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Standard Test Method for Plutonium in Water¹

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 (0.3 pCi/L) in water by means of chemical separations and alpha pulse-height analysis (alpha-particle spectrometry). ~~The isotopes, Due to overlapping alpha-particle energies, this method cannot distinguish~~ ²³⁹Pu, ~~Pu from~~ ²⁴⁰Pu, and 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 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

C 859 Terminology Relating to Nuclear Materials

~~C 1192~~ 1163 Test Method-Practice for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride

C 1284 Practice for Electrodeposition of the Actinides for Alpha Spectrometry

D 1129 Terminology Relating to Water

D 1193 Specification for Reagent Water

D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D 3084 Practice for Alpha-Particle Spectrometry of Water

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 Practices for Sampling Water from Closed Conduits

D 5847 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 D 1129 and Terminology C 859.

4. Summary of Test Method

~~4.1 The water sample is acidified and~~

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

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

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² Annual Book of ASTM Standards, Vol 12.01.

³ 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.

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 ²⁴²Pu tracer, the absolute activities of ²³⁸Pu and ^{239/240}Pu can be 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 ²²⁸Th when present at concentrations 100 times or greater than ²³⁸Pu has been 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 the sample as determined by peaks in the alpha spectrometerspectrum 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 Pulse—Height Analysis 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 FWHM 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 peak analyte isotope should be less than ten counts in 60 000 s.

TABLE 1 Radioactive Decay Characteristics of Isotopes of Interest in the Determination of Plutonium in Water^A

Isotope	Half Life Years	Principal Alpha Energies in MeV (Abundance)
²³⁶ Pu	2.858	5.767 (69.14) 5.730 (30.70)
²³⁸ Pu	87.7	5.499 (71.4) 5.456 (28.6)
²³⁹ Pu	2.4110 × 10 ⁴	5.158 (73.3) 5.144 (15.1) 5.105 (11.5)
²⁴⁰ Pu	6563	5.168 (73.51) 5.123 (26.39)
²⁴² Pu	3.733 × 10 ⁵	4.902 (79) 4.858 (21)
²⁴¹ Am ^B	432.2	5.544 (0.36) 5.485 (85.1) 5.442 (13.3)
²²⁸ Th ^B	1.9131	5.423 (73.4) 5.340 (26.6)

^ATable of Isotopes, Eighth Edition, Vol. 11, Richard B. Firestone, Lawrence Berkeley National Laboratory, University of California, 1996.

^BThese two isotopes are listed, especially in ²⁴¹Am, since they could interfere in the determination of ²³⁹Pu.

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 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)* (approximately 15 M, 28 %)—Concentrated ammonium hydroxide (NH₄OH) (OH). 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+9)*—Mix 1 volume of concentrated NH₄OH (sp gr 0.90) with 9 volumes of water. OH 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 (1+99)*—Mix 1 volume of concentrated NH₄OH (sp gr 0.90) with 99 volumes of water. OH 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 (145 g/L) (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. —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.

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 (NH₄OH or concentrated H₂SO₄). 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.

8.11 *Ethyl Alcohol Slightly Basic Ethyl Alcohol (C₂H₅OH) (OH) 95 %*— 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)* (approximately 12 M, 36 %)—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. (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 (sp gr 1.15)* (~ 29 M, 49 %)—Concentrated hydrofluoric acid (HF).

8.16 *Hydrogen Peroxide Solution (1+2)*—Standard 30%. Commercially available reagent grade. (H₂O₂)—Standard 30 %.

8.17 *Nitric Acid (sp gr 1.42)* (~ 16 M, 69 %)—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 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)*—Mix 1 volume of concentrated nitric acid (sp gr 1.42) with 8 volumes of water. (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 ²³⁶Pu or ²⁴²Pu Solutions, Standard (Approximately 0.2 Bq/mL)—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 ²⁴²Pu tracer. Those using ²³⁶Pu should validate that such a substitution does not impact the performance of the method.

