ASTM INTERNATIONAL

Designation: C 1345 – 08

Standard Test Method for
Analysis of Total and Isotopic Uranium and Total Thorium in Soils by Inductively Coupled Plasma-Mass Spectrometry[1]

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 ^{234}U, ^{235}U, ^{236}U, and ^{238}U, 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. Since this test method using quadrupole ICP-MS was approved, advances have been made in ICP-MS technology in terms of improved sensitivity and lower instrument background as well as the use of collision or reaction cells (or both) and sector field mass spectrometers with single and multiple detectors. These advances should allow this test method to be performed more effectively but it is the user's responsibility to verify performance.

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 The values stated in SI units are to be regarded as standard.

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.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

C 859 Terminology Relating to Nuclear Materials[3]

C 998 Practice for Sampling Surface Soil for Radionuclides

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

C 1255 Test Method for Analysis of Uranium and Thorium in Soils by Energy Dispersive X-Ray Fluorescence Spectroscopy

D 420 Guide to Site Characterization for Engineering Design and Construction Purposes

D 1193 Specification for Reagent Water

D 1452 Practice for Soil Investigation and Sampling by Auger Borings

D 1586 Test Method for Penetration Test and Split-Barrel Sampling of Soils

D 1587 Practice for Thin-Walled Tube Sampling of Soils for Geotechnical Purposes

D 2113 Practice for Rock Core Drilling and Sampling of Rock for Site Investigation

D 2216 Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass

D 3550 Practice for Thick Wall, Ring-Lined, Split Barrel, Drive Sampling of Soils

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E 305 Practice for Establishing and Controlling Atomic

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[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 Methods of Test.

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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] Withdrawn.

Emission Spectrochemical Analytical Curves

E 456 Terminology Relating to Quality and Statistics

E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data[3]

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

2.2 *ASTM Technical Publications:*[2]

STP 1291 Applications of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to Radionuclide Determinations

2.3 *U.S. EPA Standard:*[4]

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

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).[5]

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.

3.2.4 *reporting detection levels (RDLs)*, n—levels of each of the measured isotopes set to be above the normal background levels found in the same types of soils (see Table 1).

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

TABLE 1 ICP-MS Reporting Detection Limits (RDLs)[A]

Unit/Isotope	^{232}Th	^{234}U	^{235}U	^{236}U	^{238}U
ng/g	500	0.500	0.500	0.500	500
Bq/g	0.00203	0.1156	0.0000400	0.00120	0.00622
pCi/g	0.0549	3.12	0.00108	0.0323	0.168

[A]The reporting detection limits given for ^{232}Th and ^{238}U take into account the dilution factor of 200 from the soil sample preparation process (2.5 ng/g × 200 = 500 ng/g). They were set to exceed the normal background level found in soils and do not represent the full detection sensitivity potential of most ICP-MS instruments. Refer to 13.2.10 for the determination of the RDLs for the low abundance isotopes.

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 HNO_3/$HClO_4$, 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}U/^{238}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}U/^{235}U and ^{236}U/^{235}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}U/^{238}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 μg/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 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

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[4] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

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

[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 µg/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 bismuth 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.[6] 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 µg/mL).

8.12 *Uranium Standard Stock Solution* (1000 µg/mL).

8.13 *Thorium Standard Stock Solution* (1000 µg/mL).

8.14 *Uranium and Thorium Calibration Standard Solutions* (at 5, 50, 200, 500, 1000, and 5000 µg/L of uranium and thorium), each with 250 µg/L of bismuth 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).

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

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[6] *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

with 250µ g/L of bismuth 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 uranium)*—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 uranium)*—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 uranium)—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 uranium and thorium) 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 thorium 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 uranium and thorium plus 250 µg/L of bismuth) is prepared. This is at two times the RDL.

8.26 *Continuing Calibration Verification (CCV) Standard* (200 µg/L of uranium and thorium plus 250 µg/L of bismuth) 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 bismuth 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 uranium and thorium).

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 uranium.

8.31 *Extraction Resin*—Either prepare into columns as described by Horwitz et al (3) or use TRU resin prepacked columns.[7]

8.32 *Prefiltering Resin*—Either prepare into columns as described by Horwitz et al (3) or use prefilter resin prepacked columns.[7]

8.33 Twenty-five-mL reservoir extension connectors.[7]

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 Hydrofluoric acid is highly corrosive acid that can severly 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 untreated. 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 personnel protective equipment to protect from skin and eye contact is essential.

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

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[7] The sole source of supply of the apparatus known to the committee at this time is Eichrom Industries, Inc., 8205 S. Cass Ave., Suite 107, Darien, IL 60559, www.eichrom.com. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

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 D 2216 for a method of determining the moisture content. Also, refer to Test Method C 1255 for the initial drying and grinding sample preparation steps using a jaw tooth crusher (see 11.1 to 11.6 in Test Method C 1255) to achieve a particle size of less than 0.1 mm. It is recommended that the point of splitting out a sample to form a duplicate be prior to the sample drying process. Any process equivalent to that which is mentioned may be used to obtain a dry, ground, and homogenous soil.

Note 3—It is recommended that a Geiger-Muller counter be used to survey the dried soil as a means of segregating any with a high level of contamination, so that a reduced aliquot can be used. It is also recommended that a sample preparation log be developed by the user to detail and track the steps of preparation for each sample and batch.

11.2 Weigh out 10.00 ± 0.02 grams of each soil sample into a quartz crucible. Weigh out an additional 10.00-g aliquot of a sample to be used as a spike. It is recommended that the crucibles be scribed with identifying numbers.

