Designation: 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 Spectrometer[1]

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

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

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

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

1.5 *This standard may involve the use of hazardous materials and equipment. This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[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

C996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % ^{235}U

C1008 Specification for Sintered (Uranium-Plutonium) DioxidePellets—Fast Reactor Fuel (Withdrawn 2014)[3]

C1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry

C1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials

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[1] This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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

C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis
C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis
C1411 Practice for The Ion Exchange Separation of Uranium and Plutonium Prior to Isotopic Analysis
C1415 Test Method for ^{238}Pu Isotopic Abundance By Alpha Spectrometry
C1625 Test Method for Uranium and Plutonium Concentrations and Isotopic Abundances by Thermal Ionization Mass Spectrometry
C1816 Practice for The Ion Exchange Separation of Small Volume Samples Containing Uranium, Americium, and Plutonium Prior to Isotopic Abundance and Content Analysis
C1832 Test Method for Determination of Uranium Isotopic Composition by the Modified Total Evaporation (MTE) Method Using a Thermal Ionization Mass Spectrometer
D1193 Specification for Reagent Water
D3084 Practice for Alpha-Particle Spectrometry of Water

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

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

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

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

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

3.3 *Acronyms:*

3.3.1 *CRM*—Certified Reference Materials

3.3.2 *DU*—Depleted Uranium

3.3.3 *HEU*—High Enriched Uranium

3.3.4 *IDMS*—Isotope Dilution Mass Spectrometry

3.3.5 *IRMM*—Institute for Reference Materials and Measurements (IRMM is now known as European Commission Joint Research Center, JRC-Geel)

3.3.6 *LEU*—Low Enriched Uranium

3.3.7 *NBL*—New Brunswick Laboratory

3.3.8 *NU*—Natural Uranium

3.3.9 *TIMS*—Thermal Ionization Mass Spectrometry

3.3.10 *WRM*—Working Reference Material

4. Summary of Test Method

4.1 Uranium and plutonium are separated from each other and purified from other elements by selective anion exchange chromatography (such as in Practice C1411 or Test Method C1415 or C1816). The purified uranium or plutonium samples as nitrate solutions are drop-deposited or otherwise loaded on a refractory metal filament (typically rhenium, tungsten, or tantalum) and converted to a solid chemical form via controlled heating of the filament under atmospheric conditions. The sample filament is mounted on the sample turret, often in the double filament configuration. This configuration consists of an evaporation filament (Re or W) on which the sample is loaded, and an ionization filament (Re filament with no sample). The filaments are heated to yield a small ion current suitable for lens focusing and peak centering. Following focusing and peak centering, data acquisition begins, with the filaments heated under computer control to yield a pre-defined major isotope ion current (^{235}U or ^{238}U for uranium and ^{239}Pu or ^{240}Pu for plutonium) or a predefined sum total for all measured ion currents. Data acquisition and filament heating continues until the sample is exhausted or the ion current reaches a pre-defined lower limit. Ion intensity of each isotope is integrated over the course of the analysis, and the summed intensity for each isotope is divided by the summed intensity of a common isotope (typically the most abundant isotope) to yield ratios. The isotopic composition of the sample (formatted as amount fraction or mass fraction) may be calculated from the isotope ratios. Additional information on the total evaporation method may be found in Refs **(1-5)**.[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 ^{238}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

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

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

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

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

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

5.5 Typical uranium analyses are conducted using sample loadings between 50 nanograms and several micrograms. For uranium isotope ratios the total evaporation method had been used in several recent NBL isotopic certified reference material (CRM) characterizations (for example (**2**, **3**)). A detailed comparison of the total evaporation data on NBL uranium CRMs analyzed by the MAT 261 and TRITON^{TM} 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 should be completed within a reasonable time period after the separation of americium to minimize interference 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. For NBL CRMs 136, 137, and 138 the ^{241}Pu/^{239}Pu ratio changes by about 0.092 % per week as a 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 decay of ^{241}Pu and the accuracy and precision consistent with the data quality objectives of the facility. Other atomic and molecular species may interfere with total evaporation analyses, particularly if they cause a change in the ionization efficiency of the analyte during an analysis. Presence of carbon may disturb total evaporation measurements. It is recommended that instrument users perform validation tests on unique or complex samples by mixing known pure standards with other constituents to create a matrix-matched standard.

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

6.3 The total evaporation method may generate biases in the minor isotope ratios, especially when measuring trace amounts of ^{234}U in a HEU (highly enriched uranium, ^{235}U 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 magnitude of the peak tailing correction is a function of the design of the instrument and spread in the ion beam due to source design and particle collisions in the instrument. The peak tailing may be quantified by measuring the abundance sensitivity under experimental conditions similar to those at which samples are analyzed. A bias correction may then be applied based upon the measured abundance sensitivity. Additionally, the use of an energy filter in conjunction with an ion counting detector can significantly reduce or completely eliminate peak tailing and allow for accurate measurement of minor isotopes. The use of an energy filter, ultra-high-purity filaments and chemicals, effective sample purification, and low ionization and evaporation temperatures to minimize ^{238}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 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. The mass spectrometer used should possess the following characteristics:

7.1.1 A thermal ionization source capable of analyzing single or 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} 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 reduces the sample 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 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 chemicals shall be used in all 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] 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 ribbons shall be used, the size and configuration are instrument dependent. Tungsten or tantalum may be substituted with minor modifications to the procedure. Tungsten filaments have been reported to yield higher precision analyses via the total evaporation method. 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 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.

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 UF_6 materials

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[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.

[6] The sole source of supply of the standards known to the committee at this time are: (*1*) USDOE New Brunswick Laboratory, 9800 S. Cass Ave., Argonne, IL, 60439, 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.

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 (^{233}U spike), CRM 112–A (^{238}U spike), IRMM 040a (^{233}U spike), IRMM 052 (^{238}U spike) and IRMM 054 (^{235}U spike). For plutonium commonly used spike materials are NBL CRM 130 (^{242}Pu spike), the IRMM 049c/d/e/f series (^{242}Pu spikes), IRMM-042a (^{244}Pu spike), or the IRMM 046b/c series (mixed ^{233}U and ^{242}Pu spikes).

10. Precautions

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 in relation to the total evaporation method may be found in Ref (**9**).

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. Instrument users should perform routine electronic performance checks to ensure that the instrument meets manufacturer's specifications for stability and performance. The interval between the electronic performance checks should be established based upon manufacturer's recommendation and instrument history.

