Standard Test Method for
Determination of Uranium Isotopic Composition by the Modified Total Evaporation (MTE) Method Using a Thermal Ionization Mass Spectrometer[1]

This standard is issued under the fixed designation C1832; 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 test method describes the determination of the isotope amount ratios of uranium material as nitrate solutions by the modified total evaporation (MTE) method using a thermal ionization mass spectrometer (TIMS) instrument.

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

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

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

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder
C776 Specification for Sintered Uranium Dioxide Pellets
C787 Specification for Uranium Hexafluoride for Enrichment
C833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets
C859 Terminology Relating to Nuclear Materials
C967 Specification for Uranium Ore Concentrate
C996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % ^{235}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
C1128 Guide for Preparation of Working Reference Materials for Use in Analysis of Nuclear Fuel Cycle Materials
C1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials
C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis
C1411 Practice for The Ion Exchange Separation of Uranium and Plutonium Prior to Isotopic Analysis
C1625 Test Method for Uranium and Plutonium Concentrations and Isotopic Abundances by Thermal Ionization Mass Spectrometry
C1672 Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer
D1193 Specification for Reagent Water

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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.

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

E2586 Practice for Calculating and Using Basic Statistics

3. Terminology

3.1 The terminology standard C859 contains terms, definitions, descriptions of terms, nomenclature, and explanations of acronyms and symbols specifically associated with standards under the jurisdiction of Committee C26 on Nuclear Fuel Cycle.

3.2 *Definitions:*

3.2.1 *abundance sensitivity, n*—in isotope amount ratio measurements, the ratio of the measured intensity of an ion beam at a mass, m, to the measured intensity from the same isotope measured at one mass unit difference (for example, $m \pm 1$).

3.2.1.1 *Discussion*—Abundance sensitivity is a measure of the magnitude of the peak tailing correction. For measuring uranium on thermal ionization mass spectrometer (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS) instruments, the abundance sensitivity is typically calculated as the ratio of the measured signal intensities at masses 237 and 238 using a suitable uranium sample.

3.2.2 *total evaporation, TE, n*—analytical method for determination of isotope amount ratios of uranium or plutonium, as described in Test Method C1672, also called "classical" total evaporation in this test method.

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

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

3.3 *Acronyms:*

3.3.1 *cpm*—counts per minute

3.3.2 *cps*—counts per second

3.3.3 *CRM*—certified reference material

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

3.3.5 *DS*—double spike

3.3.6 *DU*—depleted uranium

3.3.7 *EU*—European Union

3.3.8 *FAR*—Faraday Cup

3.3.9 *HEU*—high enriched uranium

3.3.10 *IAEA*—International Atomic Energy Agency

3.3.11 *ICPMS*—inductively coupled plasma mass spectrometry

3.3.12 *IRMM*—Institute for Reference Materials and Measurements

3.3.13 *ITU*—Institute for Transuranium Elements

3.3.14 *JRC*—Joint Research Centre

3.3.15 *LEU*—low enriched uranium

3.3.16 *MTE*—modified total evaporation

3.3.17 *NBL*—New Brunswick Laboratory

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

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

3.3.20 *SD*—standard deviation—according to Practice E2586, 3.1.30: the square root of the sum of the squared deviations of the observed values in the sample divided by the sample size minus one.

3.3.21 *SE*—standard error—according to Practice E2586, 3.1.29: standard deviation of the population of values of a sample statistic (that is, the mean value) in repeated measurements, or an estimate of it.

3.3.21.1 *Discussion*—According to Practice E2586, 3.1.30: If the standard error (SE, see above) of a statistic is estimated, it will itself be a statistic with some variance that depends on the sample size, that is, the number of observed values in the sample (Practice E2586, 3.1.26).

3.3.21.2 *Discussion*—According to Guide E2655, 5.8.4.1: From statistical theory, a 95 % confidence interval for the mean of a normal distribution, given n independent observations x_1, x_2, ..., x_n drawn from the distribution is, $\bar{x} \pm t \times \mathrm{SD} / \sqrt{n}$, where $\bar{x}$ is the sample mean, SD is the standard deviation of the observations (see above), and t is the 0.975 percentile of the Student's t distribution with n-1 degrees of freedom. Because Student's t distribution approaches the Normal as n increases, the value of t approaches 1.96 as n increases. This is the basis for using the (coverage) factor 2 for expanded uncertainty. The standard error (SE) of the mean value of a series of n independent repeated measurements can be derived from that by using $t = 1$, so the standard error (SE) is given by $\mathrm{SD} / \sqrt{n}$.

3.3.22 *SEM*—secondary electron multiplier.

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

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

3.3.24 *TIMS*—thermal ionization mass spectrometry

4. Summary of Test Method

4.1 The modified total evaporation method has been developed on the basis of the "classical" total evaporation technique (**1-4**)[4], also described in Test Method C1672. By using the total evaporation technique, the mass fractionation is minimized by evaporating the entire sample amount loaded on the filament, in contrast to the "conventional" technique as described in Test Method C1625. The MTE method has already been described in detail in Refs (**5**) and (**6**). If necessary, uranium is separated from plutonium and other elements (to eliminate isobaric interferences) by selective extraction, anion exchange (see Practice C1411), or extraction chromatography. The purified uranium fraction as nitrate solution is loaded onto a degassed

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

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

4.2 The sample amount to be loaded for MTE analyses is limited to a range of about 2 to 6 µg to achieve ion beam signals of about 20 to 30 V for the major isotope – ^{238}U for DU, NU, and LEU samples and ^{235}U for HEU samples – corresponding to a ^{234}U intensity of 1 to 10 mV. This causes the ^{234}U ion beam to be suitable for an internal cross calibration of the SEM versus the Faraday cups through the entire measurement time. This also allows the ^{236}U/^{238}U isotope amount ratio to be measured in a wide dynamic range from 10^{-2} down to 10^{-10} using a Faraday cup or an SEM in combination with an energy filter for improved abundance sensitivity. For certain DU samples, the ^{236}U ion beam is used for the cross calibration and the ^{234}U is measured on the SEM (known as "reverse" MTE, see 13.8.8). For all samples with minor ratios ^{234}U/^{238}U and ^{236}U/^{238}U higher than 4 × 10^{-5}, which also includes HEU samples, the minor isotopes are only measured using Faraday cups with amplifier resistors of 10^{12} Ω yielding a favorable signal-to-noise ratio.

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

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

5. Significance and Use

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

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

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

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

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

6. Interferences

6.1 Isobaric nuclides such as ^{238}Pu interfere in the uranium measurements. The removal of interferences is generally accomplished by chemical separation leading to ionization of uranium only and improved precision of measured isotope amount ratios.

6.2 It has to be ensured that samples are not contaminated by environmental uranium. The level of effort required to minimize contamination shall be based upon the sample size and the levels of contamination present in the analytical facility. For extremely small samples or extremely low ^{236}U abundances, residual uranium from chemicals used for sample dissolution and sample preparation are possible sources for bias in the isotopic data.

6.3 Samples shall be chemically purified to assure reliable analyses by TIMS. Impurities, especially alkali elements, produce unstable ion emission leading to poor precision in the isotope amount ratios. Organic contaminants or oxide layers on the filaments also adversely influence TIMS analyses. Isobaric interferences, if not removed, will bias the isotope amount ratios. Contaminants in reagents, lab, ware, or filament material are also sources for bias in the isotope amount ratios.

6.4 The performance of the instrument can be adversely affected by changes in the environmental conditions of the laboratory, that is, temperature and humidity. For this reason, controlled laboratory environmental conditions should be maintained (within the manufacturer's specifications) during instrument operation.

7. Apparatus

7.1 The suitability of the mass spectrometer for carrying out measurements by the MTE method shall be evaluated by means of performance tests. The relevant instrument characteristics are as follows:

7.1.1 A thermal ionization source for using double filament assemblies with rhenium or tungsten filaments, or both;

7.1.2 A mass analyzer sufficient to resolve adjacent masses in the mass-to-charge range being studied, $m/z = 233$ to 238 for U^+. Resolution shall be greater than 350 (full width at 1 % of peak height) and the abundance sensitivity at mass 237 for ions of ^{238}U less than 5×10^{-6};

7.1.3 A multiple Faraday collector system to allow simultaneous detection of isotope beams from $m/z = 233$ to 238 for U^+ ions;

7.1.4 For the Faraday cups used to measure the major ion beams of ^{235}U and ^{238}U, there shall be current amplifiers equipped with 10^{11} Ω resistors and, for the minor ion beams of ^{234}U and ^{236}U, there shall be current amplifiers equipped with at least 10^{11} Ω, and preferably 10^{12} Ω (or even 10^{13} Ω) resistors to improve the signal-to-noise ratio;

7.1.5 The detection system shall include at least one secondary electron multiplier (SEM) operated in ion counting mode or a Daly detector, or similar detector, with a dark noise <0.2 cps. The SEM shall be equipped with an energy filter to improve the abundance sensitivity, which shall be better than 2×10^{-8} at mass 237 for ions from $^{238}U^+$ with the energy filter in operation;

7.1.6 A sample turret with at least ten filament positions to allow automatic measurement sequences of at least five replicate filament loadings per sample and at least five replicate filament loadings for a calibration standard (preferentially a CRM);

7.1.7 A pumping system that is able to attain a vacuum of $<4.0 \times 10^{-5}$ Pa (3×10^{-7} torr) in the ion source, the analyzer, and the detector is required. Tailing corrections are dependent on the vacuum levels inside the mass spectrometer. Analyzer pressures below 7.0×10^{-7} Pa (5×10^{-9} torr) are preferred;

7.1.8 A mechanism to scan masses by varying the magnetic field or the accelerating voltage, or both;

7.1.9 An optical pyrometer for determining the temperatures of the filaments;

7.1.10 A computer for control of the data acquisition according to a predefined sequence.

7.2 *Special MTE Capabilities*—The mass spectrometer software must be flexible enough to implement a user-defined filament-heating program for MTE.[6]

7.3 A separate filament degassing device for cleaning of the filaments before sample loading is recommended.

7.4 *Microsyringe*—Syringe to transfer microlitre volumes of solutions.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all sample preparations. 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.[7] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity and low uranium concentration to permit its use without lessening the accuracy of the MTE measurements.

8.2 Ultra-high purity reagents are necessary for processing small sample amounts or samples with extremely small isotope amount ratios. The level of uranium contamination from chemicals, water, and the sample handling environments shall be determined to ensure that the materials and the environment are sufficiently pure for the samples being analyzed.

8.3 *Nitric Acid* (HNO_3, 15.8 M)—Concentrated nitric acid.

8.4 *Nitric Acid* (HNO_3, 1 M)—One volume of concentrated nitric acid (HNO_3, 15.8 M) brought to 15.8 volumes with water.

8.5 *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.

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[6] The sole source of supply of the apparatus known to the committee at this time is Thermo Fisher Scientific Inc., 81 Wyman St., Waltham, MA 02451. 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.

[7] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K. and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.6 *Filaments*—High-purity filaments, for example, zone refined Re, are required. The size and configuration of the filament is instrument dependent. Tungsten might be used with minor modifications to the heating script. All filaments must be degassed before use. For measurement of uranium present only at the trace levels in the sample, contamination of the samples by interferences from elemental or molecular species within the $m/z = 233$ to 238 range need to be determined to ensure that biases due to contributions from the filament material will not bias the analysis results. In case a significant count rate >1 cps is determined at $m/z = 236$, a correction has to be applied for $^{236}U/^{238}U$ ratios < 10^{-6} (**6, 7**).

9. Hazards

9.1 TIMS instruments operate at 8 to 10 kV electrical potential. Ensure that the high-voltage is switched off before insertion or removal of the sample turret into/from the instrument, and working with the ion source, or accessing other electronic components.

9.2 The filaments reach temperatures in excess of 2000°C. The filament holders, sample wheel, and ion source parts are expected to be hot. Ensure that a sufficient time has lapsed since the last filament heating before accessing the filaments, sample turrets, and ion source.

9.3 Wear eye protection and suitable gloves when filling cold traps with liquid nitrogen. Protect hands, torso, and feet in the event of splashing or spilling of the liquid nitrogen.

