



# Standard Test Method for Radiochemical Determination of Uranium Isotopes in Soil by Alpha Spectrometry<sup>1</sup>

This standard is issued under the fixed designation C 1000; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the determination of uranium isotopes in soil. This test method describes one acceptable approach to the determination of uranium isotopes in soil.<sup>2</sup>

1.2 The test method is designed to analyze 10 g of soil; however, the sample size may be varied to 50 g depending on the activity level. This test method may not be able to completely dissolve all forms of uranium in the soil matrix.

1.3 The lower limit of detection is dependent on count time, sample size, detector efficiency, background, and tracer yield. The chemical recovery averaged 78 % in a single laboratory evaluation, and 66 % in an interlaboratory collaborative study.

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.* A specific precautionary statement is given in Section 10.

## 2. Referenced Documents

### 2.1 ASTM Standards:

C 998 Practice for Sampling Surface Soil for Radionuclides<sup>3</sup>

C 999 Practice for Soil Sample Preparation for the Determination of Radionuclides<sup>3</sup>

C 1163 Test Method for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride<sup>3</sup>

D 1193 Specification for Reagent Water<sup>4</sup>

D 3084 Practice for Alpha-Particle Spectrometry of Water<sup>5</sup>

D 3648 Practices for the Measurement of Radioactivity<sup>5</sup>

IEEE/ASTM SI-10 Standard for the Use of the International System of Units (SI): The Modern Metric System<sup>6</sup>

## 3. Summary of Test Method

3.1 A soil sample with uranium-232 tracer added is heated to destroy organic matter and dissolved with a mixture of hydrofluoric acid and nitric acid. The uranium is coprecipitated with ferric hydroxide and the precipitate is dissolved with hydrochloric acid. Iron is removed by extraction with isopropyl ether, and plutonium, radium, and thorium are separated from uranium by anion exchange. Uranium is electrodeposited on a stainless steel disk and determined by alpha spectrometry. As an option, the uranium may be prepared for alpha spectrometric measurement by using coprecipitation with neodymium fluoride.

## 4. Significance and Use

4.1 This test method is used to analyze soil for uranium isotopes. It can be used to establish baseline uranium levels and to monitor depositions from nuclear facilities.

## 5. Interferences

5.1 Protactinium-231 may not be completely separated by the procedure and could interfere with the determination of uranium-233 or uranium-234 because it has the following alpha energies in MeV: 5.06, 5.03, 5.01, 4.95 and 4.73 (see Appendix).

## 6. Apparatus

### 6.1 Alpha Pulse Height Analysis System:<sup>2</sup>

6.1.1 A system consisting of a charged particle detector capable of 50 keV or less resolution on samples electrodeposited on a flat mirror-finished stainless steel disk is required.

6.1.2 The resolution is defined as the width of an alpha peak when the counts on either side of the peak are equal to one-half of the counts at the maximum of the peak (full width at half maximum height (FWHM)).

6.1.3 The counting efficiency of the system should be greater than 15 % and the background in the energy region of each peak should be less than 10 counts in 1,000 min.

6.1.4 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.

### 6.2 Electrodeposition Apparatus<sup>2</sup>—A direct current power

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<sup>2</sup> Casella, V. A., Bishop, C. T., and Glosby, A. A., "Radiometric Method for the Determination of Uranium in Soil and Air," U.S. Environmental Protection Agency, EPA-600/7-80-019, Las Vegas, NV, February 1980.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 12.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 11.02.

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 14.04.

supply, 0 to 12 V and 0 to 2 A is required. A disposable electrodeposition cell is recommended. The cathode is a 20-mm diameter stainless steel disk polished to a mirror finish and the anode is a 1-mm diameter platinum wire with an 8-mm diameter loop facing the cathode.

6.3 *Beakers and Covers* (TFE-fluorocarbon), 250 mL.

6.4 *Casserole* (porcelain), 60 mL.

6.5 *Centrifuge and Bottles*, 250-mL capacity.

6.6 *Ion Exchange Columns*, 1.3 cm inside diameter by 15 cm long with 100 mL reservoir.

6.7 *Automatic Pipettes*, 0.1 to 1.0 mL with disposable tips.

## 7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>7</sup> 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.

7.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean reagent water as defined in Specification D 1193, Type III.

7.3 Reagent purity shall be such that the measured radioactivity of blank samples does not exceed the calculated probable error of measurement.

7.4 *Ammonium Hydroxide* (0.15 M)—Mix 10 mL of concentrated ammonium hydroxide with water and dilute to 1 L.

7.5 *Ammonium Hydroxide* (sp gr 0.90)—Carbonate-free, concentrated ammonium hydroxide (NH<sub>4</sub>OH).

