ASTM INTERNATIONAL

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Standard Test Method for
Determination of Uranium Isotopic Composition by the Double Spike Method Using a Thermal Ionization Mass Spectrometer[1]

This standard is issued under the fixed designation C1871; 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 double spike (DS) 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 the DS method is five to ten times better in terms of the internal and external reproducibility compared to the ("classical") total evaporation (TE) method as described in Test Method C1672 and the "modified total evaporation" (MTE) as described in Test Method C1832. This is due to the use of an *internal* rather than *external* mass fractionation correction by using a double spike material with a known or certified $^{233}U/^{236}U$ isotope ratio, which is mixed with the sample prior to the measurement, either during the sample preparation or directly on the TIMS filament.

1.3 The DS method cannot be applied for the determination of the $^{236}U/^{238}U$ minor isotope amount ratio, and is also not recommended for the determination of the $^{234}U/^{238}U$ minor isotope amount ratio.

1.4 In case the uranium amount concentration of the double spike is known or certified, the uranium amount concentration of the sample can be determined using the isotope dilution mass spectrometry (IDMS) method as described in Test Method C1672, by blending the sample gravimetrically with the double spike and performing a DS measurement.

1.5 An external mass fractionation correction by measurements of a certified reference material loaded on different filaments and measured in the same measurement sequence, as recommended for TE and required for MTE measurements, is not necessary for the DS method. However, for quality control (QC) purposes it is recommended to perform DS measure-

ments of low enriched or natural uranium isotopic reference materials on a regular basis.

1.6 The DS method can only be applied to uranium samples with relative isotope abundances $^{233}U/U$ below 10^{-5} and $^{236}U/U$ below 5×10^{-4}, the DS method is therefore mainly used for low enriched or close to natural uranium samples.

1.7 *Units*—The values stated in SI units are to be regarded as the standard. When no SI units are provided, the values are for information only.

1.8 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.9 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder

C776 Specification for Sintered Uranium Dioxide Pellets for Light Water Reactors

C787 Specification for Uranium Hexafluoride for Enrichment

C833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets for Light Water Reactors

C859 Terminology Relating to Nuclear Materials

C967 Specification for Uranium Ore Concentrate

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

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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.

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

C1672 Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer

C1832 Test Method for Determination of Uranium Isotopic Composition by Modified Total Evaporation (MTE) Method Using Thermal Ionization Mass Spectrometer

D1193 Specification for Reagent Water

E2586 Practice for Calculating and Using Basic Statistics

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

3. Terminology

3.1 Terminology 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* ± 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 *modified total evaporation, MTE, n*—analytical method for determination of isotope amount ratios of uranium, as described in Test Method C1832.

3.2.3 *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.

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

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

3.3 *Acronyms:*

3.3.1 *CRM*—certified reference material

3.3.2 *DS*—double spike

3.3.3 *DU*—depleted uranium

3.3.4 *EU*—European Union

3.3.5 *FAR*—Faraday Cup

3.3.6 *HEU*—high enriched uranium

3.3.7 *IAEA*—International Atomic Energy Agency

3.3.8 *ICPMS*—inductively coupled mass spectrometry

3.3.9 *IRMM*—Institute for Reference Materials and Measurements (since 1 July 2016 called JRC-Geel, the only unit working with nuclear materials at JRC-Geel is JRC-G.2)

3.3.10 *ITU*—Institute for Transuranium Elements (since 1 July 2016 called JRC-Karlsruhe, the only unit involved with thermal ionization mass spectrometry measurements of nuclear materials at JRC-Karlsruhe is JRC-G.II.6)

3.3.11 *JRC*—Joint Research Centre

3.3.12 *LEU*—low enriched uranium

3.3.13 *MTE*—modified total evaporation

3.3.14 *NBL*—New Brunswick Laboratory (since 15 May 2016 called NBL-Program Office)

3.3.15 *NML*—Nuclear Material Laboratory (part of the IAEA)

3.3.16 *QC*—quality control

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

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

3.3.19 *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 1.

3.3.20 *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.

3.3.20.1 *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).

3.3.20.2 *Discussion*—According to Practice 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 $\bar{x} \pm t \times SD / \sqrt{n}$, 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

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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 SD / √n.

3.3.21 *TIMS*—thermal ionization mass spectrometry

3.3.22 *WRM*—working reference material

4. Summary of Test Method

4.1 The double spike method has been developed with the intention to improve the precision and decrease the uncertainties for $^{235}U/^{238}U$ major isotope ratio measurements compared to the known methods such as the "classical" total evaporation technique (**1-4**),[4] also described in Test Method C1672, and the modified total evaporation technique (**5 and 6**), also described in Test Method C1832. For the double spike method the mass fractionation correction for the $^{235}U/^{238}U$ ratio is performed *internally throughout the measurement* rather than *externally*, by using the mass fractionation observed for a double spike material with a known or certified $^{233}U/^{236}U$ isotope ratio (also spanning three mass units), which is mixed with the sample prior to the measurement, either during the sample preparation or directly on the TIMS filament. 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 an evaporation filament (made of metals such as rhenium, zone-refined rhenium, or tungsten with high evaporation temperature), and blended with an appropriate amount of double spike solution, and converted to an oxide by controlled heating of the filament under atmospheric conditions. In case only the $^{235}U/^{238}U$ ratio of the sample has to be determined, it is recommended to mix the sample with the double spike during the loading process on the filament. In case the uranium amount concentration of the sample has to be determined, the sample solution has to be blended gravimetrically with the double spike solution prior to filament loading, for which weighable amounts have to be used.

