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# Standard Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer<sup>1</sup>

This standard is issued under the fixed designation C1672; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This method describes the determination of the isotopic composition, or the concentration, or both, of uranium and plutonium as nitrate solutions by the total evaporation method using a thermal ionization mass spectrometer (TIMS) instrument. Purified uranium or plutonium nitrate solutions are deposited onto a metal filament and placed in the mass spectrometer. Under computer control, ion currents are generated by heating of the filament(s). The ion currents are continually measured until the whole sample is exhausted. The measured ion currents are integrated over the course of the measurement and normalized to a reference isotope ion current to yield isotope ratios.

1.2 In principle, the total evaporation method should yield isotope ratios that do not require mass bias correction. In practice, samples may require this bias correction. Compared to the conventional TIMS method described in Test Method C1625, the total evaporation method is approximately two times faster, improves precision of the isotope ratio measurements by a factor of two to four, and utilizes smaller sample sizes. Compared to the C1625 method, the total evaporation method provides “major” isotope ratios  $^{235}\text{U}/^{238}\text{U}$  and  $^{240}\text{Pu}/^{239}\text{Pu}$  with improved accuracy.

1.3 The total evaporation method is prone to biases in the “minor” isotope ratios ( $^{233}\text{U}/^{238}\text{U}$ ,  $^{234}\text{U}/^{238}\text{U}$ , and  $^{236}\text{U}/^{238}\text{U}$  ratios for uranium materials and  $^{238}\text{Pu}/^{239}\text{Pu}$ ,  $^{241}\text{Pu}/^{239}\text{Pu}$ ,  $^{242}\text{Pu}/^{239}\text{Pu}$ , and  $^{244}\text{Pu}/^{239}\text{Pu}$  ratios for plutonium materials) due to peak tailing from adjacent major isotopes. The magnitude of the absolute bias is dependent on measurement and instrumental characteristics. The relative bias, however, depends on the relative isotopic abundances of the sample. The use of an electron multiplier equipped with an energy filter may eliminate or diminish peak tailing effects. Measurement of the abundance sensitivity of the instrument may be used to ensure

that such biases are negligible, or may be used to bias correct the minor isotope ratios.

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

1.5 *This standard may involve the use of hazardous materials and equipment. 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:<sup>2</sup>

- C753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder
- C757 Specification for Nuclear-Grade Plutonium Dioxide Powder for Light Water Reactors
- C776 Specification for Sintered Uranium Dioxide Pellets
- C787 Specification for Uranium Hexafluoride for Enrichment
- 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 %  $^{235}\text{U}$
- 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
- C1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials

<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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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto: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](http://www.astm.org).

- C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis
- 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
- C1415 Test Method for  $^{238}\text{Pu}$  Isotopic Abundance By Alpha Spectrometry
- C1625 Test Method for Uranium and Plutonium Concentrations and Isotopic Abundances by Thermal Ionization Mass Spectrometry
- C1816 Practice for The Ion Exchange Separation of Small Volume Samples Containing Uranium, Americium, and Plutonium Prior to Isotopic Abundance and Content Analysis
- 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
- D3084 Practice for Alpha-Particle Spectrometry of Water

### 3. Terminology

3.1 For definitions of terms used in this test method but not defined herein, refer to Terminology C859.

#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *isotopic equilibration, n*—series of chemical steps performed on a mixture of two samples (for example, a uranium sample and a uranium spike) to ensure identical valency and chemical form prior to purification of the mixture. Failure to perform isotopic equilibration of a sample-spike mixture may result in partial separation of the sample from the spike during the purification procedure, causing a bias in the results of isotope dilution mass spectrometry measurements.

3.2.2 *major ratio, n*—alternate expression for  $^{235}\text{U}/^{238}\text{U}$  (or  $^{238}\text{U}/^{235}\text{U}$ ) and  $^{240}\text{Pu}/^{239}\text{Pu}$  isotope ratios.

3.2.3 *minor ratios, n*—alternate expression for  $^{233}\text{U}/^{238}\text{U}$ ,  $^{234}\text{U}/^{238}\text{U}$ ,  $^{236}\text{U}/^{238}\text{U}$ ,  $^{234}\text{U}/^{235}\text{U}$ , and  $^{236}\text{U}/^{235}\text{U}$  or  $^{238}\text{Pu}/^{239}\text{Pu}$ ,  $^{241}\text{Pu}/^{239}\text{Pu}$ ,  $^{242}\text{Pu}/^{239}\text{Pu}$ , and  $^{244}\text{Pu}/^{239}\text{Pu}$  isotope ratios.

3.2.4 *turret, n*—holder for sample filaments, other words used: wheel, magazine.

