



# 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 C 1672; 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 and/or the concentration of uranium and plutonium as nitrate solutions by the thermal ionization mass spectrometric (TIMS) total evaporation method. Purified uranium or plutonium nitrate solutions are loaded 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 beams are continually measured until the sample is exhausted. The measured ion currents are integrated over the course of the run, and normalized to a reference isotope ion current to yield isotopic ratios.

1.2 In principle, the total evaporation method should yield isotopic ratios that do not require mass bias correction. In practice, some samples may require this bias correction. When compared to the conventional TIMS method, the total evaporation method is approximately two times faster, improves precision from two to four fold, and utilizes smaller sample sizes.

1.3 The total evaporation method may lead to biases in minor isotope ratios due to peak tailing from adjacent major isotopes, depending on sample characteristics. The use of an electron multiplier equipped with an energy filter may eliminate or diminish peak tailing effects. Measurement of instrument abundance sensitivity may be used to ensure that such biases are negligible, or may be used to bias correct minor isotope ratios.

1.4 *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>

- C 753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder
- C 757 Specification for Nuclear-Grade Plutonium Dioxide Powder, Sinterable
- C 776 Specification for Sintered Uranium Dioxide Pellets
- C 787 Specification for Uranium Hexafluoride for Enrichment
- C 833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets
- C 967 Specification for Uranium Ore Concentrate
- C 996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % <sup>235</sup>U
- C 1008 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets—Fast Reactor Fuel
- C 1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry
- C 1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials
- C 1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis
- C 1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis
- C 1411 Practice for The Ion Exchange Separation of Uranium and Plutonium Prior to Isotopic Analysis
- C 1415 Test Method for <sup>238</sup>Pu Isotopic Abundance By Alpha Spectrometry
- D 3084 Practice for Alpha-Particle Spectrometry of Water
- E 137 Practice for Evaluation of Mass Spectrometers for Quantitative Analysis from a Batch Inlet<sup>3</sup>

<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> Withdrawn.

### 3. Terminology

#### 3.1 Definitions:

3.1.1 *isotopic equilibration*—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.

3.1.2 *abundance sensitivity*—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 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.

#### 3.2 Acronyms:

3.2.1 *CRM*—Certified Reference Materials

3.2.2 *TIMS*—Thermal Ionization Mass Spectrometry

3.2.3 *IDMS*—Isotope Dilution Mass Spectrometry

3.2.4 *IRMM*—Institute for Reference Materials and Measurements, supplier of Certified Reference Materials, Geel, Belgium

3.2.5 *NBL*—New Brunswick Laboratory, supplier of Certified Reference Materials, Argonne, IL, USA

### 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 (such as in Practice C 1411) or extraction chromatography. The purified uranium or plutonium samples as nitrate solutions are mounted 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 filament is then mounted in the thermal ionization mass spectrometer, in either a single filament or double filament configuration. The filaments are initially heated to yield a small ion beam 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 or a predefined total intensity for all measured ion beams. Data acquisition and filament heating continues until the sample is exhausted or the ion beam intensity reaches a pre-defined lower limit. Each isotope ion beam intensity 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 may be calculated from the ratios. Additional information on the total evaporation method may be found in Refs (1-4).<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 <sup>233</sup>U or <sup>235</sup>U for uranium samples, and <sup>239</sup>Pu, <sup>242</sup>Pu or <sup>244</sup>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.

### 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, such as found in Specifications C 757, C 833, C 753, C 776, C 787, C 967, C 996, C 1008, or as specified by the purchaser. The uranium and/or plutonium concentration and isotopic abundances are measured by mass spectrometry following this method.

5.3 The total evaporation method allows for a wide range of sample loading with no loss in precision or accuracy, and 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. The total evaporation method and modern instrumentation allow for the measurement of minor isotopes using ion counting detectors, while the major isotopes are simultaneously measured using Faraday cup detectors.

5.4 New generations of miniaturized ion counters now allow extremely small samples, in the picogram to femtogram range, to be measured via total evaporation methods. The method may be employed for measuring environmental or safeguards inspection samples containing very small quantities of uranium or plutonium. Very small loadings require special sample handling and analysis techniques, and careful evaluation of measurement uncertainty contributors.

