



Designation: **C1672 – 07 (Reapproved 2014) C1672 – 17**

Standard Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer¹

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 (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

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

1.2 In principle, the total evaporation method should yield isotopic isotope ratios that do not require mass bias correction. In practice, ~~some~~ samples may require this bias correction. ~~When compared~~ Compared to the conventional TIMS ~~method, method~~ described in Test Method C1625, the total evaporation method is approximately two times faster, improves precision ~~from two to four fold~~, 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 may ~~lead~~ be prone to biases in ~~minor~~ 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, depending on sample characteristics. The 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 ~~instrument~~ 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:²

- [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](#)

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. Current edition approved Jan. 1, 2014/Jan. 1, 2017. Published February 2014/January 2017. Originally approved in 2007. Last previous edition approved in 2007/2014 as C1672/C1672 – 07 (2014) – 07. DOI: 10.1520/C1672-07R14.10.1520/C1672-17.

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.

- [C996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % ²³⁵U](#)
[C1008 Specification for Sintered \(Uranium-Plutonium\) Dioxide Pellets—Fast Reactor Fuel \(Withdrawn 2014\)³](#)
[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](#)
[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 ²³⁸Pu Isotopic Abundance By Alpha Spectrometry](#)
[C1625 Test Method for Uranium and Plutonium Concentrations and Isotopic Abundances by Thermal Ionization Mass Spectrometry](#)
~~[D3084](#)~~[C1816 Practice for Alpha-Particle Spectrometry of Water](#)
[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](#)
~~[E137D3084 Practice for Evaluation of Mass Spectrometers for Quantitative Analysis from a Batch Inlet](#)~~
[Alpha-Particle Spectrometry of Water](#) (Withdrawn 1992)

3. Terminology

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

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

3.2.1 *isotopic equilibration—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 *abundance sensitivity—major ratio, n*—the ratio of alternate expression for $\frac{^{235}\text{U}/^{238}\text{U}}{\text{measured U}}$ (or $\frac{^{238}\text{intensity U}/^{235}\text{of U}}{\text{and } ^{240}\text{Pu}/^{239}\text{ion beam}}$ at a mass m to the measured intensity from the same isotope measured at one mass difference (for example, $m \pm 1$). Abundance sensitivity is a measure of the magnitude of peak tailing. Typically measured using uranium at masses 237 and 238. 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 *FIMS—DU*—Thermal Ionization Mass Spectrometry 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, supplier of Certified Reference Materials, Geel, Belgium—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, supplier of Certified Reference Materials, Argonne, IL, USA 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 Typically, uranium and plutonium are separated from each other and purified from other elements by selective extraction, anion exchange chromatography (such as in Practice [C1411](#)) or extraction chromatography. Test Method [C1415](#) or [C1816](#). The purified uranium or plutonium samples as nitrate solutions are mounted drop-deposited or otherwise loaded on a degassed 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 then mounted in the thermal ionization mass spectrometer, in either a single filament or double filament configuration. mounted on the sample turret, often in the double filament

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

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 initially heated to yield a small ion beam current suitable for lens focusing and peak centering. Following focusing and peak centering, the ion beam intensity data acquisition begins, with the filaments heated under computer control to yield a pre-defined major isotope ion beam current (^{235}U or ^{238}U for uranium and ^{239}Pu or ^{240}Pu for plutonium) or a predefined sum total intensity for all measured ion beams-currents. Data acquisition and filament heating continues until the sample is exhausted or the ion beam intensity-current reaches a pre-defined lower limit. Each isotope ion beam intensity on 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 (1-45).⁴

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}U , ^{235}U , or $^{235,238}\text{U}$ for uranium samples, and ^{239}Pu , ^{242}Pu , or ^{244}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 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 specifications, criteria, such as found in Specifications C757, C833, C753, C776, C787, C967, C996, C1008, or as specified by the purchaser. The uranium and/or plutonium concentration and isotopic 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 loss-significant change in precision or accuracy, and accuracy. The method is also suitable for trace-level loadings with consequent loss of precision. Typical uranium analyses are conducted using sample loadings between 10 nanograms and several micrograms. Plutonium analyses are generally conducted using between five and 200 nanograms of plutonium per filament. 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 isotopes are isotope(s) is(are) simultaneously measured using Faraday cup detectors. 100fbc7f/astm-c1672-17

