



Standard Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer¹

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1. Scope

1.1 This method describes the determination of the isotopic composition and/or the concentration of uranium and plutonium as nitrate solutions by the thermal ionization mass spectrometric (TIMS) total evaporation method. Purified uranium or plutonium nitrate solutions are loaded onto a degassed metal filament and placed in the mass spectrometer. Under computer control, ion currents are generated by heating of the filament(s). The ion beams are continually measured until the sample is exhausted. The measured ion currents are integrated over the course of the run, and normalized to a reference isotope ion current to yield isotopic ratios.

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

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

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

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. Referenced Documents

2.1 *ASTM Standards*:²

- C753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder
- C757 Specification for Nuclear-Grade Plutonium Dioxide Powder, Sinterable
- C776 Specification for Sintered Uranium Dioxide Pellets
- C787 Specification for Uranium Hexafluoride for Enrichment
- C833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets
- C967 Specification for Uranium Ore Concentrate
- C996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % ²³⁵U
- C1008 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets—Fast Reactor Fuel
- C1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry
- C1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials
- 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
- E137 Practice for Evaluation of Mass Spectrometers for Quantitative Analysis from a Batch Inlet (Withdrawn 1992)³

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.

3. Terminology

3.1 Definitions:

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

3.1.2 *abundance sensitivity*—the ratio of the measured intensity of an ion beam at a mass m to the measured intensity from the same isotope measured at one mass difference (for example, $m \pm 1$). Abundance sensitivity is a measure of the magnitude of peak tailing. Typically measured using uranium at masses 237 and 238.

3.2 Acronyms:

3.2.1 *CRM*—Certified Reference Materials

3.2.2 *TIMS*—Thermal Ionization Mass Spectrometry

3.2.3 *IDMS*—Isotope Dilution Mass Spectrometry

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

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

4. Summary of Test Method

4.1 Typically, uranium and plutonium are separated from each other and purified from other elements by selective extraction, anion exchange (such as in Practice C1411) or extraction chromatography. The purified uranium or plutonium samples as nitrate solutions are mounted on a degassed refractory metal filament (typically rhenium, tungsten or tantalum) and converted to a solid chemical form via controlled heating of the filament under atmospheric conditions. The filament is then mounted in the thermal ionization mass spectrometer, in either a single filament or double filament configuration. The filaments are initially heated to yield a small ion beam suitable for lens focusing and peak centering. Following focusing and peak centering, the ion beam intensity data acquisition begins, with the filaments heated under computer control to yield a pre-defined major isotope ion beam or a predefined total intensity for all measured ion beams. Data acquisition and filament heating continues until the sample is exhausted or the ion beam intensity reaches a pre-defined lower limit. Each isotope ion beam intensity is integrated over the course of the analysis, and the summed intensity for each isotope is divided by the summed intensity of a common isotope (typically the most abundant isotope) to yield ratios. The isotopic composition of the sample may be calculated from the ratios. Additional information on the total evaporation method may be found in Refs (1-4).⁴

4.2 The isotope dilution mass spectrometry (IDMS) method may be used to determine the uranium or plutonium concentrations. In this method, a spike of known isotopic composition and element concentration is added to a sample prior to chemical separation. Typical spike materials include ²³³U or ²³⁵U for uranium samples, and ²³⁹Pu, ²⁴²Pu or ²⁴⁴Pu for plutonium samples. Samples containing both uranium and plutonium (for example, mixed oxide fuels or fuel reprocessing materials) may be mixed with a combined U/Pu spike prior to separation. When using a spike containing significant quantities of one or more of the isotopes present in the sample, the isotopic composition of the sample must be known in advance. The spike-sample mixture undergoes a valency adjustment, purification, and is then loaded onto a filament and the isotopic composition of the mixture is determined. Using the measured isotope ratios of the spike-sample mixture, the known isotopic composition and amount of spike added to the mixture, and the isotopic composition of the sample, the elemental concentration of the sample may be calculated.

5. Significance and Use

5.1 The total evaporation method is used to measure the isotopic composition of uranium and plutonium materials, and may be used to measure the elemental concentrations of the two elements when employing the IDMS technique.

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

5.3 The total evaporation method allows for a wide range of sample loading with no loss in precision or accuracy, and is also suitable for trace-level loadings with consequent loss of precision. Typical uranium analyses are conducted using sample loadings between 10 nanograms and several micrograms. Plutonium analyses are generally conducted using between five and 200 nanograms of plutonium per filament. The total evaporation method and modern instrumentation allow for the measurement of minor isotopes using ion counting detectors, while the major isotopes are simultaneously measured using Faraday cup detectors.