9.4 Handle radioactive materials with appropriate attention to radiological safety.

10. Sampling, Test Specimens, and Test Units

10.1 *Isotope Reference Materials*—Uranium reference materials used in the analysis should be prepared from certified reference materials (CRMs) traceable to SI units. Examples include the NBL U-Series CRMs (for example, U010 and U500), IRMM uranium standards IRMM 184-187, IRMM 019-029 (to be converted from UF_6), IRMM-074, IRMM-075, and IRMM-3100. See Guide C1128 for additional guidance on preparation of traceable working reference materials.

10.2 Uranium samples to be measured and isotope reference materials used for estimation of the mass fractionation correction factor (*K* factor) or for quality control purposes shall be in the same medium and in the same oxidation state. The solutions for loading onto the filaments are 1 *M* nitric acid solutions. The uranium concentrations of these solutions shall be similar. The loading and drying sequence of the filaments shall also be similar.

10.3 In the case of characterization studies of test materials, possible inhomogeneity between test units shall be evaluated statistically and included in the uncertainty calculations of the isotope amount ratios assigned.

11. Preparation of Apparatus

11.1 *Filament Degassing*—Degass all filaments before using them for MTE measurements. It is recommended to use a separate apparatus (see 7.3) for performing this. Start the degassing procedure when a vacuum pressure of $<4.0 \times 10^{-4}$ Pa (3×10^{-6} torr) is reached. Recommended filament currents for degassing are in the range of 4.0 to 5.0 A, corresponding to temperatures in the range of 1700 to 2000°C. Perform the degassing for a duration of at least 30 min.

11.2 *"Initialization" of the Sample Turret*—Adjust, if needed, the position of the sample turret in the ion source and verify proper electrical connections for both the evaporation and ionization filament for each sample loading position. It shall be ensured that the electrical contact is not interrupted in case the turret is slightly moved for the purpose of ion beam focusing.

11.3 *Electronics Test*—Modern mass spectrometric instruments offer an automated routine for testing the stability and performance of the electronic systems (for example, Faraday cup amplifier baselines and gains, high-voltage unit, and magnet current supply unit). A report is produced flagging systems or components that are out of specification. Users of the instruments should perform routine checks of the performance of the electronic systems and ensure that the performance is within manufacturer's specifications. The frequency for this test shall be established by the user based on manufacturer recommendations or as specified in the user's quality assurance program.

11.4 *Amplifier Signal Decay Adjustment*—Adjust the signal decay characteristics of the current amplifiers of the Faraday cups. This is important for measuring isotope amount ratios with a large dynamic range, especially for the minor isotope amount ratios of uranium. Depending on the combination of the capacitance and resistance of the current amplifier, the response time for a sudden change in the ion beam signal to the Faraday cup can reach up to 5 s. For resistances higher than the 10^{11} Ω, longer response times of about 15 s can be expected. The MTE method is designed by taking into consideration the required response times. The amplifier response can be checked either using a custom-made software module within the operating software (when available) or "manually" by means of a large ion beam that is abruptly directed into a Faraday cup to check the signal ingrowth time, or away from a Faraday cup (for example, by closing a valve between ion source and analyzer) to check the signal decay time.

11.5 *SEM Plateau Voltage*—The SEM plateau voltage, that is, the dependency of the count rate on the applied high voltage to the SEM, shall be measured on a regular basis, as recommended by the manufacturer of the SEM or the operator's quality system. Typical SEM plateau voltages range between 1700 to 3000 V. The SEM plateau voltage drifts to higher values with use and shall be readjusted to restore the original efficiency. The efficiency should be higher than 90 %.

11.6 *SEM Dark Noise*—SEM detectors are usually operated in ion counting rather than analogue mode to avoid the resistor noise of the current amplifier. The ion counting mode results in much smaller uncertainties encountered for measurements of very low intensity ion beams (10^{-19} to 10^{-16} A, equivalent to 0.6 to 600 cps). However, the dark noise, that is, the observed count rate measured without incident ion beam, shall be measured before an automated MTE measurement sequence to enable corrections to the isotope amount ratios and their uncertainties (**7**). The dark noise shall be below 0.2 cps.

11.7 *Ion Source and Analyzer Pressure*—It is important to achieve a certain level of vacuum before the isotope amount ratio measurements can begin; see 7.1.7 for the recommended pressure. The peak tailing depends strongly on the vacuum pressure in the detector system since the number of ion collisions with gas molecules inside the mass spectrometer is a direct function of the ambient pressure. Increase in the pressure within the ion source caused by the heating of the ionization and evaporation filaments can be subdued, to a certain extent, by using a cold trap filled with liquid nitrogen.

12. Calibration and Standardization

NOTE 1—The measurement method may be qualified following Guide C1068 and calibrated following Guide C1156. Additional information regarding mass spectrometer calibrations with regard to the MTE method may be found in Refs (**5, 6**).

12.1 *Mass Calibration*—The relationship between the known atomic masses and the magnetic field necessary to direct the isotope beams into the detectors shall be updated on a regular basis. Mass calibration shall be performed at intervals specified by the manufacturer or the user's quality assurance program.

12.2 *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 usually occurs via fine adjustments of the accelerating voltage, and any difference between the value optimized during peak centering from the default accelerating voltage requires a readjustment of the mass calibration curve. Peak centering shall be performed for at least three uranium masses as part of the mass calibration and also before the start of each MTE measurement sequence. During the MTE measurement, peak centering is performed on a regular basis.

12.3 *Amplifier Baseline Calibration*—The baselines of the Faraday cup amplifiers, that is, the amplifier responses without incoming ion beam to the cup, shall be measured on a regular basis and checked for stability. During the MTE measurements, baseline measurements are performed on a regular basis. Note that the integration time for the baseline measurement has a significant influence on the uncertainty of Faraday cup measurements, particularly at lower ion beam intensities. Therefore, the integration time of the baseline (within a measurement) shall be comparable to the integration time of the actual ion beam signal integration. The long-term historical baseline data shall be regularly reviewed by the user to assure that the system performance is within manufacturer specifications and quality system requirements.

12.4 *Amplifier Gain Calibration*—The stability and response of individual Faraday detector amplifiers shall be measured and differences between amplifiers corrected for via the amplifier gain calibration. Gain calibration is normally performed by sequentially applying a stable calibration current to the input of each Faraday cup amplifier and the output is then normalized to a reference value to generate a gain calibration factor for each amplifier. A gain calibration shall be performed prior to each automatic MTE sequence. Historical gain calibration data can be used to evaluate the stability of the amplifiers.

12.5 *Faraday Cup Efficiency Test*—The response of individual Faraday cups depends on several factors, for example, extent of usage, manufacturing variability, and can also be affected by an insufficient electron suppression voltage. The relative response of the Faraday cups, therefore, shall be determined periodically. Usually, the Faraday cups of a multi-collector system are only intercalibrated for the current amplifiers connected to them (see 12.4) but not for the differences in the efficiencies of the Faraday cups themselves. The efficiencies of the Faraday cups are expected to be similar to each other, which means that the relative efficiencies (relative to one reference cup) are normally close to unity. Note that an (electronic) amplifier gain calibration (see 12.4) shall be performed prior to the Faraday cup efficiency test. The Faraday cup efficiency test can be performed in several ways, as described in 12.5.1 – 12.5.4.

12.5.1 The calibration may be performed by switching a stable ion beam of ^{187}Re (from a blank filament) between each Faraday cup and a reference Faraday cup. In case a relative efficiency between the detectors is significantly different from unity, this result can be used to correct for differences in the detector response. This procedure can be performed with a relative uncertainty at the level of <0.1 %.

12.5.2 A series of peak-jumping measurements between all Faraday cups and a reference cup to be checked can also be performed using a sufficiently large uranium sample and one large stable ion beam, for example, a 10 to 20 V ion beam of ^{238}U from an LEU or natural uranium sample. The drift of the signal intensity shall be corrected for using the operating software. This procedure can be performed with a relative uncertainty at the level of <0.01 %.

12.5.3 A series of comparative neodymium (Nd) isotope amount ratio measurements can be performed in two different modes such as the multi-dynamic mode and the static mode with "amplifier rotation" (only for TRITON™ TIMS, also called "virtual amplifier": each Faraday cup is connected to each amplifier for regular time intervals during the measurement). This procedure can be performed with a relative uncertainty at the level of few ppm (**5**). It shall be repeated until all Faraday cups of interest for MTE measurements have been included.

12.5.4 A series of static measurements can be performed using special "multi-isotope" reference materials, such as IRMM-3100a (^{233}U/^{235}U/^{236}U/^{238}U = 1/1/1/1) (**8**), IRMM-072/1, IRMM-074/1, or IRMM-199 (^{233}U/^{235}U/^{238}U = 1/1/1) (**9**), to include all Faraday cups. This procedure can be performed with relative uncertainties of about 0.03 %.

12.6 *Linearity Test*—There are various procedures to check the linearity of an isotope mass spectrometer detection system. The procedures described in 12.6.1 and 12.6.2 are mainly applicable for Faraday multi-collector systems (for SEM calibration and linearity, see 12.8 and 12.9).

12.6.1 The linearity of the mass spectrometer is determined over the working range of the Faraday cups by measuring the ^{235}U/^{238}U ratios of various reference materials under identical conditions. The mass spectrometer system is linear if the *K* factor, that is, the ratio of the certified ^{235}U/^{238}U ratio to the measured ^{235}U/^{238}U ratio, is independent of the isotopic composition of the material. For this procedure, the NBL U-series of reference materials (U005a to U970, 0.5 to 97 % of ^{235}U) is ideal and can be combined with the IRMM-183-187 series (0.3 to 5 % of ^{235}U) and the IRMM 019-029 (0.17 to 5 % of ^{235}U, to be converted from UF$_6$). This procedure shall be performed sequentially for all Faraday cups of the multi-collector system needed for the MTE analyses.

12.6.2 The IRMM-072 and IRMM-074 series of reference materials are characterized by ^{238}U/^{235}U ratios of ≈1 and ^{233}U/^{235}U ratios ranging from ≈1 down to ≈10^{-6} for the 15 or 10 units, respectively, of the used series. For each unit, the bias of the measured ^{238}U/^{235}U ratios from the certified ones can be used for internal mass fractionation correction of the measured ^{233}U/^{235}U ratios. The comparison of the corrected ^{233}U/^{235}U ratios with the certified ones allows the linearity of the detection system to be checked over a dynamic range of six orders of magnitude for the ion beam intensity. A detailed description of the procedure is given in Ref (**9**). This procedure shall be performed sequentially for all Faraday cups needed for the MTE analyses.

12.7 *Peak Overlap*—When a Faraday multi-collector system for the simultaneous detection of several masses is used, it needs to be ensured that the peak overlap is acceptable. A mass scan, usually by scanning the magnetic field, shall be performed by which all ion beams are simultaneously moved through the respective cups. The measured intensities for all detectors shall be plotted versus the mass of a reference detector to make the peak overlap visible. All peaks shall have a symmetric shape with a common flat region in the center, with the peak centers reasonably close together, as specified by the manufacturer or the user quality system. After a satisfactory peak overlap is realized (by moving cups relative to one another if necessary), the positions of all detectors shall be saved, for example, as a Faraday cup configuration file. The positions shall be checked and possibly readjusted, manually or using stepping motors, as needed before a new automatic measurement sequence.

12.8 *SEM Linearity Check and Correction*—The linearity of SEM systems shall be checked carefully on a regular basis according to manufacturer's specifications or the user's quality assurance program. It is emphasized that there can be more than one reason for nonlinearity of a SEM detector. For SEM detectors operated in ion counting mode, the dead time of the pulse-counting electronic system is always one source of nonlinearity, but this can be easily corrected. As pointed out in Ref (**9**), there is also the possibility of an intrinsic nonlinearity for SEM detectors, possibly depending on the design of the ion optics, the dynode surfaces, or the electronics, which could cause the linearity investigation and correction to become more complicated. But in case the dead time is confirmed to be the only source of nonlinearity of a SEM system, the value can be determined in various ways (**9**) using CRMs, as described in 12.8.1 and 12.8.2.

