Designation: D3865 – 09 (Reapproved 2015)

Standard Test Method for Plutonium in Water[1]

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 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 (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 ^{239}Pu from ^{240}Pu. 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
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 ^{236}Pu or ^{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. The absolute activities of ^{238}Pu 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 ^{236}Pu or ^{242}Pu 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 ^{238}Pu has been

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

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[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.

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)

[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 ^{241}Am, since they could interfere in the determination of ^{238}Pu.

found to interfere with the determination of ^{238}Pu. Some ^{228}Th 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 ^{238}Pu and the ^{228}Th may appear as one peak; the principal alpha energy of ^{238}Pu is 5.50 MeV while that of ^{228}Th is 5.42 MeV. After a period of in-growth the presence of ^{228}Th 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 ^{242}Pu, in addition to other plutonium isotopes. The tracer isotope, ^{236}Pu, 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 ^{236}Pu peak into analyte regions. For samples expected to be free of plutonium analyte isotopes ^{242}Pu 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 (NH_4OH). 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 NH_4OH 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 NH_4OH 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 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. 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.

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 solution from step 12.2.4 is drying, add 75 mL of concentrated HCl and 2 g of H_3BO_3 to the undissolved residue from step 12.2.3. 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 (8 M) 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 (8 M). 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 (8 M) to convert the resin to the nitrate form.

12.4 *Anion Exchange Separation:*

12.4.1 To the solution from the coprecipitation procedure (12.1.12) or from the acid dissolution (12.2.12) that should be about 8 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 (8 M) 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 (9 M) at a flow rate no greater than 2 mL/min.

NOTE 2—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 rate, 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 NH_4I-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 column volumes of 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 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*—See Practice C1284 for guidance on electrodeposition. Alternatively see Test Method C1163 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 $NaHSO_4 \cdot H_2O$ 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 1.5 M NH_4OH 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 hours.

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

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 (0.15 M).

12.5.12 Disassemble the cell and wash the disk with slightly basic 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 Spectrometry Analysis:*

12.6.1 Count the sample with the alpha spectrometry system. See Practice D3084 for guidance.

12.6.2 Determine the total counts in the ^{238}Pu, $^{239/240}$Pu, and ^{236}Pu or ^{242}Pu energy regions and make background, blank, and tailing corrections as necessary.

13. Calculation

13.1 Calculate the concentrations of $^{239/240}$Pu, ^{238}Pu in the aliquot of water taken for analysis as follows:

$$AC_a = \frac{C_{a,n} \times AC_t \times V_t \times DF_t}{C_{t,n} \times V_a} \quad (1)$$

where:

AC_a = activity concentration of $^{239/240}$Pu, or ^{238} Pu in the water, Bq/L,
$C_{a,n}$ = net sample counts in the $^{239/240}$Pu or ^{238}Pu energy region of the alpha spectrum with any necessary correction for presence of analyte in the added tracer,
AC_t = the activity concentration of the ^{236}Pu or ^{242}Pu tracer, Bq/mL,
V_t = the ^{236}Pu or ^{242}Pu tracer added, mL,
DF_t = decay factor for the tracer from its reference date to the midpoint of the counting period,
$C_{t,n}$ = net sample counts in the ^{236}Pu or ^{242}Pu tracer energy region of the alpha spectrum, and
V_a = the water sample taken for analysis (this does not include the volume of acid added in 10.1), L.

13.1.1 If the entire energy region for each respective plutonium isotope is not used an appropriate correction will be needed to the net count value(s) used in Eq 1.

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

$$\varepsilon = \frac{R_{r,n}}{A_r} \quad (2)$$

where:

$R_{r,n}$ = net counting rate of the standard source in the energy region of the calibrated alpha emitting isotope calibrated in counts per second,
A_r = absolute alpha particle emission rate of the calibrated alpha emitting isotope in alphas per second.