11.3 Place the crucibles in a high temperature furnace maintained at $650 \pm 50°C$ for a minimum of 4 h.

11.4 Remove the samples from the furnace and allow them to cool to room temperature.

Note 4—If the samples are not going to be digested at this time, place the crucibles into a desiccator.

11.5 Transfer each sample into a 400-mL PTFE beaker and mark the beaker with the sample number. Designate an additional beaker as a preparation blank.

11.6 Add 500 µL of 1000 µg/mL bismuth internal standard solution to each beaker.

11.7 For the spike sample, add 5.0 mL of the spike solution.

11.8 Add 30 mL of concentrated HF to each sample and wait briefly for any reaction to subside.

11.9 Add 50 mL of concentrated HNO_3 to each sample.

11.10 After adding a magnetic stir bar, place each sample on a stirring hotplate maintained at $180 \pm 20°C$ until the sample reaches complete dryness. The stirring action should be reduced or turned off when the samples approach dryness.

11.11 Remove the samples from the hotplate and allow them to cool.

11.12 Add 20 mL of concentrated H_2O_2 to each beaker.

11.13 Return the samples to the stirring hotplate, and stir until an effervescent reaction occurs and the samples reach a near dryness state.

11.14 Repeat 11.11-11.13 for a second addition of H_2O_2.

11.15 If not analyzing for Th, go to 11.22.

11.16 Remove the beakers from the hotplate and allow them to cool.

11.17 Add 30 mL of concentrated $HClO_4$ into each beaker and wait briefly for any reaction to subside.

11.18 Add 50 mL of concentrated HNO_3 into each beaker.

11.19 Transfer each sample to a 250-mL glass quartz beaker. Heat the samples momentarily as needed in the PTFE beakers and rinse with more concentrated HNO_3 in order to ensure a quantitative transfer.

11.20 Place each sample on a stirring hotplate maintained at $350 \pm 50°C$ and stir until the sample reaches a near dryness state.

11.21 Repeat 11.11-11.14 to repeat the two H_2O_2 fuming steps and again allow them to cool.

11.22 Add 50 mL of 6 M HNO_3 to each beaker.

11.23 Place the samples on a stirring hotplate maintained at $120 \pm 10°C$ and stir to warm, until the residue dissolves into solution.

11.24 Remove the beakers from the hotplate and allow them to cool sufficiently for filtering as described in 11.26.

11.25 Remove the stir bar.

11.26 Filter each sample through a prewashed #40 Whatman filter paper and into a 100-mL PMP flask, marked with the sample number.

11.27 Rinse the filter paper and funnel with water, bringing the flask up to volume.

11.28 Shortly before running the samples for total uranium and thorium, as well as the $^{235}U/^{238}U$ ratio, dilute 5 mL of each sample to 100 mL with water, using a 100-mL PMP flask.

11.29 *Sample Column Extraction Process*—To further prepare the samples for analysis of the ^{234}U and ^{236}U isotopes, set up the filtration and column extraction arrangement as shown in Fig. 1.

11.29.1 The setup consists of one #542 Whatman filter paper in a funnel, followed by a prefiltering resin column and
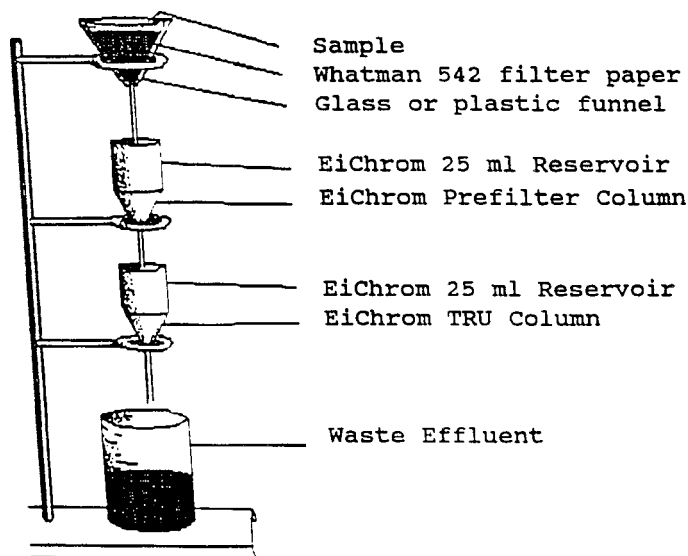

FIG. 1 Set-up of the Filtration and Column Extraction Arrangement

an extraction resin column, each using a 25-mL reservoir extension (see 8.31 to 8.33). A 100-mL glass beaker is used to collect the waste effluent.

11.29.2 Condition each column by dispensing 10 mL of 3 M HNO$_3$ into the funnel and allow time for it to pass.

11.29.3 Place 50 mL of each sample in the 3 M HNO$_3$ state (from 11.27) into a funnel. It is recommended that 15–20 mL increments be poured to avoid overflowing the reservoir.

11.29.4 Rinse the setup with 20 mL of 3 M HNO$_3$.

11.29.5 After all of the 3 M HNO$_3$ has passed through, remove the funnel, prefilter, and 100-mL beaker. Place a clean 100-mL beaker under the TRU resin column.

11.29.6 Pour 15–20 mL at a time of 0.1 M ammonium binoxalate into the TRU resin column until a total of 50 mL has been added to elute off the actinide series elements.