11.3 *Mass Calibration*—The relationship between the atomic masses and the 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 the instrument manufacturer. The stability of the mass calibration curve is dependent on the laboratory conditions and 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 on a weekly basis or as often as prior to each sample analysis. 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 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 ^{187}Re is suggested due to ease of generating a very 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 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. 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 uncertainty estimates for the sample results. The frequency at which this calibration should be performed 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 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 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**) 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, small mass biases have been reported for uranium and plutonium isotope ratio measurements using TIMS instruments (**2-8**). Therefore in several laboratories a mass bias correction 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 on the deviation of the measured major ratio of the reference material from the certified ratio. A mass bias correction factor is then applied to the measured sample ratios. Regardless of the method used, it is important 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:

$$K = \left(R_c \ / \ R_m \right) \tag{1}$$

where:

K = mass bias correction factor,
R_m = average measured atom ratio for CRM, and
R_c = certified atom ratio for the CRM.

11.10.2 To correct major and minor individual sample ratios, calculate the appropriate mass bias correction factor based upon the mass difference between 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 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 isotope ratio. Under ideal conditions, deviations from constant values are likely due to nonlinearity. Uranium CRMs are typically used for linearity checks because the range of isotopic compositions observed in safegaurds measurements. See Test Method C1832 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—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 allow convenient filament loading (for example, a 0.1 mg U/mL solution yields 100 ng of uranium in a 1 µL drop).

12.1.3 *Sample Purification*—Use Practice C1411 or similar procedure to separate uranium and 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 or with pipettes fitted with disposable tips. The tips should be changed between sample loadings to prevent cross-contamination. Typically, 1 µL 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 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 establish the current-to-temperature relationship appropriate for the sample loading. Once a suitable heating program is established, a programmable power supply may be used to ensure that the conditioning regimens for all samples and 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 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 A and hold for 2 minutes.

12.3.3 Ramp current to 1.5 A and hold for 10 s.

12.3.4 Ramp current to 2.0 A and hold for 10 s.

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 cryogenic trap, if desired.

12.4.4 Steps 11.3 through 11.6 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 (see 11.5).

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

12.4.7 If using the double filament technique, heat the ionization filament to a temperature sufficient to provide sufficient ionization. Recommended temperature for uranium is ~1800 to 2000°C and for plutonium ~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. The ^{187}Re intensity may provide a more reproducible indication of temperature than the optical pyrometer.

12.4.8 Slowly heat the sample filament to a temperature sufficient to yield a small ion beam suitable for focusing and peak centering. Typical temperatures are 1000 to 1400°C for plutonium and 1400 to 1800°C for uranium. If 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 a few thousands of counts per second when using the ion counter, or 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 Perform peak centering and focusing of the major uranium or plutonium isotopes.

12.4.10 Begin data acquisition, while 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 15 V are typical for the major isotope(s). Integration times are generally between 1 and 16 s, but may range from less than 1 s to more than 60 s, depending on sample, user preference and instrument characteristics.

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

13. Calculations

13.1 *Evaluation of the "major" ratio $^{235}U/^{238}U$*—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 $^{235}U/^{238}U$ is calculated as:

$$\left(\frac{^{235}U}{^{238}U}\right)_{TE} = \frac{\sum\limits_{ALL\_INTEGRATIONS} I\left(^{235}U\right)}{\sum\limits_{ALL\_INTEGRATIONS} I\left(^{238}U\right)} = \frac{\sum\limits_{ALL\_INTEGRATIONS}\left[\left(\frac{I\left(^{235}U\right)}{I\left(^{238}U\right)}\right)\cdot I\left(^{238}U\right)\right]}{\sum\limits_{ALL\_INTEGRATIONS} I\left(^{238}U\right)} \quad (2)$$

where:

$I(^{235}U)$ and $I(^{238}U)$ = 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 $^{235}U/^{238}U$ 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 $I(^{235}U)/I(^{238}U)$ signal intensity ratios during the measurement, weighted by the ^{238}U ion signal intensities.

13.2 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:

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

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

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

where:

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

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

M_i = nuclidic mass of the ith isotope.

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 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.

13.3 The isotope ratios obtained by total evaporation using the procedure described here can be utilized to calculate the element concentration in the sample. The calculation of the element concentration using isotope dilution mass spectrometry is illustrated below:

13.3.1 Using a ^{233}U enriched material as the spike material, the ^{235}U content in an unknown sample can be determined by isotope dilution, through a measurement of the isotope ratio $R(^{233}U/^{235}U, b)$ in the blend. The uranium amount content can be calculated using the following "full IDMS equation":

$$c(U\ ,\ X) = \frac{R\left(^{233}U/^{235}U,Y\right) - R\left(^{233}U/^{235}U,B\right)}{R\left(^{233}U/^{235}U,B\right) - R\left(^{233}U/^{235}U,X\right)}\cdot\frac{\sum\limits_m R\left(^{m}U/^{235}U,X\right)}{\sum\limits_m R\left(^{m}U/^{235}U,Y\right)}\cdot\frac{m(Y)}{m(X)}\cdot c(U\ ,\ Y) \quad (6)$$

where:

$R(^{m}U/^{235}U, X)$ = amount ratio $^{m}U/^{235}U$ in the unknown sample material X,

$R(^{m}U/^{235}U, Y)$ = amount ratio $^{m}U/^{235}U$ in the known spike material Y,

$R(^{m}U/^{235}U, B)$ = amount ratio $^{m}U/^{235}U$ in the measured blend material B,

$m(X)$ = mass of the unknown sample used in the measurement,

$m(Y)$ = mass of the spike solution used in the measurement,

$c(^{235}U, X)$ = amount content (moles) of ^{235}U / g sample material,

$c(^{233}U, Y)$ = amount content (moles) of ^{233}U / g spike solution,

$c(U, X)$ = amount content of U / kg sample material, and

$c(U, Y)$ = amount content of U / kg spike solution.

Eq 6 can be simplified as:

$$c(^{235}U,\ X)= \tag{7}$$

$$\frac{R(^{233}U/^{235}U,\ Y)-R(^{233}U/^{235}U,\ B)}{R(^{233}U/^{235}U,\ B)-R(^{233}U/^{235}U,\ X)}\cdot\frac{1}{R(^{233}U/^{235}U,\ Y)}\cdot$$

$$\frac{m(Y)}{m(X)}\cdot c(^{233}U,\ Y)$$

The use of the simplified Eq 7 is advantageous, if not all isotope ratios of the sample (X) and spike (Y) are measured or known. Eq 7 uses only the isotope ratio between the dominant "sample isotope" (in this case ^{235}U) and the dominant "spike isotope" (in this case ^{233}U) and the minor ratios are irrelevant for this equation.

