



# Standard Test Method for Determination of Uranium Isotopic Composition by the Modified Total Evaporation (MTE) Method Using a Thermal Ionization Mass Spectrometer<sup>1</sup>

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## 1. Scope

1.1 This test method describes the determination of the isotope amount ratios of uranium material as nitrate solutions by the modified total evaporation (MTE) method using a thermal ionization mass spectrometer (TIMS) instrument.

1.2 The analytical performance in the determination of the  $^{235}\text{U}/^{238}\text{U}$  major isotope amount ratio by MTE is similar to the (“classical”) total evaporation (TE) method as described in Test Method C1672. However, in the MTE method, the evaporation process is interrupted on a regular basis to allow measurements and subsequent corrections for background from peak tailing, perform internal calibration of a secondary electron multiplier (SEM) detector versus the Faraday cups, peak centering, and ion source refocusing. Performing these calibrations and corrections on a regular basis during the measurement, improves precision, and significantly reduces uncertainties for the minor isotope amount ratios  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  as compared to the TE method.

1.3 In principle, the MTE method yields major isotope amount ratios without the need for mass fractionation correction. However, depending on the measurement conditions, small variations are seen among sample turrets; therefore, a small correction based on measurements of a certified reference material is recommended to improve consistency. The uncertainty around the mass fractionation correction factor usually includes unity.

1.4 *Units*—The values stated in SI units are to be regarded as the standard. When non-SI units are provided, they are for information only.

1.5 *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.*

<sup>1</sup> 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. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- C753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder
- C776 Specification for Sintered Uranium Dioxide Pellets
- C787 Specification for Uranium Hexafluoride for Enrichment
- C833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets
- C859 Terminology Relating to Nuclear Materials
- C967 Specification for Uranium Ore Concentrate
- C996 Specification for Uranium Hexafluoride Enriched to Less Than 5 %  $^{235}\text{U}$
- C1008 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets—Fast Reactor Fuel (Withdrawn 2014)<sup>3</sup>
- 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
- C1625 Test Method for Uranium and Plutonium Concentrations and Isotopic Abundances by Thermal Ionization Mass Spectrometry
- C1672 Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer
- D1193 Specification for Reagent Water

<sup>2</sup> 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.

<sup>3</sup> The last approved version of this historical standard is referenced on www.astm.org.

**E2655** Guide for Reporting Uncertainty of Test Results and Use of the Term Measurement Uncertainty in ASTM Test Methods

**E2586** Practice for Calculating and Using Basic Statistics

### 3. Terminology

3.1 The terminology standard **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 *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.

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

3.2.3.1 *Discussion*—Alternate names for turret are carousel, magazine, wheel.

#### 3.3 Acronyms:

3.3.1 *cpm*—counts per minute

3.3.2 *cps*—counts per second

3.3.3 *CRM*—certified reference material

3.3.4 *dark noise*—observed count rate on an ion counting detector measured without incident ion beam

3.3.5 *DS*—double spike

3.3.6 *DU*—depleted uranium

3.3.7 *EU*—European Union

3.3.8 *FAR*—Faraday Cup

3.3.9 *HEU*—high enriched uranium

3.3.10 *IAEA*—International Atomic Energy Agency

3.3.11 *ICPMS*—inductively coupled plasma mass spectrometry

3.3.12 *IRMM*—Institute for Reference Materials and Measurements

3.3.13 *ITU*—Institute for Transuranium Elements

3.3.14 *JRC*—Joint Research Centre

3.3.15 *LEU*—low enriched uranium

3.3.16 *MTE*—modified total evaporation

3.3.17 *NBL*—New Brunswick Laboratory

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

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

3.3.20 *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 one.

3.3.21 *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.

3.3.21.1 *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).

3.3.21.2 *Discussion*—According to Guide **E2655**, 5.8.4.1: From statistical theory, a 95 % confidence interval for the mean of a normal distribution, given  $n$  independent observations  $x_1, x_2, \dots, x_n$  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  $SD / \sqrt{n}$ .

3.3.22 *SEM*—secondary electron multiplier.

3.3.22.1 *Discussion*—In the scientific literature the acronym SEM is also used for Scanning Electron Microscope, but within this test method SEM represents Secondary Electron Multiplier.

3.3.23 *SGAS*—Safeguards Analytical Services Laboratory of the IAEA

3.3.24 *TIMS*—thermal ionization mass spectrometry

### 4. Summary of Test Method

4.1 The modified total evaporation method has been developed on the basis of the “classical” total evaporation technique **(1-4)**<sup>4</sup>, also described in Test Method **C1672**. By using the total evaporation technique, the mass fractionation is minimized by evaporating the entire sample amount loaded on the filament, in contrast to the “conventional” technique as described in Test Method **C1625**. The MTE method has already been described in detail in Refs **(5)** and **(6)**. 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 a degassed

<sup>4</sup> The boldface numbers in parentheses refer to a list of references at the end of this standard.

