



Designation: C1625 – 19

Standard Test Method for Uranium and Plutonium Concentrations and Isotopic Abundances by Thermal Ionization Mass Spectrometry¹

This standard is issued under the fixed designation C1625; 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 covers the determination of the concentration and isotopic composition of uranium and plutonium in solutions. The purified uranium or plutonium from samples ranging from nuclear materials to environmental or bioassay matrices is loaded onto a mass spectrometric filament. The isotopic ratio is determined by thermal ionization mass spectrometry, the concentration is determined by isotope dilution.

1.2 The values stated in SI units are to be regarded as the standard. Values in parentheses are for information only.

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

1.4 *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
- C757 Specification for Nuclear-Grade Plutonium Dioxide Powder for Light Water Reactors
- C776 Specification for Sintered Uranium Dioxide Pellets for Light Water Reactors
- C833 Specification for Sintered (Uranium-Plutonium) Diox-

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.

ide Pellets for Light Water Reactors

- C859 Terminology Relating to Nuclear Materials
- C1008 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets—Fast Reactor Fuel (Withdrawn 2014)³
- C1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry
- 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
- C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis
- C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis
- C1411 Practice for The Ion Exchange Separation of Uranium and Plutonium Prior to Isotopic Analysis
- C1415 Test Method for ²³⁸Pu Isotopic Abundance By Alpha Spectrometry
- D3084 Practice for Alpha-Particle Spectrometry of Water

2.2 Other Documents

- International Target Values 2010 for Measurement Uncertainties in Safeguarding Nuclear Materials⁴

3. Terminology

3.1 For definitions of pertinent terms not listed here, see Terminology C859.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *isotope dilution mass spectrometry (IDMS)*—determination of elemental concentration of a sample, by mass spectrometry, using the addition of a spike material to the sample with significantly different isotopic composition from the sample and accurately characterized mass of the major spike isotope.

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

⁴ K. Zhao et. al., "International Target Values 2010 for Measurement Uncertainties in Safeguarding Nuclear Materials," International Atomic Energy Agency STR-368, 2010.

4. Summary of Test Method

4.1 The uranium and plutonium are separated from each other and purified from other elements by selective extraction, anion exchange (such as in C1411) or extraction chromatography. The uranium and plutonium fractions are individually mounted on filaments of rhenium, tungsten, or tantalum, and are analyzed by thermal ionization mass spectrometry to determine the relative abundance of the isotopes. If a known ^{233}U or ^{242}Pu (or ^{244}Pu) spike is added prior to chemical separation the corresponding elemental concentration may also be determined by isotope dilution mass spectrometry (IDMS).

5. Significance and Use

5.1 Uranium and plutonium oxides can be used as a nuclear-reactor fuel in the form of pellets. In order to be suitable for use as a nuclear fuel the starting material must meet certain specifications, such as found in Specifications C757, C833, C753, C776, C1008, or as specified by the purchaser. The uranium concentration, plutonium concentration, or both, and the isotopic abundances are measured by mass spectrometry following this test method.

5.2 The separated heavy element fractions placed on mass spectrometric filaments must be very pure. The quantity required depends upon the sensitivity of the instrument detection system. If an electron multiplier detector is to be used, only a few nanograms are required. If a Faraday cup is used, a few micrograms are needed. Chemical purity of the sample becomes more important as the sample size decreases, because ion emission of the sample is suppressed by impurities.

6. Interferences

6.1 Uranium-238 and ^{238}Pu interfere in the measurement of each other, and ^{241}Am interferes with the measurement of ^{241}Pu , thereby requiring chemical separation. Removal of impurities provides uniform ionization of uranium or plutonium, hence improved precision, and reduces the interference from molecular species of the same mass number as the uranium or plutonium isotopes being measured. Isotopic analysis of plutonium should be completed within a reasonable time period (approximately 20 days) after separation from americium to minimize interference of ^{241}Am ingrowth from ^{241}Pu .