11.29.7 Remove the beakers and place them on a hotplate maintained at 180 ± 20°C and heat to dryness.

11.29.8 Add 5 mL of 30 % concentrated H$_2$O$_2$ to each beaker and heat to dryness.

11.29.9 Add 5 mL of 5 % HNO$_3$ and reduce heat to 140 ± 10°C.

11.29.10 Heat just enough to dissolve the sample and then remove from the hotplate.

11.29.11 Transfer each sample to a 25-mL volumetric flask and dilute to volume while rinsing the beaker with water.

12. Preparation of Apparatus

12.1 Set up the necessary instrument software files for data acquisition, calculation, and archival, etc. The abundance setting for ^{238}U may need to be set at 99.99 + % to eliminate any abundance correction and the abundance settings of the other three isotopes set at an extremely low level (such as 0.001 %) since they are only measured by isotopic ratio. This adjustment depends on the instrument software used and is to allow for the initial concentration measurement to be strictly a measurement of the ^{238}U concentration. Corrections to the total uranium value, based on the measured abundance, are made in a separate data software file (such as Lotus 1.2.3) by combining the concentration data with the isotopic ratios. The same data file is used to calculate the uranium isotopic weight percents and activities.

12.2 Set the instrument operating conditions in accordance with the manufacturer's instructions, or as found to produce optimal results. Recommended or typical operating conditions and the data acquisition parameters are given in Table 2.

13. Calibration and Standardization

13.1 *Apparatus*—The following preliminary systems checks, with acceptance criteria, are recommended, and were performed for the data presented with this method.

13.1.1 A mass scale calibration is performed weekly, using an appropriately concentrated solution containing, at minimum, cobalt, holmium, bismuth, thorium, and uranium. The difference between the actual and measured masses shall be <0.05 AMU and the linear regression coefficient >0.98.

13.1.2 A peak resolution check is performed daily using ^{209}Bi when running the first phase of a sample batch and using ^{235}U when running the second phase. The resolution FWTM shall be within 0.75 ± 0.10 AMU.

13.1.3 A cross (or collection) calibration is performed daily using an appropriately concentrated solution containing, at minimum, cobalt, holmium, bismuth, thorium, and uranium. The regression coefficient shall be >0.96.

13.1.4 After tuning the lenses while monitoring ^{209}Bi in a sample matrix, a stability/tuning check is performed daily using an appropriately concentrated solution containing, for example, 100 µg/L of holmium, bismuth, thorium, and uranium. A minimum sensitivity response shall be established for each isotope and monitored. Also, the relative standard deviation (RSD) of each isotope from four trials shall be less than 5 %.

13.2 *Reference Standards and Blanks*—Refer to Guide E 882 for the recommended establishment of quality control charts, guidelines, and corrective actions in case the analysis of a standard is out of control. The quality control standards described in 13.2.1-13.2.9 (based in part on EPA Method 6020) are recommended for this method; however, their usage, frequency, and acceptance criteria levels are at the discretion of the user. The acceptance limits in EPA Method 6020 that apply were met for the data provided.

13.2.1 A six-point linear calibration is performed using standard solutions with concentrations of 5, 50, 200, 500, 1000, and 5000 µg/L (or as required for the user's needs). The linear coefficient of correlation can be used as one basis to determine the quality of the calibration. Refer to 7.3 in Practice E 305 for the process of fitting a regression line and evaluating the

TABLE 2 Recommended or Typical Operating Conditions and Data Acquisition Parameters

Operating Conditions		Data Acquisition Parameters	
Plasma frequency	27.12 MHz	Acquisition mode	Scanning
Incident power	1350 W	Masses scanned: 1st	^{209}Bi, ^{235}U, ^{238}U
		2nd	^{234}U, ^{235}U, ^{236}U
Reflected power	<10 W	Mass range AMU: 1st	207.6 to 239.4
		2nd	232.6 to 237.4
Nebulizer pressure	28 psi	Number of sweeps	2000
Cool gas flow	13.0 L/min	Channels per mass	20
Auxiliary gas flow	1.2 L/min	Dwell time per channel	320 µsec
Nebulizer gas flow	0.79 mL/min	Acquisition time per trial	84 s
Sample uptake flow	0.8 mL/min	Number of trials	3
Nebulizer	Meinhardt TR-C	Detector mode	Dual: pulse counting/analog
Skimmer cone	Nickel—0.75 mm aperture		
Sample cone	Nickel—1.0 mm aperture		
Analyzer pressure	2.0×10^{-6} mbar		
Ion lens tuning	^{209}Bi or ^{235}U in sample		
Sampling height	12 mm above load coil		

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linearity. Generally for the concentration range indicated for uranium and thorium, the coefficient of correlation is greater than 0.995.

13.2.2 CCVs are run every ten samples or standards. They shall be from an independent source than the calibration standards and are used to monitor the bias of the calibration. The first calibration verification standard, ICV, is run at what equates to two times the reporting detection level (RDL) for ^{238}U and ^{232}Th. These RDLs (set at 500 ng/g) are listed in Table 1, with the dilution factor of 200 taken into account. The instrumental detection limit, determined from the standard deviation of repeat trials, is below 300 ng/g, but the suggested RDLs are set with consideration of typical background and environmental concern.

13.2.3 An LCS, which is a certified standard in a soil matrix, is run with each batch to monitor the bias of the analysis, as affected by the matrix.

13.2.4 A duplicate standard is run with each batch to monitor the precision of the analysis, as affected by instrumental precision and sample homogeneity.