4.2 The sample amount to be loaded for DS analyses is within a range of about 4 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.

4.3 The $^{235}U/^{238}U$ 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 is calculated from the measured mass fractionation of the $^{233}U/^{236}U$ ratio. The peak tailing contributions are determined at two mass positions, 0.5 mass units below and 0.5 mass units above the isotope masses of interest.

4.4 For the correction of isobaric interferences, a separate measurement of the isotopic composition of the (unspiked) sample is required, unless this information is already available.

This measurement can be performed using the TE or MTE methods (Test Methods C1672 and C1832, respectively).

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 $^{235}U/^{238}U$ isotope amount ratios and the amount content of uranium material can be measured by mass spectrometry following this test method to ensure that they meet the specification.

5.2 The double spike method has been used for studies of uranium fractionation effects in isotope geochemistry and cosmochemistry, for uranium source attribution in nuclear forensics and for investigation of conversion or sampling processes in nuclear industry and nuclear safeguards (**7-11**). Most recently, the double spike method has been used for the validation of the Cristallini sampling method of UF$_6$ (**12 and 13**). The double spike method can be used for a wide range of sample sizes even in samples containing as low as 50 µg of uranium. The concentration of the loading solution for the DS method has to be in the range of 1 to 6 mg/g to allow a sample loading of 4 to 6 µg of uranium. A minimum loading of 4 µg uranium per filament is recommended.

5.3 The measurement of $^{236}U/^{238}U$ ratios using this method is not possible due to the large isobaric interference from the ^{236}U ion beam of the double spike onto the ^{236}U ion beam from the sample (>50.000 times for close to natural material, for example, like IRMM-184).

5.4 The application of the double spike method for measurements of $^{235}U/^{238}U$ ratio is limited by the isobaric interference between the ^{236}U from the double spike material and the ^{236}U contained in the sample. As a consequence, the method is not suitable for samples which contain significant amounts of ^{236}U due to prior neutron capture from ^{235}U in the predecessor materials. For samples with $^{236}U/^{238}U$ ratios higher than about 10^{-6}, the double spike method should be applied with care for the isobaric correction. For an appropriate isobaric correction, the $^{236}U/^{238}U$ ratios of the samples should be determined separately using a suitable measurement method, for example, the modified total evaporation MTE method (Test Method C1832, Ref (**5**) and (**6**)).

5.5 The measurement of $^{234}U/^{238}U$ ratios using this method is very limited in the analytical performance due to the isobaric interference of the ^{234}U from the double spike with the ^{234}U from the sample (range from 5 to 15 %). The correction algorithms are presented in 14.3, but statements for precision and bias are not given. Other methods like MTE (Test Method C1832, Ref (**5**) and (**6**)) are better suited and more reliable for measurements of $^{234}U/^{238}U$ ratios.

5.6 The DS method described here can also be extended to measurement of elements other than uranium, if a suitable double spike material is available.

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

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 For the isotopes ^{234}U, ^{235}U, ^{236}U, and ^{238}U isobaric interferences between the sample and the double spike occur. The accurate correction of isobaric interferences is a prerequisite for obtaining results for the DS method with satisfactory precision and accuracy. The corrections depend strongly on the mixing proportions between the sample and the double spike. Usually the sample/spike amount ratio is adjusted in such a manner that the ion beam intensity at mass m/z=236 is lower compared to that at mass m/z=235, in order to reduce the influences from low-mass tailings, that is, abundance sensitivities, at one mass unit below and beyond the U peaks. Therefore a sample-to-spike amount ratio of >20 is recommended. The correction of isobaric interferences is explained in detail in Section 14 ("calculations") of this test method.

6.3 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 is possible source for bias in the isotopic data.

6.4 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.

6.5 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 DS 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 single, double, or triple 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 8×10^{-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 ion beams of ^{233}U and ^{236}U, there shall be current amplifiers equipped with at least 10^{11} Ω, and preferably 10^{12} Ω resistors to improve the signal-to-noise ratio. In case the ion beam of ^{235}U is below the ion beams of ^{233}U and ^{236}U, the use of an amplifier equipped with a 10^{12} Ω resistor is recommended, if available.