5.4 New generations-The new generation of miniaturized ion counters now allow extremely small samples, in the picogram to femtogram range, to be measured via the total evaporation methods-method. The method may be employed for measuring environmental or safeguards inspection samples containing very small-nanogram quantities of uranium or plutonium. Very small loadings require special sample handling and analysis-techniques, and careful evaluation of measurement uncertainty contributors-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 TRITONTM 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}U and ^{238}Pu interfere in the measurement of each other, and ^{241}Am interferes with the measurement of ^{241}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-plutonium should be completed within a reasonable time period after the separation from Americium-of americium to minimize interference of due to ^{241}Am in-growth from ^{241}Pu . An example of a prescribed interval limiting the time between sample purification and isotopic analysis is 20 days. Operators-For NBL CRMs 136, 137, and 138 the $^{241}\text{Pu}/^{239}\text{Pu}$ ratio changes by about 0.092 % per week as a

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

result of ^{241}Pu decay. Instrument users are responsible for determining a maximum interval between purification and mass spectrometric analysis, based on an evaluation of ^{241}Am in-growth from ~~decaying~~ decay of ^{241}Pu and ~~required accuracy and precision~~. 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. ~~Carbon~~ Presence of carbon may disturb total evaporation measurements. It is recommended that ~~operators~~ 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 ~~Care~~ Precautionary steps must be taken to avoid contamination of the sample by environmental uranium or ~~traces of plutonium~~ 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 ~~care~~ 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 isotopes, ~~particularly those isotopes down mass from a major isotope, such as isotope ratios, especially when measuring trace amounts of ^{234}U in a highly enriched HEU (highly enriched uranium, ^{235}U material, or abundance > 20 %) material, or trace amounts of ^{236}U in a LEU (low enriched uranium, 1 % < ^{235}U abundance < 20 %), NU (natural or normal uranium, 0.3 % < ^{235}U abundance < 1 %), or DU (depleted uranium, ^{235}U abundance < 0.3 %) material with ^{238}U , or ^{238}Pu in the presence of ^{239}Pu . Biases in the minor isotope data occur due to peak tailing from the major isotopes. The amount/magnitude of the peak tailing correction is a function of the design of the instrument and spread in the ion beam ~~spread~~ due to source design and particle collisions in the instrument. The ~~amount of peak tailing~~ may be quantified by measuring the abundance sensitivity under ~~identical experimental conditions~~. 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 ~~placed before in conjunction with an ion counting detector~~ can ~~greatly reduce~~ significantly reduce or completely eliminate peak tailing and allow for accurate measurement of minor isotopes. The use of an energy filter, ~~ultra-high-purity~~ ultra-high-purity filaments and chemicals, effective sample purification, and low ionization and evaporation temperatures to minimize ^{238}U interferences can allow for the accurate measurement of small ^{238}Pu abundances by this technique. Another commonly used method ~~for low abundance ^{238}Pu measurement when in low abundances~~ 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 isotopes during the course of the measurement, the precision and accuracy of the minor ratio data from modified total evaporation are improved without compromising the quality of the major isotope ratio data. The modified total evaporation method had been used in several recent characterization measurements at NBL (2, 3, 7) and IRMM (8) (IRMM is now known as JRC-Geel) and shown to yield major isotope data of comparable precision and accuracy as the total evaporation method.

6.5 Chemical interferences like organics in the sample do not directly interfere with the uranium or plutonium isotope ratio measurements. These, however, adversely affect the precision and accuracy of the runs by changing the ionization efficiency. To minimize the impact of this factor, samples and standards are processed through the same preparation process and are to be analyzed in similar matrices.

7. Apparatus

7.1 *Mass Spectrometer*—The suitability of mass spectrometers for use with this method of analysis shall be evaluated by means of performance tests described in this ~~method and in Practice method~~. [E137](#). The mass spectrometer used should possess the following characteristics:

7.1.1 A thermal ionization source capable of ~~analysis utilizing analyzing single and/or double filaments~~ double filaments, or both, of rhenium; tungsten or tantalum may be substituted with minor modifications in the procedure.

7.1.2 An analyzer radius sufficient to resolve adjacent masses in the mass-to-charge range being studied, that is, $m/z = 233$ to 238 for U^+ or 238 to 244 for Pu^+ . Resolution greater than 360 (full width at 1 % of peak height) and an abundance sensitivity of less than 10^{-5} . ~~For measuring minor isotopes, an abundance sensitivity as low as achievable is recommended.~~ are recommended. For minor isotope ratio measurements, lower abundance sensitivity is preferable.

7.1.3 An instrument capable of monitoring ion beam intensity and adjusting filament currents during ion beam integration is recommended. This ~~eliminates~~ reduces the sample ~~loss~~ loss between integrations due to the time necessary to adjust the filament current.

