



Designation: ~~C1001-05~~ Designation: C1001 - 11

Standard Test Method for Radiochemical Determination of Plutonium in Soil by Alpha Spectroscopy¹

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1. Scope

1.1 This test method covers the determination of plutonium in soils at levels of detection dependent on count time, sample size, ~~detector efficiency, detector~~, background, and tracer yield. This test method describes one acceptable approach to the determination of plutonium in soil.

1.2 This test method is designed for 10 g of soil, previously collected and treated as described in Practices C998 and C999, but sample sizes up to 50 g may be analyzed by this test method. This test method may not be able to completely dissolve all forms of plutonium in the soil matrix.

~~1.3~~

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.4 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 hazard statements are given in Section 9.

2. Referenced Documents

~~2.1 ASTM Standards:~~ ASTM Standards:²

C859 Terminology Relating to Nuclear Materials

C998 Practice for Sampling Surface Soil for Radionuclides

C999 Practice for Soil Sample Preparation for the Determination of Radionuclides

C1163 Practice for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride

C1284 Practice for Electrodeposition of the Actinides for Alpha Spectrometry

D1193 Specification for Reagent Water

D3084 Practice for Alpha-Particle Spectrometry of Water

~~D3648 Practices for the Measurement of Radioactivity~~ Practices for the Measurement of Radioactivity

D7282 Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements

3. Summary of Test Method

3.1 Plutonium is extracted from the soil with a mixture of nitric, hydrofluoric, and hydrochloric acids in the presence of ²⁴²Pu or ²³⁶Pu isotopic tracer (See Appendix for purification and standardization of ²³⁶Pu tracer). Plutonium is isolated by anion exchange, then electrodeposited onto a polished metal disk for determination by alpha spectrometry. As an option, the plutonium may be prepared for alpha spectrometry measurement by using coprecipitation with neodymium fluoride. The range of chemical yield is between 40 and 90 %. The test method is based on a published procedure (1).³

4. Significance and Use

4.1 A soil sampling and analysis program provides a direct means of determining the concentration and distribution of radionuclides in soil. A soil analysis program has the most significance for the preoperational monitoring program to establish baseline concentrations prior to the operation of a nuclear facility. Soil analysis, although useful in special cases involving unexpected releases, is a poor technique for assessing small incremental releases and is therefore not recommended as a method

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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.

³ The boldface numbers in parentheses refer to the list of references at the end of this standard.

for routine monitoring releases of radioactive material. Nevertheless, because soil is an integrator and a reservoir of long-lived radionuclides, and serves as an intermediary in several of the plutonium pathways of potential importance to humans, knowledge of the concentration of plutonium in soil is essential.

5. Apparatus

5.1 *Electrodeposition Apparatus (2)*, see Practice C1284.

5.2 *Alpha Spectrometer*, capable of 40 to 50 keV resolution on actual samples electrodeposited on a flat, mirror-finished metal planchet, and a fractional counting efficiency greater than 17 %, and a background less than 0.010 cpm over each designated energy region. Resolution is defined as the full width half maximum (FWHM) in keV, the distance between those points on either side of the alpha peak where the count is equal to one-half the maximum count. Also see Practices D3084 and D3648.

NOTE 1—A regular program of measurement control operations should be conducted for the alpha spectrometry system, such as regular background checks, source check to determine system stability, control charting, and careful handling of samples during changing. See Practice D7282.

5.3 *PTFE-polytetrafluoroethylene beakers, 250-mL*.

6. Reagents

6.1 *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, where such specifications are available (3). Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined in Specification D1193, Type III.

6.3 Reagent blanks should be run to determine their contribution to the sample result.

6.4 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH₄OH).

6.5 *Ammonium Iodide (NH₄I) (1 M)*—Dissolve 14.5 g of NH₄I in 100 mL water.

6.6 *Ammonium Iodide, Hydrochloric Acid Solution (NH₄I-HCl)*—Add 25 mL 1 M ammonium iodide to 500 mL concentrated hydrochloric acid. Prepare fresh prior to use.

6.7 *Analytical Grade Anion Exchange Resin Type 1, 8 % cross-linked, 100 to 200 mesh, chloride form*⁴—Store the resin in water in a wash bottle, transfer sufficient resin to a 1.3-cm ID ion exchange column to give a 10-cm bed of settled resin. Convert the resin to the nitrate form by passing 100 mL of HNO₃ (8M) through the column at maximum flow rate.