filament (made of metals such as rhenium, zone-refined rhenium, or tungsten with high evaporation temperature) and converted to an oxide by controlled heating of the filament under atmospheric conditions. For the modified total evaporation method, the uranium load is in the range of about 2 to 6  $\mu\text{g}$ , which is about one to two orders of magnitude higher than that typically used for the “classical” total evaporation method by TIMS. The sample filament is mounted on the sample turret using a double-filament configuration. This configuration consists of an evaporation filament (Re or W) on which the sample is loaded, and an ionization filament (Re filament with no sample). For a measurement in the mass spectrometer, the ionization filament is heated to a temperature of about 1800 to 1900°C, sufficient to generate  $^{187}\text{Re}$  ion beam signals of 150 to 400 mV (corresponding to ion currents of 1.5 to  $4 \times 10^{-12}$  A using an amplifier resistor of  $10^{11} \Omega$ ). The intensity of the optimized  $^{187}\text{Re}$  signal depends on the Re material (zone-refined or non-zone-refined), thickness and the measurement conditions, but it is expected to be the same for all filaments on the same sample turret. The  $^{187}\text{Re}$  ion current is also used for the initial ion beam focusing. The evaporation filament is heated next. After ion beam re-focusing and mass re-adjustment initially using a small sum intensity (sum of  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$ , and  $^{238}\text{U}$ ) of about 1 to 3 V, the data acquisition begins under computer control to yield a predefined target sum intensity of 20 to 30 V (corresponding to ion currents of 2 to  $3 \times 10^{-10}$  A using an amplifier resistor of  $10^{11} \Omega$ ). This target value depends on the amount of uranium loaded on a filament. The MTE analysis takes between 2 and 5 h per sample filament and is about three to ten times longer than typical (“classical”) TE analyses in spite of the higher intensities at which the analyses are performed. To ensure that the whole sample is completely evaporated and analyzed before the ionization filament breaks as a result of overheating, the MTE analysis routine is programmed to increase the target sum intensity during the course of the analysis if necessary. The occurrences of outliers due to technical glitches, for example, as a result of termination before complete sample evaporation or because of early sample exhaustion, are minimized by a dynamic target intensity control feature through manipulation of the target sum intensity depending on the actual measurement conditions.

4.2 The sample amount to be loaded for MTE analyses is limited to a range of about 2 to 6  $\mu\text{g}$  to achieve ion beam signals of about 20 to 30 V for the major isotope –  $^{238}\text{U}$  for DU, NU, and LEU samples and  $^{235}\text{U}$  for HEU samples – corresponding to a  $^{234}\text{U}$  intensity of 1 to 10 mV. This causes the  $^{234}\text{U}$  ion beam to be suitable for an internal cross calibration of the SEM versus the Faraday cups through the entire measurement time. This also allows the  $^{236}\text{U}/^{238}\text{U}$  isotope amount ratio to be measured in a wide dynamic range from  $10^{-2}$  down to  $10^{-10}$  using a Faraday cup or an SEM in combination with an energy filter for improved abundance sensitivity. For certain DU samples, the  $^{236}\text{U}$  ion beam is used for the cross calibration and the  $^{234}\text{U}$  is measured on the SEM (known as “reverse” MTE, see 13.8.8). For all samples with minor ratios  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  higher than  $4 \times 10^{-5}$ , which also includes HEU

samples, the minor isotopes are only measured using Faraday cups with amplifier resistors of  $10^{12} \Omega$  yielding a favorable signal-to-noise ratio.

4.3 Similar to the TE analysis, the isotope ion beams of the major isotopes  $^{235}\text{U}$  and  $^{238}\text{U}$  are integrated over the course of the analysis, and the summed intensity for  $^{235}\text{U}$  is divided by the summed intensity for  $^{238}\text{U}$  to yield the major isotope amount ratio. The result of the major isotope amount ratio is corrected for mass fractionation using the measurement of a CRM analyzed on the same sample turret.

4.4 The minor 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 for the minor ratios is calculated from the measured mass fractionation of the major ratio. The peak tailing contributions are determined at two positions, slightly below and above the isotope masses of interest. If applicable, the SEM-versus-Faraday calibration is also performed for each integration step individually.

## 5. Significance and Use

5.1 Uranium material is used as a fuel in certain types of nuclear reactors. To be suitable for use as nuclear fuel, the starting material shall meet certain specifications such as those described in Specifications C753, C776, C787, C833, C967, C996, and C1008, or as specified by the purchaser. The isotope amount ratios of uranium material can be measured by mass spectrometry following this test method to ensure that they meet the specification.

5.2 The MTE method can be used for a wide range of sample sizes even in samples containing as low as 50  $\mu\text{g}$  of uranium. If the uranium sample is in the form of uranium hexafluoride, it can be converted into a uranium nitrate solution for measurement by the MTE method. The concentration of the loading solution for MTE has to be in the range of 1 to 6 mg/g to allow a sample loading of 2 to 6  $\mu\text{g}$  of uranium. A minimum loading of 3  $\mu\text{g}$  uranium per filament is recommended. This is needed to have a suitable ion signal especially for the two minor isotopes ( $^{234}\text{U}$  and  $^{236}\text{U}$ ) thus enabling the internal calibration of SEM versus the Faraday cups during the measurement.

5.3 Until now, the instrument capabilities for the MTE method have only been implemented on the TRITON™ TIMS instrument.<sup>5</sup> Therefore all recommendations for measurement parameters in this test method are specified for the TRITON™ TIMS instrument. The manufacturers of other TIMS instruments (for example, IsotopX and Nu Instruments) have plans to implement the modifications needed in their instruments to use the MTE method.

5.4 The MTE method described here can also be extended to measurement of elements other than uranium. Note that the MTE method has already been implemented for plutonium and calcium.

<sup>5</sup> The TRITON™ (Plus) Multicollector Thermal Ionization Mass Spectrometer is a trademark product of Thermo Fisher Scientific, <http://www.thermoscientific.com/content/tfs/en/product/triton-plus-multicollector-thermal-ionization-mass-spectrometer.html#sthash.stbDyJBG.dpuf>.