



Designation: C 1001 – 00

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

This standard is issued under the fixed designation C 1001; 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 plutonium in soils at levels of detection dependent on count time, sample size, detector efficiency, 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 C 998 and C 999, 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 *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 Sections 6 and 9.

2. Referenced Documents

2.1 ASTM Standards:

C 998 Practice for Sampling Surface Soil for Radionuclides²

C 999 Practice for Soil Sample Preparation for the Determination of Radionuclides²

C 1163 Test Method for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride²

D 1193 Specification for Reagent Water³

D 3084 Practice for Alpha-Particle Spectrometry of Water⁴

IEEE/ASTM SI-10 Standard for the Use of the International System of Units (SI): The Modern Metric System⁵

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).⁶

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 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).*

5.2 *Alpha Spectrometer*, capable of 40 to 50 keV resolution on actual samples electrodeposited on a flat, mirror-finished metal planchet, and a 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.

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

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

¹ This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Test Methods.

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² *Annual Book of ASTM Standards*, Vol 12.01.

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

⁴ *Annual Book of ASTM Standards*, Vol 11.02.

⁵ *Annual Book of ASTM Standards*, Vol 14.04.

⁶ The boldface numbers in parentheses refer to the list of references at the end of this test method.

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 D 1193, 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.

NOTE 2—**Caution:** Prepare fresh prior to use.

6.7 *Analytical Grade Anion Exchange Resin* (AG) 1-X8 (100 to 200 mesh, nitrate form)⁷—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)—Mix 1 volume of concentrated HCl (sp gr 1.19) with 3 volumes of water.

6.11 *Hydrochloric Acid* (1.7M)—Mix 1 volume of concentrated HCl (sp gr 1.19) with 6 volumes of 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)—Mix 1 volume of concentrated HNO₃ (sp gr 1.42) with 1 volume of water.

6.16 *Nitric Acid* (1.8M)—Mix 1 volume of concentrated HNO₃ (sp gr 1.42) with 8 volumes of 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 *Plutonium-236 Reagent*.

6.23 *Plutonium-242 Reagent*.⁸

7. Sampling

7.1 Collect the sample in accordance with Practice C 998.

7.2 Prepare the sample for analysis in accordance with Practice C 999.

7.3 Samples consisting of 10 to 50 g of soil can be readily analyzed by the procedure. The analysis of large soil aliquots is desirable because of more representative samples, as well as lowering the minimum detectable concentration. 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.

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 NIST-certified ²⁴¹Am source on a 2π alpha counter. The 2π counter efficiency is determined by:

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

where:

C_1 = net counts of the ²⁴¹Am source,

A_1 = certified activity of the ²⁴¹Am 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 ²³⁹Pu 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.

⁷ Resin obtainable from Bio-Rad Laboratories, or its equivalent, has been found satisfactory for this purpose.

⁸ Plutonium-242 is available as a Standard Reference Material from the National Institute of Standards and Technology, Gaithersburg, MD 20899.

9. Procedure

9.1 Weigh a 10 ± 0.01 g soil aliquot into a 250 mL PTFE beaker.

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

9.3 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.

9.4 Add 60 mL 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 4 and Note 5).

NOTE 3—Precaution: 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 rubber gloves is recommended.

NOTE 4—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 hydrochloric acid (sp gr 1.19) and digesting for an hour.

NOTE 5—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.

9.5 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.

9.6 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.

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

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

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

9.10 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 9.11-9.21 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.

9.11 Add mL of iron carrier solution (10 mg Fe (III)/mL) to each centrifuge bottle and stir (Note 6).

NOTE 6—It may not be necessary to add the iron carrier if a sufficient amount of iron is present in the soil.

9.12 Add NaOH (50 %) with stirring to each bottle to a pH of about 9 (using pH paper). Add 5 to 10 mL excess NaOH and stir for 1 min.

9.13 Centrifuge for approximately 5 min, decant, and discard the supernate(s).

9.14 Dissolve each precipitate with about 30 mL HNO_3 (8M) (60 mL total) saturated with boric acid. (Approximately 7 g of boric acid/30 mL HNO_3 (8M).) Digest in a hot water bath for 10 min.

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

9.16 Wash each residue with approximately 10 to 20 mL (20 to 40 mL total) of HNO_3 (8M) saturated with boric acid. Centrifuge for 5 min and combine the supernates with those in 9.15.

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

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

9.19 Add concentrated ammonium hydroxide dropwise with stirring to a pH of approximately 9 (using pH paper).

9.20 Centrifuge and discard the supernate.

9.21 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 molarity of the solution is not extremely critical, but should be in the range of 7 to 9.

9.22 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.

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

9.24 Pass the sample (at maximum flow rate) through an anion-exchange resin column (nitrate form).

9.25 When the solution just drains to the top of the resin bed, wash the column with six column volumes of HNO_3 (8M). A column volume is approximately 9.5 mL.

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

9.27 Elute the plutonium with four column volumes of freshly prepared $\text{NH}_4\text{I-HCl}$ solution, and collect in a 150-mL beaker.

9.28 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 HNO_3 . Add six drops of concentrated HCl and evaporate to near dryness.

9.29 Add 50 mL of HNO_3 (8M) and repeat steps 9.22-9.27, using a fresh anion-exchange resin column.

9.30 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.

NOTE 7—Plutonium can also be prepared for alpha spectrometry by coprecipitation with neodymium fluoride, see C 1163.

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