



Standard Test Method for the Determination of Uranium Content and Isotopic Composition by Isotope Dilution Mass Spectrometry¹

This standard is issued under the fixed designation C 1380; 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 a method for the determination of the uranium concentration in uranium oxides by isotope dilution mass spectrometry (IDMS). The isotopic composition of the oxide is measured simultaneously.

1.2 *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:*

D 1193 Specification for Reagent Water²

3. Summary of Test Method

3.1 For measurement of the elemental uranium concentration of uranium oxides by IDMS, a representative and accurately measured aliquot of the sample is prepared. A known quantity of ²³³U (“spike”) is added to an aliquot of the sample. The sample aliquot and spike are taken to dryness, redissolved in dilute nitric acid, and loaded on a filament for analysis in a thermal ionization mass spectrometer (TIMS). After measurement of the isotopic ratios in the spiked sample, the uranium content and isotopic composition of sample are calculated.

4. Significance and Use

4.1 Determination of percent uranium content and ²³⁵U abundance in oxides and other materials containing high concentrations of uranium is required for special nuclear materials accountability, regulatory requirements, and process control.

5. Interferences

5.1 The calculations assume any ²³³U in the sample is negligible. If the sample contains significant ²³³U, the sample must be analyzed for isotopic composition with and without added spike, and the calculations adjusted accordingly.

6. Apparatus

6.1 Thermal ionization mass spectrometer (TIMS) configured with Faraday cup detectors and an automated operating system.

6.2 Preconditioning unit for the TIMS.

6.3 Filament loading assembly for the TIMS.

6.4 Balance, analytical, with five-place range.

6.5 Vials, glass, disposable with plastic caps.

6.6 Pipet, automatic, Ranin or equivalent, variable to 1000 μL.

6.7 Pipet tips, disposable plastic, 100–1000 μL.

6.8 Liquid dispenser, Repipette[™] or equivalent.

7. Reagents and Materials

7.1 *Purity of Materials*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specification of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.³ Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall mean reagent water in conformance with Specification D 1193.

7.3 *Nitric Acid*, HNO₃, concentrated (70 %).

7.4 *Nitric Acid*, 0.8 M (5 % v/v)—Cautiously add 50 mL of concentrated nitric acid to 950 mL of water.

7.5 *Nitric Acid*, 0.1 M—Add 6.5 mL concentrated nitric acid to ≈900 mL of water, mix, and bring to 1000 mL with water.

7.6 *Hydrogen Peroxide* H₂O₂, 30 %.

7.7 *Elemental and Isotopic Uranium Standards* (New Brunswick Laboratory CRM 114, CRM 116 CRM 129, or equivalent⁴).

7.8 *Uranium-233 spike assay and isotopic standard* (NBL CRM 111–A⁴ or equivalent)—Dilute NBL CRM 111–A 1:50

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.

Current edition approved December 10, 1997. Published May 1998.

² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, Washington, D. C. 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 (USPC), Rockville, MD.

⁴ Available from the US Department of Energy, New Brunswick Laboratory, D 350, 9800 South Cass Avenue, Argonne, IL 60439.

by weight with a 5 % nitric acid to give a ^{233}U concentration of approximately $10\ \mu\text{g}\ ^{233}\text{U}/\text{g}$ solution.

NOTE 1—An exact 1:50 dilution is not required. The requirement is for precise and accurate weights of standard and diluent. Calculate the exact concentration of each isotope in the diluted spike standard in accordance with 11.2. Other dilutions of CRM-111A may be used if accurate weights are known, and the aliquot of CRM 111-A used in the measurement of test samples yields a $^{233}\text{U}/^{238}\text{U}$ ratio of at least 0.02, where X is the major uranium isotope.

8. Preparation of Apparatus

8.1 Prepare the thermal ionization mass spectrometer (TIMS) in accordance with manufacturer's recommendations.

9. Calibration and Standardization

9.1 Standardization of ^{233}U Spike Solution:

9.1.1 Prior to using a new diluted spike solution, verify the concentration of the solution with CRM 129 uranium oxide or its equivalent. If the new spike solution does not give results within control limits, its standardized concentration must be verified with another NBL certified reference material for elemental uranium, such as CRM 114 or equivalent.