³ *Annual Book of ASTM Standards*, Vol 15.02: 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).

NOTE 1—Standard ^{236}Pu and ^{242}Pu solutions usually are available from the National Institute of Standards and Technology; dilution to the required concentration may be necessary. 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 (sp gr 1.84) (~ 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 (sp gr 1.84)* (~ 18 M, 95%)—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. (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 Note2—Warning:

9.1 **Warning:** Hydrofluoric acid is extremely hazardous. Wear rubber 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 D 3370. Preserve the sample by adjusting the acidity to pH <1 with HNO_3 (1+8) (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 the National Institute for Standards and Technology, 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 Measure a known volume approximately 1 L of the water sample to be analyzed plus the volume of acid added, if any.

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 the iron-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. (If the analyst wishes to continue immediately, the iron hydroxide may be filtered out at this time.)

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 . If organic matter is believed to be present, transfer to a TFE—fluorocarbon beaker, 250 mL being a convenient size; add 2 mL 30% H_2O_2 , 2 mL concentrated HNO_3 and heat to near dryness. Repeat as necessary. Then add 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 sample solution; 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 ~~this solution~~ from step 12.2.4 is drying, add 75 mL of concentrated HCl and 2 g of H₃BO₃ 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-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)~~(8 M) 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)~~(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 HNO₃~~(+1)~~(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 ~~7 to 9~~ about 8 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)~~(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 ~~(3+1)~~(9 M) at a flow rate no greater than 2 mL/min.

~~NOTE 3—The 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 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 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 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 1.5 M NH₄OH ~~(+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 hours.

12.5.9 When the electrodeposition is to be terminated add 1 mL of concentrated NH₄OH 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 NH₄OH ~~(+9)~~(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 Pulse-Height Analysis*—Alpha Spectrometry Analysis :

12.6.1 Count the sample with the alpha pulse-height analysis spectrometry system. See Practice D 3084 for guidance.

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

13. Calculation

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

$$A_{a,i} = C_{n,i} A_i V_i / C_{n,i} V_a \quad (1)$$

$$AC_a = C_{a,n} \times AC_i \times V_i / C_{n,i} V_a \quad (1)$$

$\times DF_{t,n} \times V_a$

where:

A_a = concentration of ^{239}Pu activity concentration of $^{239/240}\text{Pu}$, or ^{238}Pu Pu in the water, Bq/L,

C_n = net sample counts in the ^{239}Pu or ^{240}Pu or ^{238}Pu energy region of the alpha spectrum with any necessary correction for presence of analyte in the added tracer,

A_{AC} = the concentration of the activity concentration of the ^{236}Pu or ^{242}Pu tracer, Bq/mL,

V_i = the ^{236}Pu or ^{242}Pu tracer added, mL,

DF_i = decay factor for the tracer from its reference date to the midpoint of the counting period,

C_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.

13.2 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:

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:

$$E = R_{n,i} / A_i \quad (2)$$

$\epsilon = R_{r,n} / A_r$

where:

$R_{n,i}$ = 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 chemical recovery/radiochemical yield as follows:

$$Y = (C_{n,i} / t) / A_i V_i E \quad (3)$$

$$RY = \frac{C_{t,n}}{AC_i \times V_i E} \quad (3)$$

$\times DF_t \times \epsilon \times t$

where:

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

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

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

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

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

$$u(A_a) = \sqrt{\frac{u^2(C_{a,n}) \times AC_i^2 \times V_i^2 \times DF_i^2}{C_{n,i}^2 \times V_a^2} + AC_a^2 \left(\frac{u^2(C_{n,i})}{C_{n,i}^2} + \frac{u^2(AC_i)}{AC_i^2} + \frac{u^2(V_i)}{V_i^2} + u^2 \right)^{1/2}} \quad (4)$$

(Va) Va2

$u(C_{a,n})$

where:

$\sigma_{C_{n,i}}$ = one sigma standard uncertainty of the net sample counts in the energy region of interest in the alpha spectrum,

$u(C_{a,n})$