12.8.1 For this procedure, the IRMM-072/8 or IRMM-074/3 (**9**) reference materials, characterized by a ^{238}U/^{235}U ratio of ≈1 and a ^{233}U/^{235}U ratio of ≈0.01, or the NBL CRM U500, characterized by a ^{238}U/^{235}U ratio of ≈1 and a ^{234}U/^{235}U ratio of ≈0.01 (using new data published in Ref (**5**)), can be used. Peak-jumping measurements are performed for count rates between 5×10^4 cps and 5×10^5 cps for ^{235}U (similar for ^{238}U). The ^{233}U/^{235}U ratios (^{234}U/^{235}U in case of NBL CRM U500) are internally normalized using the ^{238}U/^{235}U ratios of ≅1 and plotted versus the ^{235}U count rate. If the data show a linear relationship with no significant intercept, a linear regression is calculated with the intercept being zero. The slope of the regression line can be used to calculate the dead time using:

$$\tau = \{\text{slope}\} / \left(1 - \left(\frac{^{233}U}{^{235}U}\right)_{CERT}\right) \tag{1}$$

where:

τ = dead time;
slope = slope of linear regression calculation based on measured ^{233}U/^{235}U ratios versus the ^{235}U count rate; and
$(^{233}U/^{235}U)_{CERT}$ = certified isotope amount ratio of used CRM.

12.8.1.1 In case the data do not indicate a linear relationship with a non-significant intercept, the SEM detection system is likely to be affected by other sources of nonlinearity, which shall be investigated.

12.8.2 For an "external check" of the linearity of the SEM detection system, a series of reference materials can be measured by MTE, for example, the NBL U-series (**5**), the IRMM-183-187 series, the IRMM-019-029 series (converted from UF$_6$ (**7**)), or the gravimetrically prepared IRMM-075 series (**6, 10**) with ^{236}U/^{238}U rations of 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8}, and 10^{-9}.

12.9 *SEM Versus Faraday Cup Inter-Calibration*—Since the inter-calibration between a SEM detector with a Faraday cup depends on the ion source focusing and ion beam shape, this calibration shall be performed in an internal manner during the course of each measurement for MTE measurements. For this internal calibration, the ion beam of one of the uranium isotopes present in the sample is switched between the SEM and one Faraday cup within each integration step during the entire measurement. To allow such an internal calibration, there shall be at least one suitable ion beam available for this purpose. This ion beam shall be within a certain intensity range, between the lower limit of reasonable Faraday cup measurements (typically 1 mV on an amplifier with 10^{11} Ω, which is affected by about the same noise as 0.5 mV on an amplifier with 10^{12} Ω) and the upper limit for reasonable SEM measurements (typically 1.0×10^6 cps, equivalent to 16 mV on an amplifier with 10^{11} Ω). The isotope used for the internal calibration within MTE measurements is for most samples ^{234}U, in few cases ^{236}U instead ("reverse" MTE). As a consequence, the sample amount to be loaded is limited to a certain range as well. For typical TIMS conditions, the sample amount for MTE measurements is about 2 to 6 µg, which provides ion beam signals of about 20 to 30 V for the sum of the main isotopes ^{235}U and ^{238}U. The choice of the isotope used for the inter-calibration depends on the isotopic composition of the sample (based on process knowledge or sample supplier information, or estimated by a mass scan in the $m/z = 233$ to 238 mass range), in the following way:

12.9.1 Mainly for DU, NU, and LEU samples with $^{234}U/^{238}U$ ratios between 3×10^{-5} and 5×10^{-4} and with $^{236}U/^{238}U$ ratios below 3×10^{-5}, the ^{234}U ion beam is used for the internal calibration.

12.9.2 Mainly for DU (in principle also in case of NU and LEU) samples with $^{234}U/^{238}U$ ratios below 3×10^{-5} and with $^{236}U/^{238}U$ ratios higher than 3×10^{-5}, the ^{236}U ion beam is used for the internal calibration (also called "reverse" MTE).

12.9.3 In the rare case that both the $^{234}U/^{238}U$ and the $^{236}U/^{238}U$ ratios are below 3×10^{-5}, the larger one of ^{234}U and ^{236}U shall be used. This might only apply to quite highly enriched ^{235}U or ^{238}U materials, for example, for spike materials. In this case, an internal calibration using a suitable ion beam from an added ^{233}U spike (**11**) is another option, which would require isobaric corrections because of the possible ^{234}U and ^{236}U contents of the ^{233}U spike.

12.9.4 For all samples, that is, DU, NU, LEU, or HEU, with any values for the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios, an MTE measurement can always be performed using Faraday cups only, thus without using the SEM and without the need for a SEM intercalibration. This shall be carefully considered in view of the associated uncertainties originating on one hand from the SEM calibration and SEM linearity correction (see 12.8) and on the other hand from the higher relative amplifier noise in case of low signals on the Faraday cups. In case both ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ are higher than 5×10^{-4}, the SEM cannot be used for MTE, only Faraday cups shall be used.

12.9.5 For an "external" check of the SEM versus Faraday intercalibration, a suitable sample with a $^{236}U/^{238}U$ ratio being in the "overlap" range between SEM and Faraday measurements (between 3×10^{-5} and 5×10^{-4}) can be measured in a comparative way, first using the SEM and secondly using the Faraday cup for the ^{236}U ion beam. The results shall agree to each other within their uncertainties. If this is not the case, the reason shall be investigated. Using reference materials such as IRMM-187 and NBL CRM 010 with suitable $^{236}U/^{238}U$ ratios, it was shown in Ref (**6**) that the above described intercalibration procedure is accurate within uncertainties of about 0.4 % ($k = 2$).

12.10 *Mass Fractionation Correction:*

12.10.1 In theory, the "classical" total evaporation (TE) and, therefore, also the MTE methods are expected to yield isotope amount ratios that do not need correction for mass fractionation. In practice, measurable mass fractionation for uranium measurements has been observed. To be consistent in the evaluation of the data and the associated uncertainties, it is recommended to perform a mass fractionation correction also for measurement sequences in which the ratios seem to be mass fractionation free, that is, where the *K* factor (see 12.10.2) is equal to unity within its uncertainty. For MTE measurements it is recommended to perform the mass fractionation correction by measuring a certified isotope reference material in sequence with the samples, and calculate a mass fractionation correction factor based upon the deviation of the measured major ratio from the certified ratio. The mass fractionation correction factor, adjusted for isotope mass difference, is then applied to all measured sample ratios. It is important that the reference materials are prepared and measured in the same manner as the samples. For the MTE method, the major ratio $^{235}U/^{238}U$ is used to calculate a correction factor, known as the *K* factor, which is then applied also for performing corrections for the minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ internally (for details see Section 14).

12.10.2 The mass fractionation correction factor, *K*, is calculated as follows:

$$K = (R_c / R_m) \tag{2}$$

where:

K = mass fractionation correction factor;
R_m = average measured isotope amount ratio for the CRM; and
R_c = certified isotope amount ratio value for the CRM.

12.10.3 To correct individual measured isotope amount ratios, calculate the appropriate mass fractionation correction factor based upon the mass difference between isotopes (=3 for the major ratio, the $^{235}U/^{238}U$ ratio) and multiply the sample ratio by the applicable mass fractionation correction factor.

13. Procedure

13.1 *Sample Preparation:*

13.1.1 *Sample Dissolution*—Dissolve an appropriate sample amount to obtain the desired filament loading solution for the mass spectrometric analysis. See Practice C1347 for the dissolution of uranium.

13.1.2 Prepare the sample and any reference material solutions as purified nitrates, using identical chemical preparation and handling steps. For uranium samples hydrolyzed from uranium hexafluoride, it is recommended that the samples are converted to U_3O_8 before dissolution in nitric acid and analysis. The solution concentrations shall be chosen to allow for a convenient filament loading (for example, a 1-mg U/mL solution yields 1 µg of uranium per µL, see also 13.2).

13.1.3 *Sample Purification*—Use Practice C1411 or similar procedure to separate uranium from plutonium other impurities.

13.2 *Sample Loading and Conditioning*—Samples for MTE are usually directly loaded on the filament by drop deposition. Samples and reference materials shall 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. Change the tip between sample loadings to prevent cross contamination. For filaments loaded by drop deposition, the solution shall be evaporated by passing sufficient electrical current through the filament to cause gentle drying without boiling. Samples for MTE are usually prepared in a 1 *M* nitric acid with a uranium concentration between 1 to 6 mg/g, which is equivalent to 1 to 6 µg/µL. Depending on the uranium amount to be loaded, more than 1 µL may be needed. Deposit drops very carefully and slowly. It is recommended to keep the filament heated by passing 0.5 to 0.7 A current and depositing 1-µL-drops at a time. After all drops are loaded, the sample solution on the filament is heated until dryness, for at least one more minute, and then heated for 10 s at a higher current of 1.5 A for conditioning. Alternatively, a stepped-heating program can be used to condition samples, that is, to convert samples to suitable chemical forms. Avoid quick evaporation of the sample or melting the filament. At different facilities, different loading and conditioning procedures have been established and validated. Each procedure shall be applied in a consistent manner for all samples, reference materials, and quality control samples.

13.3 Mount all sample (evaporation) filaments and ionization filaments on a sample turret and insert the sample turret into the ion source of the mass spectrometer.

13.4 Seal the source and start evacuating.

13.5 Perform adjustment (also called initialization) of the sample turret. In case of problems with electrical connections, the source might have to be vented again to resolve the problem.

13.6 Evacuate ion source to the manufacturer's recommended minimum pressure or according to the user's procedure.

13.7 Add liquid nitrogen to the cold trap if desired.

13.8 *Isotope Amount Ratio Measurement*—The following steps 13.8.1 – 13.8.3 shall be performed automatically under computer control depending upon instrument. Very small samples may require manual control to avoid sample loss.

13.8.1 Perform an amplifier gain calibration for each new automatic sequence.

13.8.2 Measure the baseline during the course of each measurement of a sample and standard.

13.8.3 Usually under computer control, the ionization filament is heated up to a temperature of about 1800 to 1950°C. For automatic sequences, usually the magnitude of the ^{187}Re ion beam is used as the regulated quantity instead of the filament temperature by a pyrometer because only the narrow sides of the filaments are oriented towards the pyrometer. Typical ^{187}Re ion beams of about 300 to 600 mV (on a 10^{11} Ω resistor) are used for non-zone refined filaments and lower values of 150 to 200 mV are used for zone-refined filaments, depending on the brand.

13.8.4 The ^{187}Re ion beam is peak centered and focused. If necessary, the ^{187}Re ion beam size is readjusted towards the target value, which shall be similar (within about 10 %) for each measurement within an automatic sequence, by changing the filament current.

13.8.5 The sample filament is heated to a temperature sufficient to yield an ion beam sum intensity from ^{235}U and ^{238}U of about 1 to 4 V (on 10^{11} Ω resistor). The beam is focused and peak centered using the largest U ion beam, in most cases (DU, NU, LEU), this is the ^{238}U beam; for HEU, depending on the level of enrichment, it may be the ^{235}U beam.

13.8.6 Data acquisition is started. The data acquisition is performed on a per block basis in which each block consists of a minimum of two and a maximum of five mass cycles and each mass cycle of (usually) five integration steps. The data acquisition is continued until the whole sample is evaporated; see 13.10.

13.8.7 *MTE Mass Cycle*—The MTE mass cycle consists of five steps as shown in Table 1.

13.8.7.1 The first step is the main integration for all isotopes; the integration time is usually about 16 s. The ^{236}U isotope can be detected by either the center Faraday cup (C) or an SEM detector depending on the ^{236}U/^{238}U ratio in the sample. Usually, for ^{236}U/^{238}U ratios below 3×10^{-5}, the ^{236}U measurement is performed using the SEM. The minor isotope ^{234}U is always detected using a Faraday cup. In case the ^{236}U/^{238}U ratio is higher than 3×10^{-5}, the ^{236}U is detected using the center (C) Faraday cup.

