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# Standard Test Method for
# Determination of Uranium Isotopic Composition by the Double Spike Method Using a Thermal Ionization Mass Spectrometer[1]

This standard is issued under the fixed designation C1871; 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 describes the determination of the isotope amount ratios of uranium material as nitrate solutions by the double spike (DS) method using a thermal ionization mass spectrometer (TIMS) instrument.

1.2 The analytical performance in the determination of the $^{235}$U/$^{238}$U major isotope amount ratio by the DS method is five to ten times better in terms of the internal and external reproducibility compared to the ("classical") total evaporation (TE) method as described in Test Method C1672 and the "modified total evaporation" (MTE) as described in Test Method C1832. This is due to the use of an *internal* rather than *external* mass fractionation correction by using a double spike material with a known or certified $^{233}$U/$^{236}$U isotope ratio, which is mixed with the sample prior to the measurement, either during the sample preparation or directly on the TIMS filament.

1.3 The DS method cannot be applied for the determination of the $^{236}$U/$^{238}$U minor isotope amount ratio, and is also not recommended for the determination of the $^{234}$U/$^{238}$U minor isotope amount ratio.

1.4 In case the uranium amount concentration of the double spike is known or certified, the uranium amount concentration of the sample can be determined using the isotope dilution mass spectrometry (IDMS) method as described in Test Method C1672, by blending the sample gravimetrically with the double spike and performing a DS measurement.

1.5 An external mass fractionation correction by measurements of a certified reference material loaded on different filaments and measured in the same measurement sequence, as recommended for TE and required for MTE measurements, is not necessary for the DS method. However, for quality control (QC) purposes it is recommended to perform DS measurements of low enriched or natural uranium isotopic reference materials on a regular basis.

1.6 The DS method can only be applied to uranium samples with relative isotope abundances $^{233}$U/U and $^{236}$U/U below $10^{-5}$, the DS method is therefore mainly used for low enriched or close to natural uranium samples.

1.7 *Units*—The values stated in SI units are to be regarded as the standard. When no SI units are provided, the values are for information only.

1.8 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.9 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

2.1 *ASTM Standards:*[2]

C753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder
C776 Specification for Sintered Uranium Dioxide Pellets for Light Water Reactors
C787 Specification for Uranium Hexafluoride for Enrichment

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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.

C833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets for Light Water Reactors
C859 Terminology Relating to Nuclear Materials
C967 Specification for Uranium Ore Concentrate
C996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % $^{235}U$
C1008 Specification for Sintered (Uranium-Plutonium) DioxidePellets—Fast Reactor Fuel (Withdrawn 2014)[3]
C1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry
C1128 Guide for Preparation of Working Reference Materials for Use in Analysis of Nuclear Fuel Cycle Materials
C1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials
C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis
C1411 Practice for The Ion Exchange Separation of Uranium and Plutonium Prior to Isotopic Analysis
C1672 Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer
C1832 Test Method for Determination of Uranium Isotopic Composition by the Modified Total Evaporation (MTE) Method Using a Thermal Ionization Mass Spectrometer
D1193 Specification for Reagent Water
E2586 Practice for Calculating and Using Basic Statistics
E2655 Guide for Reporting Uncertainty of Test Results and Use of the Term Measurement Uncertainty in ASTM Test Methods

## 3. Terminology

3.1 Terminology C859 contains terms, definitions, descriptions of terms, nomenclature, and explanations of acronyms and symbols specifically associated with standards under the jurisdiction of Committee C26 on Nuclear Fuel Cycle.

3.2 *Definitions:*

3.2.1 *abundance sensitivity, n*—in isotope amount ratio measurements, the ratio of the measured intensity of an ion beam at a mass, *m*, to the measured intensity from the same isotope measured at one mass unit difference (for example, $m \pm 1$).

3.2.1.1 *Discussion*—

Abundance sensitivity is a measure of the magnitude of the peak tailing correction. For measuring uranium on thermal ionization mass spectrometer (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS) instruments, the abundance sensitivity is typically calculated as the ratio of the measured signal intensities at masses 237 and 238 using a suitable uranium sample.

3.2.2 *modified total evaporation, MTE, n*—analytical method for determination of isotope amount ratios of uranium, as described in Test Method C1832.

3.2.3 *total evaporation, TE, n*—analytical method for determination of isotope amount ratios of uranium or plutonium, as described in Test Method C1672, also called "classical" total evaporation in this test method.

3.2.4 *turret, n*—holder for sample filaments.

3.2.4.1 *Discussion*—

Alternate names for turret are carousel, magazine, and wheel.

