



Designation: D 3865 – 9702

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, ~~plutonium-239, 240,~~ ²³⁹Pu, ²⁴⁰Pu, and ~~plutonium-238,~~ ²³⁸Pu, 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

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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- 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 D-19 on Water⁴
- D 3084 Practice for Alpha Spectrometry of Water⁵
- D 3370 Practices for Sampling Water⁴
- D 3648 Practices for the Measurement of Radioactivity⁵
- 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 ~~plutonium-242~~ 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. From the recovery of the ~~plutonium-242~~ ²⁴²Pu tracer, the absolute activities of ~~plutonium-238~~ ²³⁸Pu and ~~plutonium-239, 240~~ ^{239/240}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 ~~Thorium-228~~

6.1 ~~²²⁸Th~~ when present at concentrations 100 times or greater than ~~plutonium-238~~ ²³⁸Pu has been found to interfere with the determination of ~~plutonium-238~~ ²³⁸Pu. Some ~~thorium-228~~ ²²⁸Th 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~~ ²³⁸Pu and the ~~thorium-228~~ ²²⁸Th may appear as one peak; the principal alpha energy of ~~plutonium-238~~ ²³⁸Pu is 5.50 MeV while that of ~~thorium-228~~ 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*, capable of handling 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

² Annual Book of ASTM Standards, Vol 12.01.

³ Annual Book of ASTM Standards, Vol 11.01, 15.02.

⁴ Annual Book of ASTM Standards, Vol 11.021.

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*; *ASTM Standards*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), 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)
<u>Pu-236</u> <u>²³⁶Pu</u>	<u>2.858</u> <u>2.858</u>	<u>5.767 (69.44)</u> <u>5.767 (69.14)</u> <u>5.730 (30.70)</u>
<u>Pu-238</u> <u>²³⁸Pu</u>	<u>87.7</u> <u>87.7</u>	<u>5.499 (71.4)</u> <u>5.499 (71.4)</u> <u>5.456 (28.6)</u>
<u>Pu-239</u> <u>²³⁹Pu</u>	<u>2.4110 × 10⁴</u> <u>2.4110 × 10⁴</u>	<u>5.158 (73.3)</u> <u>5.158 (73.3)</u> <u>5.144 (15.1)</u> <u>5.105 (11.5)</u>
<u>Pu-240</u> <u>²⁴⁰Pu</u>	<u>6563</u> <u>6563</u>	<u>5.168 (73.54)</u> <u>5.168 (73.51)</u> <u>5.123 (26.39)</u>
<u>Pu-242</u> <u>²⁴²Pu</u>	<u>3.733 × 10⁵</u> <u>3.733 × 10⁵</u>	<u>4.902 (79)</u> <u>4.902 (79)</u> <u>4.858 (21)</u>
<u>Am-241^B</u> <u>²⁴¹Am^B</u>	<u>432.2</u> <u>432.2</u>	<u>5.544 (0.36)</u> <u>5.544 (0.36)</u> <u>5.485 (85.1)</u> <u>5.442 (13.3)</u>
<u>Th-228^B</u> <u>²²⁸Th^B</u>	<u>1.9134</u> <u>1.9131</u>	<u>5.423 (73.4)</u> <u>5.423 (73.4)</u> <u>5.340 (26.6)</u>

^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-²⁴¹Am~~, since they could interfere in the determination of ~~Pu-²³⁸Pu~~.

reagents shall conform to the specifications of the Committee 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).

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

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).

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

NOTE 1—Standard ~~plutonium-242~~ ²⁴²Pu 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 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 of Standards and Technology plutonium-242 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 be used as a tracer, standardize or replace the plutonium-242; for guidance refer to decay-corrected traceable value. If the verification measurements fail to practices D 3084 and D 3648. These references may also be consulted in regard to energy calibration and counting efficiency determination verify the traceable activity of the counting system.~~ 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 ~~plutonium-242~~ ²³⁶Pu or ²⁴²Pu standard solution to give about 0.2 Bq of ~~plutonium-242~~ ²³⁶Pu or ²⁴²Pu. If the ~~plutonium-238~~ ²³⁹Pu, ²⁴⁰Pu, or ~~plutonium-239~~ ²³⁸Pu content of the sample is known to be high ~~plutonium-236~~ 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 NH₄ OH 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 TFE beaker, mL being a convenient size; add ~~2 mL~~ 2 mL 30 % H₂O₂, 2 mL concentrated HNO₃ and heat to near 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.

12.3.3 Wash the resin with 10 column volumes of HNO₃(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 (12.1) or from the acid dissolution (12.2) that should be 7 to 9 M in HNO₃, add 1 g of NaNO₂, 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 HNO₃(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, for example, 1 mL/min, 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 NH₄I-HCl mixture containing 1 mL of 1 M NH₄I 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 volumes of resin. concentrated HCl. 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 HNO₃.