13.2.5 A spike and serial dilution are run with each batch to examine matrix interference effects.

13.2.6 A calibration blank is initially run and used for blank spectral subtraction and to establish an initial bismuth internal standard intensity response which is monitored with each analysis to monitor uranium and thorium sensitivity loss with time.

13.2.7 A memory blank is run immediately following a memory test solution to establish an adequate rinse time. The memory test solution is at two times the maximum calibration concentration, or 10 000 µg/L.

13.2.8 An ICB followed by CCBs are run every ten samples or standards. They are used to detect any problems with sample cross contamination or memory effect as well as instability in the spectral background.

13.2.9 A preparation (or reagent) blank is run to monitor any sample contamination during preparation.

13.2.10 Two RDL sensitivity check standards [RDL-A and RDL-B] are run at the beginning (-A) and end (-B) of the low isotopic batch run to verify that sufficient sensitivity (in terms of peak intensity above background) is achieved at the beginning and maintained throughout the sample batch analysis. The intensity level must be a minimal intensity at which the ^{234}U and ^{236}U isotopes can be measured with a small standard deviation and without bias due to background interference. For example, for the data presented in this method, a 0.050 ng/g concentration of ^{234}U routinely measured greater than or equal to 100 cps with a 5 % standard deviation of the three trials and without a statistically significant bias in the $^{234}U/^{235}U$ ratio due to any background interference. The 0.050 ng/g of ^{234}U equates to 0.25 ng/g since there is a dilution factor of 5 resulting from the column extraction portion of the sample preparation. A margin factor of 2× this was used to establish the RDL (2 × 0.25 ng/g) at 0.50 ng/g. The RDLs are listed in Table 1, with the dilution factor and margin of 2 taken into account. The margin factor would allow, among other things, for the recovery from the column extraction process to be only 50 %, even though it is normally greater than 95 %, particularly for

concentrations near the RDL. These RDLs are also set to a practical level, considering typical background levels and environmental concerns. The user can refer to EPA Method 6020 to determine the instrumental detection levels, Practice E 876, or to the referenced articles by Hubaus and Vos (**4**) and Neter, Wasserman and Kutner (**5**).

13.3 *Mass Bias and Deadtime Correction Factors*:

13.3.1 To determine the mass bias factor for each of the measured isotope ratios, run the NBL U-500 isotope standard, measuring the $^{235}U/^{238}U$ ratio, and perform the calculations in 13.3.1.1 and 13.3.1.2. The NBL U-500 standard is used because the ^{235}U and ^{238}U intensities are nearly equal; therefore, no differences in deadtime exist, and a correction for mass bias can be distinctively established. The factor may be determined with each batch or less frequently based on the user's QC requirements since it is fairly constant. Refer to Appendix X1 for an optional approach.

13.3.1.1 Determine the factor M as follows:

$$\left(\frac{^{235}U}{^{238}U}\right)_{meas} = \left(\frac{^{235}U}{^{238}U}\right)_{true} (1 + M \times (\Delta m/m)) \tag{1}$$

$$M = \frac{\dfrac{\left(\frac{^{235}U}{^{238}U}\right)_{meas}}{\left(\frac{^{235}U}{^{238}U}\right)_{true}} - 1}{\dfrac{(238 - 235)}{238}} \tag{2}$$

where:

$\left(\frac{^{235}U}{^{238}U}\right)_{meas}$ = the measured ($^{235}U/^{238}U$) intensity ratio,

$\left(\frac{^{235}U}{^{238}U}\right)_{true}$ = the true or certified ($^{235}U/^{238}U$) intensity ratio,

m = the atomic mass unit of the isotope in the ratio denominator, and

Δm = the difference in atomic mass unit of the isotopes (denominator − numerator).

13.3.1.2 Calculate the mass bias factor for each isotopic ratio, as follows:

$$(B58) = 1 + (238–235)/238 \times M \tag{3}$$
$$(B45) = 1 + (235–234)/235 \times M \tag{4}$$
$$(B65) = 1 + (235–236)/235 \times M \tag{5}$$

where:

(B58) = the mass bias factor for the ($^{235}U/^{238}U$) intensity ratio,

(B45) = the mass bias factor for the ($^{234}U/^{235}U$) intensity ratio, and

(B65) = the mass bias factor for the ($^{236}U/^{235}U$) intensity ratio.

13.3.1.3 Ratios are then corrected for mass bias in the following manner:

$$(RATIO)\ corrected = \frac{(RATIO)\ measured}{B} \tag{6}$$

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The user can refer to Refs (**6**) and (**7**) for further discussion of this correction method.

13.3.2 Most instruments have incorporated into their software a deadtime correction factor. This factor minimizes the variation of the isotopic ratio measurement as a function of intensity or concentration, particularly when the two peaks have one to two orders of magnitude difference. To verify or establish a proper factor, perform steps 13.3.2.1-13.3.2.3. For an alternate approach, refer to p. 103–104 of the referenced text by Date and Gray (**2**). It is recommended that the need to redetermine this factor in the future be based on the monitoring of the $^{235}U/^{238}U$ ratio from the concentration calibration standards used, that is, the standard deviation of the six ratios. For example, if the standard deviation of the $^{235}U/^{238}U$ ratio for the six standards used is 0.005 immediately after establishing the deadtime correction factor and normally varies by ±0.002, if the standard deviation reaches 0.010, it can indicate the need to reestablish the correction factor.