### 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 <sup>238</sup>U and <sup>238</sup>Pu interfere in the measurement of each other, and <sup>241</sup>Am interferes with the measurement of <sup>241</sup>Pu, thereby requiring chemical separation. Removal of impurities provides uniform ionization of uranium or plutonium, hence improved precision, and reduces the interference

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

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 separation from Americium to minimize interference of  $^{241}\text{Am}$  in-growth from  $^{241}\text{Pu}$ . An example of a prescribed interval limiting the time between sample purification and isotopic analysis is 20 days. Operators are responsible for determining a maximum interval between purification and mass spectrometric analysis, based on an evaluation of  $^{241}\text{Am}$  in-growth from decaying  $^{241}\text{Pu}$  and required accuracy and precision. 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 may disturb total evaporation measurements. It is recommended that operators 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 must be taken to avoid contamination of the sample by environmental uranium or traces of plutonium. 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 must be taken 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 trace amounts of  $^{234}\text{U}$  in a highly enriched  $^{235}\text{U}$  material, 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 amount of peak tailing is a function of the design of the instrument and 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. A bias correction may then be applied based upon the measured abundance sensitivity. Additionally, the use of an energy filter placed before an ion counting detector can greatly reduce 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  $^{238}\text{Pu}$  measurement when in low abundances is the alpha-spectrometry technique, following Test Method C 1415 or Practice D 3084.

## 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 E 137. The mass spectrometer used should possess the following characteristics:

7.1.1 A thermal ionization source capable of analysis utilizing single and/or double filaments 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  $\text{U}^+$  or  $238$  to  $244$  for  $\text{Pu}^+$ . 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.

7.1.3 An instrument capable of monitoring ion beam intensity and adjusting filament currents during ion beam integration is recommended. This eliminates the sample lost 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  $400\ \mu\text{Pa}$  ( $3 \times 10^{-6}$  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  $7\ \mu\text{Pa}$  ( $5 \times 10^{-8}$  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 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 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 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.

8.2 *Rhenium Filaments*—High purity, the size and configuration are instrument dependent. Tungsten or tantalum may be substituted with minor modifications in 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. For small samples, the amount of uranium in the filaments should be measured to ensure 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

batch received. Zone refined filaments should be used for low-level analyses.

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.<sup>5</sup> 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 (<sup>233</sup>U spike), NBL CRM 130 (<sup>242</sup>Pu spike), IRMM 040a (<sup>233</sup>U spike), or IRMM 046b (mixed <sup>233</sup>U and <sup>242</sup>Pu 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.

## 10. Calibration and Standardization

10.1 The measurement method may be qualified following Guide C 1068 and calibrated following Guide C 1156. Additional information regarding mass spectrometer calibrations in relation to the total evaporation method may be found in Ref (5).

10.2 *Electronic Performance Check*—Modern 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 should perform routine electronic performance checks and ensure the instrument meets manufacturer's specifications for stability and performance. The interval between the electronic performance check should be established by operators based upon manufacturer's recommendation and instrument history.

10.3 *Mass Calibration*—The relationship between the known atomic masses and the necessary magnetic field 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 laboratory conditions and the stability of individual instruments. Users are advised to perform a mass calibration check prior to each day's analyses.

10.4 *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.

10.5 *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 weekly or as often as prior to each sample analysis. Operators may use historical gain calibration data to evaluate the stability of the amplifiers to determine appropriate gain calibration frequencies.

10.6 *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. The calibration may be performed by switching a stable ion beam (the use of <sup>187</sup>Re is suggested due to ease of generating a very stable, long-lived 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 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.

10.7 *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, this calibration should be performed once per day.

10.8 *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

<sup>5</sup> The sole source of supply of the apparatus known to the committee at this time is USDOE New Brunswick Laboratory, 9800 S. Cass Ave., Argonne, IL, 60439, <http://www.nbl.doe.gov>. 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,<sup>1</sup> which you may attend.

analyses. Non-linearity in the electron multiplier should be compensated for when calculating isotopic ratios and their uncertainties.