7.6 *Ammonium Sulfate Solution* (1 M)—Dissolve 132 g of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in water and dilute to 1 L.

7.7 *Anion Exchange Resin*—Bio Rad AG1-X8, 100 to 200 mesh, chloride form or equivalent. Prepare a resin slurry by soaking the resin in 8M HCl and transfer the slurry to an ion exchange column so that the resin column is approximately 10 cm high.

7.8 *Electrolyte*—Adjust the pH of 1 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution to 3.5 with concentrated H<sub>2</sub>SO<sub>4</sub> and concentrated NH<sub>4</sub>OH.

7.9 *Ethyl Alcohol Solution, basic*— Add 2 drops of 15 M NH<sub>4</sub>OH to 100 mL of 95 % alcohol.

7.10 *Ferric Chloride Solution* (0.18 M in 0.5 M HCl)—Dissolve 46 g of FeCl<sub>3</sub> · 6H<sub>2</sub>O in 0.5 M HCl and dilute to 1 L.

7.11 *Hydriodic Acid* (48 %)—Concentrated hydriodic acid (HI).

7.12 *Hydrochloric Acid* (0.5 M)—Mix 42 mL of concentrated HCl with water and dilute to 1 L.

7.13 *Hydrochloric Acid* (1 M)—Mix 83 mL of concentrated HCl with water and dilute to 1 L.

7.14 *Hydrochloric Acid* (6 M)—Mix 500 mL of concentrated HCl with water and dilute to 1 L.

7.15 *Hydrochloric Acid* (8 M)—Mix 667 mL of concentrated HCl with water and dilute to 1 L.

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

7.17 *Hydrochloric Acid-Hydriodic Acid Solution* (HCl-HI)—Mix 1 mL of concentrated HI with 50 mL of 6 M HCl. Prepare immediately before use.

7.18 *Hydrofluoric Acid* (48 %)—Concentrated hydrofluoric acid (HF).

7.19 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO<sub>3</sub>).

7.20 *Sodium Hydrogen Sulfate* (0.36 M in 1 M H<sub>2</sub>SO<sub>4</sub>)—Dissolve 10 g of NaHSO<sub>4</sub> · H<sub>2</sub>O in 88 mL of water and add 112 mL of 1.8 M H<sub>2</sub>SO<sub>4</sub>.

7.21 *Sulfuric Acid* (1.8 M)—Mix 100 mL of concentrated sulfuric acid with water and dilute to 1 L.

7.22 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).

7.23 *Thymol Blue Indicator, Sodium Salt Solution* (0.04 %).

7.24 *Uranium-232, Standard Solution*.<sup>8</sup>

7.25 *Boric Acid*.

## 8. Sampling

8.1 Collect the sample in accordance with Practice C 998.

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

## 9. Calibration and Standardization

9.1 If a standard uranium-232 solution is not available for use as a tracer, standardize a freshly prepared sample of uranium-232; for guidance refer to Practices D 3648. This standard may also be used to establish the counting efficiency of the alpha spectrometer which then can be used to calculate the chemical recovery and lower limit of detection (LLD) of the test method.

## 10. Procedure

NOTE 1—**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.

### 10.1 Acid Dissolution:

10.1.1 Weigh a 10 ± 0.01 g soil sample into a casserole.

10.1.2 Add an appropriate amount of uranium-232 tracer to the sample. (If the activity of the sample is expected to be less than 0.01 Bq/g or is unknown, add 0.1 Bq of tracer. For higher levels add uranium-232 tracer which is equivalent to the estimated activity of uranium in the sample.)

10.1.3 Heat the casserole containing the soil sample at 600°C for 4 h, remove, and cool.

10.1.4 Transfer the sample to a 250-mL TFE-fluorocarbon beaker and rinse the casserole several times with concentrated HNO<sub>3</sub> until the final volume is 60 mL.

10.1.5 Add 30 mL of 48 % HF to the beaker and cover with a TFE-fluorocarbon watchglass. Heat the sample for one hour and stir frequently with a TFE-fluorocarbon stirring rod during the heating. Cool the solution.

<sup>7</sup> "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

<sup>8</sup> Uranium-232 is available from the National Institute of Standards and Technology, Gaithersburg, MD 20899, as a Standard Reference Material.

10.1.6 Add 30 mL each of concentrated HNO<sub>3</sub> and 48 % HF and digest with some stirring for an additional hour.

10.1.7 Add 20 mL of concentrated HCl and heat. Occasionally stir the solution.

10.1.8 Evaporate the solution to approximately 20 mL. Cool the solution.

10.1.9 Add 50 mL of water and boric acid to the solution and heat while stirring for 10 min to dissolve the soluble salts.

