



Standard Test Method for Analysis of Total and Isotopic Uranium and Total Thorium in Soils by Inductively Coupled Plasma-Mass Spectrometry¹

This standard is issued under the fixed designation C 1345; 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 measurement of total uranium (U) and thorium (Th) concentrations in soils, as well as the determination of the isotopic weight percentages of ²³⁴U, ²³⁵U, ²³⁶U, and ²³⁸U, thereby allowing for the calculation of individual isotopic uranium activity or total uranium activity. This inductively coupled plasma-mass spectroscopy (ICP-MS) method is intended as an alternative analysis to methods such as alpha spectroscopy or thermal ionization mass spectroscopy (TIMS). Also, while this test method covers only those isotopes listed above, the instrumental technique may be expanded to cover other long-lived radioisotopes since the preparation technique includes the preconcentration of the actinide series of elements. The resultant sample volume can be further reduced for introduction into the ICP-MS via an electrothermal vaporization (ETV) unit or other sample introduction device, even though the standard peristaltic pump introduction is applied for this test method. The sample preparation removes organics and silica from the soil by use of a high temperature furnace and hydrofluoric acid digestion. Thus, this test method can allow for sample variability of both organic and silica content. This test method is also described in ASTM STP 1291.

1.2 The analysis is performed after an initial drying and grinding sample preparation process, and the results are reported on a dry weight basis. The sample preparation technique used incorporates into the sample any rocks and organic material present in the soil. The method of sample preparation applied differs from other techniques, such as those found in Practice C 999, which involve simply tumbling and sieving the sample; however, the user may select whichever technique is most appropriate to their needs.

1.3 A linear calibration is performed for total uranium and thorium over a concentration range from 5 to 5000 µg/L, using approximately 6 points. As with the data presented, it is suggested that the increments between points be less than or equal to a factor of ten. With a sample dilution factor of 200 resulting from the preparation, this equates to a concentration range in the samples from 1 to 1000 µg/g. For those samples

estimated to be above that range by initial activity screening, a smaller aliquot is taken to a dilution of 1000, thereby extending the range to 5000 µg/g. It is important to note that the concentration measured directly from this calibration is the concentration of ²³⁸U. The standard values are adjusted for abundance and the abundances in the instrument database are modified to eliminate any automatic correction, as discussed further in the appropriate sections. The calibration range can be changed based on the needs of the user and the expected variation among samples.

1.4 Corrections to the measured isotopic ratios for mass bias effects are made by determining and applying a mass bias factor (see 13.3.1). This can be performed for each batch analyzed. Refer to Appendix X1 for an optional correction approach where this factor is determined and applied less frequently and a calibration correction of measured versus certified ratios is determined on a batch basis in the range of the samples analyzed.

1.5 The values stated in µg/g, µg/L or ng/g concentration, and Becquerel per gram (Bq/g) activity are the acceptable SI units. However, picocurie per gram (pCi/g) is frequently used in radiochemistry and established regulatory guidelines and will, therefore, also be regarded as standard in this test method.

1.6 Many of the quality control (QC) practices or checks in this test method (such as the QC standards used, their frequency and general sequence) reflect the guidelines set forth in EPA Method 6020 in SW-846. EPA Method 6020 is not strictly followed, however, because of the fact that it does not cover uranium and thorium analysis, or radioisotopic determinations. The quality control practices and checks used is subject to the discretion of the laboratory or user, and EPA Method 6020 should be referred to as a guideline.

1.7 *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.*

2. Referenced Documents

2.1 ASTM Standards:

C 859 Terminology Relating to Nuclear Materials²

¹ This test method is under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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² Annual Book of ASTM Standards, Vol 12.01.

