



Standard Test Method for Isotopic Abundance Analysis of Uranium Hexafluoride and Uranyl Nitrate Solutions by Multi-Collector, Inductively Coupled Plasma-Mass Spectrometry¹

This standard is issued under the fixed designation C 1477; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This test method covers the isotopic abundance analysis of ^{234}U , ^{235}U , ^{236}U and ^{238}U in samples of hydrolysed uranium hexafluoride (UF_6) by inductively coupled plasma source, multi-collector, mass spectrometry (ICP-MC-MS). The method applies to material with ^{235}U abundance in the range of 0.2 to 6 % mass. This test method is also described in ASTM STP 1344.

1.2 *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

C 761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride

C 787 Specification for Uranium Hexafluoride for Enrichment

C 996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % ^{235}U

D 1193 Specification for Reagent Water

2.2 *Other Document:*

STP 1344 Applications of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to Radionuclide Determinations³

3. Summary of Test Method

3.1 Samples are received either in the form of uranium hexafluoride (UF_6) or aqueous uranic solution. The UF_6

samples are hydrolysed, diluted and acidified with nitric acid. Uranic solution samples are diluted and acidified with nitric acid. Subsequently, an internal reference of thorium isotopes is added to each diluted sample.

3.2 The samples are contained in polypropylene tubes that are inserted into the auto-sampler rack of the mass spectrometer. Sample details are input to the computer and the instrument is prepared for measurement. The automatic measuring sequence is initiated.

3.3 Uranium Isotopic Reference Materials (UIRMs) are used to calibrate the instrument. Each UIRM is prepared in aqueous solution (acidified with nitric acid) and spiked with the same internal reference as the samples. This calibration solution is measured and a mass bias parameter is calculated that is stored and subsequently imported into each of the sample measurements⁴ to correct the measured uranium isotopic ratios.

3.4 Measurements of isotopic ratios in the calibration solution and the subsequent samples are initiated by customised software. Using the $^{230}\text{Th} / ^{232}\text{Th}$ ratios (that are acquired simultaneously to the $^{234}\text{U} / ^{238}\text{U}$, $^{235}\text{U} / ^{238}\text{U}$ and $^{236}\text{U} / ^{238}\text{U}$ ratios) and the mass bias parameter imported from the calibration, the mass bias factor is computed. The mass bias factor is then used to correct the measured $^{234}\text{U} / ^{238}\text{U}$, $^{235}\text{U} / ^{238}\text{U}$ and $^{236}\text{U} / ^{238}\text{U}$ ratios in “real time.” The abundances are expressed as % atomic. Details of the mass bias correction are presented in **Appendix X1**.

4. Significance and Use

4.1 The test method is capable of measuring uranium isotopic abundances of ^{234}U , ^{235}U , ^{236}U and ^{238}U as required by Specifications **C 787** and **C 996**.

5. Interferences

5.1 *Mass Bias*—Electrostatic repulsion between uranium ions causes a so-called “mass bias” effect. Mass bias is observed as an enhancement in the number of ions detected at the collectors from the heavier uranium isotopes relative to the

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 Available from ASTM Headquarters.

⁴ The uranium isotopic measurement precision, limit of detection and uncertainty of measurement are listed in Section 15, Section 16 and **Appendix X1** respectively.

lighter uranium isotopes. A calibration procedure is used to correct the mass spectrometer for mass bias.

5.2 Adjacent Isotopic Peaks—The abundance sensitivity of the ICP-MC-MS at mass 237 is specified to be less than 0.5 parts per million of the ^{238}U ion beam. The method is limited to the measurement of ^{235}U isotopic abundances below 6 %, consequently interference effects with the ^{234}U and ^{236}U ion beams are negligible.

5.3 Isobaric Molecular Interferences—A molecular interference exists at mass 236 between ^{236}U and a hydride of ^{235}U , which is formed in the plasma. This interference is “real-time” corrected by measuring the beam height of the ^{238}U hydride at mass 239, and applying the correction defined in Eq 1, to the measured ^{236}U beam:⁵

$$^{236}\text{U}_c = ^{236}\text{U}_m - \left(^{235}\text{U} \times \frac{^{238}\text{UH}}{^{238}\text{U}} \right) \quad (1)$$

where:

- $^{236}\text{U}_c$ = the corrected ^{236}U signal,
- $^{236}\text{U}_m$ = the measured ^{236}U signal,
- $^{235}\text{U}_m$ = the measured ^{235}U signal,
- ^{238}UH = the measured ^{238}U hydride signal, and
- ^{238}U = the measured ^{238}U signal.