13.8.7.2 Step 2 of the mass cycle is dedicated to the intercalibration of the SEM versus the Faraday cup multicollector. This is achieved by measuring the ^{234}U isotope first using Cup L2 in Step 1 and then using the SEM in Step 2. The SEM efficiency is then calculated by dividing the measured ^{234}U/^{235}U ratios in Step 2 and Step 1 by each other. In this way, the signal drift over time is circumvented, which would not be the case if the ^{234}U intensities measured in Step 1 by the Faraday Cup L2 and Step 2 by the SEM would be divided directly by each other. For the SEM efficiency calculation, the ^{234}U/^{235}U ratio measured in Step 1 has also to be corrected for the tailing effect using the background measurements performed in Steps 3 and 4 (see 13.8.7.3). Because the count rate of ^{234}U is usually >60 000 cps, an integration time of 4 s is sufficient; an idle time of 6 s is typically used. Even when the Faraday cup and no SEM is used for measuring ^{236}U, this second step is retained within the mass cycle for consistency of the timing.

13.8.7.3 In Steps 3 and 4 of the MTE mass cycle, the background intensities at the low and high mass side of all uranium isotopes of interest are measured. The background for ^{234}U is mainly due to the tailing from ^{238}U and, depending on the ^{235}U enrichment, also tailing from ^{235}U contributes. As a result of the differences in the tailing effect between the low and high mass sides, an interpolation for the ^{234}U/^{238}U ratio shall be performed, usually using a linear approximation. Depending on the instrument and mass resolution, the peak areas are located well within ±0.35 u of the isotope masses, which are about 234.05, 235.05, 236.05, and 238.05 u for the

TABLE 1 Mass Cycle for MTE

Cup	L2	L1	SEM (or FAR)	H1	H2	Idle Time/ Measurement Time
Step 1	^{234}U	^{235}U	^{236}U	237 u	^{238}U	12 s/16 s
Step 2			^{234}U	^{235}U		6 s/4 s
Step 3	^{234}U - 0.35 u	^{235}U - 0.35 u	^{236}U - 0.35 u		^{238}U - 0.35 u	5 s/ 8 s
Step 4	^{234}U + 0.35 u	^{235}U + 0.35 u	^{236}U + 0.35 u		^{238}U + 0.35 u	5 s/8 s
Step 5	^{234}U	^{235}U	^{236}U	237 u	^{238}U	3 s/1 s

isotopes ^{234}U, ^{235}U, ^{236}U, and ^{238}U, respectively. By measuring the background at mass positions ±0.35 u of the isotope masses, and thereby closer to the peaks compared to the usually applied "half mass" approach, the interpolation becomes more accurate.

13.8.7.4 The isotope ^{236}U is a special case. If ^{236}U is detected using the center (C) Faraday cup, the background measurements performed at 235.7 and 236.4 u shall be interpolated logarithmically (that is, using the geometric mean) to account for the curvature of the peak tailing from ^{238}U. This type of logarithmic correction is not possible in the same way for ^{234}U because the background intensities at 233.7 and 234.4 are quite frequently at the same level as the amplifier baseline; therefore, individual baseline-corrected intensities and ratios can be negative (on a statistical basis) and would, therefore, not allow a logarithmic correction algorithm. The correction algorithms are given in 14.4.

13.8.7.5 In case ^{236}U is detected using the SEM, which is usually combined with an energy filter to improve the abundance sensitivity, the tailing effects for the ^{236}U/^{238}U ratio are of the order of 10^{-9} to 10^{-10} and can be easily corrected. Additionally, sometimes the background at mass 236 u is dominated by K_6^+ ions with a mass of about 235.78 u ($^{39}K_5{}^{41}K$-ions) emitted from the hot ionization filament, and also by unidentified possibly organic interferences. The K_6^+ ions interfere only partially with the ^{236}U isotope at mass 236.05 u and can therefore, not be accurately corrected. Thus, in case of a high background measurement ($\geq 10^{-9}$) at mass 235.7 u, this value shall not be used for correction. Unknown organic interferences around mass 236 u shall be investigated by checking blank filaments or measuring certified isotope reference materials with ^{236}U/^{238}U ratios in the order of 10^{-8} to 10^{-9}, for example, the IRMM-075 series (**10**). In this case, the background at the ^{236}U mass position shall be corrected externally.

13.8.7.6 For the measurement of ^{234}U using the SEM combined with an energy filter in Step 2, the intensity is usually large enough (>60 000 cps) and the background in the vicinity of 234.05 u small enough so that additional background measurements are not needed.

13.8.7.7 Step 5 is an optional "dummy" step, which might be needed to move the mass setting back to the main cup configuration (as in Step 1) for checking the ion beam signals at the very end of each block. This is needed to determine the ion beam intensity before the next heating step (see 13.10).

13.8.8 The mass cycle for "reverse" MTE consists of eight steps shown in Table 2.

13.8.8.1 The first step is used for the data acquisition for all isotopes on Faraday cups. In Step 2, ^{236}U is measured on the SEM for the intercalibration. In Steps 3 and 4, the background intensities for the tailing correction are determined. The correction algorithms are described in 14.5.

13.8.8.2 Step 5 is used for measuring the ^{234}U in the SEM, and because of the possibly low abundance of ^{234}U in the sample, Steps 6 and 7 are introduced to measure background intensities also for ^{234}U in this case. Step 8 is needed again (similar to Step 5 for the "non-reverse MTE") to switch the mass back to the main cup configuration.

13.8.8.3 The mass cycles can be extended, for instance if low levels of ^{233}U have to be determined using the SEM for specific samples.

13.9 *Interblock Actions and Filament Heating for MTE:*

13.9.1 *Peak Centering and Baseline*—Each measurement block usually consists of a maximum of five mass cycles, with each cycle having a duration of about 60 to 90 s. Before each block a peak centering is performed using the most abundant isotope, usually the major isotope ^{238}U (^{235}U for HEU samples). Additionally, an ion source focusing is performed before each block. Typically, every five blocks, the electronic baselines of all the Faraday cup amplifiers are remeasured. In case 10^{12} Ω resistors are used in some of the amplifiers, the idle times for the baseline measurements have to be sufficiently long, for example, at least 15 s.

13.9.2 *MTE Interblock Heating*—The filament heating is controlled by a special program script executed after each measurement block. This program script first measures the actual sum intensity (mainly from ^{235}U and ^{238}U) and compares it with the predefined (initial) target sum intensity. This predefined target sum intensity is typically in the range of 20 to 30 V, selected by the operator depending on the sample amount loaded, the experience with the ion source and the instrument transmission. Based on the comparison of the actually measured sum intensity with the target sum intensity, the following filament heating step is calculated. The heating step, that is, the difference between the new evaporation filament current and the actual one, is calculated based on the relative difference between the actually measured and the target sum intensity using a quadratic polynomial with empirical parameters:

$$\mathrm{HS} = P1 \times (\mathrm{RD\ sum\ intensity})^2 + P2 \times (\mathrm{RD\ sum\ intensity}) + P3 \quad (3)$$

TABLE 2 Mass Cycle for "Reverse" MTE

Cup	L2	L1	SEM (or FAR)	H1	H2	Idle Time/ Measurement Time
Step 1	^{234}U	^{235}U	^{236}U (FAR)	237 u	^{238}U	12 s/16 s
Step 2	^{234}U	^{235}U	^{236}U (SEM)	237 u	^{238}U	3 s/8 s
Step 3	^{234}U - 0.35 u	^{235}U - 0.35 u	^{236}U - 0.35 u (FAR)		^{238}U - 0.35 u	5 s/8 s
Step 4	^{234}U + 0.35 u	^{235}U + 0.35 u	^{236}U + 0.35 u (FAR)		^{238}U + 0.35 u	5 s/8 s
Step 5			^{234}U (SEM)	^{235}U		5 s/8 s
Step 6			^{234}U - 0.35 u (SEM)			5 s/4 s
Step 7			^{234}U + 0.35 u (SEM)			5 s/4 s
Step 8	^{234}U	^{235}U	^{236}U (FAR)	237 u	^{238}U	3 s/1 s

where:

HS = difference between evaporation filament current (in A) after and before the heating step (in A);

RD sum intensity = relative difference between target sum intensity and measured sum intensity; and

P1, P2, and P3 = empirical parameters for the quadratic polynomial.

13.9.2.1 Typical values for *P*1, *P*2, and *P*3 are about 0.35 A, 0.1 A, and 0 A, respectively, but shall be optimized by the user. If the measured sum intensity is very close to the target sum intensity (for example, within 1 %), the filament current is recommended not be changed.

13.9.3 *Dynamic Target Intensity Concept*—This is a programming feature within the MTE heating script that is needed to avoid extremely long measurement times. This is achieved by automatically readjusting the target sum intensity during the measurement. If the measurement time becomes too long, for example, 5 h or more, this could cause the ionization filament to become hotter and thinner over time and possibly break. By means of the "dynamic target intensity concept," the value for the target sum intensity is itself increased on a block-by-block basis as long as the measurement is running below a defined filament current threshold (for example, about 1.6 A for Re filaments and 2.2 A for W filaments), which is considered too low for a not-too-long measurement time. This increase is applied between each two blocks, with the exception of the starting period of Block 1 to 5 where the filament current is intentionally still low. The stepwise increase of the target sum intensity is continued until the filament current has exceeded the defined threshold. This rule is not only applied to one defined filament current threshold, it is applied cumulatively for multiple filament current thresholds, such as 1.6, 1.7, 1.8, 1.9, 2.0, 2.1 and 2.2 A, associated with different programmed steps for increasing the target sum intensity, such as 10 %, 5 %, 4 %, 3 %, 2 %, 1.5 %, and 1 % respectively; for more details, see Ref (**6**).

13.9.4 In addition to the implementation of the dynamic target intensity concept, the MTE program script reacts on unusually low or high ion beam intensities from individual sample filaments. This is achieved by increasing the target sum intensity by a certain percentage (for example, 10 %) if the starting filament current at block one is extremely low (for example, below 0.8 A) for a sample appearing as "too large," or by decreasing the target intensity if the starting filament current is extremely high (for example, more than 2.0 A) for a sample appearing as "too small."

13.9.5 The MTE heating program script shall be adapted for different instruments and different types and brands of filaments, for example, rhenium versus zone-refined rhenium versus tungsten. For example, if tungsten is used for the evaporation filaments, which require much higher filament currents to achieve the same sample temperatures, the script shall be adapted accordingly. The script parameters shall be optimized to obtain reproducible MTE measurements in terms of the number of blocks and mass cycles, the heating, and the intensity versus time patterns.

13.10 *Termination of MTE Measurement*—The MTE measurement is terminated when the sum intensity is below a user-defined limit of 1 to 2 V.

14. Calculations

14.1 Within this section, the MTE data evaluation and calculation of the various correction factors will be discussed. Despite the application of the total evaporation principle, it is recommended for consistency reasons to perform a mass fractionation correction for MTE measurements. For the major ratio $^{235}U/^{238}U$, the mass fractionation correction is performed externally using a reference material measured on the same sample turret under similar conditions in terms of sample loading and sample matrix as well as the same MTE interblock heating script. The mass fractionation correction for the minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ is performed internally based on the result of the corrected $^{235}U/^{238}U$ ratio using the exponential fractionation law. The differences between different fractionation laws, for example, power law, exponential law, linear law, or Rayleigh law are at the level of few parts per million for heavy elements like uranium, which is insignificant for the MTE measurements (**6**).

14.2 The calculations to be performed for MTE measurements are rather method specific, so there is currently no commercial software available. Up until now, two spreadsheets exist, one by IRMM (and used/modified also by NBL, ITU, and IAEA, regularly updated at IRMM) and another one from ITU using visual basic for calculations and graphic display. Within this test method, only the mathematical equations are presented.

14.3 *Evaluation for 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 and MTE methods, the major ratio $^{235}U/^{238}U$ is calculated as:

$$\left(\frac{^{235}U}{^{238}U}\right)_{TE} = \frac{\Sigma_{ALL\_INTEGRATIONS}I\left(^{235}U\right)}{\Sigma_{ALL\_INTEGRATIONS}I\left(^{238}U\right)} = \frac{\Sigma_{ALLINTEGRATIONS}\left[\left(\frac{I\left(^{235}U\right)}{I\left(^{238}U\right)}\right)\cdot I\left(^{238}U\right)\right]}{\Sigma_{ALL\_INTEGRATIONS}I\left(^{238}U\right)} \qquad (4)$$

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, baselines, and backgrounds on the low and high mass sides.