Eq 6 and Eq 7 cannot be used if there is no ^{235}U in the spike. In this case, Eq 8 or Eq 9 are to be used and all isotope ratios are expressed as ^{m}U/^{233}U, that is, using ^{233}U as the normalizing isotope.

13.3.2 Using a ^{233}U enriched material as spike, the ^{235}U content in an unknown sample can be determined by IDMS, through a measurement of the isotope ratio R(^{235}U/^{233}U, B) in the blend. The U amount content can be calculated using the following (full IDMS) equation:

$$c(U,\ X)= \tag{8}$$

$$\frac{R(^{235}U/^{233}U,\ Y)-R(^{235}U/^{233}U,\ B)}{R(^{235}U/^{233}U,\ B)-R(^{235}U/^{233}U,\ X)}\cdot\frac{\sum_{m}R(^{m}U/^{233}U,\ X)}{\sum_{m}R(^{m}U/^{233}U,\ Y)}\cdot$$

$$\frac{m(Y)}{m(X)}\cdot c(U,\ Y)$$

where:

$R(^{m}U/^{233}U,\ X)$ = amount ratio ^{m}U/^{233}U in the unknown sample material X,

$R(^{m}U/^{233}U,\ Y)$ = amount ratio ^{m}U/^{233}U in the known spike material Y,

$R(^{m}U/^{233}U,\ B)$ = amount ratio ^{m}U/^{233}U in the measured blend material B,

$m(X)$ = mass of the unknown sample used in the measurement,

$m(Y)$ = mass of the spike solution used in the measurement,

$c(^{235}U,\ X)$ = amount content (moles) of ^{235}U / g sample material,

$c(^{233}U,\ Y)$ = amount content (moles) of ^{233}U / g spike solution,

$c(U,\ X)$ = amount content of U / kg sample material, and

$c(U,\ Y)$ = amount content of U / kg spike solution.

Eq 8 can be simplified as:

$$c(^{235}U,\ X)= \tag{9}$$

$$\frac{R(^{235}U/^{233}U,\ Y)-R(^{235}U/^{233}U,\ B)}{R(^{235}U/^{233}U,\ B)-R(^{235}U/^{233}U,\ X)}\cdot\frac{R(^{235}U/^{233}U,\ X)}{1}\cdot$$

$$\frac{m(Y)}{m(X)}\cdot c(^{233}U,\ Y)$$

The use of the simplified Eq 9 is advantageous, if not all isotope ratios of the sample (X) and spike (Y) are measured or known. Eq 9 uses only the isotope ratio between the dominant "sample isotope" (in this case ^{235}U) and the dominant "spike isotope" (in this case ^{233}U) and the minor ratios are irrelevant for this equation. The choice of the Eq 6 to Eq 9 depends on the particular IDMS task, that is, the way the ratios are defined, which ratios are known or measured, and which spike is used.

Eq 8 and Eq 9 cannot be used if there is no ^{233}U within the sample. In this case, Eq 6 and Eq 7 are to be used and all isotope ratios are expressed as ^{m}U/^{235}U, that is, using ^{235}U as the normalizing isotope.

Eq 6 to Eq 9 can be adapted for other situations, for example, calculation of the uranium content using ^{235}U or ^{238}U as spike materials instead of a ^{233}U spike, and for calculation of the plutonium content using ^{240}Pu, or ^{242}Pu or ^{244}Pu as spike materials. The most common spike isotope for Pu IDMS is ^{242}Pu, the IDMS can be calculated using Eq 10 to Eq 13.

13.3.3 Using a ^{242}Pu enriched material as the spike, the ^{239}Pu content in an unknown sample can be determined by isotope dilution, through a measurement of the isotope ratio R(^{242}Pu/^{239}Pu, B) in the blend. The plutonium amount content can be calculated using the following (full IDMS) equation:

$$c(Pu,\ X)= \tag{10}$$

$$\frac{R(^{242}Pu/^{239}Pu,\ Y)-R(^{242}Pu/^{239}Pu,\ B)}{R(^{242}Pu/^{239}Pu,\ B)-R(^{242}Pu/^{239}Pu,\ X)}\cdot\frac{\sum_{m}R(^{m}Pu/^{239}Pu,\ X)}{\sum_{m}R(^{m}Pu/^{239}Pu,\ Y)}\cdot$$

$$\frac{m(Y)}{m(X)}\cdot c(Pu,\ Y)$$

where:

$R(^{m}Pu/^{239}Pu,\ X)$ = amount ratio ^{m}Pu/^{239}Pu in the unknown sample material X,

$R(^{m}Pu/^{239}Pu,\ Y)$ = amount ratio ^{m}Pu/^{239}Pu in the known spike material Y,

$R(^{m}Pu/^{239}Pu,\ B)$ = amount ratio ^{m}Pu/^{239}Pu in the measured blend material B,

$m(X)$ = mass of the unknown sample used in the measurement,

$m(Y)$ = mass of the spike solution used in the measurement,

$c(^{239}Pu,\ X)$ = amount content (moles) of ^{239}Pu / g sample material,

$c(^{242}Pu,\ Y)$ = amount content (moles) of ^{242}Pu / g spike solution,

$c(Pu,\ X)$ = amount content of Pu / kg sample material, and

$c(Pu,\ Y)$ = amount content of Pu / kg spike solution.

Eq 10 can be simplified as:

$$c(^{239}Pu,\ X)= \tag{11}$$

$$\frac{R(^{242}Pu/^{239}Pu,\ Y)-R(^{242}Pu/^{239}Pu,\ B)}{R(^{242}Pu/^{239}Pu,\ B)-R(^{242}Pu/^{239}Pu,\ X)}\cdot\frac{1}{R(^{242}Pu/^{239}Pu,\ Y)}\cdot$$

$$\frac{m(Y)}{m(X)}\cdot c(^{242}Pu,\ Y)$$

The use of the simplified Eq 11 is advantageous, if not all isotope ratios of the sample (X) and spike (Y) are measured or known, Eq 11 uses only the isotope ratio between the dominant "sample isotope" (in this case ^{239}Pu) and the dominant "spike isotope" (in this case ^{242}Pu) and the minor ratios are irrelevant for this equation.

Eq 10 and Eq 11 cannot be used if there is no ^{239}Pu in the spike. In this case, Eq 12 or Eq 13 are to be used and all isotope ratios are expressed as ^{m}Pu/^{242}Pu, that is, using ^{242}Pu as the normalizing isotope.