7.1.4 A mechanism for changing samples.

7.1.5 Multiple direct-current detectors (Faraday cups) or a combination of Faraday cups and electron multiplier detector in a multi-collector design. Very small samples may be measured utilizing a multi-ion counting array.

7.1.6 A pumping system to attain a vacuum of less than 400 μPa (3×10^{-6} torr) in the source, the analyzer, and the detector regions. The ability to accurately measure minor isotopes is directly related to analyzer pressure. Analyzer pressures below approximately 7 μPa (5×10^{-8} torr) are preferable.

7.1.7 A mechanism to scan masses by means of varying the magnetic field and the accelerating voltage.

7.1.8 A computer to automate the instrument operation and to collect and process data produced by the instrument.

7.2 An optical pyrometer is recommended for determining filament temperatures.

7.3 Filament preheating/degassing unit for cleaning filaments.

8. Reagents and Materials

8.1 *Purity of Reagents*—~~Reagent-grade~~ Reagent grade chemicals shall be used in all steps. ~~Ultra-high purity reagents may be necessary for small samples, those with extreme ratios, or those otherwise susceptible to isotope ratio biases from cross-contamination. Distilled water is sufficient for routine tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁵ analysis of large samples; deionized water is recommended. For small samples, those with extreme ratios, or those otherwise susceptible to biases from cross-contamination, the level of uranium and/or plutonium contamination in chemicals, water, and the sample handling environment should be determined to ensure that the materials and environment are sufficiently pure for the sample being analyzed. 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. Ultra-high purity reagents may be necessary for small samples, samples with extreme ratios, or samples otherwise susceptible to isotope ratio biases from cross-contamination.~~

8.1.1 For small samples, or samples with extreme ratios, or samples otherwise susceptible to biases from cross-contamination, the level of uranium or plutonium contamination, or both, in chemicals, water, and the sample handling environment should be determined to ensure that the materials used and analytical environment are sufficiently pure for the samples being analyzed.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean laboratory accepted demineralized or deionized water as described by Type I of Specification D1193.

8.3 *Rhenium Filaments*—~~High purity, purity ribbons shall be used, the size and configuration are instrument dependent. Tungsten or tantalum may be substituted with minor modifications into the procedure. Tungsten filaments have been reported to yield higher precision analyses via the total evaporation method. All filaments should be degassed prior to use. Degassed filaments are preferred. For small samples, the amount of uranium in the filaments should be measured to ensure that the uranium content of the filament material will not bias sample analysis results.~~

NOTE 1—The purity of the filaments should be confirmed with each new batch received. Zone refined filaments should be used for low-level analyses.

<https://standards.iteh.ai/catalog/standards/sist/8bb1fed6-0c06-47fd-9004-65b4d00fbc7f/astm-c1672-17>

⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on 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, Inc. (USPC), Rockville, MD.

8.3 *Isotopic Reference Materials*—Uranium or plutonium standard reference solutions, of varying isotopic composition depending on sample. The standard solutions should preferably be made from certified reference materials traceable to a national standard body.⁵ Examples include the NBL U-series CRM's (for example, U010, U500), NBL plutonium CRM 128, and IRMM uranium standards IRMM 184–187.

8.4 *Elemental Concentration and Isotopic Reference Materials (IDMS Spikes)*—Materials of known isotopic and chemical composition, preferably CRMs traceable to a national standard body, for use in the determination of elemental concentration by IDMS. Examples include NBL CRM 111-A (²³³U spike), NBL CRM 130 (²⁴²Pu spike), IRMM 040a (²³³U spike), or IRMM 046b (mixed ²³³U and ²⁴²Pu spike).

9. Hazards

9.1 Thermal ionization mass spectrometers operate at electrical potentials in excess of 10 kV. Care must be taken to ensure that high voltage electronics are switched off prior to handling the source or accessing electronic components.

9.2 The filaments can reach temperatures in excess of 2000°C, with consequent heating of the filament holders and source areas. Care should be taken when adding or removing filaments/turrets.

9.3 Liquid nitrogen is used in cold traps. Care should be taken to shield eyes and face when filling cold traps, and to protect hands, torso and feet in the event of splashing or spilling.