6.8 *Boric Acid (H₃BO₃)*.

6.9 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

6.10 *Hydrochloric Acid (3M)*—Add 250 mL of concentrated HCl (sp gr 1.19) to 500 mL of water, mix, and dilute to 1.0 L with water.

6.11 *Hydrochloric Acid (1.7M)*—Add 142 mL of concentrated HCl (sp gr 1.19) to 500 mL of water, mix, and dilute to 1.0 L with water.

6.12 *Hydrofluoric Acid (48 to 51 %)*—Concentrated hydrofluoric acid (HF).

6.13 *Iron Carrier solution (10 g Iron (III)/L)*—Dissolve 10.0 g iron metal in HCl (1.7M) and dilute to 1 L with HCl (1.7M).

6.14 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO₃).

6.15 *Nitric Acid (8M)*—Add 500 mL of concentrated HNO₃ (sp gr 1.42) to 400 mL of water, mix, and dilute to 1.0 L with water.

6.16 *Nitric Acid (1.8M)*—Add 112 mL of concentrated HNO₃ (sp gr 1.42) to 500 mL of water, mix, and dilute to 1.0 L with water.

6.17 *Octyl alcohol*.

6.18 *Sodium Bisulfite (NaHSO₃)*.

6.19 *Sodium Hydroxide (50 %)*—Dissolve 500 g of NaOH in 500 mL water. A 50 % NaOH solution is available commercially.

6.20 *Sodium Nitrite (NaNO₂)*.

6.21 *Thymol Blue Indicator, Sodium Salt, 0.02 % Solution*.

6.22 *National Standard Traceable Plutonium-236 Reagent*. National Standard Traceable Plutonium-236 Reagent.⁴

6.23 *National Standard Traceable Plutonium-242 Reagent*. National Standard Traceable Plutonium-242 Reagent.⁴

7. Sampling

7.1 Collect the sample in accordance with Practice C998.

7.2 Prepare the sample for analysis in accordance with Practice C999.

7.3 Samples consisting of 10 to 50 g of soil can be readily analyzed by the procedure. In order to obtain more representative samples, as well as lowering the minimum detectable concentration, the analyses of large soil samples is desirable. In general, it is poor practice to use less than 10 g of sample, unless replicate analyses are performed, because of needed sensitivity to determine lower levels of activity.

⁴ Resin obtainable from BioRad Laboratories (Hercules, CA) and from Eichrom Technologies, Inc. (Darien, IL).

⁴ Plutonium-236 is available from NBL and is traceable to NIST. Plutonium-242 is available as a Standard Reference Material from the National Institute of Standards and Technology, Gaithersburg, MD 20899.

8. Calibration and Standardization

8.1 The counting efficiency of the alpha spectrometer is used to determine the minimum detectable concentration (MDC), lower limit of detection (LLD), and chemical recovery. The efficiency of the alpha spectrometer is determined as the ratio of the observed count rate to the known disintegration rate times the counting efficiency of the 2π counter. The procedure is as follows:

8.1.1 Count a ^{241}Am source traceable to a national standards organization on a 2π alpha counter. The 2π counter efficiency is determined by:

$$(1) \quad CE_{2\pi} = C_1 / (A_1)(T)(1.023)$$

where:

C_1 = net counts of the ^{241}Am source,

A_1 = certified activity of the ^{241}Am source (cps), corrected for decay,

T = duration of the count time, s, and

1.023 = backscatter factor correcting the counting efficiency of a source on platinum to that on stainless steel.

8.1.2 Electrodeposit ^{239}Pu on a polished metal disk, using the equipment and procedure listed in this method, and counting on the 2π counter. This gives the known disintegration rate, $C_{2\pi}$.

8.1.3 The counting efficiency of the alpha spectrometer is determined as follows:

$$CE = (C_s)(CE_{2\pi}) / (C_{2\pi}) \quad (2)$$

where:

C_s = net count rate of the electroplated source over the entire energy region on the alpha spectrometer (cps); the observed count rate,

$CE_{2\pi}$ = counting efficiency of the 2π counter, and

$C_{2\pi}$ = net counting rate of the same source on the 2π counter (cps).