10.9 *Mass Bias Calibration*—In theory, the total evaporation method should yield mass bias-free ratios. In practice, some operators have experienced mass biases for uranium and/or plutonium measurements. There are several variations that may be used for the determination of mass bias correction factors in static multi-collector measurements. A commonly employed method is to measure certified isotopic reference materials in sequence with the samples, and calculate a mass bias correction factor based upon the deviation of the measured major ratio for the standard from the certified ratio. A mass bias correction factor, adjusted for isotope mass difference, is then applied to measured sample ratios. Regardless of 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.

10.9.1 Calculate the mass bias correction factor,  $K$ , as follows:

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

where:

$K$  = mass bias correction factor,

$R_m$  = average measured atom ratio for CRM, and

$R_c$  = certified atom ratio value for the CRM.

10.9.2 To correct individual measured sample ratios, calculate the appropriate mass bias correction factor based upon the mass difference between isotopes, and multiply the sample ratio by the applicable mass bias correction factor.

10.10 *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 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. Under ideal conditions, any deviation from a constant value greater than 4 in 10 000 is likely to be nonlinearity. Uranium CRMs are typically used because the range of isotopic ratios of existing plutonium CRMs is not adequately large.

## 11. Procedure

### 11.1 *Sample Preparation:*

11.1.1 *Sample Dissolution*—Dissolve an appropriate sample to obtain the desired filament loading for the mass spectrometric analysis. See Practice C 1347 for the dissolution of uranium or Practice C 1168 for 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.

NOTE 2—Spike addition and equilibration must be performed prior to chemical purification if determining concentration by IDMS.

11.1.2 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 convenient filament loading (for example, a 1 mg U/mL solution yields 1  $\mu$ g of uranium in a 1  $\mu$ L drop).

11.1.3 *Sample Purification*—Use Practice C 1411 or similar procedure to separate uranium and/or plutonium from each other and from other impurities.

11.2 *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 should be changed between sample loadings to prevent cross-contamination.

11.3 *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. After 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 the filament. The use of an optical pyrometer or salt crystals of varying melting points can help to characterize the current-to-temperature relationship of a sample loading protocol. Once a suitable heating program is established, a programmable power supply may be used to ensure repeatable conditioning regimens for all samples and standards. A typical sample conditioning program would consist of:

11.3.1 Ramp electrical current to 1 A and hold until the drop disappears.

11.3.2 Ramp current to 1.5 A and hold for 2 minutes.

11.3.3 Ramp current to 1.8 A and hold for 1 minute.

11.3.4 Ramp current to 2.1 A and hold for 10 seconds.

### 11.4 *Isotopic Ratio Measurement:*

11.4.1 Insert the filament assembly into the mass spectrometer.

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

11.4.3 Add liquid nitrogen to the cryo trap if desired.

11.4.4 Steps 11.4.5 through 11.4.9 may be performed automatically under computer control, depending upon instrument. Very small samples may require manual control to avoid sample loss.

11.4.5 Perform a gain calibration if desired.

11.4.6 Perform a baseline (amplifier noise) measurement.

11.4.7 If using the double filament technique, heat the ionization filament to a temperature sufficient to provide satisfactory ionization. Typical temperatures for uranium are 2000°C and for plutonium 1850°C. In the absence of an optical pyrometer, the magnitude of the  $^{187}Re$  beam may be used as an indication of filament temperature. In certain cases this technique may provide a more reproducible indication of temperature than the optical pyrometer.

11.4.8 Slowly begin heating 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 for plutonium and 1650–1850°C for uranium. If so equipped, 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 counts per second when using the ion counter, or 10–30 mV when using Faraday cup detectors.

11.4.9 Locate the major uranium or plutonium isotope and perform peak centering and focusing.

11.4.10 Begin data acquisition, while simultaneously heating the sample filament to yield a predetermined major isotope ion beam intensity. The maximum beam intensity to be maintained during analysis depends upon the sample size and the capabilities of the detectors. Intensities between 4 and 30V are typical for the major isotope(s). Integration times are generally between 1 and 16 seconds, but may range from less than 1 second to more than 60 seconds, depending on sample, operator preference and instrument capability.