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

6. Interferences

6.1 Ions with atomic masses in the uranium and plutonium ranges cause interference if they have not been removed or if they are generated as part of the chemical handling or analysis of the samples. Both ²³⁸U and ²³⁸Pu interfere in the measurement of each other, and ²⁴¹Am interferes with the measurement

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

of ^{241}Pu , thereby requiring chemical separation. Removal of impurities provides uniform ionization of uranium or plutonium, hence improved precision, and reduces the interference from molecular species of the same mass number as the uranium or plutonium isotopes being measured. Isotopic analysis of Plutonium should be completed within a reasonable time period after separation from Americium to minimize interference of ^{241}Am in-growth from ^{241}Pu . An example of a prescribed interval limiting the time between sample purification and isotopic analysis is 20 days. Operators are responsible for determining a maximum interval between purification and mass spectrometric analysis, based on an evaluation of ^{241}Am in-growth from decaying ^{241}Pu and required accuracy and precision. Other atomic and molecular species may interfere with total evaporation analyses, particularly if they cause a change in the ionization efficiency of the analyte during an analysis. Carbon may disturb total evaporation measurements. It is recommended that operators perform validation tests on unique or complex samples by mixing known pure standards with other constituents to create a matrix-matched standard.

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

6.3 The total evaporation method may generate biases in the minor isotopes, particularly those isotopes down mass from a major isotope, such as trace amounts of ^{234}U in a highly enriched ^{235}U material, or ^{238}Pu in the presence of ^{239}Pu . Biases in the minor isotope data occur due to peak tailing from the major isotopes. The amount of peak tailing is a function of the design of the instrument and ion beam spread due to source design and particle collisions in the instrument. The amount of peak tailing may be quantified by measuring the abundance sensitivity under identical experimental conditions. A bias correction may then be applied based upon the measured abundance sensitivity. Additionally, the use of an energy filter placed before an ion counting detector can greatly reduce peak tailing and allow for accurate measurement of minor isotopes. The use of an energy filter, ultra high-purity filaments and chemicals, effective sample purification, and low ionization and evaporation temperatures to minimize ^{238}U interferences can allow for the accurate measurement of small ^{238}Pu abundances by this technique. Another commonly used method for ^{238}Pu measurement when in low abundances is the alpha-spectrometry technique, following Test Method **C1415** or Practice **D3084**.

7. Apparatus

7.1 *Mass Spectrometer*—The suitability of mass spectrometers for use with this method of analysis shall be evaluated by means of performance tests described in this method and in

Practice **E137**. The mass spectrometer used should possess the following characteristics:

7.1.1 A thermal ionization source capable of analysis utilizing single and/or double filaments of rhenium; tungsten or tantalum may be substituted with minor modifications in the procedure.

7.1.2 An analyzer radius sufficient to resolve adjacent masses in the mass-to-charge range being studied, that is, $m/z = 233$ to 238 for U^+ or 238 to 244 for Pu^+ . Resolution greater than 360 (full width at 1 % of peak height) and an abundance sensitivity of less than 10^{-5} . For measuring minor isotopes, an abundance sensitivity as low as achievable is recommended.

7.1.3 An instrument capable of monitoring ion beam intensity and adjusting filament currents during ion beam integration is recommended. This eliminates the sample lost between integrations due to the time necessary to adjust the filament current.

7.1.4 A mechanism for changing samples.

7.1.5 Multiple direct-current detectors (Faraday cups) or a combination of Faraday cups and electron multiplier detector in a multi-collector design. Very small samples may be measured utilizing a multi-ion counting array.

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

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

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

7.2 An optical pyrometer is recommended for determining filament temperatures.

7.3 Filament preheating/degassing unit for cleaning filaments.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all steps. Ultra-high purity reagents may be necessary for small samples, those with extreme ratios, or those otherwise susceptible to isotope ratio biases from cross-contamination. Distilled water is sufficient for routine analysis of large samples; deionized water is recommended. For small samples, those with extreme ratios, or those otherwise susceptible to biases from cross-contamination, the level of uranium and/or plutonium contamination in chemicals, water, and the sample handling environment should be determined to ensure that the materials and environment are sufficiently pure for the sample being analyzed.

8.2 *Rhenium Filaments*—High purity, the size and configuration are instrument dependent. Tungsten or tantalum may be substituted with minor modifications in the procedure. Tungsten filaments have been reported to yield higher precision analyses via the total evaporation method. All filaments should be degassed prior to use. For small samples, the amount of uranium in the filaments should be measured to ensure the uranium content of the filament material will not bias sample analysis results.