8.2 The quantity of the tracer to be used should be in the expected range (but not less than 0.17 Bq) of the isotopic activity being determined so that the statistical uncertainty in the yield determination will not be larger than that of the nuclide being determined.

8.1 The fractional counting efficiency of the alpha spectrometer is used to determine the chemical yield. The fractional efficiency of the alpha spectrometer is determined as the ratio of the observed count rate to the known disintegration rate.

8.2 The quantity of the tracer to be used should be in the expected range (but not less than 0.17 Bq) of the isotopic activity being determined so that the statistical uncertainty in the chemical yield determination will not be larger than that of the nuclide being determined.

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9. Precautions

9.1 Adequate laboratory facilities, such as fume hoods and controlled ventilation, along with safe techniques, must be used in this procedure. Extreme care should be exercised in using hydrofluoric and other hot, concentrated acids. Use of proper gloves is recommended. Refer to the laboratory's chemical hygiene plan and other applicable guidance for handling chemical and radioactive materials and for the management of radioactive, mixed, and hazardous waste.

9.2 Hydrofluoric acid is a highly corrosive acid that can severely burn skin, eyes, and mucous membranes. Hydrofluoric acid is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid. Hydrofluoric acid differs from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers. Unlike other acids that are rapidly neutralized, hydrofluoric acid reactions with tissue may continue for days if left unattended. Due to the serious consequences of hydrofluoric acid burns, prevention of exposure or injury of personnel is the primary goal. Utilization of appropriate laboratory controls (hoods) and wearing adequate personal protective equipment to protect from skin and eye contact is essential.

10. Procedure

10.1 Weigh a $10.0 \pm 0.010.1$ g soil aliquot into a 250 mL PTFE beaker.

10.2 Wet sample with distilled water and add a known quantity of ^{236}Pu or ^{242}Pu tracer.

10.3 Add concentrated HNO_3 (sp gr 1.42) a few drops at a time as fast as the frothing and vigor of the reaction will permit until the entire sample is covered.

10.4 Add 60 mL more of the concentrated HNO_3 (sp gr 1.42) and 30 mL of concentrated HF (48 to 51 %) and digest on a hotplate with frequent stirring (TFE fluorocarbon stirring rod) for about 1 h (Note 2 and Note 3).

NOTE 2—For organic soils, first add the nitric acid only in small portions while stirring. If the solution threatens to overflow as a result of froth generation, add a few drops of octyl alcohol and stir. Digest on a hotplate until the evolution of reddish-brown fumes is reduced to a barely visible level. Cool to room temperature before carefully adding the concentrated hydrofluoric acid (48 to 51 %) and digesting for an hour.

NOTE 3—For larger soil aliquots, larger amounts of the acids (in the same proportions) should be used. For example, for a 50 g sample, use 200 mL concentrated HNO_3 and 100 mL HF, etc., with appropriately sized containers.

10.5 Remove from the hotplate and cool somewhat before adding 30 mL concentrated HNO_3 (sp gr 1.42) and 30 mL concentrated HF (48 to 51 %). Digest on the hotplate with intermittent stirring for an additional 1 h.

10.6 Remove from the hotplate and cool. Carefully add 20 mL concentrated HCl (sp gr 1.19) and stir. Heat on hotplate for 45 min with occasional stirring.

10.7 Add about 5 g of powdered boric acid and digest for an additional 15 min with occasional stirring.

10.8 Add approximately 200 mg of sodium bisulfite and continue heating until the solution has evaporated to a liquid volume of approximately 20 mL.

10.9 Add 50 mL of water and digest on a hotplate while stirring for 10 min to dissolve soluble salts.

10.10 Cool and transfer approximately equal parts of the total sample into centrifuge bottles with a minimum of water from a wash bottle. If equipment for large volume centrifugation is not available, the two precipitations in 10.11-10.21 may be performed in a beaker, allowing the precipitate to settle, decanting the supernate, and then completing the separation by centrifugation on a smaller scale.

10.11 Add 1.0 mL of iron carrier solution (10 mg Fe (III)/mL) to each centrifuge bottle and mix (Note 4).

NOTE 4—It may not be necessary to add the iron carrier if a sufficient amount of iron is present in the soil.

10.12 Add NaOH (50 %) with mixing to each bottle to a pH of about 9 (using pH paper) to precipitate ferric hydroxide. Add 5 to 10 mL excess NaOH and mix for 1 min.