13.3.4 Using a ^{242}Pu enriched material as the spike, the ^{239}Pu content in an unknown sample can be determined by IDMS, through a measurement of the isotope ratio R(^{239}Pu/^{242}Pu, B) in the blend. The Pu amount content can be calculated using the following (full IDMS) equation:

$$c(Pu,\ X)= \tag{12}$$

$$\frac{R(^{239}Pu/^{242}Pu,\ Y)-R(^{239}Pu/^{242}Pu,\ B)}{R(^{239}Pu/^{242}Pu,\ B)-R(^{239}Pu/^{242}Pu,\ X)}\cdot\frac{\sum_{m}R(^{m}Pu/^{242}Pu,\ X)}{\sum_{m}R(^{m}Pu/^{242}Pu,\ Y)}\cdot$$

$$\frac{m(Y)}{m(X)}\cdot c(Pu,\ Y)$$

where:

$R(^{m}Pu/^{242}Pu,\ X)$ = amount ratio ^{m}Pu/^{242}Pu in the unknown sample material X,
$R(^{m}Pu/^{242}Pu,\ Y)$ = amount ratio ^{m}Pu/^{242}Pu in the known spike material Y,
$R(^{m}Pu/^{242}Pu,\ B)$ = amount ratio ^{m}Pu/^{242}Pu in the measured blend material B,
$m(X)$ = mass of the unknown sample used in the measurement,
$m(Y)$ = mass of the spike solution used in the measurement,
$c(^{239}Pu,\ X)$ = amount content (moles) of ^{239}Pu / g sample material,
$c(^{242}Pu,\ Y)$ = amount content (moles) of ^{242}Pu / g spike solution,
$c(Pu,\ X)$ = amount content of Pu / kg sample material, and
$c(Pu,\ Y)$ = amont content of Pu / kg spike solution.

Eq 12 can be simplified as:

$$c(^{239}Pu,\ X)= \tag{13}$$

$$\frac{R(^{239}Pu/^{242}Pu,\ Y)-R(^{239}Pu/^{242}Pu,\ B)}{R(^{239}Pu/^{242}Pu,\ B)-R(^{239}Pu/^{242}Pu,\ X)}\cdot\frac{R(^{239}Pu/^{242}Pu,\ X)}{1}\cdot$$

$$\frac{m(Y)}{m(X)}\cdot c(^{242}Pu,\ Y)$$

The use of the simplified Eq 13 is advantageous, if not all isotope ratios of the sample (X) and spike (Y) are measured or known. Eq 13 uses only the isotope ratio between the dominant "sample isotope" (in this case ^{239}Pu) and the dominant "spike isotope" (in this case ^{242}Pu) and the minor ratios are irrelevant for this equation. The choice of the Eq 10 to Eq 13 depends on the particular IDMS task, that is, the way the ratios are defined, which ratios are known or measured, and which spike is used.

Eq 12 and Eq 13 cannot be used if there is no ^{242}Pu within the sample. In this case, Eq 10 or Eq 11 are to be used and all isotope ratios are expressed as ^{m}Pu/^{239}Pu, that is, using ^{239}Pu as the normalizing isotope.

If using a ^{244}Pu spike, Eq 10 to Eq 13 can be reformulated accordingly, but the simplified Eq 13 cannot be used if there is no ^{244}Pu in the sample.

13.4 The mass concentration of the sample can then be calculated by multiplying the result of Eq 6 to Eq 13 by the atomic weight (according to Eq 5) of the element in the sample.

13.5 In case that the ratios from the unknown sample material X, the known spike material Y, or the blend material B have been obtained by an isotope ratio measurement using the same reference material for the mass bias correction factor (that is, K-factor, see Eq 1) or even within the same measurement sequence, the corrected ratios cannot be considered truly independent. In this case, it is recommended that the uncorrected ratios multiplied by the appropriate K-factors be entered into Eq 6 to Eq 13 instead of the corrected ratios. This is important for properly calculating the combined uncertainty of the (U or Pu) amount content.

13.6 *Correction of the Peak-Tailing Effects on Minor Isotopes:*

13.6.1 Peak-tailing from adjacent isotopes may cause a bias in minor isotope measurements. A correction may be performed using the individually-measured ratios and an estimate of the abundance sensitivity. 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.

13.6.2 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. As an illustration, the peak-tailing correction at ^{234}U is shown below (tailing corrections at ^{234}U/^{238}U ratios arise due to ^{235}U isotope).

$$I_{234,meas}=I_{243}+I_{235,tail}=I_{234}+t\cdot I_{235} \tag{14}$$

$$\frac{I_{234,meas}}{I_{238}}=\frac{I_{234}}{I_{238}}+t\cdot\frac{I_{235}}{I_{238}} \tag{15}$$

$$R_{4/8corr}=R_{4/8meas}-t\cdot R_{5/8meas} \tag{16}$$

where:

$I_{234,meas}$ = measured ion beam intensity at mass 234,
I_{234} = ion beam intensity at 234 from ^{234}U ions,
$I_{235,tail}$ = ion beam intensity at 234 from tailing of ^{235}U ions,
t = abundance sensitivity,
I_{238} = ion beam intensity at mass 238,
$R_{4/8corr}$ = tailing corrected ^{234}U/^{238}U ratio,
$R_{4/8meas}$ = measured ^{234}U/^{238}U ratio, and

$R_{5/8meas}$ = measured $^{234}U/^{238}U$ ratio.

13.6.3 Eq 16 is used to perform bias corrections for peak-tailing, with Eq 14 and Eq 15 showing the derivation. Tail correction equations for other isotopes of U and or minor isotopes of Pu may be similarly derived.

13.6.3.1 In case of a sample with low or no ^{235}U enrichment, the tailing correction for ^{234}U may rather be due to the ^{238}U beam, in that case the correction has to be performed according to:

$$R_{4/8corr} = R_{4/8meas} - t \tag{17}$$

13.6.4 Alternatively, the tailing correction can be performed on the averaged and mass-bias corrected ratios according to Eq 16 and Eq 17.