#### 3.3 Acronyms:

- 3.3.1 CRM—Certified Reference Materials
- 3.3.2 DU—Depleted Uranium
- 3.3.3 HEU—High Enriched Uranium
- 3.3.4 IDMS—Isotope Dilution Mass Spectrometry
- 3.3.5 IRMM—Institute for Reference Materials and Measurements (IRMM is now known as European Commission Joint Research Center, JRC-Geel)
- 3.3.6 LEU—Low Enriched Uranium
- 3.3.7 NBL—New Brunswick Laboratory
- 3.3.8 NU—Natural Uranium
- 3.3.9 TIMS—Thermal Ionization Mass Spectrometry
- 3.3.10 WRM—Working Reference Material

### 4. Summary of Test Method

4.1 Uranium and plutonium are separated from each other and purified from other elements by selective anion exchange chromatography (such as in Practice C1411 or Test Method C1415 or C1816). The purified uranium or plutonium samples as nitrate solutions are drop-deposited or otherwise loaded on a refractory metal filament (typically rhenium, tungsten, or tantalum) and converted to a solid chemical form via controlled heating of the filament under atmospheric conditions. The sample filament is mounted on the sample turret, often in the 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). The filaments are heated to yield a small ion current suitable for lens focusing and peak centering. Following focusing and peak centering, data acquisition begins, with the filaments heated under computer control to yield a pre-defined major isotope ion current ( $^{235}\text{U}$  or  $^{238}\text{U}$  for uranium and  $^{239}\text{Pu}$  or  $^{240}\text{Pu}$  for plutonium) or a predefined sum total for all measured ion currents. Data acquisition and filament heating continues until the sample is exhausted or the ion current reaches a pre-defined lower limit. Ion intensity of each isotope is integrated over the course of the analysis, and the summed intensity for each isotope is divided by the summed intensity of a common isotope (typically the most abundant isotope) to yield ratios. The isotopic composition of the sample (formatted as amount fraction or mass fraction) may be calculated from the isotope ratios. Additional information on the total evaporation method may be found in Refs (1-5).<sup>4</sup>

4.2 The isotope dilution mass spectrometry (IDMS) method may be used to determine the uranium or plutonium concentrations. In this method, a spike of known isotopic composition and element concentration is added to a sample prior to chemical separation. Typical spike materials include  $^{233}\text{U}$ ,  $^{235}\text{U}$ , or  $^{238}\text{U}$  for uranium samples, and  $^{239}\text{Pu}$ ,  $^{242}\text{Pu}$ , or  $^{244}\text{Pu}$  for plutonium samples. Samples containing both uranium and plutonium (for example, mixed oxide fuels or fuel reprocessing materials) may be mixed with a combined U/Pu spike prior to separation. When using a spike containing significant quantities of one or more of the isotopes present in the sample, the isotopic composition of the sample must be known in advance. The spike-sample mixture undergoes a valency adjustment, purification, and is then loaded onto a filament and the isotopic composition of the mixture is determined. Using the measured isotope ratios of the spike-sample mixture, the known isotopic composition and amount of spike added to the mixture, and the isotopic composition of the sample, the elemental concentration of the sample may be calculated. The IDMS method yield results that are directly traceable to the SI unit of mole, provided the spike is SI traceable.

### 5. Significance and Use

5.1 The total evaporation method is used to measure the isotopic composition of uranium and plutonium materials, and

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

may be used to measure the elemental concentrations of the two elements when employing the IDMS technique.

5.2 Uranium and plutonium compounds are used as nuclear reactor fuels. In order to be suitable for use as a nuclear fuel the starting material must meet certain criteria, such as found in Specifications [C757](#), [C833](#), [C753](#), [C776](#), [C787](#), [C967](#), [C996](#), [C1008](#), or as specified by the purchaser. The uranium concentration, plutonium concentration, or both, and isotope abundances are measured by thermal ionization mass spectrometry following this method.

5.3 The total evaporation method allows for a wide range of sample loading with no significant change in precision or accuracy. The method is also suitable for trace-level loadings with some loss of precision and accuracy. The total evaporation method and modern instrumentation allow for the measurement of minor isotopes using ion counting detectors, while the major isotope(s) is(are) simultaneously measured using Faraday cup detectors.

5.4 The new generation of miniaturized ion counters allow extremely small samples, in the picogram range, to be measured via the total evaporation method. The method may be employed for measuring environmental or safeguards inspection samples containing nanogram quantities of uranium or plutonium. Very small loadings require special sample handling and careful evaluation of measurement uncertainties.