10.13 Centrifuge for approximately 5 min, decant, and discard the supernate.

10.14 Dissolve each precipitate with about 30 mL HNO₃ (8M) (60 mL total) saturated with boric acid. (Approximately 7 g of boric acid/30 mL HNO₃ (8M).) Digest in a hot water bath for 10 min.

10.15 Cool and centrifuge for approximately 5 min. Decant the supernate into the original 250 mL PTFE beaker and save.

10.16 Wash each residue with approximately 10 to 20 mL (20 to 40 mL total) of HNO₃ (8M) saturated with boric acid. Centrifuge for 5 min and combine the supernates with that in 10.15. Discard the undigested soil.

10.17 Heat the supernate on a hotplate and evaporate to approximately 5 mL.

10.18 Add approximately 30 mL water and heat to dissolve the salts. Cool and transfer into a centrifuge tube.

10.19 Add concentrated ammonium hydroxide dropwise with mixing to a pH of approximately 9 (using pH paper) to precipitate ferric hydroxide.

10.20 Centrifuge and discard the supernate.

10.21 Dissolve the precipitate with a volume of concentrated nitric acid approximately equal to the volume of the precipitate and transfer using nitric acid (8M) into a 250-mL beaker. Add nitric acid (8M) to a total volume of approximately 75 mL. If the volume of the hydroxide precipitate is considerably greater than should be expected from the 10 mg of Fe(III) added, the final volume should be brought up to approximately 100 mL with nitric acid (8M) or, alternatively, the dissolved hydroxides should be evaporated to salts before the addition of the nitric acid (8M) solution. The final nitric acid molarity of the solution is not extremely critical, but should be in the range of 7 to 9.

10.22 Add approximately 200 mg of sodium nitrite crystals and stir with a stirring rod. Bring to a quick gentle boil on a hotplate and cool. Avoid prolonged heating.

10.23 Prepare an anion-exchange column as described in 6.7.

10.24 Pass the sample (at maximum flow rate) through the anion-exchange resin column.

10.25 When the solution just drains to the top of the resin bed, wash the column with six column volumes of HNO₃ (8M). A column volume is approximately 9.5 mL.

10.26 Wash the resin column with six column volumes of concentrated HCl.

10.27 Elute the plutonium with four column volumes of freshly prepared NH₄I-HCl solution, and collect in a 150-mL beaker.

10.28 Evaporate the solution to approximately 5 mL on a hotplate. Rinse down the sides of the beaker dropwise with 1 to 2 mL of concentrated HNO₃. Add six drops of concentrated HCl and evaporate to near dryness.

10.29 Add 50 mL of HNO₃(8M) and repeat steps 10.22-10.27, using a fresh anion-exchange resin column.

10.30 Continue heating the final plutonium elution just to dryness on the hotplate. Rinse down the sides of the beaker with a few mL of concentrated HCl, and evaporate to approximately 0.5 mL. See Note 5. Assemble the electrodeposition cell as described in Practice C1284.

NOTE 5—Plutonium can also be prepared for alpha spectrometry by coprecipitation with neodymium fluoride, see ~~Test Method~~ Practice C1163. If samples are determined by coprecipitation, then the counting standards must be prepared in a similar manner.

10.31 Add 1.5 to 2 mL of HCl (3M) solution into the beaker, rinse as above, and add the rinses to the plating cell.

10.32 Add ~~three~~ drops of thymol blue indicator solution and then add concentrated NH₄OH dropwise until the color changes to yellow.

10.33 Add HCl (1.7M) dropwise to a salmon pink endpoint.

10.34 Electroplate at 1.5 amps for 20 min. See Note 6.

NOTE 6—**Caution:** The electrodeposition should be performed in a fume hood due to the chlorine gas evolved during the electrodeposition.

10.35 At the end of 20 min, quickly add 2 to 3 mL of concentrated NH₄OH and leave the current on for another 20 s.

10.36 Turn off the current, rinse out the solution into a beaker with water, and dismantle the cell. Rinse the disk with water and dry it in a clean planchet on a hotplate at medium heat for 5 min, or flame with a burner.

10.37 Count the sample in an alpha spectrometer long enough to obtain the desired sensitivity (see Table 1).