14. Precision and Bias

14.1 A total of four thermal ionization mass spectrometers were employed to determine the precision and bias for uranium and plutonium ratio measurements via the method. A Finnigan MAT 261 and a Thermo TRITON^{TM} instrument were used for uranium analyses, and a Finnigan MAT 262 and a different Thermo TRITON^{TM} instrument were used for plutonium isotope ratio measurements. Uranium and plutonium CRMs were used for the estimation of the bias and precision. The CRMs were analyzed on each instrument using a minimum of three turrets on three different days. Uranium CRMs U010, U030A, U050, U100, U200, U500, U750, and U900 from New Brunswick Laboratory were used. These CRMs covered the range of ^{235}U enrichments from 1 to 90 %. Plutonium reference materials used were CRM 122, CRM 136, CRM 137, CRM 138 and CRM 128. The range of ^{239}Pu abundance spanned by these materials is from 85 to 92 %, with ^{240}Pu abundances between 8 and 18 %. CRM 128 is certified only for ^{239}Pu and ^{242}Pu ($^{239}Pu/^{242}Pu \cong 1$) and the minor isotope ratios of this CRM were not evaluated for the bias and precision.

14.2 *Precision:*

14.2.1 For uranium, the major ratio ($^{235}U/^{238}U$) precision expressed as relative standard deviation varied between 0.016 and 0.028 % for the suite of reference materials analyzed. Similar precisions had also been reported in published literature for the ($^{235}U/^{238}U$) ratio using both TRITON^{TM} and MAT 261 instruments (**5**), with the TRITON^{TM} showing significantly improved precision compared to the MAT 261, especially for DU, NU, and LEU CRMs. Table A1.3 shows that the precision of the major ratio measurement is independent of the value of the ratio. Minor ratio precision varied over a large range, dependent upon minor isotope abundance.

14.2.2 For plutonium, the $^{240}Pu/^{239}Pu$ ratio precision varied between 0.0045 and 0.0077 % as relative standard deviation. For CRM 128, the precision of the $^{242}Pu/^{239}Pu$ ratio was 0.017 % as relative standard deviation, this corresponds to precision of 0.0057 % per amu, similar to that reported for the $^{240}Pu/^{239}Pu$ ratio of other CRMs. Minor ratio precision varied over a large range, dependent upon minor isotope abundance.

14.3 *Bias:*

14.3.1 Measurements of a gravimetric mixture with $^{235}U/^{238}U$ = 1 at JRC-Geel shows that the major ratio bias is <0.05 % (2σ). This data is included as Fig. A1.1. For uranium, there was statistically significant deviation from the certified value for a number of the measured $^{236}U/^{238}U$ ratios. The biases detected in the $^{236}U/^{238}U$ ratios are due to tailing from the ^{238}U ion beam into the low-abundance ^{236}U as all of the measured values were higher than the certified value. Biases in the $^{234}U/^{238}U$ ratio of the HEU (high enriched uranium, ^{235}U abundance ≥ 20 %) CRMs and biases similar to those reported in A1.3, for the $^{236}U/^{238}U$ ratio, had been reported in literature (**5**).

14.3.2 Measurements of a gravimetric mixture with $^{242}Pu/^{239}Pu$ = 1, at JRC-Geel shows that the major ratio bias is <0.05 % (2σ). This data is included as Fig. A1.2. For plutonium, there was no detected bias (no significant difference between measured and certified value) in neither the measured major nor the minor ratios. However, instrument users are cautioned that significant bias is possible, particularly in $^{238}Pu/^{239}Pu$ due to peak tailing from the ^{239}Pu ion beam into the ^{238}Pu beam or due to an incomplete separation of the Pu fraction and the U fraction or due to U background from the processing of the samples (chemical and process blanks).

14.4 Due to the extremely good precision, particularly for plutonium, significant day-to-day variations in the isotope ratios are possible. These variations were detected in the data for all plutonium ratios measured on the Thermo TRITON^{TM} instrument. However, the magnitude of the variations was much smaller than the uncertainties of the certified ratios. The major ratio uncertainties for the CRMs are generally around 0.1 %, while the precision of the major ratio measurements were generally <0.0050 %. Therefore, the significance of these day-to-day variation in the total uncertainty of the measurements is negligible.

14.5 Additional precision and bias information are shown in Annex A1.

15. Measurement Uncertainty

15.1 The uncertainties in the major isotope ratios for the analyzed sample are dominated by: (*1*) the precision in the analysis of the reference material standard used for mass bias correction; (*2*) precision of the sample analysis; and (*3*) certified uncertainty of the reference material standard used for mass bias correction. For the minor isotope ratios, peak-tailing corrections due to the major isotopes and variability in the major ratio that is used for estimation of the mass bias correction effects are significant contributors in addition to the precision of the isotope ratio measurement itself. For the major ratios often, uncertainties in the isotope ratios are dominated by the certified uncertainties of the isotopic CRM used for estimation of the mass bias effects and used for instrument calibration. In case no mass fractionation is performed for total evaporation data, the uncertainties may be underestimated if they are calculated purely from the reproducibility of the measurements. Additional uncertainty components arising from the dependency of total evaporation data from the measurement parameters, for example, sample loading, filament temperatures, and measurement procedures, may have to be investigated and included. A more detailed discussion of the uncertainty components relevant to isotope ratio measurements is beyond the scope of the current document.

15.2 The uncertainties in the elemental amount contents determined by IDMS are dominated by (*1*) uncertainties in the isotope ratio measurements (isotope ratios in the sample, spike, and sample-spike mixture are required); (*2*) uncertainties in the masses (or volumes, if the mixture preparation involves mixing of the volume aliquots); (*3*) uncertainties in the concentration of the spike solution; and (*4*) uncertainties in the amount content of the spike. Often, weight uncertainties dominate the amount content uncertainty budget. Biases in the IDMS results are mostly caused by lack of equilibration between the spike and sample in the mixture. The spike must be added before column separation, if any. A more detailed discussion of the uncertainty components relevant to amount content determinations of U and Pu by the IDMS technique is beyond the scope of this standard.

16. Keywords

16.1 certified reference materials; isotope amount fraction; isotope mass fraction; isotope dilution mass spectrometry; isotopic composition; mass fractionation; plutonium; thermal ionization mass spectrometry; total evaporation; uranium

ANNEX

(Mandatory Information)

A1. PRECISION AND BIAS STATEMENT

A1.1 Introduction

A1.1.1 A series of turrets loaded with CRMs were measured 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^{TM}) 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 were made 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 certified $^{235}U/^{238}U$ ratio for the reference material used for bias correction is divided by the measured $^{235}U/^{238}U$ ratio to calculate the correction factor for a mass difference of 3 u (u stands for atomic mass units). A linear model was then used to calculate correction factors for mass differences of 1 u, 2 u, and 4 u, in case of the minor ratios. All other reference materials on the turret were then corrected using the turret specific 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.

A1.1.4 Mathew et al (5) performed a detailed study of the performance of the total evaporation method using TRITON^{TM} and MAT 261 instruments. Filament loads in the range of 200 ng to 1 µg were analyzed. Different CRMs were used as comparator standard. Summary data from this study (mass bias corrected) is shown as Table A1.3.

