



Designation: C 1477 – 06

# Standard Test Method for Isotopic Abundance Analysis of Uranium Hexafluoride and Uranyl Nitrate Solutions by Multi-Collector, Inductively Coupled Plasma-Mass Spectrometry<sup>1</sup>

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 approval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the isotopic abundance analysis of  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$  and  $^{238}\text{U}$  in samples of hydrolysed uranium hexafluoride ( $\text{UF}_6$ ) by inductively coupled plasma source, multi-collector, mass spectrometry (ICP-MC-MS). The method applies to material with  $^{235}\text{U}$  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:*<sup>2</sup>

**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 %  $^{235}\text{U}$

**D 1193** Specification for Reagent Water

2.2 *Other Document:*

**STP 1344** Applications of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to Radionuclide Determinations<sup>3</sup>

## 3. Summary of Test Method

3.1 Samples are received either in the form of uranium hexafluoride ( $\text{UF}_6$ ) or aqueous uranic solution. The  $\text{UF}_6$

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 measurements<sup>4</sup> 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  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$  and  $^{238}\text{U}$  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

<sup>1</sup> 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.

Current edition approved July 1, 2006. Published August 2006. Originally approved in 2000. Last previous edition approved in 2000 as C 1477 – 00.

<sup>2</sup> 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.

<sup>3</sup> Available from ASTM Headquarters.

<sup>4</sup> 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  $^{238}\text{U}$  ion beam. The method is limited to the measurement of  $^{235}\text{U}$  isotopic abundances below 6 %, consequently interference effects with the  $^{234}\text{U}$  and  $^{236}\text{U}$  ion beams are negligible.

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

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

where:

- $^{236}\text{U}_c$  = the corrected  $^{236}\text{U}$  signal,
- $^{236}\text{U}_m$  = the measured  $^{236}\text{U}$  signal,
- $^{235}\text{U}_m$  = the measured  $^{235}\text{U}$  signal,
- $^{238}\text{UH}$  = the measured  $^{238}\text{U}$  hydride signal, and
- $^{238}\text{U}$  = the measured  $^{238}\text{U}$  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  $^{235}\text{U}$  are measured after enriched samples. Memory effects can be readily assessed by aspirating a 2 % nitric acid solution and measuring the background  $^{238}\text{U}$  ion beam. The sample introduction system should be periodically disassembled and cleaned, to minimise the background  $^{238}\text{U}$  ion beam.

**5.4.2 A background correction is performed during the measurement** run by monitoring the  $^{230}\text{Th}$ ,  $^{232}\text{Th}$ ,  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$  and  $^{238}\text{U}$  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.<sup>6</sup>

**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 ×50 dilution of the concentrated acid).

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

**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  $^{230}\text{Th}$  to a calculated quantity of  $^{232}\text{Th}$  from a 1000 µg/mL stock standard which is then diluted with 2 % nitric acid. The quantity of  $^{230}\text{Th}$  added is such that the final diluted reference should contain 14 ng/mL of  $^{230}\text{Th}$  and 0.7 µg/mL of  $^{232}\text{Th}$ . 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 µg/mL of uranium. The resultant concentration of  $^{230}\text{Th}$  is 4.7 ng/mL and that of  $^{232}\text{Th}$  is 0.23 µg/mL.

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

**NOTE 2**—The decay of  $^{234}\text{U}$  to  $^{230}\text{Th}$  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  $\text{UF}_6$  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 Measurements<sup>8</sup> (IRMM) reference material IRMM-024 is used for enriched samples and the New Brunswick Laboratory<sup>9</sup> Certified Reference Material CRM U005-A is used for samples of natural or depleted  $^{235}\text{U}$  abundances. The UIRMs are prepared as uranyl nitrate solutions containing 1.5 µg/mL of

<sup>7</sup>  $^{230}\text{Th}$  was supplied by AEA Technology, Harwell, Didcot, Oxfordshire, UK.

<sup>8</sup> Institute for Reference Materials and Measurement, Retieseweg, B-2440 Geel, Belgium.

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

<sup>5</sup> This correction can only be applied to samples which do not contain  $^{239}\text{Pu}$ .

<sup>6</sup> The Nu Instruments “Nu Plasma” is such a mass spectrometer.

