroxide Solution* (H_2O_2)—Standard 30 %.

8.17 *Nitric Acid* (~ 16 M, 69 %)—Concentrated nitric acid (HNO_3).

8.18 *Nitric Acid Solution* (8 M)—Add 500 mL of 16 M nitric acid to 250 mL of water and dilute to 1 L with water.

8.19 *Nitric Acid Solution* (1.8 M)—Add 110 mL of 16 M nitric acid to 500 mL of water and dilute to 1 L with water.

8.20 *^{236}Pu or ^{242}Pu Solutions, Standard (Approximately 0.2 Bq/mL)*—The study which generated the precision and bias data referenced in section 15 was performed using only a ^{242}Pu tracer. Those using ^{236}Pu should validate that such a substitution does not impact the performance of the method.

NOTE 1—Standard ^{236}Pu and ^{242}Pu tracer solutions usually are available from the National Institute of Standards and Technology (NIST), vendors with traceability to NIST, or other national standards laboratories; 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 H_2SO_4 (~ 18 M, 95 %) while stirring. This solution contains approximately 5 g of $NaHSO_4$ per 100 mL of 9 M H_2SO_4 .

8.22 *Sodium Nitrite* ($NaNO_2$).

8.23 *Sulfuric Acid* (~ 18 M, 95%)—Concentrated sulfuric acid (H_2SO_4).

8.24 *Sulfuric Acid Solution* (1.8 M)—Carefully add 100 mL of 18 M sulfuric acid to 750 mL of water and dilute to 1 L with water. **Warning:** Add the acid slowly to water, with stirring, to prevent boiling and spattering.

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

9. Hazards

9.1 **Warning:** Hydrofluoric acid is extremely hazardous. Wear suitable protective 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 **D3370**. Preserve the sample by adjusting the acidity to pH <1 with HNO_3 (1.8 M) 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 ^{236}Pu or ^{242}Pu tracer used in this method shall be traceable to NIST or another national standards laboratory. 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 ^{236}Pu or ^{242}Pu tracer solution the laboratory will resolve this with the supplier.

12. Procedure

12.1 Coprecipitation:

12.1.1 Accurately measure a known volume of the water sample. The volume should be approximately 1 litre. Document the known volume.

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 ^{236}Pu or ^{242}Pu standard solution to give about 0.2 Bq of ^{236}Pu or ^{242}Pu . If the ^{239}Pu , ^{240}Pu , or ^{238}Pu content of the sample is known to be high ^{236}Pu 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 iron hydroxide. 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. Alternatively, the iron hydroxide precipitate may be filtered out.

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 HNO_3 . Transfer to a beaker, add 2 mL 30 % H_2O_2 , 2 mL concentrated HNO_3 and heat to near dryness. Repeat twice if necessary to achieve dissolution. Then add an additional 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 solution resulting from 12.1.11, 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.