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 formatted as a percent.

A1.2.3 The relative standard deviation is the standard deviation of the measurement set, divided by the reference value and formatted as a percent.

A1.2.4 For each reference material, 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^{TM} 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^{TM} 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 isotope 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 ^{236}U/^{235}U ratio with enrichment levels of less than 90 % consistently showed statistically significant bias from the reference values, due to tailing effects from the major isotopes. No other ratio measured indicated any significant bias from the reference values.

A1.2.8 For plutonium, TRITON^{TM} 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 %).

A1.2.9 The U major isotope data from Mathew et al. (**5**) are included as Table A1.3. As minor isotope ratio measurements by TE are prone to biases because they are not corrected for peak tailing effects, these data are not reproduced here (see (**5**) for a detailed discussion of the uranium minor ratio biases during U isotope ratio measurements using TE). Note that isotope data generated using multiple CRMs as comparator standards and by multiple analysts are included in Table A1.3.

A1.3 References

A1.3.1 Goodnight, J. H., "Computing MIVQUE Estimates of Variance Components," SAS Institute, Raleigh, NC, 1978.

A1.3.2 Bowen, W. M. and Bennett, C. A., Editors, "Statistical Methods for Nuclear Material Management," NUREG/CR-4604, U.S. Nuclear Regulatory Commission, Washington, DC, 1988, pp. 168-171.

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

TABLE A1.1 Precision and Bias Data for U CRMs

NOTE 1—Data shown here was included as part of reapproved standard. Precision and bias data on Pu CRMs included as part of the reapproved standard is shown as Table A1.2. Additional literature data on U CRMs analyzed by the MAT 261 and by TRITON™ (Mathew et al. (**5**)) are included as Table A1.3. In addition, measurements of gravimetric mixtures with $^{235}\text{U}/^{238}\text{U} \approx 1$ are shown as Fig. A1.1 and Fig. A1.2.

		Instrument: MAT 261			
Isotope Ratio	CRM	U010	U100	U500	U900
$^{234}\text{U}/^{235}\text{U}$	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
$^{236}\text{U}/^{235}\text{U}$	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
$^{238}\text{U}/^{235}\text{U}$	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

		Instrument: TRITON™			
Isotope Ratio	CRM	U200	U500	U750	U900
$^{234}\text{U}/^{235}\text{U}$	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
$^{236}\text{U}/^{235}\text{U}$	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	No	No	No	No
	Significant Difference From Ref. Value	No	No	No	No
$^{238}\text{U}/^{235}\text{U}$	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

Isotope Ratio	CRM	U010	U030A	U050	U500	U030A	U050
$^{234}\text{U}/^{238}\text{U}$	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
$^{236}\text{U}/^{238}\text{U}$	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
$^{235}\text{U}/^{238}\text{U}$	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

TABLE A1.2 Precision and Bias Data for Pu CRMs

NOTE 1—Data shown here was included as part of the approved standard. No additional data are included.

Instrument: MAT 261

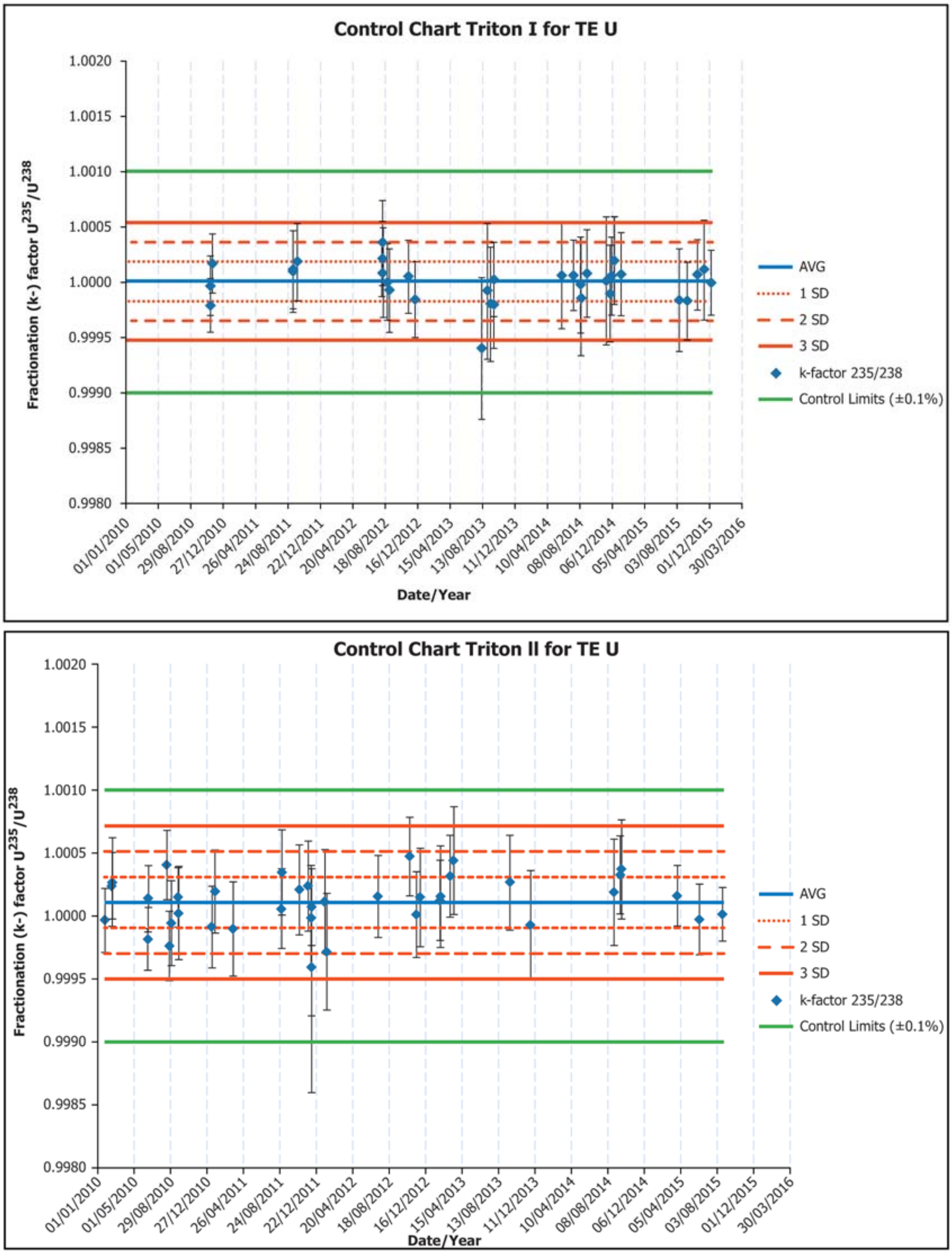
Isotope Ratio	CRM	CRM 122	CRM 136	CRM137
^{238}Pu/^{239}Pu	Reference Value	0.00052	0.00234	0.00308
	Mean Relative Difference, %	-0.0172	0.6127	0.6200
	Rel. Std. Dev, %	0.4909	0.0851	0.0995
	Number of Observations	8	9	9
	Number of Turrets	3	3	3
	Significant Turret-to-Turret Variation	No	No	No
	Significant Difference From Ref. Value	No	No	No
^{240}Pu/^{239}Pu	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
^{241}Pu/^{239}Pu	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	No	No	No
^{242}Pu/^{239}Pu	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