10.1.10 Cool and transfer the sample solution to a 250-mL centrifuge bottle and wash the beaker with a minimum amount of water.

10.1.11 Centrifuge and transfer the supernate to a 250-mL centrifuge bottle. Wash the residue with 10 mL of 1 M HCl and add the washing to the supernate.

#### 10.2 Co-Precipitation:

10.2.1 Add 2 mL of 0.18 M ferric chloride solution to the centrifuge bottle and stir. It may not be necessary to add the iron carrier if a sufficient amount of iron is present in the soil.

10.2.2 Add carbonate-free concentrated NH<sub>4</sub>OH to the sample solution while stirring to precipitate the iron and until the pH reaches 9 to 10.

10.2.3 Add 5 mL of concentrated NH<sub>4</sub>OH in excess.

10.2.4 Centrifuge the sample for 5 min, discard the supernate. Dissolve the precipitate with a minimum addition of concentrated HCl and bring the volume to 50 mL with 8 M HCl.

10.2.5 Transfer the sample to a 250-mL separatory funnel and rinse the centrifuge bottle with two 5 mL rinses of 8 M HCl.

#### 10.3 Ether Extraction:

10.3.1 Add 60 mL of isopropyl ether to the funnel, stopper, and shake for 2 min. Allow the phases to separate and drain the aqueous phase into a second separatory funnel.

10.3.2 Add 5 mL of concentrated HCl to the second funnel and mix. Add 60 mL of isopropyl ether and repeat the extraction twice to remove iron. (Additional extractions may be necessary if the third extract is yellow, indicating incomplete removal of the iron).

10.3.3 Transfer the aqueous phase to a 150-mL beaker and boil the solution for 15 min.

#### 10.4 Anion Exchange Separation:

10.4.1 Condition the anion exchange column (7.7) by rinsing with four column volumes of 8 M HCl.

10.4.2 Transfer the sample to the anion exchange column and pass the sample through the column at a rate of 2 mL per min.

10.4.3 Wash the column with six column volumes of 6 M HCl containing 1 mL of concentrated HI per 50 mL of 6 M HCl, prepared immediately before use, to remove iron and plutonium.

10.4.4 Wash the column with two column volumes of 6 M HCl.

10.4.5 Elute the uranium with six column volumes of 1 M HCl and collect in a 150-mL beaker.

10.4.6 Evaporate the sample to 20 mL and add 5 mL of concentrated HNO<sub>3</sub>. Evaporate the sample to near dryness.

#### 10.5 Electrodeposition:

NOTE 2—Uranium can also be prepared for alpha spectrometry by

coprecipitation with neodymium fluoride, see C 1163.

10.5.1 Add 2 mL of 0.36 M NaHSO<sub>4</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> to sample and then add 5 mL of concentrated HNO<sub>3</sub>. Mix and evaporate just to dryness but do not bake.

10.5.2 Dissolve the residue in 5 mL of electrolyte solution and warm the solution.

10.5.3 Transfer the sample to the electrodeposition cell. Rinse the beaker with 5 to 10 mL of electrolyte.

10.5.4 Add 3 to 4 drops of thymol blue indicator to the sample and adjust the pH with 1.8 M H<sub>2</sub>SO<sub>4</sub> or concentrated NH<sub>4</sub>OH, or both, until a salmon pink color is obtained.

10.5.5 Place the platinum anode into the solution so that it is 1 cm above the stainless steel slide cathode.

10.5.6 Turn the current on and adjust to 1.2 amps. Electrodeposit for 1 h.

10.5.7 After 1 h, add 1 mL of concentrated NH<sub>4</sub>OH and continue electrodeposition for 1 min.

10.5.8 Remove the anode from the cell and turn off the power. Discard the solution in the cell and rinse the cell 3 times with 0.15 M NH<sub>4</sub>OH.

10.5.9 Disassemble the cell and wash the slide with the basic ethyl alcohol solution. Touch the edge of the slide with a tissue to absorb the excess alcohol and dry the slide. Count the sample within 1 week or sooner to prevent interferences from uranium-232 daughters.

#### 10.6 Alpha Pulse Height Analysis:

10.6.1 Count the sample on an alpha spectrometer for 1,000 min or longer to resolve the uranium isotopes.<sup>2</sup>

10.6.2 Determine the background and reagent blank activities and correct the count for each peak.

## 11. Calculation

11.1 The activity of each uranium isotope is calculated as follows:

$$X_i = (C_i A_i) / (C_t W_s) \quad (1)$$

where:

$X_i$  = concentration of a uranium isotope in Bq/g,

$A_i$  = activity of the internal standard added in Bq,

$C_i$  = net sample counts in the energy region of the uranium isotope being measured,

$C_t$  = net sample counts in the energy region of the uranium-232 tracer, and

$W_s$  = the sample weight in g.