5.4 Memory Effects:

5.4.1 Contamination of the sample introduction system from previous samples produces memory interference effects. Such effects are accentuated when samples that are depleted in ^{235}U are measured after enriched samples. Memory effects can be readily assessed by aspirating a 2 % nitric acid solution and measuring the background ^{238}U ion beam. The sample introduction system should be periodically disassembled and cleaned, to minimise the background ^{238}U ion beam.

5.4.2 A background correction is performed during the measurement run by monitoring the ^{230}Th , ^{232}Th , ^{234}U , ^{235}U , ^{236}U and ^{238}U signals of the 2 % nitric acid wash solution. The background correction is measured prior to the mass calibration and is re-measured before each subsequent sample.

6. Apparatus

6.1 Mass Spectrometer:

6.1.1 The mass spectrometer has an inductively coupled plasma (ICP) source and a double focussing electrostatic/magnetic sector analyser equipped with twelve Faraday detectors and two ion counters.⁶

6.1.2 The mass spectrometer is fully computer controlled using customised software and is equipped with an auto-sampler.

6.2 Polypropylene Sample Tubes, Screw-Cap, 50 mL.

6.3 Polypropylene Sample Tubes, Screw-Cap, 10 mL.

6.4 Fixed-Volume Pipette, and Tips to Suit, 0.01 mL.

6.5 Fixed-Volume Pipette, and Tips to Suit, 1 mL.

6.6 Variable-Volume Dispenser, 1 to 5 mL, fitted to a 1-L glass storage bottle.

7. Reagents

7.1 Purity of Water—Demineralised water as defined by Type I of Specification D 1193.

7.2 Nitric Acid Solution, high purity, various concentrations. Necessary dilutions can be inferred from the stated acid strength (for example, 2 % nitric acid solution requires a $\times 50$ dilution of the concentrated acid).

7.3 Reference Solution containing 140 ng/mL of $^{230}\text{Th}^7$ and 7 $\mu\text{g/mL}$ of ^{232}Th .

7.4 Uranium Isotopic Reference Materials (see Section 9 for details).

8. Internal References

8.1 Requirements—As described in Section 3, thorium is used as an internal reference to be added to the UIRMs and uranium samples. The internal reference must contain at least one pair of isotopes in a fixed ratio. It is not necessary for this isotopic ratio to be accurately known as the same reference is added to both the calibration material and the subsequent samples. Minor fluctuations in instrument calibration (mass bias) are reflected in the measured ratio of the internal reference in the samples. Subsequent correction of the mass bias parameter using the measured ratio of the internal reference provides the necessary adjustment to the mass bias factor prior to result calculation.

8.2 Thorium—The $^{230}\text{Th} / ^{232}\text{Th}$ ratio is monitored. The thorium solution is prepared by adding ^{230}Th to a calculated quantity of ^{232}Th from a 1000 $\mu\text{g/mL}$ stock standard which is then diluted with 2 % nitric acid. The quantity of ^{230}Th added is such that the final diluted reference should contain 14 ng/mL of ^{230}Th and 0.7 $\mu\text{g/mL}$ of ^{232}Th . This solution is stored in a 1 L bottle fitted with an adjustable dispenser set to 1.0 mL. A 1.0 mL aliquot of thorium solution is dispensed into 2.0 mL of sample solution containing 1.5 $\mu\text{g/mL}$ of uranium. The resultant concentration of ^{230}Th is 4.7 ng/mL and that of ^{232}Th is 0.23 $\mu\text{g/mL}$.

NOTE 1—The quantity of ^{230}Th is minimised to comply with local disposal safety regulations.

NOTE 2—The decay of ^{234}U to ^{230}Th may present a problem with the analysis of aged-uranic solutions. This should not present a problem with uranium hexafluoride samples that are taken in the gaseous phase, as gaseous UF_6 separates from any non-volatile thorium compounds.

9. Uranium Isotopic Reference Materials (UIRMs)

9.1 UIRMs are used to calibrate the instrument for multi-collection measurements. The Institute for Reference Materials and Measurements⁸ (IRMM) reference material IRMM-024 is used for enriched samples and the New Brunswick Laboratory⁹ Certified Reference Material CRM U005-A is used for samples of natural or depleted ^{235}U abundances. The UIRMs are prepared as uranyl nitrate solutions containing 1.5 $\mu\text{g/mL}$ of

⁷ ^{230}Th was supplied by AEA Technology, Harwell, Didcot, Oxfordshire, UK.

⁸ Institute for Reference Materials and Measurement, Retieseweg, B-2440 Geel, Belgium.

⁹ New Brunswick Laboratory, D-350, 9800 South Cass Avenue, Argonne, Illinois 60439.

⁵ This correction can only be applied to samples which do not contain ^{239}Pu .

⁶ The Nu Instruments “Nu Plasma” is such a mass spectrometer.