13.3 Calculate the plutonium radiochemical yield as follows:

$$RY = \frac{C_{t,n}}{AC_t \times V_t \times DF_t \times \varepsilon \times t} \quad (3)$$

where:

t = counting duration in seconds for both the sample test source and the background subtraction count (BSC).

13.4 The combined standard uncertainty (1σ) for each individual plutonium isotope concentration is calculated as follows:

$$u(AC_a) = \sqrt{\frac{u^2(C_{a,n}) \times AC_t^2 \times V_t^2 \times DF_t^2}{C_{t,n}^2 \times V_a^2} + AC_a^2 \left(\frac{u^2(C_{t,n})}{C_{t,n}^2} + \frac{u^2(AC_t)}{AC_t^2} + \frac{u^2(V_t)}{V_t^2} + \frac{u^2(V_a)}{V_a^2} \right)} \quad (4)$$

where:

$u(C_{a,n})$ = standard uncertainty of the net sample counts in the energy region of interest in the alpha spectrum,
$u(AC_t)$ = standard uncertainty of the concentration of the ^{236}Pu or ^{242}Pu tracer, Bq/mL,
$u(V_t)$ = standard uncertainty in the volume of the ^{236}Pu or ^{242}Pu tracer added, mL,
$u(C_{t,n})$ = standard uncertainty of the net sample counts in the ^{236}Pu or ^{242}Pu tracer energy region of the alpha spectrum, and
$u(V_a)$ = standard uncertainty of the volume of the water sample taken for analysis.

The standard uncertainty for the net count, $C_n = C_s - C_b$, in an analyte or and tracer energy region of interest is calculated from:

$$u(C_n) = \sqrt{C_s + C_b + 2 + u^2(C_c)} \quad (5)$$

where:

C_s = the gross counts in the region of interest for the sample count,
C_b = the background counts for the same counting duration in the region of interest, and
$u(C_c)$ = (for an analyte region of interest) the uncertainty of the counts C_c contributed by analyte contamination in the ^{236}Pu or ^{242}Pu tracer.

13.5 The critical net activity concentration is calculated as follows:

$$L_C = \frac{1.35 + 2.33\sqrt{0.34 + C_{a,b}}}{V_a \times RY \times \varepsilon \times t} \quad (6)$$

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

$$MDC\,(Bq/L) = \frac{5.41 + 4.65\sqrt{R_{a,b} \times t}}{V_a \times RY \times \varepsilon \times t} \quad (7)$$

where:

$R_{a,b}$ = background count rate in the analyte region of interest.

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. The batch size should not exceed 20 samples, not including QC samples.

14.2 *Tracer*—As indicated in 12.1.3 an accurately added amount of ^{236}Pu or ^{242}Pu is used as a tracer (for example, internal standard) in the determination of the $^{239/240}$Pu and ^{238}Pu in the sample. As noted in 11.1 the activity of the ^{236}Pu or ^{242}Pu tracer used shall be traceable to a national standards laboratory (such as NIST or NPL).

14.2.1 The radiochemical yield of the ^{236} Pu or ^{242}Pu 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 standard uncertainty of the radiochemical yield (1-sigma) should be less than 5 % (approximately 400 net counts).

14.3 *Detector Efficiency*—While not required to determine the $^{239/240}$Pu or ^{238}Pu activity of the sample, the detector

efficiency is necessary to determine the ^{236}Pu or ^{242}Pu radiochemical yield. The efficiency of each detector shall be verified monthly or prior to use, whichever is longer, using a source traceable to NIST, vendors with traceability to NIST, or other national standards laboratories.

14.4 *Initial Demonstration of Laboratory Capability:*

14.4.1 If the laboratory or analyst has not previously performed this test, or if there has been a major change in the measurement system, for example, significant instrument change, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory/instrument capability.