- C 998 Practice for Sampling Surface Soil for Radionuclides²
- C 999 Practice for Soil Sample Preparation for the Determination of Radionuclides²
- C 1255 Test Method for Analysis of Uranium and Thorium in Soils by Energy Dispersive X-Ray Fluorescence Spectroscopy²
- D 420 Guide to Site Characterization for Engineering, Design, and Construction Purposes³
- D 1193 Specification for Reagent Water⁴
- D 1452 Practice for Soil Investigation and Sampling by Auger Borings³
- D 1586 Test Method for Penetration Test and Split-Barrel Sampling of Soils³
- D 1587 Practice for Thin-Walled Tube Geotechnical Sampling of Soils³
- D 2113 Practice for Diamond Core Drilling for Site Investigation³
- D 2216 Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock³
- D 3550 Practice for Ring-Lined Barrel Sampling of Soils³
- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials⁵
- E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves⁵
- E 456 Terminology Relating to Quality and Statistics⁶
- E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data⁷
- E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory⁷
- STP 1291 “Applications of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to Radionuclide Determinations”

2.2 U.S. EPA Standard:

Method 6020, SW-846, Inductively Coupled Plasma-Mass Spectrometry⁸

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms relating to analytical atomic spectroscopy, refer to Terminology E 135.

3.1.2 For definitions of terms relating to statistics, refer to Terminology E 456.

3.1.3 For definitions of terms relating to nuclear materials, refer to Terminology C 859.

3.1.4 For definitions of terms specifically related to ICP-MS in addition to those found in 3.2, refer to Appendix 3 of Ref (1).⁹

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *mass bias or fractionation, n* —the deviation of the observed or measured isotope ratio from the true ratio as a

function of the difference in mass between the two isotopes. This deviation is the result of several different processes; however, the primary cause is “Rayleigh fractionation associated with sample evaporation in which lighter isotopes are carried away preferentially” (2). With solution nebulization in ICP-MS, source fractionation would be expected to be relatively insignificant and independent of time, but with other methods of introduction, it could be more significant.

3.2.2 *dead time, n* —the interval during which the detector and its associated counting electronics are unable to record another event or resolve successive pulses. The instrument signal response becomes non-linear above a certain count rate due to deadtime effects, typically about 1×10^6 counts/s.

3.2.3 *specific activity, n* —the radioactivity of a radioisotope of an element per unit weight of the element in a sample, in units of Bq/g or pCi/g.

4. Summary of Test Method

4.1 A representative sample of soil is obtained by first taking a sizeable amount (>150 grams) and drying it, then running it through a crusher, or placing it on a shaker/tumbler to homogenize it, or both. A portion of the dried and ground sample is weighed out and placed in a high temperature furnace to remove organics. It is then digested in HNO_3/HF , followed by a rapid fuming with H_2O_2 , and ^{209}Bi (bismuth) is used as an internal standard. For an analysis of total and isotopic uranium, the sample can be filtered and diluted at this time. A secondary digestion, using $\text{HNO}_3/\text{HClO}_4$, followed by another H_2O_2 fuming, is performed, if thorium analysis is required. Two separate runs of a sample batch are performed on the instrument; the first run (at a dilution factor of 200) is to obtain the total uranium and thorium results and measure the $^{235}\text{U}/^{238}\text{U}$ isotopic ratio, and the second run (after a portion of the digestate has been concentrated and the actinides separated out by solid phase extraction) is to measure the $^{234}\text{U}/^{235}\text{U}$ and $^{236}\text{U}/^{235}\text{U}$ ratios. If the ^{234}U and ^{236}U information is not needed, the second run can be omitted and the measured ^{238}U concentration data (with abundance correction) can be combined with the $^{235}\text{U}/^{238}\text{U}$ ratio data to obtain the total uranium concentration (assuming that ^{234}U and ^{236}U have negligible concentration). A standard peristaltic pump is used as the means of sample introduction into the plasma; however, as mentioned in Section 1, an ETV unit, or other method more efficient at sample introduction, may be used to improve sensitivity, which would be necessary to look at other actinide series radioisotopes.

5. Significance and Use

5.1 This test method measures the presence of uranium and thorium in soil that occurs naturally and as a result of contamination from nuclear operations and uranium ore processing. The reporting detection levels (RDLs) of total uranium and thorium are well below the normal background in soil. The normal background level for uranium is between 3 and 5 $\mu\text{g/g}$ in most geographic areas and slightly higher for thorium. The ^{235}U enrichment is also measured from an initial sample pass through the instrument. The other less abundant uranium isotopes (^{234}U and ^{236}U) are measured down to a typical soil background level after sample concentration and a second

³ Annual Book of ASTM Standards, Vol 04.08.