NOTE 5—It is also important that the instrument have an accurate detector cross calibration or that both peaks be measured with the same detector mode. In examining the $^{235}U/^{238}U$ ratios for the six calibration standards, the user can make note of when the calibration standard intensities cross from a pulse counting to an analog detection. Thus if the point where the ^{235}U peak is measured by pulse counting while the ^{238}U peak is measured in an analog mode results in an outlying ratio within the set, it can indicate an inaccurate detector cross calibration.

13.3.2.1 Run the calibration standards from 50 to 5000 µg/L to determine the $^{235}U/^{238}U$ ratio for each standard at several deadtime correction factor settings.

13.3.2.2 Plot the (RATIO)meas/(RATIO)true versus correction factor and determine the correction factor with the minimum deviation between the standards.

13.3.2.3 Enter that correction factor into the instrument software.

14. Procedure

14.1 Allow the ICP-MS instrument time to warm up and reach a stable state of detection.

14.2 Perform any instrumental system checks or calibrations and mass bias or deadtime factor determinations, in accordance with 13.1 and 13.3 and the frequencies established.

14.3 *Total uranium and thorium and $^{235}U/^{238}U$ Batch Run*:

14.3.1 Calibrate for total uranium and thorium by running the calibration blank and the calibration standards (see 13.2.1 and 13.2.6).

14.3.2 Establish an acceptable rinse time (or verify that which has been previously established) by running the memory test solution through the system followed by the analysis of the memory blank (see 13.2.7).

14.3.3 Run the ICV and ICB standards (see 13.2.2 and 13.2.8) to verify accuracy of the calibration.

14.3.4 Run the preparation blank (see 13.2.9).

14.3.5 Run the LCS (see 13.2.3).

14.3.6 Run the first sample followed by its associated duplicate, serial dilution, and spike to check precision and matrix interferences (see 13.2.4 and 13.2.5).

14.3.7 Analyze all of the batch samples with a CCV and CCB after every ten samples.

14.3.8 Run the NBL U-500 mass bias correction standard if it is to be run on a batch basis (see 13.3.1) or the optional $^{235}U/^{238}U$ isotopic correction standards under Appendix X1.

14.4 Examine the ^{235}U and ^{238}U intensities for the samples. Based on a prior established intensity level (typically near background soil levels) and the statistical uncertainty of the ratio, those samples below the intensity level may have the $^{235}U/^{238}U$ ratio determined from the more concentrated digestate in conjunction with the other two ratios below.

14.5 $^{234}U/^{235}U$ and $^{236}U/^{235}U$ Ratio Batch Run:

14.5.1 If this second phase of the sample batch analysis is performed on a separate day, repeat the steps in 14.1 and 14.2. It is recommended that they be performed on separate days to allow for sufficient sample cleanup of the system.

14.5.2 Run a calibration blank to be used for blank subtraction.

14.5.3 Run the NBL U-500 mass bias correction standard if it is to be run on a batch basis (see 13.3.1) or the optional isotopic ratio calibration standards under Appendix X1.

14.5.4 Establish an acceptable rinse time (or verify that which has been previously established) by running a memory test solution through the system followed by the analysis of a memory blank.

14.5.5 Run the RDL-A standard and verify that the ^{234}U and ^{236}U intensities are above a prior established intensity acceptance level (see Note 6).

14.5.6 Run the LCS.

14.5.7 Run the first sample followed by its associated duplicate, serial dilution, and spike to check precision and matrix interferences.

14.5.8 Analyze all of the batch samples.

14.5.9 Run the RDL-B standard and repeat the verification made in 14.5.5.

NOTE 6—Before any samples are analyzed, the RDL-A standard is run to verify adequate sensitivity down to the established RDL level. It is verified by the ^{234}U and ^{236}U intensities of a standard being above a prior established intensity acceptance level. The intensity level is established based on a minimal intensity at which the ^{234}U and ^{236}U isotopes can be measured with a standard deviation of less than 5 % and no bias present due to background interference. The RDL-B is a repeat check of the same RDL-A standard. If the RDL-B standard is above the acceptance level, then those samples whose ^{234}U or ^{236}U, or both, are below the acceptance level are calculated with that ratio equal to zero and reported as less than the RDL values listed in Table 1. In this sense, the RDL-A and RDL-B act as a low level sensitivity or intensity monitor at the beginning and end of the batch.

15. Calculations

15.1 The mass bias correction factors are applied to the measured ratio data, as discussed in 13.3.

15.2 Using the corrected ratios, calculate the weight percents of the isotopes as follows:

$$(R48) = (R58) \times (R45) \qquad (7)$$

$$(R68) = (R58) \times (R65) \qquad (8)$$

$$W = \frac{100 \times m \times R}{238.05 + 234.04\,(R48) + 235.04\,(R58) + 236.05\,(R68)} \qquad (9)$$

where:
R45 = the ratio of ^{234}U to ^{235}U,

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$R48$ = the ratio of ^{234}U to ^{238}U,
$R58$ = the ratio of ^{235}U to ^{238}U,
$R65$ = the ratio of ^{236}U to ^{235}U,
$R68$ = the ratio of ^{236}U to ^{238}U,
m = mass of a given isotope,
R = ratio of a given isotope to ^{238}U, and
W = weight percent of a given isotope.

The user can refer to Refs (6) and (7) for further discussion of this calculation.

15.3 Once the weight percents have been determined for each of the isotopes, calculate the total uranium by dividing the measured ^{238}U concentration (from the first batch run determination) by the weight percent of ^{238}U. Subsequently, using the calculated total U value, determine the concentrations of the other isotopes from their weight percentages.