11.4.11 Under computer control, the sample filament temperature is continually adjusted to maintain the target ion beam intensity, until the sample is exhausted or a pre-determined minimum ion beam intensity is reached.

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

11.4.13 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 ratios.

11.4.14 Record and correct if necessary (see Section 8) the isotopic ratios of the samples.

## 12. Calculations

12.1 Calculation of atom percent, weight percent and atomic weight:

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

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

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

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.

12.2 Calculation of sample element mass via isotope dilution mass spectrometry:

$$\text{Moles of element in sample} = \frac{b(B_i - R_{ik}B_k)}{R_{ik}A_k - A_i} \quad (5)$$

where:

$b$  = moles of element in spike added to sample,

$R_{ik}$  = measured ratio of spike/sample isotopes in the sample-spike mix,

$A_i$  = atom fraction spike isotope in pure sample,

$B_i$  = atom fraction spike isotope in pure spike (for example,  $^{242}\text{Pu}$  or  $^{233}\text{U}$ ),

$A_k$  = atom fraction sample isotope in pure sample, and

$B_k$  = atom fraction sample isotope present in pure spike.

12.2.1 The concentration of the sample can then be calculated by multiplying the result of Eq 5 by the atomic weight of

the element in the sample and then dividing by the weight of the sample in the aliquant.

12.3 Calculation to correct peak-tailing effects on minor isotopes:

12.3.1 Peak-tailing from adjacent isotopes may cause a bias in minor isotope measurements. A correction may be performed using the individually-measured ratios for each integration and an estimate of the abundance sensitivity during sample analysis. The accuracy of the correction is dependent on the accuracy of the abundance sensitivity estimate. For the most accurate results, the abundance sensitivity should be measured just prior to sample analysis, under conditions (pressure, sample load, ion beam intensities) similar to those used in sample analysis. Additionally, the analyzer pressure should be monitored to ensure it does not exceed the pressure at which the abundance sensitivity measurement is performed. Minor isotope ratio measurement uncertainties should include contributions from the correction and estimates of the abundance sensitivity.

12.3.2 The peak-tailing correction generally requires modification or adaptation of the instrument software or export of individual ratio values into a spreadsheet with subsequent data manipulation. An example derivation of the correction equation is given in Eq 6-8 for correcting  $^{234}\text{U}/^{238}\text{U}$  ratios for peak tailing into the  $^{234}\text{U}$  mass from  $^{235}\text{U}$ .

$$I_{234,meas} = I_{234} + I_{235,tail} = I_{234} + t \cdot I_{235} \quad (6)$$

$$\frac{I_{234,meas}}{I_{238}} = \frac{I_{234}}{I_{238}} + t \cdot \frac{I_{235}}{I_{238}} \quad (7)$$

$$R_{4/8corr} = R_{4/8meas} + t \cdot R_{5/8meas} \quad (8)$$

where:

$I_{234,meas}$  = measured ion beam intensity at mass 234,  
 $I_{234}$  = intensity of ion beam at mass 234 from  $^{234}\text{U}$  ions,

$I_{235,tail}$  = intensity of ion beam at mass 234 from tailing  $^{235}\text{U}$  ions,

$t$  = abundance sensitivity,

$I_{238}$  = intensity of ion beam at mass 238,

$R_{4/8corr}$  = tail-corrected  $^{234}\text{U}/^{238}\text{U}$  ratio,

$R_{4/8meas}$  = measured  $^{234}\text{U}/^{238}\text{U}$  ratio, and

$R_{5/8meas}$  = measured  $^{235}\text{U}/^{238}\text{U}$  ratio.

12.3.3 Eq 8 is the equation used to perform bias corrections for peak-tailing, with Eq 6 and Eq 7 indicating the derivation. Tail correction equations for other isotopes and ratios may be similarly derived for the isotopes of uranium and plutonium.