9.4 Appropriate care should be taken when handling radioactive materials.

9. Reference Materials

9.1 *Isotopic Reference Materials*—Uranium or plutonium standard reference solutions, of varying isotopic composition depending on sample. The standard solutions should preferably be made from CRMs traceable to a national standard body.⁶ Examples for uranium isotope reference materials include the NBL U-series CRM's (for example, U005A, U010, U030A, U045, U200, U500, U630, U900, U970), and IRMM materials series IRMM 184–187, the IRMM-074 series, and the IRMM-2019-2029 series (in preparation, to be based on UF₆ materials IRMM-019-029). Plutonium isotope reference materials include the NBL plutonium standards CRM 128, CRM 136, CRM 137, and CRM 138, and the IRMM-290, IRMM-290a, and IRMM-290b series.

9.2 *Elemental Concentration and Isotopic Reference Materials (IDMS Spikes)*—Materials of known isotopic and chemical composition, preferably CRMs traceable to a national standard body, for use in the determination of elemental concentration by IDMS. Examples for uranium include NBL CRM 111-A (²³³U spike), CRM 112-A (²³⁸U spike), IRMM 040a (²³³U spike), IRMM 052 (²³⁸U spike) and IRMM 054 (²³⁵U spike). For plutonium commonly used spike materials are NBL CRM 130 (²⁴²Pu spike), the IRMM 049c/d/e/f series (²⁴²Pu spikes), IRMM-042a (²⁴⁴Pu spike), or the IRMM 046b/c series (mixed ²³³U and ²⁴²Pu spikes).

10. Precautions

ASTM C1672-17

10.1 Appropriate precautions should be taken when handling radioactive materials. A detailed discussion of the necessary precautions is beyond the scope of this test method. Personnel involved in the handling of radioactive material analyses should be familiar with safe handling practices for these materials and be trained appropriately. The safe handling practices, at a minimum, shall include use of glove boxes or fume hoods with filtered air and use of personnel protective equipment.

10.2 Because of the toxicity of plutonium, all operations involving plutonium in the solid state should be performed within glove boxes to prevent ingestion/inhalation of plutonium. After dissolution, plutonium samples can be handled in a fume hood or glovebox with filtered air and use of personal protective equipment.

10.3 Thermal ionization mass spectrometers operate at electrical potentials of up to 10 kV. Care must be taken to ensure that high voltage electronics are switched off prior to handling the source or accessing electronic components.

10.4 The filaments can reach temperatures in excess of 2000°C, with consequent heating of the filament holders and of the source region. Allow the turret and source parts to cool before handling and exercise caution when adding or removing filaments/turrets.

10.5 Liquid nitrogen is used in cryogenic cold traps. Care should be taken to shield eyes and face when filling cold traps, and to protect hands, torso, and feet in the event of splashing or spilling of the liquid nitrogen.

11. Calibration and Standardization

11.1 The measurement method may be qualified following Guide C1068 and calibrated following Guide C1156. Additional information regarding calibration of the mass spectrometer ~~calibrations~~ in relation to the total evaporation method may be found in Ref (59).

⁶ The sole source of supply of the apparatus standards known to the committee at this time is are: (1) USDOE New Brunswick Laboratory, 9800 S. Cass Ave., Argonne, IL, 60439, <http://www.nbl.doe.gov>—<http://science.energy.gov/nbl> and (2) European Commission Joint Research Centre, Retiesweg 111, B-2440 Geel, Belgium, <http://ec.europa.eu/jrc>. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

11.2 *Electronic Performance Check*—Modern mass spectrometer instruments normally offer an automated routine which tests the stability and performance of the electronic systems of the instrument and reports results, flagging systems or components which are out of specification. Operators—Instrument users should perform routine electronic performance checks and to ensure that the instrument meets manufacturer’s specifications for stability and performance. The interval between the electronic performance check checks should be established by operators—based upon manufacturer’s recommendation and instrument history.

11.3 *Mass Calibration*—The relationship between the ~~known~~ atomic masses and the ~~necessary~~ magnetic field necessary to direct the isotope beam into the detectors shall be updated on a periodic basis. The interval between mass calibrations is determined by instrument manufacturers and operators based upon the instrument manufacturer. The stability of the mass calibration curve is dependent on the laboratory conditions and the stability of individual instruments. Users are advised to perform may vary between different instruments. It is recommended that a mass calibration check be performed prior to each day’s analyses.

11.4 *Peak Centering*—The peak centering routine is used as a fine adjustment to ensure that the ion beam is centered within the detector. Peak centering occurs via fine adjustments of the accelerating high voltage. Peak centering should be performed as part of the mass calibration, and at the start of each sample analysis.