3.3 *Acronyms:*

3.3.1 *CRM*—certified reference material

3.3.2 *DS*—double spike

3.3.3 *DU*—depleted uranium

3.3.4 *EU*—European Union

3.3.5 *FAR*—Faraday Cup

3.3.6 *HEU*—high enriched uranium

3.3.7 *IAEA*—International Atomic Energy Agency

3.3.8 *ICPMS*—inductively coupled mass spectrometry

3.3.9 *IRMM*—Institute for Reference Materials and Measurements (since 1 July 2016 called JRC-Geel, the only unit working with nuclear materials at JRC-Geel is JRC-G.2)

3.3.10 *ITU*—Institute for Transuranium Elements (since 1 July 2016 called JRC-Karlsruhe, the only unit involved with thermal ionization mass spectrometry measurements of nuclear materials at JRC-Karlsruhe is JRC-G.II.6)

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[3] The last approved version of this historical standard is referenced on www.astm.org.

3.3.11 *JRC*—Joint Research Centre

3.3.12 *LEU*—low enriched uranium

3.3.13 *MTE*—modified total evaporation

3.3.14 *NBL*—New Brunswick Laboratory (since 15 May 2016 called NBL-Program Office)

3.3.15 *NML*—Nuclear Material Laboratory (part of the IAEA)

3.3.16 *QC*—quality control

3.3.17 *RSD*—relative standard deviation—SD (see below) divided by the mean value of the observations in repeated sampling.

3.3.18 *RSE*—relative standard error—SE (see below) divided by the mean value of the observations in repeated sampling.

3.3.19 *SD*—standard deviation—according to Practice E2586, 3.1.30: The square root of the sum of the squared deviations of the observed values in the sample divided by the sample size minus 1.

3.3.20 *SE*—standard error—according to Practice E2586, 3.1.29: Standard deviation of the population of values of a sample statistic (that is, the mean value) in repeated measurements, or an estimate of it.

3.3.20.1 *Discussion—*

According to Practice E2586, 3.1.30: If the standard error (SE, see above) of a statistic is estimated, it will itself be a statistic with some variance that depends on the sample size, that is, the number of observed values in the sample (Practice E2586, 3.1.26).

3.3.20.2 *Discussion—*

According to Practice E2655, 5.8.4.1: From statistical theory, a 95 % confidence interval for the mean of a normal distribution, given n independent observations $x_1$, $x_2$, ..., $x_n$ drawn from the distribution, is $\bar{x} \pm t \times SD / \sqrt{n}$, where $\bar{x}$ is the sample mean, SD is the standard deviation of the observations (see above), and t is the 0.975 percentile of the Student's t distribution with n-1 degrees of freedom. Because Student's t distribution approaches the normal as n increases, the value of t approaches 1.96 as n increases. This is the basis for using the (coverage) factor 2 for expanded uncertainty. The standard error (SE) of the mean value of a series of n independent repeated measurements can be derived from that by using t = 1, so the standard error (SE) is given by $SD / \sqrt{n}$.

3.3.21 *TIMS*—thermal ionization mass spectrometry

3.3.22 *WRM*—working reference material

## 4. Summary of Test Method

4.1 The double spike method has been developed with the intention to improve the precision and decrease the uncertainties for $^{235}U/^{238}U$ major isotope ratio measurements compared to the known methods such as the "classical" total evaporation technique (**1-4**),[4] also described in Test Method C1672, and the modified total evaporation technique (**5 and 6**), also described in Test Method C1832. For the double spike method the mass fractionation correction for the $^{235}U/^{238}U$ ratio is performed *internally throughout the measurement* rather than *externally*, by using the mass fractionation observed for a double spike material with a known or certified $^{233}U/^{236}U$ isotope ratio (also spanning three mass units), which is mixed with the sample prior to the measurement, either during the sample preparation or directly on the TIMS filament. If necessary, uranium is separated from plutonium and other elements (to eliminate isobaric interferences) by selective extraction, anion exchange (see Practice C1411), or extraction chromatography. The purified uranium fraction as nitrate solution is loaded onto an evaporation filament (made of metals such as rhenium, zone-refined rhenium, or tungsten with high evaporation temperature), and blended with an appropriate amount of double spike solution, and converted to an oxide by controlled heating of the filament under atmospheric conditions. In case only the $^{235}U/^{238}U$ ratio of the sample has to be determined, it is recommended to mix the sample with the double spike during the loading process on the filament. In case the uranium amount concentration of the sample has to be determined, the sample solution has to be blended gravimetrically with the double spike solution prior to filament loading, for which weighable amounts have to be used.

4.2 The sample amount to be loaded for DS analyses is within a range of about 4 to 6 µg to achieve ion beam signals of about 20 to 30 V for the major isotope $^{238}U$ for DU, NU, and LEU samples.

4.3 The $^{235}U/^{238}U$ isotope amount ratios are corrected for mass fractionation for each integration step individually. This is accomplished in an internal manner, the magnitude of the mass fractionation is calculated from the measured mass fractionation of the $^{233}U/^{236}U$ ratio. The peak tailing contributions are determined at two mass positions, 0.5 mass units below and 0.5 mass units above the isotope masses of interest.

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[4] The boldface numbers in parentheses refer to a list of references at the end of this standard.