## 13. Precision and Bias

13.1 A total of four thermal ionization mass spectrometers were employed to determine the precision and bias for uranium and plutonium ratio determinations via the method. A Finnigan MAT 261 and a Thermo Triton instrument were used for uranium analyses, and a Finnigan MAT 262 and a different Thermo Triton instrument were used for plutonium analyses. Uranium and plutonium Certified Reference Materials were used, and all were analyzed on each instrument using a minimum of three turrets on three different days. Uranium reference materials used were New Brunswick Laboratory CRMs U010, U030A, U050, U100, U200, U500, U750 and U900. These materials covered the range of  $^{235}\text{U}$  enrichments

from 1 to 90 %. Plutonium reference materials used were CRMs C122, C136, C137, C138 and C128. The range of  $^{239}\text{Pu}$  abundance spanned by these materials is from 85 to 92 %, with  $^{240}\text{Pu}$  abundances between 8 and 18 %. C128 is certified only for  $^{239}\text{Pu}$  and  $^{242}\text{Pu}$  (equal atom) and the minor isotopes were not included in this study.

### 13.2 Precision:

13.2.1 For uranium, the major ratio ( $^{235}\text{U}/^{238}\text{U}$ ) precision varied between 0.016 and 0.028 % as relative standard deviation for the suite of reference materials analyzed. Minor ratio precision varied over a large range, dependent upon minor isotope abundance.

13.2.2 For plutonium, with the exception of CRM 128, the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio precision varied between 0.0045 and 0.0077 % as relative standard deviation. For CRM 128, the  $^{242}\text{Pu}/^{239}\text{Pu}$  ratio precision was 0.017 % as relative standard deviation. Minor ratio precision varied over a large range, dependent upon minor isotope abundance.

### 13.3 Bias:

13.3.1 For uranium, there was statistically significant deviation from the certified value for a number of the measured  $^{236}\text{U}/^{238}\text{U}$  ratios. This was detected more often on the Finnigan MAT 261 instrument. All other measured ratios did not exhibit any bias from the certified value. It is most likely that the biases detected in the  $^{236}\text{U}/^{238}\text{U}$  ratios are due to

tailing from the  $^{238}\text{U}$  ion beam into the low-abundance  $^{236}\text{U}$  beam as all of the measured values were larger than the certified value.

13.3.2 For plutonium, there was no detected bias (no significant difference between measured and certified value) in any of the measured ratios. Users should be cautioned that significant bias is possible, particularly in  $^{238}\text{Pu}/^{239}\text{Pu}$ , due to peak tailing from the  $^{239}\text{Pu}$  ion beam into the  $^{238}\text{Pu}$  beam.

13.4 Due to the methods capability for extremely good precision, particularly for plutonium, significant day-to-day variations are possible. These variations were detected in the data for all plutonium ratios measured on the Thermo Triton instrument. However, the magnitude of the variations was much smaller than the certified uncertainties (that is, major ratio uncertainties for the CRM's are generally around 0.1 %, while the major ratio precision's were generally <0.0050 %). Therefore, the significance of these day-to-day variation in the total uncertainty of the measurements is negligible and may be ignored in most cases.

## 14. Keywords

14.1 atom percent; isotope dilution mass spectrometry; isotopic composition; mass fractionation; plutonium; thermal ionization mass spectrometry; total evaporation; uranium; weight percent

## ANNEX

### (Mandatory Information)

#### A1. PRECISION AND BIAS STATEMENT

##### A1.1 Introduction

A1.1.1 A series of turrets loaded with Certified Reference Materials were run by the total evaporation mass spectrometric method with the purpose of validating and qualifying the method for use at a single laboratory.

A1.1.2 For both uranium and plutonium, two different mass spectrometers were employed (Finnigan MAT 261 and a Thermo Triton) to generate the precision and bias data. All samples were loaded on degassed, high-purity rhenium filaments as nitrate solutions after an ion exchange purification. Plutonium filament loads contained 40 ng Plutonium, and uranium filament loads contained 200 ng uranium. All analyses took place at a single laboratory, with turret loading and analysis taking place on different days.