Instrument: TRITON^{TM}

Isotope Ratio	CRM	CRM 122	CRM 136	CRM 137	CRM 138	CRM 128
^{238}Pu/^{239}Pu	Reference Value	0.0005	0.0023	0.0031	0.0001	0.0001**
	Mean Relative Difference, %	0.5350	0.8573	0.7115	14.2649	N/A
	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
^{240}Pu/^{239}Pu	Reference Value	0.132	0.1448	0.241	0.0862	0.0007**
	Mean Relative Difference, %	0.0135	-0.0182	-0.022	0.0432	N/A
	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
^{241}Pu/^{239}Pu	Reference Value	0.0044	0.0106	0.0132	0.0012	0.0003**
	Mean Relative Difference, %	0.0117	0.0383	0.1315	-0.0425	N/A
	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
^{242}Pu/^{239}Pu	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

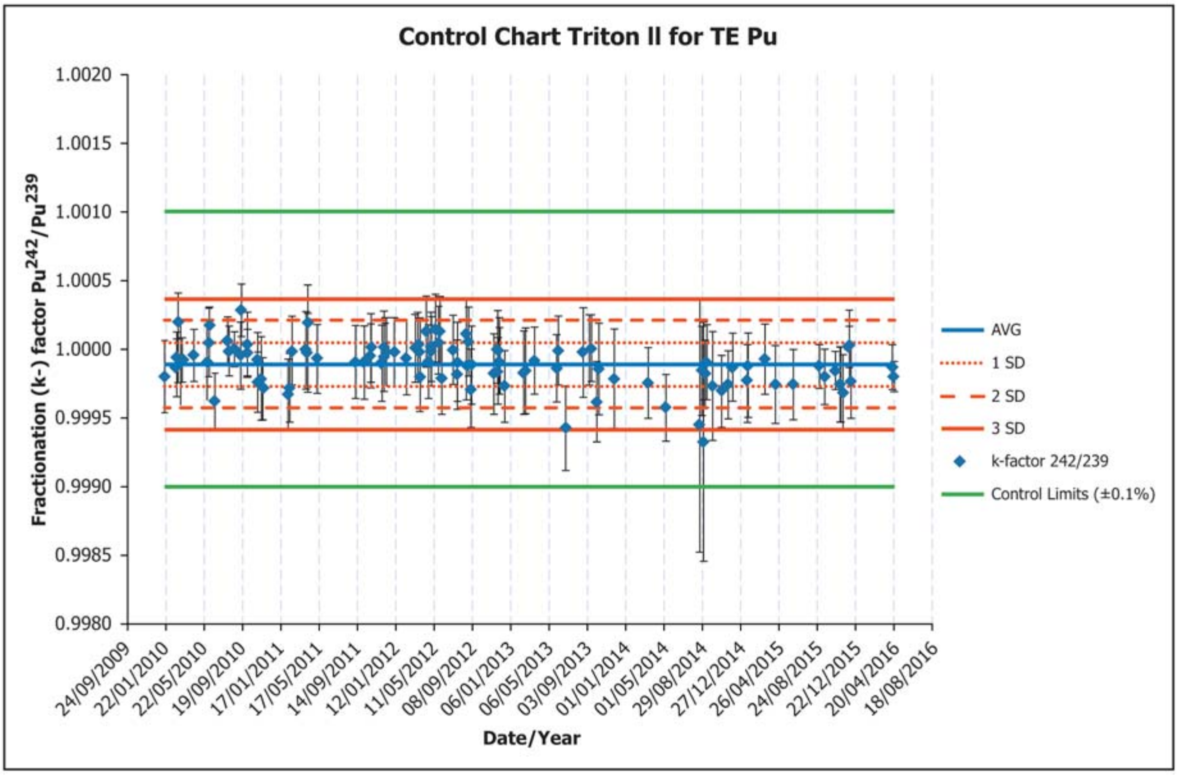
TABLE A1.3 Within-turret Precision (Rel. Std. Dev, %) and Bias (Rel. Diff., %) for TE Measurements of ^{235}U/^{238}U Major Ratio Using TRITON™ and MAT 261 Instruments