11.5 *Amplifier Gain Calibration*—The stability and response of each Faraday detector amplifier system should be measured, and differences between amplifier systems compensated for, via a gain calibration. The gain calibration is normally performed by sequentially applying a stable calibration signal to the inputs of the different detector channels. The output of each channel is then normalized to a reference channel to generate a gain calibration factor for each channel. Depending upon the stability of the amplifier system, a gain calibration may be performed ~~once on a weekly basis~~ or as often as prior to each sample analysis. ~~Operators—Instrument users may use historical gain calibration data to evaluate the stability of the amplifiers to determine appropriate gain calibration frequencies.~~

11.6 *Amplifier Baseline Calibration*—The baselines of the Faraday detector amplifiers, that is, the amplifier response without ion beam to the detector, shall be measured on a regular basis and checked for stability. The integration time for the baseline measurement influences the uncertainty of Faraday detector measurements, particularly at the lower ion beam intensities. The long-term historical baseline data shall be regularly reviewed by the user to assure that the system performance is within manufacturer specifications and facility specific quality requirements. Amplifier baseline calibration should be performed before each analysis day.

11.7 *Faraday Detector Calibration*—The response of individual Faraday cups may differ depending on history of use, manufacturing variability or other factors. The relative response of the Faraday cups should be determined periodically, or at least once per year—frequencies established based on the data quality objectives of the facility. The calibration may be performed by switching a stable ion beam (the use of ¹⁸⁷Re is suggested due to ease of generating a very stable, long-lived stable ion beam from a blank filament) between a Faraday cup and a reference cup. The relative gain between detectors can be used to compensate for differences in detector response, or the test can be used to ensure that individual detector responses are within sufficient appropriate limits to allow for the necessary level of accuracy for sample measurements. In either case, the precision and accuracy of the detector calibration should be evaluated to ensure that the calibration factor or detector response is of sufficient accuracy for sample measurement. Note that a gain calibration should be performed immediately prior to Faraday detector calibration.

11.8 *Electron Multiplier/Faraday Intercalibration*—When using an electron multiplier to measure minor isotopes, a calibration factor shall be determined to correct for differences in detector responses. This calibration factor may be determined by switching a stable beam repeatedly between the ion counter and a reference Faraday detector. The measurement uncertainty of this factor should be determined and incorporated into the ~~sample analysis results. At a minimum, uncertainty estimates for the sample results. The frequency at which this calibration should be performed once per day may be established based on the data quality objectives of the specific task at hand.~~

11.9 *Electron Multiplier Calibration*—Recommended for the most accurate measurements of minor isotopes. When using an electron multiplier, the electronic dead time and the multiplier linearity should be accounted for. The multiplier linearity, a function of count rate, may be determined ~~once at the time of multiplier installation, or for the most accurate corrections should be determined immediately prior to sample analyses. Non-linearity in the electron multiplier should be compensated for when calculating isotope isotope ratios and their uncertainties. At a minimum, the electronic dead time should be performed once per year.~~

11.10 *Mass Bias Calibration*—Even though the sum integrated major isotope ratio data using the total evaporation method is minimally biased compared to the certified ratio of the CRMs, the major and minor isotope ratios evolve throughout the evaporation process (5) In theory, the due to preferential release of the lighter isotopes in the early stages of the filament heating process. All isotope ratios, major and minor, are affected by this process. In theory, if the ionization efficiency and ion transmission are constant, the total evaporation method should yield mass bias-free ratios. In practice, some operators have experienced mass biases small mass biases have been reported for uranium and/or plutonium measurements. There are several variations that and plutonium isotope ratio measurements using TIMS instruments may (2-8), be used for the determination of Therefore in several laboratories a mass bias correction factors in static multi-collector measurements. A on the total evaporation data for uranium and plutonium is performed. In this case, additional components are included in the uncertainty evaluation to account for the mass bias

calibration uncertainties. When a mass bias correction is performed, a commonly employed method is to measure multiple filament loadings of a certified isotopic reference material in sequence with replicate loadings for the samples, and calculate a mass bias correction factor based upon the deviation of the measured major ratio for the standard reference material from the certified ratio. A mass bias correction factor, adjusted for isotope mass difference, factor is then applied to the measured sample ratios. Regardless of the method used, it is vital that the reference materials are treated, prepared, and measured in exactly the same manner as the samples. For uranium samples hydrolyzed from uranium hexafluoride, it is recommended that the samples be converted to U_3O_8 prior to dissolution and analysis. Mass bias calibrations are, generally, performed on a turret-by-turret basis.

11.10.1 Calculate the mass bias correction factor, K , for the major ratio as follows:

$$K = (R_m/R_c) \quad (1)$$

$$K = (R_c / R_m) \quad (1)$$

where:

K = mass bias correction factor,

R_m = average measured atom ratio for CRM, and

R_c = certified atom ratio value for the CRM.

