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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Plutonium in Water[1]

This standard is issued under the fixed designation D 3865; 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 reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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 Materials[2]
D 1129 Terminology Relating to Water[3]
D 1193 Specification for Reagent Water[3]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[3]
D 3084 Practice for Alpha Spectrometry of Water[4]
D 3370 Practices for Sampling Water[3]
D 3648 Practices for the Measurement of Radioactivity[4]

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 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 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)

[A] *Table 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 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.

8.4 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

8.5 *Ammonium Hydroxide Solution* (1+9)—Mix 1 volume of concentrated NH_4OH (sp gr 0.90) with 9 volumes of water.

8.6 *Ammonium Hydroxide Solution* (1+99)—Mix 1 volume of concentrated NH_4OH (sp gr 0.90) with 99 volumes of water.

8.7 *Ammonium Iodide Solution* (145 g/L)—Dissolve 14.5 g of NH_4I 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 (H_3BO_3)*—Powdered or crystalline.

8.10 *Electrolyte, Preadjusted*—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. The solution is 1 *M* $(NH_4)_2SO_4$.

8.11 *Ethyl Alcohol* (C_2H_5OH)—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* (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 (HNO_3).

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 H_2SO_4(sp gr 1.84) 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* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

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

[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).