6.2 Extreme care must be taken to avoid contamination of the sample by environmental uranium. The level of uranium contamination should be measured by analyzing an aliquot of 8M nitric acid as a reagent blank and calculating the amount of uranium it contains.

6.3 When ^{238}Pu is present in low abundance it may be necessary to measure it by alpha-spectrometry following Test Method C1415 or Practice D3084.

7. Apparatus

7.1 *Mass Spectrometer*—The suitability of mass spectrometers for use with this test method of analysis shall be evaluated by means of performance tests described in this test method. The mass spectrometer used should possess the following characteristics:

7.1.1 A thermal ionization source with single or multiple filaments of rhenium, tungsten or tantalum.

7.1.2 An analyzer radius sufficient to resolve adjacent masses in the mass-to-charge range being studied, that is, $m/z = 233$ to 238 for U^+ or 238 to 244 for Pu^+ . Abundance sensitivity must be great enough to detect one part of ^{236}U in 400 parts ^{235}U .

7.1.3 A minimum of one stage of magnetic deflection. Since the resolution is not affected, the angle of deflection may vary with the instrument design.

7.1.4 A mechanism for changing samples.

7.1.5 A direct-current (Faraday cup) or electron multiplier detector, as a single detector system or, several detectors in a multi collector design, followed by a current measuring device.

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

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

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

7.2 An *Optical Pyrometer* should be available to determine the filament temperature.

7.3 Filament preheating and degassing unit for cleaning unloaded filaments.

8. Materials and Reagents

8.1 *Purity of Reagents*—all reagents used in the final purification and filament loading steps should be of the highest purity available. Other grades may be used if they are determined not to affect the final result.

8.2 *Filaments*—high purity, the size and configuration are instrument dependent. Filaments should be degassed, and maybe carbon saturated, prior to use.

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

8.3 *Certified Reference Materials (CRM)*—of varying isotopic composition, traceable to a national standard body⁵, for use as calibration and quality control standards.

8.4 *Spikes*—Materials, preferably CRMs, for use in the determination of elemental concentration by IDMS, examples of spikes used for uranium concentration include NBL CRM 111-A (^{233}U spike), NBL CRM 112-A (^{238}U spike), IRMM 040a (^{233}U spike), and IRMM 054 (^{235}U spike). For plutonium commonly used spikes include NBL CRM 130 (^{242}Pu spike), and IRMM 049c/d/e/f series (^{242}Pu spikes).

9. Instrument Calibration

9.1 The measurement method may be qualified following Guide C1068 and calibrated following Guide C1156.

⁵ Available from USDOE NBL Program Office, Argonne, IL, or other equivalent source.

9.2 *Mass Calibration*—The relationship between the masses to be analyzed and the magnetic field needed to direct the ion beam for those masses to the detector shall be updated on a periodic basis. The interval between mass calibrations is determined by the manufacturer. The stability of the mass calibration is affected by laboratory conditions. It is recommended that a mass calibration check be performed prior to each day’s analysis.

9.3 *Peak Centering*—The peak centering routine is used as fine adjustment to ensure that the ion beam is centered within the detector. This routine should be used during the mass calibration check, and at the start of each sample analysis.

9.4 *Amplifier Baseline/Background Calibration*—The baseline, or background, for the Faraday cup amplifiers is the background signal that can be measured when there is no ion beam to the detector. This shall be measured on a routine basis and checked for stability. The amplifier baseline should be performed at the beginning of each analysis day.

9.5 *Amplifier Gain Calibration*—The amplifier gain calibration is typically performed as a programmed routine on the mass spectrometer. A constant voltage is applied to each amplifier and the amplifier response is recorded. The output for each amplifier is normalized to a single amplifier to determine a gain factor for each amplifier. This calibration is not required for single collector systems. Depending on the stability of the amplifier system, the amplifier gain may be performed on a weekly basis, or as often as prior to each analysis.