14.4.2 Analyze seven replicates of a standard solution prepared from an IRM (independent reference material) containing ^{238}Pu or ^{239}Pu (or both) activities sufficient to minimize the standard counting uncertainty (1-sigma) to less than 1 %. Each replicate must be taken through the complete analytical test method including any sample pretreatment steps. The matrix used for the demonstration should represent a water sample 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, ^{241}Am and ^{228}Th should be included in the matrix because they can interfere in the determination of ^{238}Pu. These two isotopes should each be included at a level of at least ten times the *a priori* MDC of the analysis. The level of tracer may also be adjusted to match the level of analyte in these samples.

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.[4] Test Method D5847 should be consulted on the manner by which precision and mean bias are determined from the initial demonstration study. The method shall not be used for official samples until precision and bias criteria are met.

14.4.4 Analyze at least seven replicates of a blank (in plutonium) solution matrix. The matrix used for the demonstration should represent a water sample 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 ^{241}Am and ^{228}Th should be included in the matrix because they can interfere in the determination of ^{238}Pu. These two isotopes should each be included at a level of at least five times the MDC of the plutonium analyte.

14.4.5 Calculate the $^{239/240}$Pu and ^{238}Pu activity for each of these seven blank solutions. This method shall not be used for official samples until the Laboratory has conducted an absolute bias t-test using results of the seven or more blank replicates. Attachment 6A (Bias-Testing Procedure) of the MARLAP[5] manual provides guidance in the performance of such a bias test.

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 reagent water should be appropriate for the type of samples analyzed and allow sufficient precision to 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 ±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 the blank should be less than half the MDC. If the concentration of the analytes is above the limit, provide an explanation in the case narrative.

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 radiochemical yield would indicate any problems with interferences in a specific sample matrix. Section 14.2.1 addresses the use of the tracer radiochemical 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 [duplicate error ratio (DER)] between the two results. This calculation is performed using the combined standard uncertainty of each result as shown below.

$$DER = \frac{|\, AC_{original} - AC_{dup} \,|}{\sqrt{u_c^2(AC_{original}) + u_c^2(AC_{dup})}} \quad (8)$$

where:

$AC_{original}$ = original sample activity concentration,
AC_{dup} = duplicate sample activity concentration,
$u_c(AC_{original})$ = combined standard uncertainty of the original sample, and
$u_c(AC_{dup})$ = combined standard uncertainty of the duplicate sample.

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) should be performed and analyzed using the same DER criteria.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1063. Contact ASTM Customer Service at service@astm.org.

[5] NUREG 1576, EPA 402-B-04-001A-C, NTIS PB2004-105421, MARLAP, Multi-Agency Radiological Laboratory Protocols Manual, Volumes 1-3, Washington, DC, July 2004. Available at www.epa.gov/ radiation/marlap/ index.html.

14.8.3 The value of DER should be less than or equal to 3.0. If the sample duplicate or LCS duplicate calculated DER value is greater than 3.0 all samples in the batch must be reanalyzed, or an explanation must be provided in a case narrative.

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 national standards laboratory traceable reference 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.

14.9.2 In the absence of other acceptance criteria for the IRM sample, compare the IRM sample result to the IRM known value as follows:

$$R = \frac{|\ IRM_{found} - IRM_{known}\ |}{\sqrt{u_c^2(IRM_{found}) + u_c^2(IRM_{known})}} \quad (9)$$

where:

R = relative difference,
IRM_{found} = found concentration of the IRM,
IRM_{known} = known concentration of the IRM,
$u_c(IRM_{found})$ = combined standard uncertainty of the IRM found concentration, and
$u_c(IRM_{known})$ = combined standard uncertainty of the IRM known concentration.

14.9.3 The value of R should be less than or equal to 3.0. If the value of R is greater than 3.0, the method should be investigated to determine the cause.

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

^{238}Pu			PRECISION (Bq/L)	
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
^{239}Pu			PRECISION (Bq/L)	
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

15. Precision and Bias[4]

15.1 A limited collaborative test of this test method was conducted for the plutonium isotopes of ^{238}Pu and ^{239}Pu.[6] 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 D2777. 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 chromotography; plutonium; water

[6] 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.