14.3.1 Therefore according to Eq 4, 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. This algorithm was already applied for the TE method for which the signal integration continues without interruption until the sample is consumed. For the MTE method, the major change is that the measurement is interrupted on a regular basis to perform additional operations during each mass cycle, such as the SEM versus Faraday calibration and background measurements, which mainly serve to improve the accuracy for the measurement of the minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$. These interruptions amount to about 20 % of the measurement time (preheating time not included) and, because of their strict regularity, no significant effects on the $^{235}U/^{238}U$ ratios from these interruptions have been observed.

14.3.2 The mass fractionation correction for the $^{235}U/^{238}U$ ratio is calculated from the average values for all replicate measurements of the reference material used for mass fractionation correction and a given sample according to Eq 5 and Eq 6. For both, the reference material and each sample, a suitable number of replicates, typically at least five, shall be measured on the same turret under similar conditions.

14.3.3 The *K* factor is defined as:

$$K = \frac{\left(\frac{^{235}U}{^{238}U}\right)_{ST-CE}}{\left(\frac{^{235}U}{^{238}U}\right)_{ST-ME}} \qquad (5)$$

14.3.4 The *K* factor is applied as:

$$\left(\frac{^{235}U}{^{238}U}\right)_{SA-CO} = K \cdot \left(\frac{^{235}U}{^{238}U}\right)_{SA-ME} \qquad (6)$$

where:

SA-CO = sample, corrected ratio;
SA-ME = sample, measured ratio;
ST-CE = certified ratio of the certified reference material; and
ST-ME = measured ratio for reference material.

14.4 *Evaluation for Minor Ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ for "Non-Reverse" MTE*—The corrections for the minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ are performed internally on a per mass cycle basis for each reference material and each sample on the same turret. The $^{234}U/^{238}U$ ratio is corrected for peak tailing from the ^{235}U and ^{238}U ion beams, which is determined using the background measurements at masses 233.7 and 234.4 u performed in Steps 3 and 4 of the same mass cycle for "non-reverse MTE." The mass fractionation correction of the $^{234}U/^{238}U$ ratio is then performed internally using the measured ratio $(^{235}U/^{238}U)_{SA\text{-}ME}$ from the same mass cycle and the corrected ratio $(^{235}U/^{238}U)_{SA\text{-}CO}$ determined using Eq 5 and Eq 6. The correction formula for the $^{234}U/^{238}U$ ratio is given by:

$$\left(\frac{^{234}U}{^{238}U}\right)_{SA-CO} = \left(\frac{\left(\frac{^{235}U}{^{238}U}\right)_{SA-CO}}{\left(\frac{^{235}U}{^{238}U}\right)_{SA-ME}}\right)^{R234} \left(\left(\frac{^{234}U}{^{238}U}\right)_{SA-ME} - \left(\left(\frac{233.7}{^{238}U}\right)_{SA-ME} + \left(\frac{234.4}{^{238}U}\right)_{SA-ME}\right)/2\right) \qquad (7)$$

Where SA-CO and so forth are the same as defined for Eq 6. The exponent R234 is given by R234 $=[\ln(M(^{234}U)/M(^{238}U))/\ln(M(^{235}U)/M(^{238}U))] \cong 1.33617$ (which is close to $4/3$) with, $M(^{m}U)$ being the molar mass of the isotope ^{m}U.

14.4.1 If the $^{236}U/^{238}U$ ratio is measured on the (center, "C") Faraday cup, the correction is calculated according to:

$$\left(\frac{^{236}U}{^{238}U}\right)_{SA-CO} = \left(\frac{\left(\frac{^{235}U}{^{238}U}\right)_{SA-CO}}{\left(\frac{^{235}U}{^{238}U}\right)_{SA-ME}}\right)^{R236} \left(\left(\frac{^{236}U}{^{238}U}\right)_{SA-ME} - \sqrt{\left(\left(\frac{235.7}{^{238}U}\right)_{SA-ME}\left(\frac{236.4}{^{238}U}\right)_{SA-ME}\right)}\right) \qquad (8)$$

Where SA-CO and so forth are the same as defined for Eq 6. The exponent R236 is given by R236 $=[\ln(M(^{236}U)/M(^{238}U))/\ln(M(^{235}U)/M(^{238}U))] \cong 0.66526$ (which is close to $2/3$) are used.

14.4.2 If the $^{236}U/^{238}U$ ratio is measured using the SEM, the relative detection efficiency, *G*, of the SEM (that is also called yield) has to be included. The value, *G*, is calculated according to Eq 9, where FAR stands for Faraday cup:

$$G = \left(\frac{\left(\frac{^{234}U_{SEM}}{^{235}U_{FAR}}\right)_{Step2}}{\left(\frac{^{234}U_{FAR}}{^{235}U_{FAR}}\right)_{Step1}}\right) \frac{\left(\frac{^{234}U_{FAR}}{^{238}U_{FAR}}\right)_{Step1}}{\left(\left(\frac{^{234}U_{FAR}}{^{238}U_{FAR}}\right)_{Step1} - \left(\left(\frac{233.7_{FAR}}{^{238}U_{FAR}}\right)_{Step3} + \left(\frac{234.4_{FAR}}{^{238}U_{FAR}}\right)_{Step4}\right)/2\right)} \qquad (9)$$

14.4.3 This formula includes the correction for the tailing contribution from the ^{235}U and ^{238}U ion beams to the ^{234}U beam detected on the Faraday cup. On the SEM, no tailing correction for the calibrating ^{234}U ion beam (>60 000 cps) is necessary if an energy filter with an abundance sensitivity of $<5 \times 10^{-8}$ at mass 237 u is used. The corrected $^{236}U/^{238}U$ ratio measured using the SEM is given by:

$$\left(\frac{^{236}U}{^{238}U}\right)_{SA-CO} = \frac{1}{G}\left(\frac{\left(\frac{^{235}U}{^{238}U}\right)_{SA-CO}}{\left(\frac{^{235}U}{^{238}U}\right)_{SA-ME}}\right)^{R236} \left(\left(\frac{^{236}U}{^{238}U}\right)_{SA-ME} - \left(\left(\frac{235.7}{^{238}U}\right)_{SA-ME} + \left(\frac{236.4}{^{238}U}\right)_{SA-ME}\right)/2 - B\right) \qquad (10)$$

where:

B = (optional) constant background ratio calculated by dividing a background count rate intensity at mass 236 u, for example, predetermined using blank filaments or suitable reference materials such as IRMM-075 (**10**), by the observed average ^{238}U intensity during the MTE measurement.

14.4.4 Because of relatively low ion beam intensities during the start and the end periods of each MTE measurement, the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios are only taken into consideration for the main part of the measurement as defined by the sum intensity being above a threshold of 30 % of the maximum sum intensity during the measurement. This threshold shall be applied in a consistent way for reference materials and samples. Note that this threshold of 30 % only applies to the corrected minor isotope amount ratios and not to the major ratio $^{235}U/^{238}U$.

14.4.5 The minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ for the reference material(s) are calculated in the same way using Eq 7-10 as for the samples; SA-ME has to be replaced by ST-ME and SA-CO by ST-CO. The ST-CO results obtained for the minor isotope amount ratios of reference materials can be compared to the certified ratios and, therefore, serve as a quality control.

14.5 *Evaluation for Minor Ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ for "Reverse" MTE*—The corrections for the minor ratio, $^{236}U/^{238}U$, measured on Faraday cups only are calculated according to Eq 8 as before.

14.5.1 If the $^{234}U/^{238}U$ ratio is measured using the SEM, the relative detection efficiency, *G*, of the SEM (that is also called yield) has to be included. The value, *G*, is calculated according to Eq 11 where FAR stands for Faraday cup:

$$G = \left(\frac{\left(\frac{^{236}U_{SEM}}{^{235}U_{FAR}} \right)_{Step2}}{\left(\frac{^{236}U_{FAR}}{^{235}U_{FAR}} \right)_{Step\ 1}} \right) \frac{\left(\frac{^{236}U_{FAR}}{^{238}U_{FAR}} \right)_{Step1}}{\left(\left(\frac{^{236}U_{FAR}}{^{238}U_{FAR}} \right)_{Step1} - \left(\left(\frac{235.7_{FAR}}{^{238}U_{FAR}} \right)_{Step3} + \left(\frac{236.4_{FAR}}{^{238}U_{FAR}} \right)_{Step4} \right) / 2 \right)} \qquad (11)$$

14.5.2 This formula includes the correction for the tailing contribution from the ^{235}U and ^{238}U ion beams to the ^{236}U beam detected on the Faraday cup. On the SEM, no tailing correction for the calibrating ^{236}U ion beam (>60 000 cps) is necessary if an energy filter with high abundance sensitivity is used. The corrected $^{234}U/^{238}U$ ratio measured using the SEM is given by:

$$\left(\frac{^{234}U}{^{238}U} \right)_{SA-CO} = \frac{1}{G} \left(\frac{\left(\frac{^{235}U}{^{238}U} \right)_{SA-CO}}{\left(\frac{^{235}U}{^{238}U} \right)_{SA-ME}} \right)^{R234} \left(\left(\frac{^{234}U}{^{238}U} \right)_{SA-ME} - \left(\left(\frac{234.7}{^{238}U} \right)_{SA-ME} + \left(\frac{234.4}{^{238}U} \right)_{SA-ME} \right) / 2 \right) \qquad (12)$$

14.5.3 There is no background ratio to be taken into account for typical count rates observed for ^{234}U, in contrast to those low count rates encountered for ^{236}U, for example, in case of natural samples.

14.6 *Uncertainty Estimation:*

14.6.1 The uncertainties for MTE measurements are estimated according to the principles described in the Guide to the Expression of Uncertainty in Measurements (GUM) (**12**), see also Refs (**13**) and (**14**). For MTE measurements, the uncertainty evaluation steps are explained in the following.

14.6.2 For the uncertainty of the corrected major ratio $^{235}U/^{238}U$ calculated according to Eq 6, the relative uncertainties of the measured ratios of the reference material used for mass fractionation correction and the sample as well as the relative uncertainty in the certified value of the reference material are added in quadrature to obtain the relative uncertainty of the corrected ratio of the sample. This correction and the uncertainty calculation are performed on the averages of all measurements on the same sample turret. Because of the good repeatability of MTE measurements (about 0.01 to 0.02 % RSD, independent of the value of the ratio), this uncertainty is often dominated by the uncertainty of the known certified ratio of the reference material (typically in the range of 0.015 to 0.1 %). Typical values for the expanded uncertainty (coverage factor $k = 2$) are about 0.04 to 0.12 % (see 16.1 for additional details).

14.6.3 A relative uncertainty of 0.020 % ($k = 2$) for the external (rather than internal) type of mass fractionation of the major ratio, $^{235}U/^{238}U$, is added in quadrature to the uncertainties of MTE measurements to take potential unaccounted fractionation effects into consideration, which might be slightly different between the reference material and sample(s) (**6**).

14.6.3.1 If two samples with the same origin but different processing are measured on the same sample turret for the purpose of directly comparing their (uncorrected) $^{235}U/^{238}U$ ratios, for the relative difference of the measured $^{235}U/^{238}U$ ratios between the two samples also an additional uncertainty of 0.020 % ($k = 2$) shall be added in quadrature.