12.4.8 Evaporate the sample to near dryness.

12.4.9 Add 20 mL of concentrated HNO₃ and evaporate to near dryness.

12.5 *Electrodeposition:*—See Practice C 1284 for guidance on electrodeposition. Alternatively see Test Method C 1163 for guidance on coprecipitation using neodymium fluoride but it is the user's responsibility to ensure the validity of this modification.

12.5.1 Add 2 mL of a 5 % solution of NaHSO₄·H₂O in 9 M H₂SO₄ to the sample.

12.5.2 Add 5 mL of concentrated HNO₃, 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 NH₄OH (1+9) until a salmon pink color is obtained. If too much is added, pH may be readjusted with 1.8 M H₂SO₄.

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 NH₄OH 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 NH₄OH (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, ²³⁸Pu, ²³⁹Pu, and plutonium-242 ²⁴²Pu energy

regions and make background, blank, and tailing corrections as necessary.

13. Calculation

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

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

$$A_{a,i} = C_{n,i} A_t V_t / C_{n,t} V_a \quad (1)$$

C_{n, i}, C_{n, t}, t, V_a

where:

A_{a, i} = concentration of ~~plutonium-239, ²³⁹Pu, or plutonium-238~~ ²³⁸Pu in the water, Bq/L₂

N_i / C_{n, i} = net sample counts in the ~~plutonium-239~~ ²³⁹Pu or ~~plutonium-238~~ ²³⁸Pu energy region of the alpha spectrum with any necessary correction for presence of analyte in the added tracer,

A_t = the concentration of the ~~plutonium-242~~ ²³⁶Pu or ²⁴²Pu tracer, Bq/mL₂

V_t = the ~~plutonium-242~~ ²³⁶Pu or ²⁴²Pu tracer added, mL,

N_t / C_{n, t} = net sample counts in the ~~plutonium-242~~ ²³⁶Pu or ²⁴²Pu tracer energy region of the alpha spectrum, and

V_{sa} = 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:

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

$$E = R_{n,r} / A_r \quad (2)$$

A_r

where:

R_{sn, r} = net counting rate of the standard source in the energy region of the calibrated alpha emitting isotope calibrated in counts per second,

R_{αA_r} = absolute alpha particle emission rate of the calibrated alpha emitting isotope in alphas per second.

13.3 Calculate the plutonium chemical recovery as follows:

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

$$Y = (C_{n,t} / t) / A_t V_t E \quad (3)$$

where:

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

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

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

$$\sigma_{A_{a,i}} (Bq/L) = A_{a,i} (Bq/L) * [(\sigma_{n,i} / C_{n,i})^2 + (\sigma_{A_t} / A_t)^2 + (\sigma_{V_t} / V_t)^2 + (\sigma_{C_{n,t}} / C_{n,t})^2 + (\sigma_{V_a} / V_a)^2]^{1/2} \quad (4)$$

σ_{N_i / C_{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~~ ²³⁶Pu or ~~Pu-236~~ ²⁴²Pu tracer, Bq/mL,

σ_{V_t} = one sigma uncertainty in the volume of the ~~236Pu or 242Pu~~ tracer added, mL,

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

σ_{V_{sa}} = 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:

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

$$\sigma_C = (C + C_b + U_{c,t}^2)^{1/2} \quad (5)$$

C_b

where:

GC = the gross counts in the region of ~~interest and interest,~~

BC_b = the expected background counts for the same counting duration in the region of interest, and

U_{c,t} = the estimated uncertainty of the contribution of analyte contamination in the ²³⁶Pu or ²⁴²Pu tracer.

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

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

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

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 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test the following QC procedures must be followed when running the test:

14.2 *Internal Standard*—As indicated in 12.1.3 an accurately added amount of ²³⁶Pu or ²⁴²Pu is used as a tracer (for example, internal standard) in the determination of the external quality control program, ^{239/240}Pu and ²³⁸Pu in the sample. As noted in 11.1 the activity of the ²³⁶Pu or ²⁴²Pu tracer used shall submit blind quality control samples be traceable to the National Institute of Standards and Technology.

14.2.1 The yield of the ²³⁶Pu or ²⁴²Pu tracer will be calculated for each sample and associated QC sample. This yield should be reported along with the reported analytical data.

14.2.2 The 2-sigma uncertainty of the yield should be less than 10% (approximately 400 net counts).

14.3 *Detector Efficiency*—While not required to determine the ^{239/240}Pu or ²³⁸Pu activity of the sample, the detector efficiency is necessary to determine the ²³⁶Pu or ²⁴²Pu tracer chemical yield. The efficiency of each detector shall be verified monthly or prior to use, whichever is longer, using a source traceable to the National Institute for Standards and Technology.