15.4 Calculate the activity of each uranium isotope as follows and then determine the total uranium activity by adding them together:

$$A = 10^{-9} \times S \times C \qquad (10)$$

where:
A = activity of a given isotope in Bq/g,
S = isotope specific activity in Bq/g, and
C = isotope concentration in µg/kg.

The same equation may be used if both A and S are in units of pCi/g. Refer to Table 3 for a list of the specific activities and half-lives of the radionuclides of interest.

NOTE 7—All of the calculations listed in 15.1-15.4, as well as calculating the data on an as-received versus a dry weight basis, can be performed in a Lotus 1.2.3 (or equivalent) master file for batch entry and analysis.

16. Precision and Bias

16.1 Four batches of nuclide reference material (NRM) certified soil standards, which were supplied by RUST Geotech (8), were analyzed for total uranium only. Each batch contained five NRM 4 standards, four NRM 5, and four NRM 6 standards. The four batches were run on separate days over a period of three weeks. The last of the four batches was also analyzed for isotopic uranium (see 16.3). The total uranium contained in each of the NRM standards was calculated from the certified isotopic uranium activities of the NRM standards. See Table 4 for the analysis results. The thorium analysis results presented in Table 4 are a compilation of laboratory control standard (LCS) results from separate batches.

16.2 Additionally, three batches of NBL certified isotopic uranium standards of U_3O_8 were analyzed on separate days

TABLE 3 Specific Activities and Half-Lives of the Uranium and Thorium Radionuclides[A]

Radio-nuclide	Specific Activity			Half-life (year)
	(dec/min-µg)	(pCi/g)	(Bq/g)	
^{232}Th	2.435 E – 01	1.097 E + 05	4.058 E + 03	1.405 E + 10
^{234}U	1.387 E + 04	6.248 E + 09	2.312 E + 08	2.445 E + 05
^{235}U	4.798 E + 00	2.161 E + 06	7.997 E + 04	7.038 E + 08
^{236}U	1.436 E + 02	6.468 E + 07	2.393 E + 06	2.342 E + 07
^{238}U	7.463 E – 01	3.362 E + 05	1.244 E + 04	4.468 E + 09

[A]From Kocher, D. C., *Radioactive Decay Data Tables, A Handbook of Decay Data for Application to Radiation Dosimetry and Radiological Assessments*, U.S. Department of Energy, Technical Information Center, DOE-TIC-11026.

TABLE 4 NRM Certified Standard Data for Total Uranium and Thorium by ICP-MS (in units of µg/g)

	NRM 4	NRM 5	NRM 6
Certified total thorium[A]	86.6	164.1	313.6
Measured mean value	82.9	159.3	303.6
Relative sample standard deviation (%)	4.4	3.4	7.6
Percent recovery of the mean value	95.7	97.1	96.7
Certified total uranium[A]	35.6	67.5	128.2
Measured mean value	34.6	65.5	124.4
Relative sample standard deviation (%)	4.8	5.1	7.0
Percent recovery of the mean value	97.2	97.0	97.1

[A]The "certified total uranium and thorium" concentrations are based on the certified isotope activities and a normal ^{235}U enrichment of these standards.

over a period of one week for uranium isotopic weight percents only. Each batch consisted of three standards that were certified for the weight percents of the four uranium isotopes of interest: U-005, U-010, and U-030-A. Each batch contained five aliquots each from the three standards. They were analyzed consecutively without removal from the instrument or washes in between. See Table 5 for a summary of these analysis results.

16.3 For the fourth batch of NRM standards, the uranium isotopic weight percents were determined and they are given in Table 6. Because each NRM standard (4, 5, and 6) was made from uranium mill tailings diluted to different concentrations with river sediment or sand, the ^{235}U enrichment was considered to be normal (0.712 wt. %), and the isotopic data are combined for the three standards. Since ^{236}U is not naturally

TABLE 5 NBL Isotopic Standard Data

NBL Standard	^{234}U Results		
	U-005	U-010	U-030A
Certified $^{234}U/^{235}U$ atomic % ratio	0.004454	0.005390	0.009137
Mean $^{234}U/^{235}U$ atomic % ratio	0.004529	0.005361	0.008911
Relative sample std. dev. of the ratio	1.67	0.70	3.59
Percent recovery of the mean ratio	101.7	99.5	97.5
Certified wt. percent ^{234}U	0.00214	0.00532	0.02732
Mean wt. percent ^{234}U	0.00213	0.00526	0.02700
Relative sample std. dev. of wt. % ^{234}U	3.84	1.96	2.46
Percent recovery of mean wt. % value	99.4	98.9	98.8
	^{236}U Results		
Certified $^{236}U/^{235}U$ atomic % ratio	0.009520	0.006785	0.000197
Mean $^{236}U/^{235}U$ atomic % ratio	0.009462	0.006768	0.000209
Relative sample std. dev. of the ratio	1.10	0.85	12.14
Percent recovery of the mean ratio	99.4	99.7	106.3
Certified wt. percent ^{236}U	0.00462	0.00675	0.00059
Mean wt. percent ^{236}U	0.00449	0.00670	0.00064
Relative sample std. dev. of wt. % ^{236}U	4.09	1.37	11.85
Percent recovery of mean wt. % value	97.1	99.2	107.1
	^{235}U Results		
Certified $^{235}U/^{238}U$ atomic % ratio	0.004919	0.010140	0.031367
Mean $^{235}U/^{238}U$ atomic % ratio	0.004806	0.010079	0.031815
Relative sample std. dev. of the ratio	4.76	1.64	2.57
Percent recovery of the mean ratio	97.7	99.4	101.4
Certified wt. percent ^{235}U	0.48330	0.99110	3.0032
Mean wt. percent ^{238}U	0.47231	0.98525	3.0448
Relative sample std. dev. of wt. % ^{235}U	4.73	1.61	2.48
Percent recovery of mean wt. % value	97.7	99.4	101.4
	^{238}U Results		
Certified wt. percent ^{235}U	99.510	98.997	96.969
Mean wt. percent ^{238}U	99.521	99.003	96.928
Relative sample std. dev. of wt. % ^{235}U	0.02	0.02	0.08
Percent recovery of mean wt. % value	100.0	100.0	100.0