⁴ Annual Book of ASTM Standards, Vol 11.01.

⁵ Annual Book of ASTM Standards, Vol 03.05.

⁶ Annual Book of ASTM Standards, Vol 14.02.

⁷ Annual Book of ASTM Standards, Vol 03.06.

⁸ Available from the U.S. Government Printing Office, Washington, DC 20402.

⁹ The boldface numbers in parentheses refer to a list of references at the end of this test method.

sample analysis. This allows for calculation of individual isotopic uranium and total uranium activity. The majority of the uranium activity results from ^{234}U and ^{238}U .

6. Interferences

6.1 *Adjacent Isotopic Peak Effects*—Interferences can occur from adjacent isotopes of high concentration, such as an intense ^{235}U peak interfering with the measurement of ^{234}U and ^{236}U . This is particularly the case for instruments that provide only nominal unit mass resolution at 10 % of the peak height. For this test method, the ICP-MS peak resolution for ^{209}Bi was set to within 0.75 ± 0.10 AMU full-width-tenth-maximum (FWTM) peak height to reduce adjacent peak interference effects. The analysis of spiked and serial dilution QC standards are used to check for good analyte recovery, which would give indication of such matrix interferences.

6.2 *Isobaric Molecular Ion Interferences*—Uranium-235 could interfere with ^{236}U determinations by forming a UH^+ ion. A laboratory control standard (LCS) is run with each batch, which is from a certified soil source of known natural enrichment (thus containing no ^{236}U). The measurement of any ^{236}U peak from this standard is used to monitor this molecular ion interference. At the $300\text{ }\mu\text{g/g}$ concentration level used, there is no ^{236}U peak presence above the ^{236}U reporting detection limit (RDL). Another possible molecular ion interference would be the formation of NaBi^+ , which would interfere with ^{232}Th , since Bi is used as an internal standard. Follow the instrument manufacturer's instructions to minimize these molecular ion formations, for example by optimizing the nebulizer gas flow rate. Correction factors can be established if the above interferences are found to be significant.

6.3 *Memory and Sample Matrix Interference Effects*—Memory effects or sample carryover can occur from previously run samples. These effects can be detected by looking at the standard deviation of the repeat trials from a sample analysis. Also, with each batch, a memory check is performed to establish an acceptable rinse time. Sample matrix effects can occur due to the high ion flux through the electrostatic lenses. Biases are possible since pure solution standards are used for calibration which do not reflect the same high ion flux from the digested soil sample matrix of unknowns. The soil LCS, mentioned in 6.2, is used to determine if this error is significant. Also, this error may be reduced if the lenses are tuned while monitoring the Bi in a sample matrix.

7. Apparatus

- 7.1 *Stirring hotplate,*
- 7.2 *High temperature furnace,*
- 7.3 *Balance, with precision of 0.0001 g,*
- 7.4 *ICP-MS instrument, controlled by computer and fitted with the associated software and peripherals,*
- 7.5 *Peristaltic pump,*
- 7.6 *Desiccator,*
- 7.7 *400-mL polytetrafluoroethylene (PTFE) beaker,*
- 7.8 *10.0 cm PTFE watch glasses,*
- 7.9 *Magnetic stirring bars,*
- 7.10 *30-mL quartz crucibles,*
- 7.11 *Whatman #40 and #542 filter paper,*
- 7.12 *Funnels, 10 to 7 cm diameter size,*

- 7.13 *Funnel rack or stand setup,*
- 7.14 *100-mL and 250-mL polymethylpentene (PMP) volumetric flasks,*
- 7.15 *100- and 250-mL glass quartz beakers,*
- 7.16 *25-mL glass (or PMP) volumetric flasks, and*
- 7.17 *25- and 50-mL graduated cylinders, or optional 25-mL acid bottle-top dispensers.*

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 conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.¹⁰ 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.

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

8.3 *Nitric Acid* (sp gr 1.42)—70 % w/w concentrated nitric acid (HNO_3).

8.4 *Hydrofluoric Acid* (sp gr 1.18)—49 % w/w concentrated hydrofluoric acid (HF).