14.4 *Initial Demonstration of Laboratory Capability:*

14.4.1 If the laboratory or analyst has not previously performed this method a precision and bias study must be performed to demonstrate laboratory capability.

14.4.2 Analyze seven replicates of a standard solution prepared from an IRM (independent reference material) containing ²³⁸Pu and/or ²³⁹Pu activities sufficient to minimize counting uncertainty to less than 2% at 2-sigma. The matrix used for the demonstration should represent a water sample typical for which the method will be used, e.g. a surface water. The total dissolved solids (TDS) of the matrix should approximate that which may be encountered in normal use. In addition ²⁴¹Am and ²²⁸Th should be included in the matrix because they can interfere in the determination of ²³⁸Pu. These two isotopes should each be included at a level of at least ten times the *a priori* MDC of the analysis.

14.4.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of precision and mean bias of 10% and ± 10%, respectively, based on a review of the collaborative study data^{7,3}. Test Method D5847 should be consulted on the manner by which usually include duplicate precision and mean bias are determined from the initial demonstration study. The study should be repeated until the precision and bias are within the given limits.

14.4.4 Analyze three replicates of a blank samples, shall test (in plutonium) solution matrix. The matrix used for the demonstration should represent a water sample collection and preparation as well as sample analysis whenever possible, typical for which the method will be used, for example, a surface water. The total dissolved solids (TDS) of the matrix should approximate that which may be encountered in normal use. In addition; ²⁴¹Am and ²²⁸Th should be included in the matrix because they can interfere in the determination of ²³⁸Pu. These two isotopes should each be included at a level of at least five times the MDC of the plutonium analyte.

² 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.

⁷ Supporting data are available from ASTM Headquarters, Request RR: D19-1063.

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

Plutonium- ²³⁸ Pu		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 Pu		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

14.4.5 Calculate the $^{239/240}\text{Pu}$ and ^{238}Pu activity for each of these three blank solutions. This study should be repeated until the $^{239/240}\text{Pu}$ and ^{238}Pu result of each of the three blank solutions is below half the associated MDC for each of the plutonium analytes.

14.5 Laboratory Control Sample (LCS) :

14.5.1 To ensure that the test method is in control, analyze an LCS with each batch of no more than 20 samples. The activity added to ~~run internal quality control~~ reagent water should be appropriate for the type of samples ~~that will indicate~~ analyzed and allow sufficient precision to ~~them whether~~ insure a meaningful assessment of accuracy. The LCS must be taken through all the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within the limit of $\pm 25\%$ of the expected value.

14.5.2 If the result is not within these limits reporting of the results is halted until the problem is resolved. An indication of the occurrence should accompany the reported results.

14.6 *Method Blank (Blank)*—Analyze a reagent water test blank with each batch of no more than 20 samples. The concentration of analytes found in ~~control~~. Both the external and internal quality control samples ~~need to blank~~ should be less than half the MDC. If the concentration of the analytes is found above this level the results must be flagged.

14.7 Matrix Spike (MS):

14.7.1 The performance of a matrix spike analysis with every batch is not required given the use of a tracer with each sample. The tracer chemical yield would indicate any problems with interferences in ~~such a way~~ specific sample matrix. 14.2.2 addresses the use of the tracer chemical yield as measure of result quality.

14.8 Duplicate:

14.8.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch of no more than 20 samples. Calculate the statistical agreement between the two results to insure they agree within a 99% confidence level. This calculation is performed using the determined uncertainty associated with each result.

14.8.2 In those cases where there is in-sufficient sample volume to allow performance of a duplicate sample analysis a duplicate LCS (LCS-D) shall be performed.

14.8.3 If the ~~routine samples~~, insofar as this result is practical. The quality control not within these limits all samples that are routinely used ~~consist~~ in the batch must be reanalyzed or the results must be flagged with an indication that they do not fall within the performance criteria of five basic types: blank samples, replicate samples, the test method.

14.9 Independent Reference Material (IRM):

14.9.1 In order to verify the quantitative value produced by the test method, analyze an IRM submitted on at least single-blind basis (if practical) to the laboratory at least once per quarter. The concentration of analyte in the NIST traceable reference materials, control samples, and “spiked” samples ~~material~~ should be appropriate to the typical purpose for which the method is used. The value obtained shall demonstrate acceptable performance as defined by the program or the outside source.

15. Precision and Bias ⁷

15.1 A limited collaborative test of this test method was conducted for the plutonium isotopes of ~~Pu-238~~ ^{238}Pu and ~~Pu-~~ ^{239}Pu .⁸ 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

⁸ 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.

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