14.6.4 For the minor ratios, $^{234}U/^{238}U$ and $^{236}U/^{238}U$, the corrections are performed on a "per mass cycle" basis according to Eq 7-12. Average values and their uncertainties for each sample (or the reference material) on the turret are calculated. The uncertainty of the average value is also known as the standard error (SE), which is calculated as the "internal" SD divided by the square root of the number of mass cycles for an individual measurement. The typical (or average) derived SE for a given sample (or the standard) can be compared to the "external" SD of the replicate measurements for the same material on the turret. For a sufficient number (≥5) of replicate measurements, the "external" SD can be relied upon, but, in case of very few replicates, the average internal SE shall be used instead of the "external" SD as a more reasonable estimate of the uncertainty. The larger of these two values can be used as a conservative estimate of the uncertainty. Within the MTE evaluation software, this conservative estimate of the uncertainty value is selected, and then divided by the square root of the number of replicate MTE measurements for the sample (or reference material) on the turret to obtain the uncertainty for the average $^{234}U/^{238}U$ or $^{236}U/^{238}U$ ratio for the turret sequence. This uncertainty for the average ratio is then combined with other uncertainty components arising from, for example, mass fractionation correction, SEM-Faraday intercalibration, SEM linearity correction, dark noise, and background correction, which are described in detail in Ref (**6**). To facilitate the uncertainty calculations for some of these components, constant (relative) uncertainty contributions can be assigned, for example, 0.4 % for all SEM-related corrections (**6**) ($k = 2$). For minor ratios of 10^{-4} or larger, the mass fractionation correction is typically the dominant contribution to the uncertainty. For ratios between 3 × 10^{-5} and 10^{-4} measured on the Faraday collector, the uncertainty calculated from the repeatability, which is due to the amplifier noise, is dominant. For ratios close to 3 × 10^{-5} and below measured using the SEM, the uncertainty is given by a combination of counting statistics and the constant uncertainty contribution stemming from the SEM-related corrections. For the extremely low ratios, the uncertainty is a combination of the background correction uncertainty and counting statistics.

14.6.5 The detection limit for the ^{236}U/^{238}U ratio by MTE can be expressed by the sum of the absolute deviation of the measured from the true (or certified) value plus the uncertainty (coverage factor $k = 2$) of the measured value. The value depends on the measurement conditions, for example, the loaded sample amount, the ion beam intensities, and measurement time. For 5-µg loadings, a detection limit of about 6 × 10^{-10} was found (**6**, **15**). For 2.5-µg loadings, it is slightly higher (that is, inferior), about 3 × 10^{-9} (**6**).

14.7 *Calculation of Isotope Amount Fractions ("Atom Percent"), Isotope Mass Fractions ("Weight Percent"), and Molar Mass ("Atomic Weight"):*

14.7.1 *Isotope Amount Fraction for Isotope i (i = 234, 235, 236, 238):*

$$A({}^{i}U) = \frac{n({}^{i}U)}{n(U)} = \frac{n({}^{i}U)}{\sum\limits_{j=234,\,235,\,236,\,238} n({}^{j}U)} = \frac{R_i}{\sum\limits_{j=234,\,235,\,236,\,238} R_j} \tag{13}$$

14.7.2 *Isotope Mass Fraction for Isotope i (i = 234, 235, 236, 238):*

$$W({}^{i}U) = \frac{m({}^{i}U)}{m(U)} = \frac{R_i M_i}{\sum\limits_{j=234,\,235,\,236,\,238} R_j M_j} \tag{14}$$

14.7.3 *Molar Mass:*

$$M(U) = \frac{\sum\limits_{j=234,\,235,\,236,\,238} R_j M_j}{\sum\limits_{j=234,\,235,\,236,\,238} R_j} \tag{15}$$

where:

$n({}^{i}U)$ = number of moles for isotope i;
$n(U)$ = number of moles for all isotopes, usually ^{234}U, ^{235}U, ^{236}U, and ^{238}U;
$m({}^{i}U)$ = mass for isotope i;
$m(U)$ = mass for all isotopes, usually ^{234}U, ^{235}U, ^{236}U, and ^{238}U;
R_i = isotope amount ratio (i = 234, 235, 236, and 238) relative to one (no matter which) of the isotopes; and
M_i = molar mass for isotope i.

15. Evaluation and Statements for Precision and Bias

15.1 A total of six thermal ionization mass spectrometers at IRMM, ITU, NBL, and the SGAS (at the IAEA) were used to determine the precision and bias for uranium isotope amount ratio measurements via the MTE method. Only TIMS instruments of the type TRITON™ were used for the analyses, because this is currently the only TIMS instrument with MTE capabilities. The following uranium certified reference materials were used:

15.1.1 From New Brunswick Laboratory (NBL, U.S.DOE): the original U-series CRMs: U010, U030A, U050, U100, U200, U500, U750, and U900 and, additionally, CRMs U005a, U045, U630, 112A, 113B, 115, 116A, and 145.

15.1.2 From the Institute for Reference Materials and Measurements (IRMM-JRC-EU): the IRMM-183-187 series, IRMM-072/1, the IRMM-075/1-6 series, the IRMM-074/1-10 series, IRMM-199, and the IRMM-019-029 series (converted from UF_6).

15.1.3 These materials cover the range of ^{235}U enrichments from 0.2 to 95 %. The reference materials used for testing the MTE method were different for each of the instruments depending on the operating facility and the projects for which the measurements were performed. Therefore, common general observations and some examples for precision and bias are presented within this test method.

15.2 *Precision for MTE Measurements of the Major Ratio* $^{235}U\,/\,^{238}U$*:*

15.2.1 For the un-corrected major ratio, ^{235}U/^{238}U, the within-turret precision varies within a range of 0.005 and 0.030 % relative standard deviation (RSD) for replicate (>5) filament loadings of reference materials analyzed (**5-7**, **14**, **16-18**). For uranium nitrate solutions prepared directly from uranium metal reference materials such as CRM112A and CRM116A, the precision is usually better (RSD < 0.01 %) (**16**, **17**) compared to solutions prepared from oxides or other uranium compounds (RSD only < 0.03 %). Examples for within-turret precisions obtained in MTE measurements are given in A1.1.1.

15.2.2 For the corrected major ratio, ^{235}U/^{238}U, the between-turret precision varies between 0.005 and 0.01 % RSD as reported in Refs (**5-7**, **13**, **14**, **16-18**). An example for between-turret precisions obtained in MTE measurements is shown in A1.1.2.

15.2.3 Both the within-turret precision and the between-turret precision are found to be independent of the value of the major isotope amount ratio (**5-7**, **13**, **14**, **16-18**).

15.3 *Bias for MTE Measurements of the Major Ratio,* $^{235}U\,/\,^{238}U$*:*

15.3.1 No significant biases (that is, deviations of measured and corrected ratios from the known or certified ratios) for the major ratios, ^{235}U/^{238}U, were observed for CRMs of the NBL U series CRMs (**5**, **6**, **14**).

15.3.2 For the IRMM reference materials, the IRMM-183-187 series (**19**), IRMM-072/1, the IRMM-075/1-6 series, the IRMM-074/1-10 series, and IRMM-199, also no significant biases were observed (**6**, **9**, **14**). As an example discussed in detail in Ref (**9**) and with data shown in A1.1.3, MTE measurements of the ^{235}U/^{238}U isotope amount ratios for the gravimetrically prepared mixtures IRMM-072, IRMM-199, IRMM-074-1, and IRMM-074-Mix1 are presented within this test method to serve for a bias statement. The sample loading was 5 µg of uranium for all materials. IRMM-072-1 was used as a CRM for the K-factor calculation. According to Table A1.3, the results for the corrected ^{235}U/^{238}U ratios for IRMM-199, IRMM-074-1, and IRMM-074-Mix1 agree well with their respective certified values, showing that the used MTE method provides accurate data. As a conclusion from these results, the maximum bias for MTE measurements of the $^{235}U/^{238}U$ isotope amount ratio can be stated to be 0.02 %.

15.3.3 A series of comparative measurements using the MTE method and the "double spike" (DS) method using a $^{233}U/^{236}U$ double spike was performed (**6**) to investigate the effect of the external mass fractionation correction used for MTE measurements in comparison to the internal mass fractionation correction, which is used for the much more precise DS method. The double spike IRMM-3636 is characterized by a $^{233}U/^{236}U$ ratio of about one with a relative uncertainty of 0.016 % (coverage factor *k* = 2) (**20**). Because of this low uncertainty and the much better precision of the DS method (RSD < 0.003 %) compared to MTE (RSD < 0.03 %), the comparison between the MTE and the DS results is also a measure of the bias of the MTE method. As shown in Ref (**6**), the relative difference between MTE and DS results for the major ratio, $^{235}U/^{238}U$, is below 0.02 %, thereby supporting the bias statement made in 15.3.2.

15.4 *Precision for the Minor Ratios* $^{234}U\,/\,^{238}U$ *and* $^{236}U\,/\,^{238}U$*:*

15.4.1 In contrast to the major ratios, the precision for the minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ strongly depends on the value (in particular on the order of magnitude) of the ratios, as well as on the loaded sample amount and the detector used and is discussed in detail in several publications (**5-7**, **14**, **16**, **17**, **18**, **21**). There is no difference between the within-turret and the between-turret precisions because all minor ratios are corrected for mass fractionation internally using the (corrected) major ratios.

15.4.1.1 An example for precisions of the minor ratios, $^{234}U/^{238}U$ and $^{236}U/^{238}U$, obtained in MTE measurements using Faraday cups (equipped with 10^{12} Ω resistors) is shown in A1.1.4. Data are taken from Ref (**7**). The precision is characterized by the (Johnson's) noise of the amplifier resistors. Therefore, the absolute precision (SD) of repeated measurements is independent on the ratios. As a consequence, the relative precision RSD is decreasing (and thereby improving) logarithmically with increasing value of the ratios. The slope in the double logarithmic plot in Fig. A1.2 is, therefore, close to minus one.

15.4.1.2 An example for precisions for the minor ratios, $^{234}U/^{238}U$ and $^{236}U/^{238}U$, obtained in MTE measurements using SEM detectors is shown in A1.1.5. Data are taken from Refs (**7**, **10**, and **22**). In this case, the precision is characterized by the counting (Poisson) statistics; therefore, the RSD is decreasing (and thereby improving) with the square root of the increasing number of counts and, therefore, also with square root of the increasing ratios (**6**, **7**). The slope in the double logarithmic plot in Fig. A1.3 is, therefore, close to minus one half.

15.5 *Bias for Minor Ratios* $^{234}U\,/\,^{238}U$ *and* $^{236}U\,/\,^{238}U$*:*

15.5.1 The evaluation of biases for the minor ratios, $^{234}U/^{238}U$ and $^{236}U/^{238}U$ by MTE is primarily performed using CRMs for which also the minor ratios are assigned using a gravimetrical preparation. One available reference material of this kind is the IRMM-075 series (**10**) for which the $^{236}U/^{238}U$ ratios are directly traceable to the SI because of the gravimetrical mixing of a highly enriched (>99.96 %) ^{236}U spike with a natural uranium sample with proven low ^{236}U ($<10^{-10}$) relative abundance. The "bias" for measuring minor ratios using the MTE method obtained at IRMM and IAEA-SGAS using the IRMM-075 series (and some further materials with minor ratios confirmed by several laboratories, for example, IRMM-184 and samples from the REIMEP-18 interlaboratory comparison (**21**)) is shown in A1.1.6 by tables and figures (similar to Fig. 4 and 5 in Ref (**6**)). In Fig. A1.5, on the ordinate the absolute values of the (absolute) deviation of the measured from the certified values are added to the (absolute) measurement uncertainties (with coverage factor *k* = 2) and plotted against the values of the measured ratios. This parameter on the ordinate was introduced as the "performance" of MTE measurements in Ref (**6**), and is more meaningful to characterize the MTE method in terms of bias or accuracy compared to only the absolute (or relative) difference between the measured and certified values. The advantage is that by adding the uncertainties (see Section 16) to the difference, the full range of possible deviations or biases according to the measurement conditions is included. All ratios below about 3×10^{-5} are measured using the SEM detector; all ratios above this limit were measured using Faraday cups only.

15.5.2 For comparative TE measurements on a TRITON™ TIMS and a predecessor MAT261 TIMS, the performances (as defined in 15.5.1) are almost ratio independent at a level of about 10^{-6} (that is, 1 ppm) and 10^{-5} (that is, 10 ppm), respectively, which is more than a factor of 30 to 10 000 higher (that is, inferior) compared to the performance of the MTE measurements. The reason for the performance for TE measurements being almost independent of the ratio is given by the fact that peak tailing corrections were not performed for the TE measurements and no SEM detector with energy filter for improved abundance sensitivity was used.