A1.1.3 For the uranium analyses, each turret contained multiple samples of either U500 or U030A used to generate a bias correction factor for the turret. The measured 235/238 ratio for the bias correction standards was divided by the certified 235/238 ratio to calculate the three-mass correction factor. A linear model was then used to calculate one-mass and two-mass correction factors. All other reference materials on the turret were then corrected using the specific turrets bias

correction factors. No bias correction was performed for plutonium analyses; the results reported in the tables are directly taken from instrument output without subsequent modification.

##### A1.2 Data Analysis

A1.2.1 For each ratio, the given reference value is the value taken from the certificate of analysis for that reference material. If ratio values were not given on the certificate, the ratio values and their uncertainties were directly calculated from the certified abundance values.

A1.2.2 The mean relative difference is the difference of the reference value from the observed mean value of the ratio, divided by the reference value and expressed in percent.

A1.2.3 The relative standard deviation is the standard deviation of the measurement set, divided by the reference value and expressed in percent.

A1.2.4 For each standard, standard Analysis of Variance (ANOVA) techniques were used to test for significant turret-to-turret variation in the results. For both instruments measuring uranium and the Mat 261 measuring Plutonium, no statistical evidence of turret-to-turret variation was detected.

For the Triton measuring plutonium, however, significant turret-to-turret variation was found for all isotopic ratios.

A1.2.5 Thus for Plutonium isotopic measurements made with the Triton instrument, both a “Relative Standard Deviation (simple)” is calculated which is the relative standard deviation as calculated for the other measurement sets. Additionally, a “Relative Standard Deviation (complex)” is also calculated. This quantity is determined by estimates of variance components due to both analytical error and turret-to-turret variation. The components are calculated using the MIVQUE algorithm (Goodnight) and then added in quadrature to obtain the standard deviation quantity, which is then divided by the reference value and expressed as percent.

A1.2.6 The “Significant Difference From Ref. Value” is determined by a two-sample *t*-test (Bowen and Bennet) incorporating the standard error of the measurement set and the uncertainty of the reference value. Where the reference value uncertainty is stated on the certificate, that quantity is used. Where the uncertainty is not stated on the certificate, the uncertainty for the ratios is calculated from the stated uncertainties for the isotopic abundances, using standard propagation of uncertainty techniques (Bevington).

A1.2.7 The mean relative difference is an indication of potential bias. The Relative Standard Deviation is an indication of precision. The test method when performed on uranium materials with the Mat 261 instrument for the U236/U235 ratio with enrichment levels of less than 90 % consistently showed

statistically significant bias from the reference values. No other ratio measured indicated any significant bias from the reference values.

A1.2.8 For plutonium, many of the Triton instrument results indicated a significant turret-to-turret variation. However, the magnitude of the variation is, in all cases, much smaller than the certified uncertainty. The total evaporation technique is capable of extremely low precisions, on the order of 0.005 % for plutonium major ratios, and thus significant turret-to-turret variations are commonly detected though their effect on the overall uncertainty of the measured ratio is negligible due to the contribution of the uncertainty in the certified values (which is on the order of 0.1 %).

### A1.3 References

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A1.3.3 Bevington, P. R., “Data Reduction and Error Analysis for the Physical Sciences,” McGraw-Hill, New York, NY, 1969, pp. 56-65.