9.6 The measurement and correction for mass discrimination and dead time are critical factors in obtaining precise and accurate results. Equally critical to the accuracy of the measurement is the linearity of the total measuring circuit including the collector. Calibration of the mass spectrometer is based on the assumption that these are the only sources of significant (>1 in 10^4) systematic error in the measurement. Thus, accurate calibration is made by analyzing standards of known isotopic composition under conditions in which cross-contamination between samples does not occur.

9.6.1 For multi-collector systems, the bias between collectors may also be an important factor in the systematic error and thus must also be evaluated prior to making measurements.

9.6.2 For very low-level samples, or samples with extreme ratios, other corrections may need to be made, for example, dark count data/dark current.

9.7 *Mass Discrimination*—Use a traceable isotopic standard to determine the mass discrimination. The deviation from the certified value of the 235/238 ratio (for U) or the 239/242 ratio (for Pu) is a measure of the mass discrimination of the mass spectrometer.

9.7.1 Calculate the elemental mass discrimination bias factor, B , as follows:

$$B = (1/c)[(aR_{ij}/R_s) - 1] \quad (1)$$

where:

- B = mass discrimination factor,
- aR_{ij} = average measured atom ratio of isotope i to isotope j
- R_s = certified atom ratio value of the CRM

c = Δ mass/mass. The values for c for various ratios and ion species include:

ratio	U ⁺ or Pu ⁺
²³⁵ U/ ²³⁸ U	+3/238
²³⁶ U/ ²³⁵ U	-1/235
²³³ U/ ²³⁸ U	+5/238
²³⁴ U/ ²³⁵ U	+1/235
²⁴² Pu/ ²³⁹ Pu	-3/239
²⁴⁰ Pu/ ²³⁹ Pu	-1/239
²⁴¹ Pu/ ²³⁹ Pu	-2/239
²³⁸ Pu/ ²³⁹ Pu	+1/239

9.7.2 Correct every measured ratio, R_{ij} , for mass discrimination as follows:

$$R_{ij} = a R_{ij}/(1 + cB) \quad (2)$$

where R_{ij} is the corrected atom ratio of isotope i to isotope j

9.8 *Dead Time Correction*—Required for counting detectors, at high count rates. Use laboratory protocols for this correction with high count rate samples.

9.9 *Linearity*—The linearity of the mass spectrometer may be determined over the working ratio range by measuring the ²³⁵U/²³⁸U ratio, under identical conditions, of appropriate CRMs. The ratio of the certified ²³⁵U/²³⁸U ratio to the experimental ²³⁵U/²³⁸U ratio is independent of isotopic ratio if the system is linear. Under ideal conditions, any deviation from a constant value greater than 4 in 10 000 is likely to be nonlinearity. Uranium CRMs are used because the range of isotopic ratios of existing plutonium CRMs is not adequately large.

10. Procedure

10.1 Sample Preparation:

10.1.1 *Sample Dissolution*—Dissolve an appropriate sample to obtain the desired filament loading for the mass spectrometric analysis. See Practice C1347 for the dissolution of uranium or Practice C1168 for plutonium. Add the appropriate amount of spike, by weight or volume, as appropriate, if concentration is to be determined by isotope dilution methods.

NOTE 2—Spike addition and equilibration are performed to ensure identical valency and chemical form between the sample and spike material prior to chemical purification if determining concentration by IDMS. Failure to perform spike equilibration may result in partial separation of the sample to the spike during purification procedure, resulting in a bias in the results of the IDMS measurement.

10.1.2 *Sample Purification*—Purify samples by selective extraction, extraction chromatography, or ion exchange chromatography (such as Practice C1411 or similar procedure) to separate the uranium and plutonium from each other and from other impurities.

10.2 *Filament Loading*—Samples may either be directly loaded by evaporation, electroplated, or loaded onto a resin bead for mounting on the filament. Samples and standards should be prepared for analysis by the same method at similar mass loadings.

10.3 Sample Heating and Isotopic Ratio Measurement:

10.3.1 Insert the filament assembly into the mass spectrometer. If the instrument contains a turret to allow loading of several samples, load at least one QC sample (preferably a