16. Measurement Uncertainty

16.1 *Major Isotope Amount Ratios* $^{235}U\,/\,^{238}U$—The proportions of the uncertainty contributions (see 14.6.2) depend on the precisions and number of replicates of the MTE measurements for sample and reference material, as well as on the uncertainty of the certified major isotope amount ratio of the reference material. The uncertainties of the $^{235}U/^{238}U$ major isotope amount ratios using MTE were found to be independent of the ratios and their magnitude range between 0.04 and 0.12 %.

16.2 *Minor Isotope Amount Ratios* $^{234}U\,/\,^{238}U$ *and* $^{236}U/^{238}U$—Considering the minor isotope amount ratios, the uncertainty budgets are quite complex because of the large dynamic range of the isotope amount ratios and the different types of detectors used.

16.2.1 When ^{234}U is measured on the SEM ("reverse" MTE), usually the main source of uncertainty is the contribution from the SEM calibration versus the Faraday cups using the ^{236}U isotope. The same can be observed when ^{236}U is measured on SEM and ^{234}U used for the intercalibration ("non-reverse" MTE), except for low count rates.

16.2.1.1 For the calibrations of the SEM versus the Faraday cups (see 12.9) and the correction in terms of linearity (see 12.8), a (combined) relative uncertainty of 0.4 % (with coverage factor $k = 2$) can be assigned, as explained, for example, in Ref (**6**). This estimation was confirmed by measuring ^{236}U/^{238}U ratios of IRMM-187 and NBL CRM U010 using both the SEM and Faraday cups at various facilities and instruments (see Ref (**6**)), see also 12.9.5.

16.2.1.2 With decreasing count rate on the SEM for the minor isotopes, the counting statistics and a possible background correction become increasingly dominant in the uncertainty budget.

16.2.2 When the minor isotopes are measured on Faraday cups, the two main contributions come from the mass fractionation correction and the amplifier noise, which influences the precision (see 15.4.1.1). Therefore, the uncertainties depend on the values of the isotope amount ratios.

16.2.2.1 If the isotope amount ratios are below 10^{-4}, the main contribution comes from the amplifier noise and precision, whereas the mass fractionation correction represents only a minor contribution for the uncertainty budget.

16.2.2.2 If the minor isotope amount ratios are above 3×10^{-4}, the contribution of the mass fractionation correction is the main source of uncertainty. Because of the larger mass difference, this contribution is larger for the ^{234}U/^{238}U ratios than for the ^{236}U/^{238}U ratios. To avoid this effect, for example, for HEU samples with better measurement precision for the minor ratios, the uranium isotope amount ratios are usually expressed using ^{235}U in the denominator, which means as ^{234}U/^{235}U, ^{236}U/^{235}U, and ^{238}U/^{235}U. In this case, the uncertainty contribution from the mass fractionation correction becomes smaller as a result of the smaller mass differences for the minor ratios ^{234}U/^{235}U, ^{236}U/^{235}U compared to the major ratio ^{238}U/^{235}U.

16.2.2.3 For minor isotope amount ratios between these two ranges, that is, between 10^{-4} and 3×10^{-4}, a varying contribution of 40 and 60 % to the uncertainty budget comes from the precision of the measurements and the mass fractionation correction.

16.2.3 Expanded uncertainties for the minor isotope amount ratios ^{234}U/^{238}U and ^{236}U/^{238}U (coverage factor $k = 2$ corresponding to a level of confidence of about 95 %) are represented versus the isotope amount ratios in A1.1.6 (Table A1.6 and Table A1.7 and Fig. A1.4).

17. Keywords

17.1 certified reference materials; ion counting; isotope amount-ratios; mass fractionation correction; secondary electron multiplier; thermal ionization mass spectrometry; total evaporation; uranium

ANNEX

(Mandatory Information)

A1. PRECISION AND BIAS FOR MTE MEASUREMENTS

A1.1 A discussion and statements regarding precision and bias for MTE measurements are given in Section 15. Associated tables and figures are presented in A1.1.1 – A1.1.6.

A1.1.1 See Table A1.1.

A1.1.2 See Table A1.2.

A1.1.2.1 The data are also shown in Fig. A1.1.

A1.1.3 MTE measurements of the ^{235}U/^{238}U isotope amount ratio for IRMM-072-1, IRMM-199, IRMM-074-1, and IRMM-074-Mix 1 (**9**). See Table A1.3.

A1.1.4 Precision (% RSD) for MTE measurements of minor ratios ^{234}U/^{238}U and ^{236}U/^{238}U on Faraday cups (amplifiers with 10^{12} Ω resistors), taken from Ref (**7**). See Table A1.4 and Fig. A1.2.

A1.1.5 Precision (% RSD) for MTE measurements of minor ratios ^{234}U/^{238}U and ^{236}U/^{238}U using a SEM detector, taken from Refs (**7, 10,** and **22**). See Table A1.5 and Fig. A1.3.

A1.1.6 In Table A1.6 and Table A1.7 and Fig. A1.4 and Fig. A1.5 are shown the MTE measurement uncertainty (coverage factor $k = 2$) and the measurement "performance," defined as the sum of the (absolute) deviation of the measured from the certified value plus the (absolute) uncertainty (see 15.5.1), for MTE measurements of minor ratios ^{234}U/^{238}U and ^{236}U/^{238}U using a TRITON™ TIMS. The sample loading is 5 µg, for ^{236}U a SEM detector or a Faraday detector is used, and only a Faraday detector for ^{234}U. Additionally, regression lines for the performance of TE measurements performed on MAT262 and TRITON™ TIMS instruments are shown for comparison.

TABLE A1.1 Within-Turret Precision (% RSD) for MTE Measurements of the Major Ratio $^{235}U/^{238}U$

CRM	$^{235}U/^{238}U$	$^{235}U/U$, %	Average RSD, %
Ref **(5)** in 2003			
U005a	0.005 090	0.5	0.028
U010	0.010 140	1.0	0.028
U030A	0.031 367	3.0	0.017
U050	0.052 784	5.0	0.024
U100	0.113 596	10.2	0.016
U200	0.251 259	20.1	0.040
U500	0.999 698	50.0	0.025
U750	3.166 130	76.0	0.022
U900	10.375 704	91.2	0.019
Ref **(7)** in 2013/2014			
IRMM-019	0.00177	0.2	0.014
IRMM-020	0.00296	0.2	0.013
IRMM-021	0.00405	0.4	0.018
IRMM-022	0.00756	0.7	0.009
IRMM-023	0.03381	3.3	0.012
IRMM-024	0.05354	5.1	0.009
IRMM-025	0.02036	2.0	0.010
IRMM-026	0.02579	2.5	0.018
IRMM-027	0.04117	4.0	0.010
IRMM-028	0.03776	3.6	0.022
IRMM-029	0.04452	4.2	0.018
Ref **(18)** in 2013			
CRM 115	0.002034	0.2	0.019
Ref **(16)** in 2013			
CRM112A (from metal)	0.00754	0.7	<0.010
CRM145 (from metal)	0.00754	0.7	<0.010
CRM030A	0.03167	3.0	<0.020
Ref **(17)** in 2014			
CRM116A (from metal)	19.498803	93.2	<0.010
CRM U900	10.375704	91.2	0.010

TABLE A1.2 Between-Turret Precision

Relative Deviation of corrected $^{235}U/^{238}U$ ratios from certified values. Additional IRMM-187 samples loaded on each turret 1–6 were used for *K*-factor determination.

Turret	IRMM-187, %	IRMM-186, %	IRMM-185, %	IRMM-184, %
1	0.001	0.022	0.016	-0.020
2	-0.001	0.026	0.022	-0.026
3	0.001	0.032	0.016	-0.019
4	0.000	0.023	0.017	-0.011
5	-0.002	0.020	0.016	-0.023
6	0.001	0.019	0.015	-0.018
Summary:				
RSD[A]	0.0012	0.0048	0.0027	0.0050

[A] The between-turret precision (% RSD) varies between 0.0012 and 0.0050 % RSD.

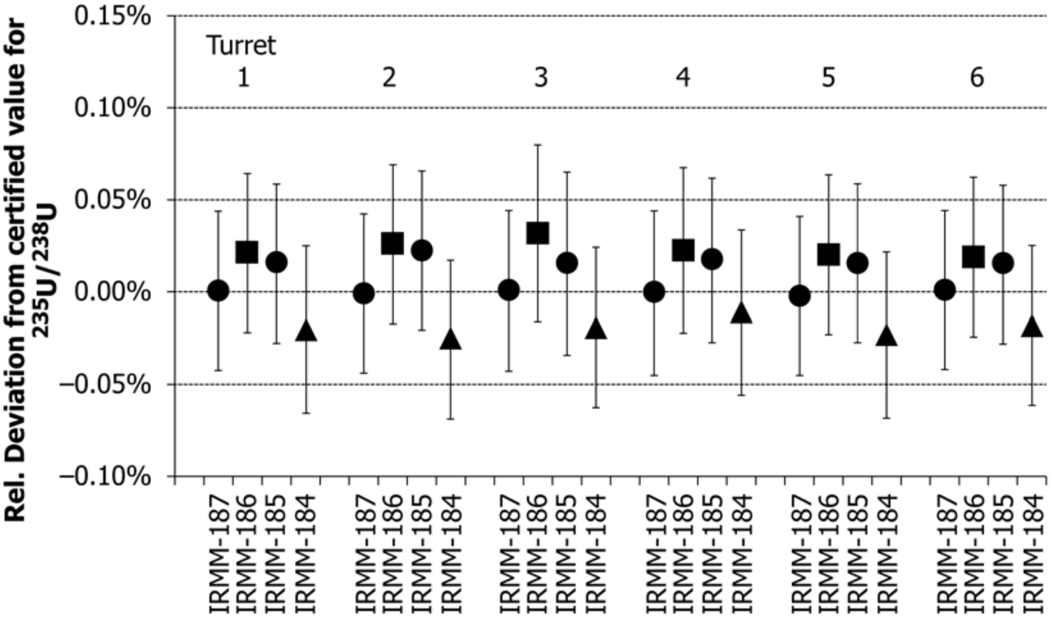

FIG. A1.1 Between-Turret Precision

TABLE A1.3 Bias for MTE Measurements of the Major Ratio $^{235}U/^{238}U$

	Corrected $^{235}U/^{238}U$	Certified $^{235}U/^{238}U$	Rel. Dev. from Certified Value
IRMM-072-1	Used for K-Factor	0.991 03(20)	N/A
IRMM-199	1.000 18(36)	1.000 15(20)	0.003(42) %
IRMM-074-Mix1	1.000 09(43)	1.000 26(15)	-0.017(44) %
IRMM-074-1	1.000 22(32)	1.000 25(15)	-0.003(33) %

TABLE A1.4 Precision (% RSD) for MTE Measurements of Minor Ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ on Faraday Cups

CRM	Ratio	Ratio Value	Average % RSD
IRMM-021	$^{234}U/^{238}U$	0.000 024 85	0.17
IRMM-019	$^{236}U/^{238}U$	0.000 036 52	0.25
IRMM-022	$^{234}U/^{238}U$	0.000 053 28	0.12
IRMM-025	$^{234}U/^{238}U$	0.000 122 45	0.042
IRMM-025	$^{236}U/^{238}U$	0.000 148 39	0.030
IRMM-026	$^{234}U/^{238}U$	0.000 149 41	0.041
IRMM-026	$^{236}U/^{238}U$	0.000 207 30	0.060
IRMM-027	$^{234}U/^{238}U$	0.000 231 59	0.037
IRMM-020	$^{236}U/^{238}U$	0.000 286 15	0.033
IRMM-024	$^{234}U/^{238}U$	0.000 290 75	0.016
IRMM-023	$^{234}U/^{238}U$	0.000 339 50	0.016
IRMM-027	$^{236}U/^{238}U$	0.000 387 39	0.020
IRMM-024	$^{236}U/^{238}U$	0.000 516 96	0.014
IRMM-028	$^{234}U/^{238}U$	0.000 610 41	0.0066
IRMM-029	$^{234}U/^{238}U$	0.000 844 4	0.014
IRMM-028	$^{236}U/^{238}U$	0.005 194 3	0.0015
IRMM-029	$^{236}U/^{238}U$	0.010 556 3	0.0022