9.2 Calibration of TIMS:

9.2.1 Calibrate the TIMS in accordance with manufacturer's recommendations to achieve the user's performance and quality assurance criteria.

10. Procedure

10.1 Weigh, to the nearest 0.01 mg, a labeled vial and cap for each sample; record the weight.

10.2 Tare the balance and weight, to the nearest 0.01 mg, a 0.35–0.45 g aliquot of the sample into the vial. Record the weight.

NOTE 2—Smaller or larger aliquots of sample may be used. However, the sample size should be sufficient to obtain a representative sample of the material and the ratio of the measured ^{233}U to major uranium isotope in the material must be greater than 0.02. It is recommended that samples be prepared in duplicate.

10.3 Cautiously add 5 mL concentrated HNO_3 to the sample and heat slowly on a hot plate to dissolve the sample.

10.4 Heat the sample/ HNO_3 to dryness.

10.5 Remove the sample from the hot plate and examine the residue.

NOTE 3—If conversion of the sample to orange/red uranium nitrate/oxide was incomplete, repeat Steps 10.3–10.5.

10.6 After conversion is complete and the sample is dry, cool the vial, add 40 mL 0.8 M HNO_3 , and cap with the appropriate plastic lined cap.

10.7 Mix the vial contents thoroughly by inverting vigorously.

10.8 Weigh the vial and its contents to the nearest 0.1 mg and record the weight.

10.9 Label a new 20-mL vial with sample identification number and "Dil 1."

10.10 Place the labeled vial and a plastic lined cap on the balance, and zero the balance.

10.11 Add 0.5 mL of the original dilution (from step 10.8), set the cap on the vial, and record the weight to the nearest 0.01 mg.

10.12 Tare the balance, add 20 mL of 0.8 M HNO_3 , and record the weight to the nearest 0.01 mg.

10.13 Cap the vial and mix the contents thoroughly by inverting vigorously.

10.14 Label a third vial with sample identification and "Dil 2," place the vial and a plastic lined cap on the balance, and zero the balance.

10.15 Add 0.5 mL of Dilution 1, set the cap on the vial, and record the weight to the nearest 0.01 mg.

10.16 Tare the balance, add 0.5 mL of ^{233}U spike solution to the vial, and record the weight to the nearest 0.01 mg.

10.17 Add five drops of 30 % H_2O_2 and 1 mL of concentrated HNO_3 to the vial, set it on the hot plate, and heat to dryness.

10.18 Remove from the hot plate, cool, and add 0.02 mL 0.1 M HNO_3 .

10.19 Swirl or agitate the vial to dissolve the sample.

10.20 Load 4 μL of the dissolved sample (Step 10.19) on a filament for analysis in the TIMS.

10.21 Analyze in accordance with the user's standard operating procedure for TIMS analysis.

NOTE 4—Follow the requirements for analysis of duplicate samples, standards, or controls as recommended in the user's quality control plan.

11. Calculation

11.1 From the certified reference values of the ^{233}U spike standard (obtained from the certificate of analysis) and any standardization performed per Step 9.1, calculate the exact concentration of each isotope (in $\mu\text{g}/\text{g}$) in the spike solution.

$$\frac{\mu\text{g isotope}}{\text{g certified solution}} = \frac{\mu\text{moles U (total)}}{\text{g certified solution}} \times \text{at fract'n isotope} \times \text{at mass isotope} \quad (1)$$

where the atomic mass for each isotope⁵ is as follows:

$$\begin{aligned} ^{233}\text{U} &= 233.039627\ \mu\text{g}/\mu\text{mol}, \\ ^{234}\text{U} &= 234.040945\ \mu\text{g}/\mu\text{mol}, \\ ^{235}\text{U} &= 235.043922\ \mu\text{g}/\mu\text{mol}, \\ ^{236}\text{U} &= 236.045561\ \mu\text{g}/\mu\text{mol}, \text{ and} \\ ^{238}\text{U} &= 238.050784\ \mu\text{g}/\mu\text{mol}. \end{aligned}$$