7.1.5 A sample turret to allow automatic measurement sequences of several replicate filament loadings per sample and per quality control standard (preferentially a CRM);

7.1.6 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;

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

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

7.2 *Special MTE Capabilities*—It is recommended to have a mass spectrometer software to be flexible enough to implement a user-defined filament-heating program as for MTE.[5]

7.3 A separate filament degassing device for cleaning of the filaments before sample loading can be used.

7.4 A pipette or microsyringe to transfer microliter volumes of solution.

7.5 A separate filament heating device for drying and oxidizing the sample on the filament ribbon after loading.

8. Reagents and Materials

8.1 *Purity of Reagents*—Ultra-high purity reagents shall be used 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.

8.2 *Nitric Acid (HNO₃, 15.8 M)*—Concentrated nitric acid.

8.3 *Nitric Acid (HNO₃, 1 M)*—One volume of concentrated nitric acid (HNO$_3$, 15.8 M) brought to 15.8 volumes with water.

8.4 *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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[5] 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.

8.5 *Filaments*—Filaments with sufficient purity, for example, zone refined or high purity Re or W, should be used. The size and configuration of the filament is instrument dependent.

8.6 *Liquid Nitrogen*—Liquid nitrogen can be filled into the cold trap of a mass spectrometer to improve the vacuum pressure.

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 sources 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.

9.5 Handle chemical hazards and toxins like uranium with appropriate care.

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 Double Spikes IRMM-3636 (1 mg U/g), IRMM-3636a (0.1 mg U/g), and IRMM-3636b (0.01 mg U/g), which all have the same isotopic composition (uncertainties with coverage factor $k = 2$, 95 % confidence level):

$^{233}U/^{236}U = 1.01906(16)$,
$^{234}U/^{236}U = 0.00036606(48)$,
$^{235}U/^{236}U = 0.000045480(74)$, and
$^{238}U/^{236}U = 0.00023481(38)$.

In addition, various in-house double spike materials are being used at numerous facilities, which have been calibrated using isotope reference materials, like NBL CRM U500 ($^{235}U/^{238}U \cong 1$) or IRMM-184 (close to natural U). For the preparation of in-house double spike reference materials, 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 quality control purposes shall be in the same medium, same concentration and in the same oxidation state. The solutions for loading onto the filaments are usually 1 to 5 *M* nitric acid solutions. 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*—Filaments can be degassed before using them for DS measurements. This is recommended in case the heating of the filaments during the mass spectrometric measurement is causing the vacuum pressure in the ion source to increase beyond 1.3×10^{-4} Pa (1×10^{-6} torr) is reached. Recommended filament currents for degassing are in the range 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 units). 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, high precision and accuracy, or both. 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 amplifier resistances higher than the 10^{11} Ω, longer response times of about 15 s can be expected. The DS method has to be 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 *Ion Source and Analyzer Pressure*—It is important to achieve a certain level of vacuum before the isotope amount ratio measurements can be started; see 7.1.6 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. An increase of 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.

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12. Calibration and Standardization

Note 1—The measurement method may be qualified following Guide C1068 and calibrated following Guide C1156.

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 at three uranium masses as part of the mass calibration before the start of each DS measurement sequence. During the DS 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 DS 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 DS 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 multicollector 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 a 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 of 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 DS 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), IRMM-072/1, IRMM-074/1, or IRMM-199 (^{233}U/^{235}U/^{238}U=1/1/1), 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.

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 series (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 multicollector system needed for the DS 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 (**14**). This procedure shall be performed sequentially for all Faraday cups needed for the DS 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 *Mass Fractionation Correction:*

12.8.1 For the double spike method the mass fractionation correction for the $^{235}U/^{238}U$ ratio is performed for each integration step (called "mass cycle," see below) internally throughout the measurement rather than externally, by using the mass fractionation observed for a double spike material with a known or certified $^{233}U/^{236}U$ isotope ratio (also spanning three mass units).

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

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

where:

K = mass fractionation correction factor,
R_m = measured $^{233}U/^{236}U$ isotope amount ratio for the double spike, and
R_c = known or certified $^{233}U/^{236}U$ isotope amount ratio value for the double spike.

Details about the mass fractionation and further correction algorithms are presented in 14.2.

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 2-mg U/mL solution yields 2 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 and other impurities, if necessary.

13.2 *Sample Loading and Conditioning*—Samples for the DS method are usually directly loaded on the filament by drop deposition. Samples and QC 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 or pipette fitted with a plastic tip. Change the tip between sample loadings to prevent cross contamination. In particular for loading and mixing a sample solution and the double spike solution on the same filament, cross contamination between these solutions has to be prevented by changing pipette tips. It is recommended to load the double spike solution first and the sample afterwards in order to minimize the risk of contaminating the double spike solution with any sample material. 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 DS are usually prepared in a 1 to 5 *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 of the sample solution may be needed. The recommended uranium amount for loading is 4 to 6 μg. 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 solution on the filament is heated until dryness, for at least one more minute, and then heated for several seconds at a higher current of 1.5 to 2.0 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, and quality control samples.

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

13.4 Close the source and start evacuating.

13.5 Perform adjustment (also called initialization) of the sample turret if needed. 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 – 13.10 are typically performed automatically under computer control depending upon the instrument.

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 QC standard.