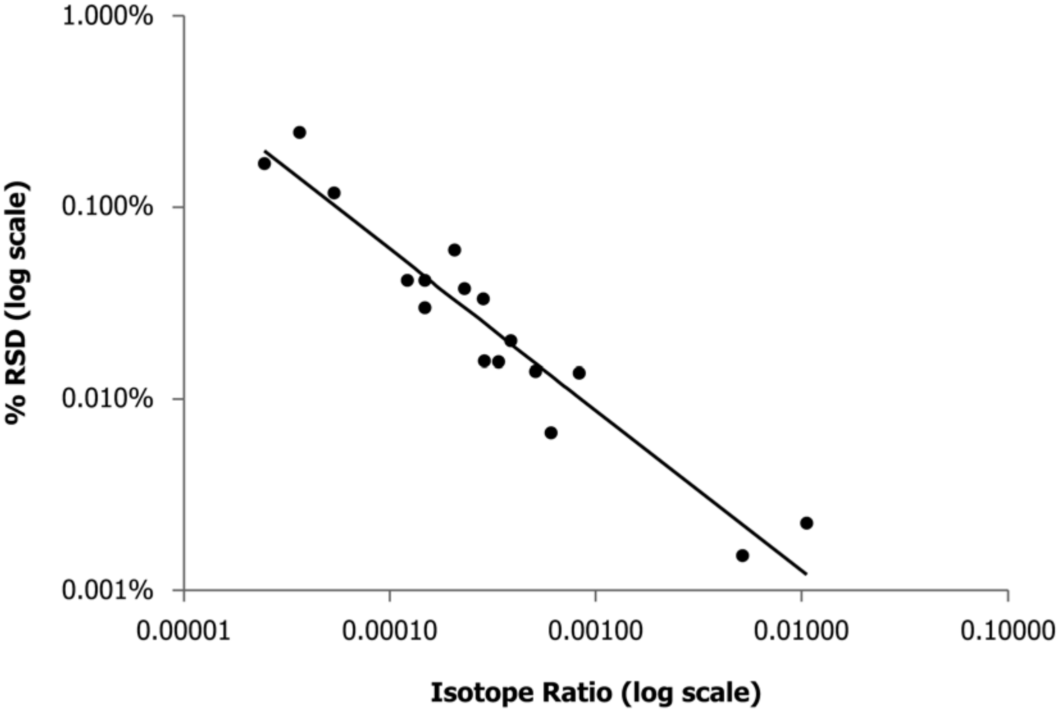

FIG. A1.2 Precision (% RSD) for MTE Measurements of Minor Ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ on Faraday Cups

TABLE A1.5 Precision (% RSD) for MTE Measurements for Minor Ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$, Using a SEM Detector for ^{234}U or ^{236}U

CRM	Ratio	Ratio Value	Average % RSD
IRMM-075-6	$^{236}U/^{238}U$	0.000 000 001 088 9	11.5
IRMM-075-5	$^{236}U/^{238}U$	0.000 000 010 651 9	0.91
S3-1-2, BC 2692	$^{236}U/^{238}U$	0.000 000 011 9	0.33
IRMM-021	$^{236}U/^{238}U$	0.000 000 026 6	0.67
S3-1-1, BC 2691	$^{236}U/^{238}U$	0.000 000 105 1	0.27
IRMM-023 (also IRMM-075-4)	$^{236}U/^{238}U$	0.000 000 115 3	0.49
IRMM-022	$^{236}U/^{238}U$	0.000 000 241 5	0.35
IRMM-075-3	$^{236}U/^{238}U$	0.000 001 040 93	0.12
IRMM-019	$^{234}U/^{238}U$	0.000 006 85	0.25
IRMM-075-2	$^{236}U/^{238}U$	0.000 011 416	0.073
IRMM-020	$^{234}U/^{238}U$	0.000 011 92	0.037

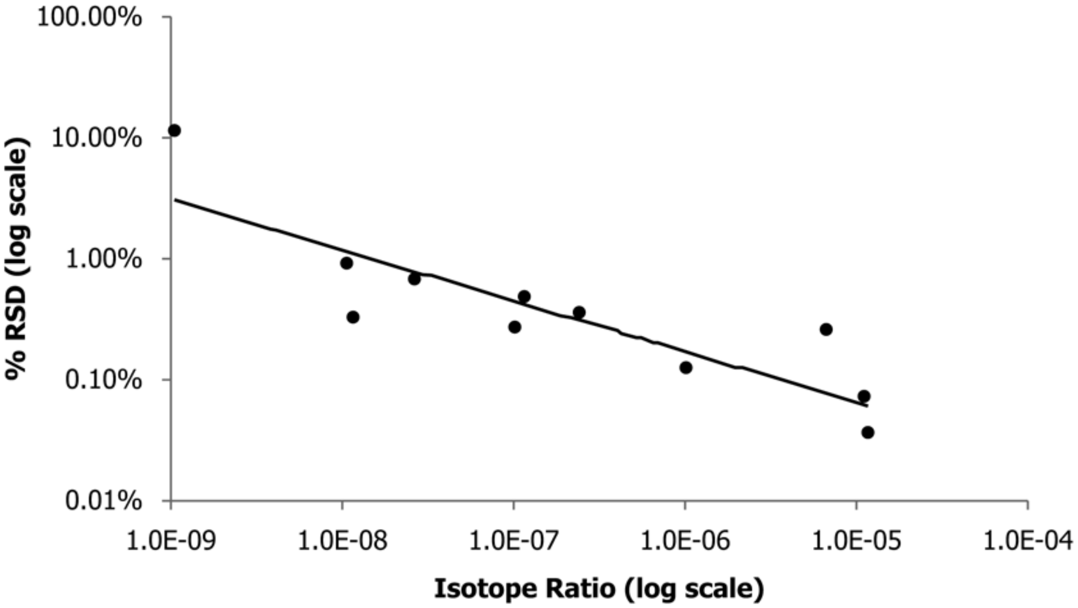

FIG. A1.3 Precision (% RSD) for MTE Measurements for Minor Ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$, Using a SEM Detector for ^{234}U or ^{236}U

TABLE A1.6 MTE Measurement Uncertainty and Measurement Performance

CRM, Sample	$^{236}U/^{238}U$	Rel. U, *k* = 2, %	"Performance" ABS (Dev.) + U (*k* = 2)
REIMEP 18-C	0.000 982 015	0.036	6.30×10^{-7}
REIMEP 18-B	0.000 388 280	0.034	1.89×10^{-7}
IRMM-075-1	0.000 104 433	0.050	1.18×10^{-7}
IRMM-187	0.000 071 965	0.074	7.57×10^{-8}
IRMM-075-2	0.000 011 416	0.23	3.73×10^{-8}
IRMM-075-3	0.000 001 040 93	0.30	3.49×10^{-9}
IRMM-184	0.000 000 124 46	0.47	7.43×10^{-10}
IRMM-075-5	0.000 000 010 651 9	4.03	4.92×10^{-10}

TABLE A1.7 MTE Measurement Uncertainty and Measurement Performance

CRM, Sample	$^{234}U/^{238}U$	Rel. U, *k* = 2, %	"Performance" ABS (Dev.) + U (*k* = 2)
Close to natural[A]	0.00005286	0.12	8.70×10^{-8}
NBL 005a	0.00003417	0.16	7.47×10^{-8}
REIMEP 18-C	0.00007947	0.092	1.11×10^{-7}
REIMEP 18-D	0.00020931	0.071	1.96×10^{-7}
REIMEP 18-B	0.00033272	0.067	2.33×10^{-7}
IRMM-187	0.00038700	0.056	3.15×10^{-7}

[A] Average from measurements of IRMM-184, IRMM-075-1, NBL U010, and NBL CRM 129A.

$^{236}U/^{238}U$, using a SEM Detector for ^{234}U or ^{236}U

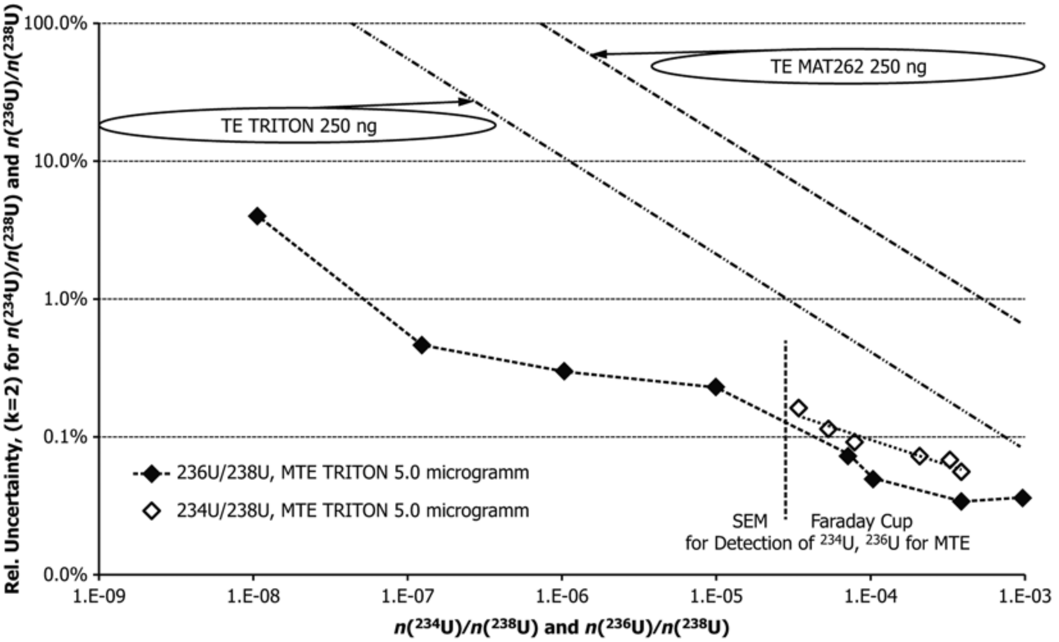

FIG. A1.4 MTE Measurement Uncertainty

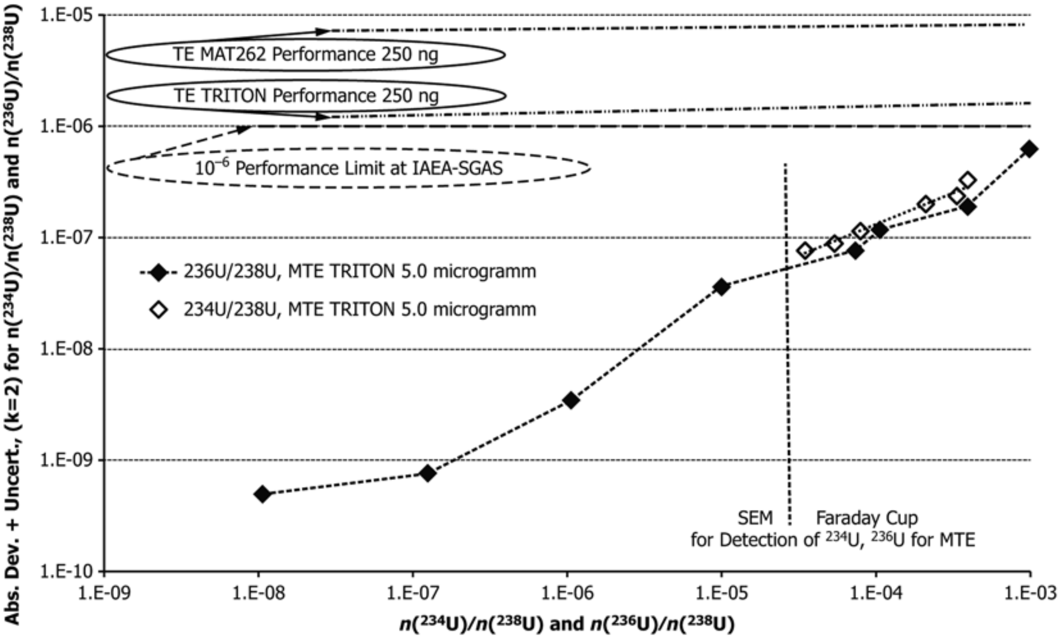

FIG. A1.5 MTE Measurement Performance

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