CRM	^{235}U/^{238}U	^{235}U/U, %	Rel. Std. Dev, %	Rel. Diff., %
		Instrument: TRITON™		
U900	10.3757	91.2	0.0217	-0.0131
U900	10.3757	91.2	0.0234	-0.0120
U750	3.16613	76.0	0.0313	0.0116
U750	3.16613	76.0	0.0238	0.0297
U630	1.806679	63.1	0.0106	-0.0281
U045	0.047310	4.5	0.0088	-0.0086
U045	0.047310	4.5	0.0308	0.0340
U045	0.047310	4.5	0.0230	-0.0290
U045	0.047310	4.5	0.0257	0.0180
U030A	0.03137	3.0	0.0226	0.0199
U030A	0.03137	3.0	0.0333	0.0375
U010	0.01014	1.0	0.0222	-0.0611
U010	0.01014	1.0	0.0138	-0.0033
U010	0.01014	1.0	0.0076	-0.0448
U010	0.01014	1.0	0.0432	-0.0412
129-A	0.0072614	0.7	0.0139	0.0065
129-A	0.0072614	0.7	0.0080	-0.0078
129-A	0.007261	0.7	0.0035	0.0053
129-A	0.0072614	0.7	0.0065	-0.0113
129-A	0.0072614	0.7	0.0246	0.0341
129-A	0.0072614	0.7	0.0147	0.0046
112-A	0.0072543	0.7	0.0035	0.0034
112-A	0.0072543	0.7	0.0048	0.0003
112-A	0.0072543	0.7	0.0038	-0.0052
112-A	0.0072543	0.7	0.0398	-0.0138
112-A	0.0072543	0.7	0.0702	0.0166
112-A	0.0072543	0.7	0.0092	-0.0348
112-A	0.0072543	0.7	0.0042	-0.0220
U005A	0.00509	0.5	0.0293	0.0008
115	0.0020337	0.2	0.0202	0.0276
115	0.0020337	0.2	0.0484	0.0145
115	0.0020337	0.2	0.0192	0.0267
CRM	^{235}U/^{238}U	^{235}U/U, %	Rel. Std. Dev, %	Rel. Diff., %
		Instrument; MAT 261		
C149	17.4986	93.2	0.0102	-0.0082
U900	10.3757	91.2	0.0319	-0.0216
U900	10.3757	91.2	0.0110	-0.0159
U900	10.3757	91.2	0.0104	-0.0046
U900	10.3757	91.2	0.0144	-0.0082
U750	3.16613	76.0	0.0378	0.0123
U630	0.806679	63.1	0.0154	-0.0362
U630	1.806679	63.1	0.0199	-0.0088
U045	0.047310	4.5	0.0438	0.0156
U045	0.047310	4.5	0.0118	-0.0142
U045	0.047310	4.5	0.0882	0.0087
U045	0.047310	4.5	0.0388	0.0093
U045	0.047310	4.5	0.0158	0.0507
125-A	0.042301	4.0	0.0162	-0.0218
U030A	0.03137	3.0	0.0386	-0.0061
U010	0.010140	1.0	0.0250	-0.0296
U010	0.010140	1.0	0.0118	-0.0376
112-A	0.0072543	0.7	0.0674	-0.0189
112-A	0.0072543	0.7	0.0215	-0.0114



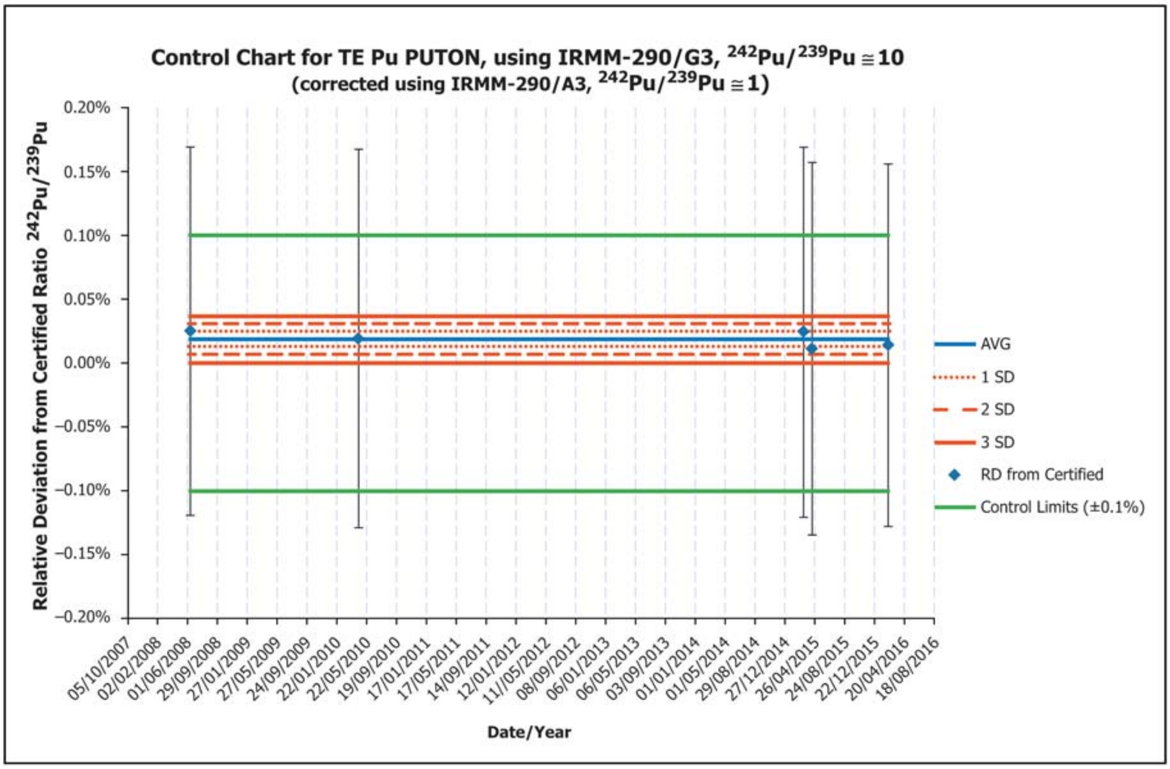
NOTE 1—Measured using two TRITON™ instruments at the IRMM (now known as JRC-Geel). The error bars represent the uncertainties (with coverage factor *k* = 2) calculated only as two times the standard error of the replicate measurements within the same turret sequence. The relative uncertainty of the certified value is 0.016 %.

FIG. A1.1 Control Charts Showing Data for U TE Measurements of IRMM-074/10 with a Certified ^{235}U/^{238}U Ratio of 1.00026(16) from Gravimetrical Preparation



NOTE 1—Measured using a TRITON™ instrument at the IRMM (now known as JRC-Geel). The error bars represent the uncertainties (with coverage factor *k* = 2) calculated only as two times the standard error of the replicate measurements within the same turret sequence. The relative uncertainty of the certified value is 0.1 %.

FIG. A1.2 Control Chart Showing Data for Pu TE Measurements of IRMM-290/A3 with a Certified ^{242}Pu/^{239}Pu Ratio of 0.9993(10) (01/07/1986) from Gravimetrical Preparation



NOTE 1—Measured using a TRITON™ instrument at the IRMM (now known as JRC-Geel). The mass bias correction was performed according to Eq 1 using IRMM-290/A3 with a certified $^{242}\text{Pu}/^{239}\text{Pu}$ ratio of 0.9993(10) (01/07/1986) from gravimetrical preparation. The error bars represent the uncertainties (with coverage factor $k = 2$) calculated including the uncertainties of the certified values for IRMM-290/A3 and IRMM-290/G3, that is, a relative uncertainty of about 0.14 % for all data points.

FIG. A1.3 Control Chart Showing Mass Bias Corrected Data for Pu TE Measurements of IRM-290/G3 with a Certified $^{242}\text{Pu}/^{239}\text{Pu}$ Ratio of 10.007(10) (01/07/1986) from Gravimetrical Preparation

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