5.5 Typical uranium analyses are conducted using sample loadings between 50 nanograms and several micrograms. For uranium isotope ratios the total evaporation method had been used in several recent NBL isotopic certified reference material (CRM) characterizations (for example ([2](#), [3](#))). A detailed comparison of the total evaporation data on NBL uranium CRMs analyzed by the MAT 261 and TRITON™ instruments is provided in Ref ([5](#)). For total evaporation, plutonium analyses are generally conducted using sample loads in the range of 30 to 400 nanograms of plutonium.

## 6. Interferences

6.1 Ions with atomic masses in the uranium and plutonium ranges cause interference if they have not been removed or if they are generated as part of the chemical handling or analysis of the samples. Both  $^{238}\text{U}$  and  $^{238}\text{Pu}$  interfere in the measurement of each other, and  $^{241}\text{Am}$  interferes with the measurement of  $^{241}\text{Pu}$ , thereby requiring chemical separation. Removal of impurities provides uniform ionization of uranium or plutonium, hence improved precision, and reduces the interference from molecular species of the same mass number as the uranium or plutonium isotopes being measured. Isotopic analysis of plutonium should be completed within a reasonable time period after the separation of americium to minimize interference due to  $^{241}\text{Am}$  in-growth from  $^{241}\text{Pu}$ . An example of a prescribed interval limiting the time between sample purification and isotopic analysis is 20 days. For NBL CRMs 136, 137, and 138 the  $^{241}\text{Pu}/^{239}\text{Pu}$  ratio changes by about 0.092 % per week as a result of  $^{241}\text{Pu}$  decay. Instrument users are responsible for determining a maximum interval between purification and mass spectrometric analysis, based on an evaluation of  $^{241}\text{Am}$  in-growth from decay of  $^{241}\text{Pu}$  and the accuracy and

precision consistent with the data quality objectives of the facility. Other atomic and molecular species may interfere with total evaporation analyses, particularly if they cause a change in the ionization efficiency of the analyte during an analysis. Presence of carbon may disturb total evaporation measurements. It is recommended that instrument users perform validation tests on unique or complex samples by mixing known pure standards with other constituents to create a matrix-matched standard.

6.2 Precautionary steps must be taken to avoid contamination of the sample by environmental uranium or plutonium from the analytical laboratory environment. The level of effort needed to minimize the effect of contamination of the sample should be based upon the sample size, planned handling and processing of the sample, and knowledge of the levels of contamination present in the laboratory. For very small uranium or plutonium samples, extreme measures are often warranted to ensure that the sample is not contaminated. For these samples, residual uranium or plutonium in the mass spectrometer and trace uranium in chemicals or the filaments may bias measurement data.

6.3 The total evaporation method may generate biases in the minor isotope ratios, especially when measuring trace amounts of  $^{234}\text{U}$  in a HEU (highly enriched uranium,  $^{235}\text{U}$  abundance > 20 %) material, or trace amounts of  $^{236}\text{U}$  in a LEU (low enriched uranium, 1 % <  $^{235}\text{U}$  abundance < 20 %), NU (natural or normal uranium, 0.3 % <  $^{235}\text{U}$  abundance < 1 %), or DU (depleted uranium,  $^{235}\text{U}$  abundance < 0.3 %) material with  $^{238}\text{U}$ , or  $^{238}\text{Pu}$  in the presence of  $^{239}\text{Pu}$ . Biases in the minor isotope data occur due to peak tailing from the major isotopes. The magnitude of the peak tailing correction is a function of the design of the instrument and spread in the ion beam due to source design and particle collisions in the instrument. The peak tailing may be quantified by measuring the abundance sensitivity under experimental conditions similar to those at which samples are analyzed. A bias correction may then be applied based upon the measured abundance sensitivity. Additionally, the use of an energy filter in conjunction with an ion counting detector can significantly reduce or completely eliminate peak tailing and allow for accurate measurement of minor isotopes. The use of an energy filter, ultra-high-purity filaments and chemicals, effective sample purification, and low ionization and evaporation temperatures to minimize  $^{238}\text{U}$  interferences can allow for the accurate measurement of small  $^{238}\text{Pu}$  abundances by this technique. Another commonly used method for low abundance  $^{238}\text{Pu}$  measurement is the alpha-spectrometry technique, following Test Method [C1415](#) or Practice [D3084](#).

6.4 The modified total evaporation method, following Test Method [C1832](#), was developed to correct for the peak tailing interferences at the minor isotopes. It utilizes total evaporation of larger sample loads of uranium, sample loads of up to 5 micrograms are analyzed ([6](#)). In this method, the total evaporation process is interrupted on a regular basis to perform measurement of the peak tail intensities for all isotopes of interest and for peak centering, focusing, baseline measurements, inter-calibration of the detectors, etc. As a result of the ability to perform the tailing corrections on the minor