11.2 The absolute counting efficiency of the alpha spectrometer,  $E$ , must be determined if it is desired to calculate the uranium recovery and lower limit of detection (LLD). Calculate the fractional efficiency as follows:

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

where:

$R_s$  = net counting rate of the standard source in the region of the alpha emitter of interest in cps, and

$R_\alpha$  = absolute alpha particle emission rate of the standard source in Bq.

11.3 Calculate the fractional uranium recovery as follows:

$$Y = (C_i) / (TA_i E) \quad (3)$$

**TABLE 1 Summary of Uranium Results**

Isotope	Reference Value (Bq/g)	Number of Laboratories	$\bar{X}$	Percent Relative Standard Deviation	
				Within Laboratory	Between Laboratories
<sup>238</sup> U	0.0035 ± 0.0005	4	0.0032	26.3	33.0
	0.032 ± 0.001	7	0.031	8.9	...
	0.378 ± 0.027	5	0.36	8.8	4.6
	0.342 ± 0.0038	3	0.35	4.8	1.0
<sup>234</sup> U	0.004 ± 0.0007	4	0.0042	44.0	64.0
	0.046 ± 0.0013	7	0.0447	10.0	2.6
	0.342 ± 0.0038	3	0.344	4.5	...
	0.730 ± 0.0057	5	0.632	16.0	9.8
<sup>235</sup> U	0.0016 ± 0.0001	5	0.0015	11.0	16.0
	0.0148 ± 0.0003	2	0.017	6.0	37.0
	0.0317 ± 0.0012	4	0.028	16.0	21.0
<sup>236</sup> U	0.022 ± 0.0005	5	0.022	12.0	...

where:

$T$  = counting time in s,

$C_i$  = the net sample counts in the energy region of the uranium-232 tracer,

$A_i$  = activity of the internal standard added in Bq, and

$E$  = absolute counting efficiency of the alpha spectrometer.

11.4 The lower limit of detection (LLD) in Bq is calculated as follows:<sup>9</sup>

$$LLD_{95} = \frac{2.71 + 4.66(C_b/T_b)^{1/2}}{E} \quad (4)$$

where:

$C_b$  = counter and reagent background in cps, in the region of interest,

$T_b$  = background counting time in s, and

$E$  = absolute counting efficiency of the alpha spectrometer.

## 12. Precision and Bias

12.1 *Precision*—Reference samples were sent to fourteen laboratories. Analytical data on some or all of the samples was returned by eight of the laboratories.<sup>2</sup> It is not known if these eight laboratories are typical of the laboratories that will use this test method. Table 1 summarizes the results from these laboratories.

12.2 *Bias*—There is no indication of bias over the samples. In all cases except one (<sup>235</sup>U in Samples 2 and 3), the computed  $\bar{X}$  was within the two standard deviation limits on the reference value. For the Sample 3 cases, the uncertainty on the computed  $\bar{X}$  was so large, the reference value was covered.

## 13. Keywords

13.1 alpha spectrometry; radiochemistry; soil; uranium

<sup>9</sup> Available from "Upgrading Environmental Radiation Data," U.S. Environmental Protection Agency, EPA 520/1-80-012, August 1980.

## APPENDIX

### (Nonmandatory Information)


#### X1. ENVIRONMENTAL SAMPLES

X1.1 See Table X1.1

**TABLE X1.1 Properties of Uranium Isotopes of Interest in Environmental Samples<sup>A</sup>**

Isotope	Half-Life (years)	Alpha Energies, MeV (abundance)
<sup>232</sup> U	68.9	5.320 (68.6 %), 5.263 (31.2 %)
<sup>233</sup> U	1.592 × 10 <sup>5</sup>	4.825 (84.4 %), 4.783 (13.2 %)
<sup>234</sup> U	2.454 × 10 <sup>5</sup>	4.776 (72.5 %), 4.723 (27.5 %)
<sup>235</sup> U	7.037 × 10 <sup>8</sup>	4.395 (85 %), 4.370 (6 %), 4.597, (5 %)
<sup>236</sup> U	2.342 × 10 <sup>7</sup>	4.494 (74 %), 4.445 (26 %)
<sup>238</sup> U	4.468 × 10 <sup>9</sup>	4.196 (77 %), 4.147 (23 %)

<sup>A</sup>Available from Browne, E. and Firestone, R. B., *Table of Radioactive Isotopes*, (Shirley, V. S., Ed.), John Wiley and Sons, Inc., 1986.

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