11.2 Using the weights obtained during standard dilution in Step 7.8, calculate the exact concentrations of each isotope present in the working spike solution:

$$\frac{\mu\text{g isotope}}{\text{g working solution}} = \frac{\mu\text{g isotope}}{\text{g certified solution}} \times \frac{\text{g certified solution (dispensed)}}{\text{g working spike solution (prepared)}} \quad (2)$$

11.3 From the sample analysis, obtain the isotopic ratios for the spiked sample for ^{233}U , ^{234}U , ^{235}U , and ^{236}U to ^{238}U .

11.4 Using the amount of spike added to the sample in Step 10.16 and the concentrations obtained from Step 11.2, calculate the amounts of spike added for each isotope:

$$\mu\text{g isotope added} = \text{g working spike solution added} \times \frac{\mu\text{g isotope}}{\text{g working spike solution}} \quad (3)$$

11.5 Using the $^{233}\text{U}/^{238}\text{U}$ ratio, the ^{233}U added in the spike,

⁵ CRC Handbook of Chemistry & Physics, 77th Edition (1996–1997), CRC Press, Inc., Boca Raton, FL, pp. 135–136.

and the sample mass, calculate the amount of ^{238}U present in the sample. The value is corrected for any ^{238}U present in the spiking solution as calculated in Step 11.2:

$$\frac{\mu\text{g } ^{238}\text{U}}{\text{g sample}} = \frac{R \times \mu\text{g } ^{233}\text{U added} \times A - \mu\text{g } ^{238}\text{U added}}{\text{#g sample}} \quad (4)$$

where:

R = $1/R_1$,
 R_1 = $^{233}\text{U}/^{238}\text{U}$ atomic ratio,
 A = atomic mass ^{238}U /atomic mass ^{233}U , and
 #g sample = $F1 \times F2 \times W2$.

where:

$F1$ = weight sample aliquot, g*/total weight, g⁺,
 $F2$ = weight used for Dil 1, g**/total weight Dil 1, g⁺⁺,
 $W2$ = weight Dil 1 analyzed, g[@],

g* is from Step 10.2;

g** is from Step 10.11;

g⁺ is weight from Step 10.8—tare of vial and cap Step 10.1;

g⁺⁺ is from Steps 10.11 and 10.12; and

g[@] is from Step 10.15.

11.6 Using the individual ratios from the sample analysis for ^{234}U , ^{235}U , and ^{236}U , calculate the amount of each isotope present in the sample. The individual values are corrected for the amount of each isotope present in the spiking solutions as calculated in Step 11.2:

$$\frac{\mu\text{g isotope}}{\text{g sample}} = \frac{RX \times \mu\text{g } ^{233}\text{U added} \times AX - \mu\text{g } ^{23X}\text{U added}}{\text{#g sample}} \quad (5)$$

where:

$R2$ = $^{23X}\text{U}/^{238}\text{U}$ atomic ratio,

RX = $R2/R1$ (see Step 11.5), and

AX = atomic mass ^{23X}U /atomic mass ^{233}U .

11.7 To calculate the concentration of total uranium, add up the concentrations calculated for each isotope in Steps 11.5 and 11.6.

12. Precision and Bias

12.1 Aliquots of NBL CRM-129 were prepared and analyzed over a 12-month period by four analysts. Two hundred data points were collected. The average for total uranium content was 0.84788 g U/g oxide with a relative standard deviation of 0.42 % (the certified value is 0.84773 g U/g oxide). The average percent ^{235}U content was 0.714 %, with a relative standard deviation of 0.87 % at the 0.72 % ^{235}U level (also 200 points collected). The percent ^{235}U value is not yet certified for NBL CRM-129, but the preliminary value is 0.72 %. The t-test for bias showed no significant bias in this data at the 95 % confidence level.

13. Keywords

13.1 isotope dilution mass spectrometry (IDMS); uranium concentration; uranium isotopes

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).