R_c = certified atom ratio for the CRM.

11.10.2 To correct individual measured major and minor individual sample ratios, calculate the appropriate mass bias correction factor based upon the mass difference between isotopes, and isotopes in the numerator and denominator, and multiply the sample ratio by the applicable mass bias correction factor.

11.11 In case a mass bias correction is not performed on the total evaporation data, it is recommended to measure quality control samples, certified reference materials, on a predefined frequency to ensure that any bias from mass fractionation is insignificant or within the limits specified in the user's quality system. See Fig. A1.1 and Fig. A1.2 for examples of control charts for U and Pu total evaporation measurements of certified reference materials.

11.12 It is emphasized that precision and accuracy achieved in a total evaporation analysis without mass bias correction using an SI traceable CRM is dependent on the method parameters such as sample loading, filament heating, etc. and cannot be considered SI-traceable. SI-traceable total evaporation data can only be obtained through the use of an SI traceable, that is, gravimetrically prepared, CRM for performing the mass bias correction.

11.13 In case a mass bias correction is performed on the total evaporation data according to Eq 1, it is recommended to measure additional quality control samples, different certified reference materials, on a predefined frequency to ensure that the mass bias correction applied is correct and under control. See Fig. A1.3 for an example of a control chart for mass bias corrected Pu total evaporation measurements of a certified reference material.

11.14 In cases when no reference materials as mentioned in 9.1 are available, working reference materials (WRM) can be used for quality control purposes, as described in 11.11 and 11.13.

11.15 During conventional analyses routinely utilized for uranium and plutonium isotope ratio measurements (Test Method C1625), only a portion of the uranium or plutonium released from the sample is utilized for analysis. The mass biases at the minor isotope ratios are estimated assuming that the deviations of the major ratio from certified values are due to mass bias effects. Thus, the major ratio values, by definition, are identical to certified ratios. This is explained in detail in (2, 3) for NBL characterization measurements on isotopic standards.

11.16 *Linearity*—The linearity of the mass spectrometer may be determined over the working ratio range by measuring the $^{235}U/^{238}U$, under identical conditions, of appropriate certified reference materials. The CRMs. The system is linear if the ratio of the certified $^{235}U/^{238}U$ ratio to the experimental $^{235}U/^{238}U$ is independent of isotopic ratio if the system is linear. isotope ratio. Under ideal conditions, any deviation deviations from a constant value greater than 4 in 10 000 is likely to be constant values are likely due to nonlinearity. Uranium CRMs are typically used for linearity checks because the range of isotopic ratios of existing plutonium CRMs is not adequately compositions observed in safeguards measurements. See Test Method C1832 large. for details on how to perform the linearity test using U CRMs.

12. Procedure

12.1 Sample Preparation:

12.1.1 *Sample Dissolution*—Dissolve an appropriate sample to obtain the desired filament loading for the mass spectrometric analysis. See Practice C1347 for the dissolution of uranium or Practice C1168 for the dissolution of plutonium. If performing isotope dilution mass spectrometry, add the appropriate amount of spike, by weight or volume as appropriate to sample size and desired accuracy, to the previously-weighed sample. Spike addition and equilibration must be performed prior to chemical purification if determining concentration by IDMS.

NOTE 2—Spike addition and equilibration must be performed prior to chemical purification if determining concentration by IDMS. Independent of whether known amount of sample is added to the vial in which known spike amounts are stored or known weights/volumes of spike is added to container in which known weights/volumes of sample are stored, quantitative transfer is critical to avoid biases in the concentration results. Measures to ensure

quantitative transfer are rinsing the caps of the container in which the sample or spike was stored and transferring the rinsate to the mixture and rinsing the walls of the container by slowly adding drops of 8 M nitric acid and transferring the rinsate to the mixture.

12.1.2 Prepare the sample and any standard solutions as purified nitrates, using identical chemical preparation and handling steps. The solution concentrations should be chosen to allow for a allow convenient filament loading (for example, a ± 0.1 mg U/mL solution yields ± 100 ng of uranium in a 1 μ L drop).

12.1.3 *Sample Purification*—Use Practice C1411 or similar procedure to separate uranium and/or plutonium from each other and from other impurities.