TABLE 6 NRM Soil Standards Isotopic Data

NOTE 1—The "certified" values of these ratios and weight percents are an average of the values from NRMs 4, 5, and 6. The certified activities were used to calculate isotope concentrations and subsequent weight percents (assuming 0.712 wt. % of ^{235}U and 0.0 wt. % of ^{236}U). The weight percents were then used to calculate the ratios.

^{234}U Results	
Certified ^{234}U/^{235}U atomic % ratio	0.007356
Mean ^{234}U/^{235}U atomic % ratio	0.007757
Relative sample std. dev. of the ratio	5.30
Percent recovery of the mean ratio	105.4
Certified wt. percent ^{234}U	0.00522
Mean wt. percent ^{234}U	0.00558
Relative sample std. dev. of wt. % ^{234}U	6.43
Percent recovery of mean wt. % value	107.0

^{235}U Results	
Certified ^{235}U/^{238}U atomic % ratio	0.007263
Mean ^{235}U/^{238}U atomic % ratio	0.007373
Relative sample std. dev. of the ratio	1.30
Percent recovery of the mean ratio	101.5
Certified wt. percent ^{235}U	0.71200
Mean wt. percent ^{235}U	0.72250
Relative sample std. dev. of wt. % ^{235}U	1.32
Percent recovery of mean wt. % value	101.5

^{238}U Results	
Certified wt. percent ^{238}U	99.283
Mean wt. percent ^{238}U	99.272
Relative sample std. dev. of wt. % ^{238}U	0.01
Percent recovery of mean wt. % value	100.0

occurring, there was not expected to be any ^{236}U present in these standards, and, in fact, there was none detected above the RDL. This data in comparison to the NBL standard data from Table 5, examines the effects of the matrix presence and the variation in soil concentration to the precision and bias of the isotopic data.

16.4 Having determined the total uranium concentrations together with the isotopic weight percents for the fourth NRM batch, the individual isotopic activities were then calculated. They are shown in Table 7. This data combines the effects of

TABLE 7 NRM Soil Isotopic Activity Data (in units of pCi/g)

NOTE 1—The certified activity of ^{235}U assumes the weight % of ^{235}U is 0.712.

	^{234}U	^{235}U	^{238}U
NRM 4 Results			
Mean value	12.79	0.537	11.32
Relative sample standard deviation	1.32	0.90	0.95
Certified activity	11.40	0.549	11.90
Percent recovery of the mean	112.2	97.8	95.1
NRM 5 Results			
Mean value	21.93	0.993	21.23
Relative sample standard deviation	2.03	0.52	0.55
Certified activity	22.20	1.042	22.60
Percent recovery of the mean	98.8	95.3	93.9
NRM 6 Results			
Mean value	40.13	1.905	41.24
Relative sample standard deviation	1.39	0.41	0.31
Certified activity	42.40	1.978	42.90
Percent recovery of the mean	94.6	96.3	96.1

the precision and accuracy of the total U measurements (in Table 4) with that of the isotopic weight percents (in Table 6).

16.5 *Precision*—For the three NRM standards analyzed for total uranium and thorium, the relative standard deviations (RSDs) indicate that the precision of the method is very good. It should be pointed out that the NRM standards are finely divided and very homogeneous; thus, the data do not indicate the variability that may be expected from preparation of routine soil samples.

16.5.1 With one exception, for the three NBL standards and the three intensity ratios measured, the RSDs of the 15 measurements were very low. For the one exception, the RSD of the ^{236}U/^{235}U ratio for standard U-030-A was 12.1 %. This was due to the ^{236}U abundance being very low for this standard and insufficient discrimination of the peak from the background. This indicated the necessity of running a blank subtraction standard for the second phase of the analysis. To reduce this error effect, it can be run more than once during the batch. The precisions were similar after the calculations were made to determine weight percents from the isotopic ratios. Again the highest RSD was for ^{236}U in the U-030-A standard. Overall, the standard deviations of the replicate measurements indicate excellent precision of the method for isotopic uranium analysis.

16.5.2 The precision of ^{234}U and ^{235}U in the NRM soil standards (see Table 6) is similar to the NBL standard results in Table 5, with the ^{234}U data only slightly worse for the NRMs. Thus, in comparing solution standards data (no soil matrix and constant intensity) to soil standards data varied over the concentration range of NRM 4 to NRM 6, there is no significant difference in precision. The precisions for each set of four data points for NRM isotopic activity in Table 7 is very good as well, with RSDs between 0.3 and 2.0 %.