Uranium	MAT 261 Reference Material	U010	U100	U500	U900
U234/U235	Reference Value	0.00539	0.00663	0.01043	0.00862
	Mean Relative Difference, %	-0.8497	0.2043	0.0720	0.0752
	Rel. Std. Dev	4.4115	0.2505	0.0234	0.0311
	Number of Observations	9	9	10	9
	Number of Turrets	3	3	3	3
	Significant Turret-to Turret Variation	No	No	No	No
	Significant Difference From Ref. Value	No	No	No	No
U236/U235	Reference Value	0.00678	0.00372	0.00152	0.00369
	Mean Relative Difference, %	3.5464	0.6496	0.5968	0.0448
	Rel. Std. Dev	2.3572	0.45	0.1481	0.0629
	Number of Observations	9	9	10	9
	Number of Turrets	3	3	3	3
	Significant Turret-to Turret Variation	No	No	No	No
	Significant Difference From Ref. Value	Yes	Yes	Yes	No
U238/U235	Reference Value	98.61911	8.80314	1.00030	0.09638
	Mean Relative Difference, %	0.0214	-0.0107	N/A	0.0098
	Rel. Std. Dev	0.0194	0.0278	0.0158	0.0163
	Number of Observations	9	9	10	9
	Number of Turrets	3	3	3	3
	Significant Turret-to Turret Variation	No	No	No	No
	Significant Difference From Ref. Value	No	No	N/A	No
Triton	Standard	U200	U500	U750	U900
U234/U235	Reference Value	0.00623	0.01043	0.00786	0.00862
	Mean Relative Difference, %	0.0508	-0.0705	-0.0590	-0.0586
	Rel. Std. Dev	0.0520	0.0485	0.0326	0.0525
	Number of Observations	8	8	8	7
	Number of Turrets	2	2	2	2
	Significant Turret-to Turret Variation	No	No	No	No
	Significant Difference From Ref. Value	No	No	No	No
U236/U235	Reference Value	0.01057	0.00152	0.00332	0.00369
	Mean Relative Difference, %	-0.0687	0.2707	0.0765	-0.039
	Rel. Std. Dev	0.0162	0.0329	0.0148	0.0271
	Number of Observations	8	8	8	7
	Number of Turrets	2	2	2	2



Significant Turret-to Turret Variation Significant Difference From Ref. Value		No No	No No	No No	No No		
U238/U235	Reference Value	3.97996	1.00030	0.31584	0.09638		
	Mean Relative Difference, %	0.0301	#N/A	-0.0050	0.0041		
	Rel. Std. Dev	0.0312	0.0229	0.0205	0.0360		
	Number of Observations	8	8	8	7		
	Number of Turrets	2	2	2	2		
	Significant Turret-to Turret Variation	No	No	No	No		
	Significant Difference From Ref. Value	No	#N/A	No	No		
Triton (Continued)		Standard	U010	U030A	U050	U030A	U050
U234/U238	Reference Value	0.00005	0.00029	0.00029	0.01043	0.00029	0.00029
	Mean Relative Difference, %	-0.3306	0.1892	-0.0110	0.0272	0.1846	-0.0299
	Rel. Std. Dev	0.1336	0.0513	0.0483	0.0296	0.0649	0.0572
	Number of Observations	7	7	8	8	35	37
	Number of Turrets	2	2	2	2	8	8
	Significant Turret-to Turret Variation	No	No	No	No	No	No
	Significant Difference From Ref. Value	No	No	No	No	No	No
U236/U238	Reference Value	0.00007	0.00001	0.00051	0.00152	0.00001	0.00051
	Mean Relative Difference, %	0.6664	-1.0262	0.2810	0.3095	-0.6150	0.2720
	Rel. Std. Dev	0.2762	1.9417	0.0237	0.0204	2.5890	0.0297
	Number of Observations	7	7	8	8	35	37
	Number of Turrets	2	2	2	2	8	8
	Significant Turret-to Turret Variation	No	No	No	No	No	No
	Significant Difference From Ref. Value	No	Yes	No	No	No	No
U235/U238	Reference Value	0.01014	0.03137	0.05276	0.99970	0.03137	0.05278
	Mean Relative Difference, %	-0.0129	0.0105	-0.0430	N/A	#N/A	-0.0586
	Rel. Std. Dev	0.0217	0.0188	0.0282	0.0235	0.0191	0.0224
	Number of Observations	7	7	8	8	35	37
	Number of Turrets	2	2	2	2	8	8
	Significant Turret-to Turret Variation	No	No	No	No	No	No
	Significant Difference From Ref. Value	No	No	No	N/A	N/A	No
Plutonium		Mat 261 Standard	CRM 122	CRM 136	CRM 137		
Pu238/Pu239	Reference Value		0.00052	0.00234	0.00308		
	Mean Relative Difference, %		-0.0172	0.6127	0.6200		
	Rel. Std. Dev		0.4909	0.0851	0.0995		
	Number of Observations		8	9	9		
	Number of Turrets		3	3	3		
	Significant Turret-to Turret Variation		No	No	No		
	Significant Difference From Ref. Value		No	No	No		
Pu240/Pu239	Reference Value		0.13199	0.14484	0.24104		
	Mean Relative Difference, %		0.0153	-0.023	-0.0142		
	Rel. Std. Dev		0.0045	0.0058	0.008		
	Number of Observations		8	9	9		
	Number of Turrets		3	3	3		
	Significant Turret-to Turret Variation		No	No	No		
	Significant Difference From Ref. Value		No	No	No		
Pu241/Pu239	Reference Value		0.00460	0.01105	0.01376		
	Mean Relative Difference, %		0.2741	0.1157	0.3666		
	Rel. Std. Dev		0.0403	0.0157	0.0176		
	Number of Observations		8	9	9		
	Number of Turrets		3	3	3		
	Significant Turret-to Turret Variation		No	No	No		
	Significant Difference From Ref. Value		Yes	No	No		
Pu242/Pu239	Reference Value		0.00205	0.00679	0.0156		
	Mean Relative Difference, %		0.0758	-0.0384	-0.2232		
	Rel. Std. Dev		0.0739	0.0349	0.025		
	Number of Observations		8	9	9		
	Number of Turrets		3	3	3		
	Significant Turret-to Turret Variation		No	No	No		
	Significant Difference From Ref. Value		No	No	No		
Triton		Standard	CRM 122	CRM 136	CRM 137	CRM 138	CRM 128
Pu238/Pu239	Reference Value		0.0005	0.0023	0.0031	0.0001	0.0001**
	Mean Relative Difference, %		0.5350	0.8573	0.7115	14.2649	-45.5288
	Rel. Std. Dev (Simple)		1.0953	0.3520	0.2434	6.1923	13.5615
	Rel. Std. Dev (Complex)		1.1782	0.3803	0.2586	6.5895	14.1712
	Number of Observations		20	22	25	18	28
	Number of Turrets		6	6	7	5	7
	Sig. Turret-to Turret Variation		Yes	Yes	Yes	Yes	Yes
	Sig. Difference From Ref. Value		No	No	No	No	N/A