12.2 *Filament Loading*—Samples may either be directly loaded on the filament by drop deposition, electroplated onto the filament, or loaded onto a resin bead for subsequent mounting on the filament. Samples and standards should be prepared for analysis by the same method at similar mass loadings. Drop deposition onto the filament can be accomplished with the use of a microsyringe fitted with a plastic tip. ~~The tip or with pipettes fitted with disposable tips. The tips should be changed between sample loadings to prevent cross-contamination. Typically, 1 μ L drops are loaded.~~

12.3 *Sample Conditioning*—For filaments loaded by drop deposition, the solution should be evaporated by passing sufficient electrical current through the filament to cause gentle drying without boiling-splattering. After the initial drying, a stepped-heating program can be employed to convert samples to suitable chemical forms. Care should be taken to avoid evaporation of the sample or melting of the filament. The use of an optical pyrometer or salt crystals of varying melting points can help to ~~characterize~~ establish the current-to-temperature relationship of a ~~sample loading protocol~~ appropriate for the sample loading. Once a suitable heating program is established, a programmable power supply may be used to ensure repeatable that the conditioning regimens for all samples and standards. ~~A typical standards are applied consistently. At different facilities, different loading and conditioning practices have been established and validated. Each practice shall be applied in a consistent manner for all samples and standards. An example of sample conditioning program would consist of:~~ is shown below (steps 12.3.1 through 12.3.4):

12.3.1 Ramp electrical current to ± 0.5 to 0.7 A and hold until the drop disappears. The aim is to evaporate the liquid gently without causing splattering.

12.3.2 Ramp current to ± 1.5 A and hold for 2 minutes.

12.3.3 Ramp current to ± 1.5 A and hold for ~~1 minute~~ 10 s.

12.3.4 Ramp current to ± 2.0 A and hold for 10 seconds.

12.4 *Isotopic Ratio Measurement:*

12.4.1 Insert the filament assembly into the mass spectrometer.

12.4.2 Seal the source and evacuate to the manufacturer's recommended minimum pressure.

12.4.3 Add liquid nitrogen to the ~~eryo trap~~ cryogenic trap, if desired.

12.4.4 Steps ~~H-4.511.3~~ through ~~H-4.911.6~~ may be performed automatically under computer control, depending upon instrument. Very small samples may require manual control to avoid sample loss.

12.4.5 Perform a gain calibration if ~~desired~~ desired (see 11.5).

12.4.6 Perform a baseline (amplifier noise) ~~measurement~~ measurement (see 11.6).

12.4.7 If using the double filament technique, heat the ionization filament to a temperature sufficient to provide ~~satisfactory~~ sufficient ionization. ~~Typical temperatures~~ Recommended temperature for uranium are ~ 1800 to 2000°C and for plutonium 1850°C – 1750 to 1850°C (current required will depend on the filament material and even for the same type of filaments will vary from batch to batch. Typical currents required for U analysis is in the range of 5 A to 5.8 A). In the absence of an optical pyrometer, the magnitude of the ^{187}Re beam may be used as an indication of filament temperature. ~~In The ^{187}Re certain cases this technique~~ Re intensity may provide a more reproducible indication of temperature than the optical pyrometer.

12.4.8 Slowly ~~begin heating~~ heat the sample filament to a temperature sufficient to yield a small ion beam suitable for beam focusing and peak centering. Typical ~~emitting~~ temperatures are 1450 – 1650°C – 1000 to 1400°C for plutonium and 1650 – 1850°C – 1400 to 1800°C for uranium. If ~~so equipped~~, available, the ion counter may be used to minimize sample loss during the focusing and peak centering steps. Typical ion intensities for these purposes are ~~50 000~~ a few thousands of counts per second when using the ion counter, or ~~10–30~~ 10 to 30 mV when using Faraday cup detectors. Alternatively, also the use of the Re beam for focusing purposes is generally acceptable. The use of carburized filaments is recommended if the U (or Pu) beams are quite high even when the evaporation filament current is zero.

12.4.9 ~~Locate~~ Perform peak centering and focusing of the major uranium or plutonium isotope and perform peak centering and focusing isotopes.

12.4.10 Begin data acquisition, while ~~simultaneously~~ continuously heating the sample filament to yield a predetermined major isotope ion beam intensity. The maximum beam intensity (the intensity of the major isotope or sum of the intensities of the most abundant isotopes could be used for controlling the heating of the evaporation filament) to be maintained during analysis depends upon the sample size and the capabilities of the detectors. Intensities between 4 and ~~30V~~ 15 V are typical for the major isotope(s). Integration times are generally between 1 and 16 seconds, but may range from less than 1 seconds to more than 60 seconds, depending on sample, operator user preference and instrument ~~capability~~ characteristics.