8.5 *Hydrogen Peroxide* (sp gr 1.41)—30 % w/w concentrated hydrogen peroxide (H_2O_2).

8.6 *Perchloric Acid* (sp gr 1.67)—69–72 % w/w concentrated perchloric acid (HClO_4).

8.7 *Nitric Acid (6 M)*—Add 380 mL concentrated HNO_3 to water, dilute to 1 L, and mix.

8.8 *Nitric Acid (3 M)*—Add 190 mL concentrated HNO_3 to water, dilute to 1 L, and mix.

8.9 *Nitric Acid (5 % w/v)*—Add 71 mL concentrated HNO_3 to water, dilute to 1 L, and mix.

8.10 *Nitric Acid (1 % w/v)*—Add 14 mL concentrated HNO_3 to water, dilute to 1 L, and mix.

8.11 *Bismuth Internal Standard Stock Solution* (1000 $\mu\text{g/mL}$).

8.12 *Uranium Standard Stock Solution* (1000 $\mu\text{g/mL}$).

8.13 *Thorium Standard Stock Solution* (1000 $\mu\text{g/mL}$).

8.14 *Uranium and Thorium Calibration Standard Solutions* (at 5, 50, 200, 500, 1000, and 5000 $\mu\text{g/L}$ of U and Th), each with 250 $\mu\text{g/L}$ of Bi internal standard in 1 % HNO_3 .

NOTE 1—The standard stock solutions of uranium available from chemical suppliers are usually depleted in ^{235}U and the isotopic abundance of the solution used must be predetermined by this test method or by TIMS so that an accurate ^{238}U concentration can be used for calibration. The uranium concentrations of the calibration standard solutions are then adjusted for the abundance to actually represent the concentration of ^{238}U .

8.15 *Isotopic Enrichment U_3O_8 Standards*, NBL-005, NBL-010, and NBL-030-A (used for optional isotopic calibration: Appendix X1).

¹⁰ *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), Rockville, MD.

8.16 *Isotopic Enrichment Standard Stock Solutions* (200 µg/mL of U)—59.0 mg of each U_3O_8 isotopic standard heated to dissolution with 18 mL of concentrated HNO_3 and diluted to 250 mL with 5 % HNO_3 in a 250-mL PMP flask (used for optional isotopic calibration: Appendix X1).

8.17 *Uranium-235/Uranium-238 Isotopic Ratio Calibration Standards* (400 µg/L of U)—Add 200 µL of each isotopic enrichment standard stock solution to a separate 25-mL flask with 250 µg/L of Bi internal standard and dilute to volume with 1 % HNO_3 (used for optional isotopic calibration: Appendix X1).

8.18 *Uranium-234/Uranium-235 and $^{236}U/^{235}U$ Isotopic Ratio Calibration Standards* (40 µg/mL of U)—Add 5 mL of each isotopic enrichment standard stock solution to a separate 25-mL flask and dilute to volume with water (resulting in a 1 % HNO_3 concentration) (used for optional isotopic calibration: Appendix X1).

8.19 *Uranium-234/Uranium-235, $^{235}U/^{238}U$, and $^{236}U/^{235}U$ Isotopic Ratio Calibration Standards* (10 µg/mL of U)—Add 5 mL of each isotopic enrichment standard stock solution to a separate 100-mL PMP flask and dilute to volume with 1 % HNO_3 (used for optional isotopic calibration: Appendix X1).

8.20 *RDL-A and RDL-B Isotopic RDL Solution Standards*, analyzed at the beginning (-A) and end (-B) of the low abundant isotopic batch run, (1 µg/mL of U)—Add 500 µL of NBL-010 isotopic enrichment standard stock solution to a 100-mL PMP flask, and dilute to volume with 1 % HNO_3 .

8.21 *Oxalic Acid* ($H_2C_2O_4 \cdot 2H_2O$), mol wt 126.07.

8.22 *Ammonium Oxalate* ($(NH_4)_2C_2O_4 \cdot H_2O$), mol wt 142.11.