Pu240/Pu239	Reference Value	0.132	0.1448	0.241	0.0862	0.0007**
	Mean Relative Difference, %	0.0135	-0.0182	-0.022	0.0432	-2.6312
	Rel. Std. Dev (Simple)	0.0064	0.0067	0.0072	0.0060	0.5581
	Rel. Std. Dev (Complex)	0.0064	0.0073	0.0074	0.0064	0.5892
	Number of Observations	20	22	25	18	28
	Number of Turrets	6	6	7	5	7
	Sig. Turret-to Turret Variation	Yes	Yes	Yes	Yes	Yes
	Sig. Difference From Ref. Value	No	No	No	No	N/A
Pu241/Pu239	Reference Value	0.0044	0.0106	0.0132	0.0012	0.0003**
	Mean Relative Difference, %	0.0117	0.0383	0.1315	-0.0425	-2.1116
	Rel. Std. Dev (Simple)	0.1285	0.0611	0.0799	0.3890	2.1632
	Rel. Std. Dev (Complex)	0.1387	0.0654	0.0854	0.4151	2.2526
	Number of Observations	20	22	25	18	28
	Number of Turrets	6	6	7	5	7
	Sig. Turret-to Turret Variation	Yes	Yes	Yes	Yes	Yes
	Sig. Difference From Ref. Value	No	No	No	No	N/A
Pu242/Pu239	Reference Value	0.0021	0.0068	0.0156	0.0004	1.0011
	Mean Relative Difference, %	0.0365	-0.0887	-0.2698	-0.7284	0.0079
	Rel. Std. Dev (Simple)	0.212	0.1322	0.0619	2.8322	0.0167
	Rel. Std. Dev (Complex)	0.2228	0.1415	0.0627	2.9794	0.0172
	Number of Observations	20	22	25	18	28
	Number of Turrets	6	6	7	5	7
	Sig. Turret-to Turret Variation	Yes	Yes	Yes	Yes	Yes
	Sig. Difference From Ref. Value	No	No	No	No	No

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