12.4.11 Under computer control, the sample filament temperature is ~~continually~~ continuously adjusted to maintain the target ion beam intensity, until the sample is exhausted ~~or~~ and thus the measured intensity is dropped below a pre-determined minimum ion beam intensity ~~is reached~~ intensity.

12.4.12 Turn off filament currents (if not performed via automated computer control).

12.4.13 The computer integrates the total ion beam intensity for each isotope, applies baseline, gain and any other applicable corrections (dead time, multiplier linearity, etc.), and reports isotope ratios.

12.4.14 Record and correct if necessary (see Section 8) the ~~isotope~~ isotope ratios of the samples.

13. Calculations

13.1 Evaluation of the “major” ratio $^{235}\text{U}/^{238}\text{U}$ —The total evaporation principle is associated with a particular way of calculating isotope amount ratios. For uranium measurements using the TE method, the major ratio $^{235}\text{U}/^{238}\text{U}$ is calculated as:

$$\left(\frac{^{235}\text{U}}{^{238}\text{U}}\right)_{TE} = \frac{\sum_{ALL_INTEGRATIONS} I(^{235}\text{U})}{\sum_{ALL_INTEGRATIONS} I(^{238}\text{U})} = \frac{\sum_{ALL_INTEGRATIONS} \left[\left(\frac{I(^{235}\text{U})}{I(^{238}\text{U})} \right) \cdot I(^{238}\text{U}) \right]}{\sum_{ALL_INTEGRATIONS} I(^{238}\text{U})} \quad (2)$$

where:

$I(^{235}\text{U})$ and $I(^{238}\text{U})$ = signal intensities (in V) for ^{235}U and ^{238}U measured on Faraday cups, corrected for the Faraday cup amplifier gains and baselines.

13.1.1 According to Eq 3, the $^{235}\text{U}/^{238}\text{U}$ ratio is calculated as the sum of all ^{235}U ion beam intensity integrations during the measurement divided by the respective sum of the ^{238}U ion beam intensity integrations. This is the same as the average of all measured $I(^{235}\text{U})/I(^{238}\text{U})$ signal intensity ratios during the measurement, weighted by the ^{238}U ion signal intensities.

13.2 Calculation of atom percent, weight percent and atomic weight: For mass spectrometer instruments, measured quantities are isotope ratios. Therefore, control limits for monitoring the performance of the analytical method are generally set by evaluating the accuracy and precision of isotopic standards traceable to the SI units. Isotope amount fractions (also known as atom percent abundances), and isotope mass fractions (also known as weight percent abundances), and atomic weight are calculated using the measured isotope ratios as input quantities using Eq 3-5, respectively. The isotope amount fractions, isotope mass fractions, and atomic weight are calculated as follows:

$$\text{Isotope amount fraction of isotope } i = 100 \cdot \frac{R_i}{\sum R_i} \quad (3)$$

$$\text{Isotope mass fraction of isotope } i = 100 \cdot \frac{R_i \cdot M_i}{\sum (R_i \cdot M_i)} \quad (4)$$

$$\text{Atomic weight} = \frac{\sum (R_i \cdot M_i)}{\sum R_i} \quad (5)$$

where:

R_i = isotope ratio, corrected for mass bias (if necessary),

$\sum R_i$ = sum of all ratios (corrected for mass bias), including the reference isotope ratio (for example, $^{238}\text{U}/^{238}\text{U} = 1$ or $^{239}\text{Pu}/^{239}\text{Pu} = 1$), and

M_i = nuclidic mass of the i^{th} isotope.

$$\text{Atom percent for isotope } i = 100 \times \frac{R_i}{\sum R_i} \quad (2)$$

NOTE 3—The ^{238}Pu isotope abundance measurement is a special case. Measurement of this ratio using thermal ionization mass spectrometry is prone to biases, due to isobaric interference from ^{238}U . The preferred analytical technique for measurement of the ^{238}Pu isotope abundances is α -spectrometry. In this case, the ^{238}Pu isotope abundances from α -spectrometry must be combined with the ^{239}Pu isotope abundance by TIMS to perform the above calculations.

$$\text{Weight percent for isotope } i = 100 \times \frac{R_i \times M_i}{\sum (R_i \times M_i)} \quad (3)$$

$$\text{Sample atomic weight} = \frac{\sum (R_i \times M_i)}{\sum R_i} \quad (4)$$

where:

R_i = an isotopic ratio, corrected for mass bias if necessary,

$\sum R_i$ = sum of all corrected isotope ratios, including reference isotope ratio (that is, $^{238}\text{U}/^{238}\text{U} = 1$), and

M_i = the nuclidic mass for the i^{th} isotope.