16.6 *Bias*—With regard to accuracy of the total uranium analysis, for each NRM standard, the mean of the 16 measurements (20 measurements for NRM 4) was within one standard deviation of the certified value (see Table 4). The percent recovery (PR), as defined below, of each mean value, was 97 %. Thus, there is a slight low bias; however, this is within the uncertainty (5 to 7 %) of the mean values, and is not considered significant. The percent recoveries of the mean values and the range of recoveries from the individual measurements demonstrate that the method yields accurate results for total uranium measurements.

$$PR = \frac{\text{measured value}}{\text{certified value}} \times 100 \% \qquad (11)$$

The accuracy of the total thorium analysis data, although determined with limited data, is shown to be the same. The PRs of the means are 96 to 97 %.

16.6.1 The mean values of the NBL isotopic ratios and weight percents for the 15 trials were within one standard deviation of the certified value, as indicated by the recovery data in Table 5. The ^{236}U measurements of standard U-030-A showed a bias for each given batch even though the mean of all three batches was not largely biased, as indicated by the poor ratio precision. As discussed above, this was due to the very low abundance of ^{236}U in the U-030-A standard and insufficient discrimination and removal of the background. Other than that,

there does not appear to be any dominant bias effects present in the isotopic ratio measurements. The potential bias due to deadtime (resulting from varying total uranium concentration) is examined with the NRM standards in 16.6.3.

16.6.2 For the NRM isotopic analyses given in Table 6, the mean values (ratios and wt. %) for the 12 trials were within a 95 % confidence interval from the certified values. The mean values had recoveries from 101.5 % to 107.0 %, thus indicating only a slightly high overall bias.

16.6.3 The NRM isotopic activities shown in Table 7 have mean value recoveries between 94 and 112 %. Biases in the isotopic weight percent measurement and concentration measurement can have an additive or cancelling effect when combined to calculate the isotopic activities. Any bias for ^{238}U activity is essentially the same as for the total uranium concentration since the RPD for ^{238}U wt. % is negligible. The slightly biased high (112 % recovery) activity for the ^{234}U isotope of NRM 4 is mainly the result of biased high weight percent measurements. Initially this bias might be interpreted as being due to a varying degree of multiplier deadtime between the three standards; however, based on an examination of the data it is apparent that it was due to one or both of the following: the isotopic calibration standards were much higher in intensity than the soil standards; and the NRM 4 standard exhibited poor recovery resulting in low intensity. In the first case, for the ^{234}U/^{235}U analyses, the ^{235}U intensities exhibited a much lower intensity in the samples compared to the NBL standards. The high NBL ^{235}U intensities could have resulted in a deadtime effect present in the calibration standards that was not comparably present in the samples and therefore the samples were not similarly corrected. Care should be taken to ensure that the NBL standard intensities are on the same order of magnitude as the samples. Also, acceptance limits can be placed on the slope of the calibration to identify this potential bias or a maximum intensity, or both, established. The magnitude of this error effect can be determined by running the isotopic standards in a series of dilutions. Thus the intensity in which any instrument deadtime correction software becomes no longer valid can be determined. The second and probably more dominant factor contributing to the ^{234}U bias is that the ^{234}U intensities for NRM 4 were just below the 100 cps RDL intensity requirement established, ranging from 93 to 96 cps. This poor recovery most likely occurred during the extraction of the NRM 4s since the instrument sensitivity checks were acceptable. The lapse of time between digestion and extraction should be monitored to see if it has an effect. Also, a more frequent analysis of a blank subtraction standard would have improved the background subtraction process and therefore the low intensity data.

17. Keywords

17.1 inductively coupled plasma-mass spectrometry (ICP-MS); isotopic ratio; soil; thorium; uranium

APPENDIX

(Nonmandatory Information)

X1. ALTERNATIVE ISOTOPIC RATIO CALIBRATION

X1.1 Corrections to the mass bias and deadtime effects can be performed as described in this test method: by establishing a mass bias factor using the NBL U-500 standard on a routine or batch basis, and verifying or adjusting the deadtime correction factor. Alternatively, the factors can be determined less frequently (such as weekly) and a linear calibration performed on a batch basis for each of the three isotopic ratios measured:

^{234}U/^{235}U, ^{236}U/^{235}U, and ^{235}U/^{238}U. A three-point calibration is suggested, using the standards in 8.16-8.19. The isotopic calibrations of measured versus certified ratios could then be used to make any short-term corrections to the measured ratios for mass bias and deadtime effects, while the factors would be determined weekly and applied to the data. The range of the ratio calibrations can be set according to the weight percents normally found in the soils analyzed by the user and the NBL standards selected as such. For the data presented, the ^{235}U/^{238}U calibration was from 0.5 to 3.0 weight %.

X1.2 The three NBL isotopic standards are run with both phases of the batch analysis to perform the isotopic ratio calibration for the three measured ratios. The mass bias correction factors are applied to the measured ratio data, including the data from the isotopic calibration standards analyzed with each batch, as discussed in 13.3. A linear isotopic calibration curve is then established for each of the three ratios of interest:

$$[(RATIO) \text{ certified} = (RATIO) \text{ measured} \times \text{slope} + Y \text{ intercept}] \quad (X1.1)$$

The three ratios for each sample are then corrected as follows:

$$[(RATIO) \text{ corrected} = (RATIO) \text{ measured} \times \text{slope} + Y \text{ intercept}] \quad (X1.2)$$

The user may find this to be unnecessary or beyond the data QC level desired and that adequate corrections can be achieved with the mass bias factor determinations. The significance or need for the calibration can be examined by checking how close the slopes are to 1 and the Y intercepts are to 0. The frequency of the mass bias factor determination can also be changed, and the data quality control can be assessed against its statistical variation over time. In any type of calibration or

correction, the ion intensity of the standard(s) should not be largely different from the samples in order to avoid differing deadtime effects.

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