



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

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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:*²

D1193 Specification for Reagent Water

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 μ L.

6.7 Pipet tips, disposable plastic, 100–1000 μ L.

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 D1193.

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

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 *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. Pharmacopeial Convention (USPC), Rockville, MD.

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 \approx 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 by weight with a 5 % nitric acid to give a ²³³U concentration of approximately 10 μ g ²³³U/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 111–A may be used if accurate weights are known, and the aliquot of CRM 111–A used in the measurement of test samples yields a ²³³U/²³⁵U 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 ²³³U 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 weigh, 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 ²³³U 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 HNO₃ to the sample and heat slowly on a hot plate to dissolve the sample.

10.4 Heat the sample/HNO₃ 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 HNO₃, 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 HNO₃, 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 ²³³U spike solution to the vial, and record the weight to the nearest 0.01 mg.

10.17 Add five drops of 30 % H₂O₂ and 1 mL of concentrated HNO₃ 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 HNO₃.

10.19 Swirl or agitate the vial to dissolve the sample.

10.20 Load 4 μ L 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 ²³³U spike standard (obtained from the certificate of analysis) and any standardization performed per Step 9.1, calculate the exact concentration of each isotope (in μ g/g) in the spike solution.

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

⁴ Available from the US Department of Energy, New Brunswick Laboratory, D350, 9800 South Cass Avenue, Argonne, IL 60439. CRM 114 and CRM 129 have been replaced by CRM 129A.

where the atomic mass for each isotope 55CRC Handbook of Chemistry & Physics, 77th Edition (1996–1997), CRC Press, Inc., Boca Raton, FL, pp. 135–136. is as follows:

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

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, 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:

$$\begin{aligned}R &= 1/R1, \\ R1 &= ^{233}\text{U}/^{238}\text{U} \text{ atomic ratio}, \\ A &= \text{atomic mass } ^{238}\text{U}/\text{atomic mass } ^{233}\text{U}, \text{ and} \\ \text{\#g sample} &= F1 \times F2 \times W2.\end{aligned}$$

where:

$$\begin{aligned}F1 &= \text{weight sample aliquot, g}^*/\text{total weight, g}^+, \\ F2 &= \text{weight used for Dil 1, g}^{**}/\text{total weight Dil 1, g}^{++}, \\ W2 &= \text{weight Dil 1 analyzed, g}^{\textcircled{a}},\end{aligned}$$

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

$g^{\textcircled{a}}$ 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:

$$\begin{aligned}R2 &= ^{23X}\text{U}/^{238}\text{U} \text{ atomic ratio}, \\ RX &= R2/R1 \text{ (see Step 11.5), and} \\ AX &= \text{atomic mass } ^{23X}\text{U}/\text{atomic mass } ^{233}\text{U}.\end{aligned}$$

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 One hundred aliquants of CRM 114, a normal oxide with certified value of 0.847396 g U/g, were analyzed by four analysts on two Thermal Ionization Mass Spectrometers over a period of several months. The average measured uranium content was 0.847689 gU/g, with a relative standard deviation of 0.18 %. In the same time period, analysis of 80 aliquants of CRM 129, certified value 0.847726, gave a measured uranium content of 0.847906, with a relative standard deviation of 0.17 %. For CRM 116, a highly enriched metal uranium standard containing 0.999673 gU/g, 53 aliquants were analyzed over the same time period. The average measured value was 0.999422 gU/g with a relative standard deviation of 0.15 %. The average measured percentage of U-235 for CRM 116 was 93.124, with a relative standard deviation of 0.004 %. The certified value for this standard is 93.1215 wt % ^{235}U . The t -test for bias showed no significant bias in this data at the 95 % confidence level.

12.2 For each attribute being measured, the measurement data set was tested for bias. The test calculates the t statistic:

$$t = \frac{|Meas - Ref|}{\sqrt{U^2(Meas) + U^2(Ref)}} \quad (6)$$

where:

$$\begin{aligned}Meas &= \text{mean of the measured attribute value data set,} \\ Ref &= \text{reference value,} \\ U(Meas) &= \text{standard uncertainty of the measured value,} \\ &\text{which is the standard deviation of the data set} \\ &\text{divided by the square root of the number of} \\ &\text{observations in the data set; that is, the standard} \\ &\text{error of the data set, and} \\ U(Ref) &= \text{standard uncertainty of the reference value,} \\ &\text{which is half of the 95 \% confidence interval} \\ &\text{radius associated with the reference value; for} \\ &\text{example, if the reference value and its associated} \\ &\text{95 \% confidence interval of an attribute is } 10 \pm \\ &\text{1, its standard uncertainty would be half of 1, or} \\ &\text{0.5.}\end{aligned}$$

This statistic is compared to values for a two-sided t -statistic with degrees of freedom (df) determined by the following formula:

$$df = \frac{(U^2(Meas) + U^2(Ref))^2}{\frac{U^4(Meas)}{N - 1} + \frac{U^4(Ref)}{60}} \quad (7)$$

which is a particular application of Satterthwaite's approximation for effective degrees of freedom, with an assignment of 60 degrees of freedom to the reference value uncertainty.

13. Keywords

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

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