8.23 *0.10 M Ammonium Binoxalate* ($NH_4HC_2O_4 \cdot H_2O$), mol wt 125.08—Add 12.607 g of oxalic acid and 14.211 g of ammonium oxalate to a 1-L beaker. Add approximately 900 mL of water and stir until dissolved. Transfer to a 1-L volumetric flask and dilute to the 1 L volume with water.

8.24 *Spike Solution Standard*, (200 µg/mL of U and Th) 59.0 mg of NBL-010 U_3O_8 isotopic standard, heated to dissolution with 18 mL of concentrated HNO_3 . Add 50 mL of 1000 µg/mL Th standard solution and dilute to 250 mL with DI water in a PMP flask.

8.25 *Initial Calibration Verification (ICV) Standard* (5 µg/L of U and Th plus 250 µg/L of Bi) is prepared. This is at two times the RDL.

8.26 *Continuing Calibration Verification (CCV) Standard* (200 µg/L of U and Th plus 250 µg/L of Bi) is prepared.

NOTE 2—It is recommended that the calibration verification standards be prepared from an independent source, that is, other than that used for the calibration standards.

8.27 *Calibration Blank*, initial calibration blank (ICB), continuing calibration blank (CCB), and memory blank (250 µg/L Bi internal standard) in 1 % HNO_3 .

8.28 *LCS*, a matrix soil standard, certified for the radioisotopes of interest.

8.29 *Memory Test Solution* (10 µg/mL of U and Th).

8.30 *Isotopic Enrichment U_3O_8 Standard NBL U-500* used for mass bias determination, prepared in accordance with 8.16 and 8.17 to a concentration of approximately 400 µg/L of U.

8.31 *Extraction Resin*—Either prepare into columns as de-

scribed by Horwitz et al (3) or use TRU resin prepacked columns that are available from EiChrom Industries, Inc. which have been found satisfactory for this purpose.¹¹

8.32 *Prefiltering Resin*—Either prepare into columns as described by Horwitz et al (3) or use prefilter resin prepacked columns that are available from EiChrom Industries, Inc. which have been found satisfactory for this purpose.¹¹

8.33 Twenty-five-mL reservoir extension connectors (recommended for use with EiChrom prepacked columns).¹¹

9. Hazards

9.1 Since uranium- and thorium-bearing materials are radioactive and toxic, adequate laboratory facilities and fume hoods along with safe handling techniques must be used. A detailed discussion of all safety precautions needed is beyond the scope of this test method. Follow site- and facility-specific radiation protection and chemical hygiene plans.

9.2 Acute exposure to HF can cause painful and severe burns upon skin contact that require special medical attention. Chronic or prolonged exposure to low levels on the skin may cause fluorosis.

9.3 Perchloric acid reacts vigorously with organic material. All samples and materials coming in contact with perchloric acid must first be muffled or wet-ashed to remove organic material. A perchloric acid fume hood must be used whenever fuming operations are performed with perchloric acid present.

10. Sampling, Test Specimens, and Test Units

10.1 Practice C 998 provides a practice for sampling of surface soil to obtain a representative sample for analysis of radionuclides. Guide D 420 provides a guide for investigating and sampling soil and rock materials at subsurface levels, but is mainly concerned with geological characterization. The method described in Practice D 1587 may be used to sample the soil, using a thin-walled tube. If the soil is too hard for pushing, the tube may be driven, or Practice D 3550 may be used. The method described in Test Method D 1586 may also be used to sample the soil, and includes discussion on drilling procedures and collecting samples, which are representative of the area. In the case of sampling rocky terrain, diamond core drilling may be used (Practice D 2113). Where disturbed sampling techniques can be afforded, Practice D 1452 can be used, that is, using an Auger boring technique. The size of the sample is based on achieving a representative sample. Tube samples can be composited to achieve such a sample. Refer to Test Method D 1586, which discusses obtaining a representative sample.

11. Sample Preparation

11.1 As stated in Section 1, the analysis is performed on a dry weight basis. The percent moisture of the soil sample can be determined during the drying steps by measuring the weight before and after drying. This provides the opportunity to calculate and report the data on an as-received basis, with the percent moisture reported separately. Refer to Test Method

¹¹ Available from Eichrom Industries, Inc., 8205 S. Cass Ave., Suite 107, Darien, IL 60559.