**TABLE 1**

Collector	L6	L5	L4	IC1	L3	IC0	L2	L1	Ax	H1	H2	H3	H4	H5
Separation	2U	1U	1U	1U	1U	1U	1U	1U	1U	1U	1U	1U	2U	2U
Ion Beam	<sup>230</sup> Th	<sup>232</sup> Th	–	<sup>234</sup> U	<sup>235</sup> U	<sup>236</sup> U	–	<sup>238</sup> U	<sup>238</sup> UH	–	–	–	–	–

where:

- Ax = Axial Faraday collector,  
 L and H = low and high mass Faraday collectors (with respect to the Axial collector),  
 IC = ion counters, and  
 U = unit mass dispersion for uranium isotopes.

uranium and the same quantity of internal reference as described in Section 8 (which reduces the uranium content down to 1 µg/mL).

## 10. Instrument Setup

10.1 Many ICP-MC-MS designs require the Faraday collectors to be mechanically positioned to align with the ion beams. The instrument used for this work adopts a different approach, where a “zoom lens,” which alters the dispersion of the instrument, is used to focus the beams onto a fixed array of detectors. The zoom lens settings were adjusted under software control to achieve the configuration shown in Table 1.

10.2 To minimise measurement uncertainty all minor isotope (<sup>234</sup>U and <sup>236</sup>U) measurements are on the ion counters. The analyser magnet must be calibrated across the mass range 230 to 238, however the instrument manufacturer recommends calibrating across the mass range 80 to 238 (achieved using the beam from the Argon dimer). The magnet must be re-calibrated if the calibration drifts by more than the 0.2 atomic mass units (at uranium).

## 11. Sample and Blank Preparation

11.1 *Samples Received as UF<sub>6</sub>:*

11.1.1 Transfer between 0.2 g and 0.25 g of UF<sub>6</sub> gas into a glass sample tube cooled by liquid nitrogen.<sup>10</sup>

11.1.2 Working in a fumecupboard, hydrolyse the UF<sub>6</sub> using demineralised water from a wash bottle. The operator should keep the sample tube pointed away at all times since some toxic HF gas is produced.

11.1.3 Pour the hydrolysed UF<sub>6</sub> into a 50 mL screw-cap polypropylene tube and dilute so that the final concentration of UF<sub>6</sub> is 5 mg/mL. For example, if the weight of UF<sub>6</sub> transferred is 0.2 g, dilute to 40 mL with demineralised water.

11.1.4 Using a fixed volume pipette, take a 0.01 mL aliquot of solution and transfer to a clean 50 mL screw-cap polypropylene tube. Dilute to a volume of 23 mL using a 2 % nitric acid solution. The resulting solution contains 2.2 µg/mL of UF<sub>6</sub> which is equivalent to 1.5 µg/mL of uranium.

11.1.5 Pour 2 mL of solution into a 10 mL polypropylene tube.

11.1.6 Add 1 mL of the 0.7 µg/mL thorium internal reference and thoroughly mix the solution.

11.1.7 Place the tube in the designated rack position in accordance with Section 13.

11.2 *Samples Received As Aqueous Uranyl Nitrate Solutions Of Known Uranic Concentration:*

11.2.1 Dilute the sample with a 2 % nitric acid solution so that the uranium concentration is 1.5 µg/mL

11.2.2 Proceed in accordance with 11.1.5-11.1.7.

## 12. Calibration

12.1 Calibration of the mass spectrometer using a UIRM produces a mass bias factor. The mass bias factor for the UIRM in question is defined in Eq 2.

$$\text{Mass Bias Factor} = \left( \frac{\frac{^{235}\text{U}}{^{238}\text{U}} \text{ quoted}}{\frac{^{235}\text{U}}{^{238}\text{U}} \text{ measured}} \right)^{\frac{1}{\Delta m}} \quad (2)$$

where

$\Delta m$  = ratio mass difference (that is, 3).

12.2 The mass bias factor is applied to the measured isotope ratio of the internal reference to produce a mass bias parameter. This parameter is exported to all subsequent sample measurements to correct for mass bias effects. Details of how the mass bias correction is applied can be found in Appendix X1. As stated in Section 9, IRMM-024 is used to calibrate for mass bias for samples enriched in <sup>235</sup>U and NBL CRM 005-A is used to calibrate for mass bias for natural samples or samples depleted in <sup>235</sup>U. Stock solutions of both these uranium reference materials (containing 1.5 µg/mL of uranium in a 2 % nitric acid solution) are held in the laboratory. Mass bias calibration is an integral part of each sample run (that is, no separate calibration procedure is necessary).

## 13. Operational Procedure

13.1 The instrument software is used to assign sample names, measurement procedures and auto-sampler rack positions to UIRMs and samples. Two sample racks are used. The first rack contains the UIRM IRMM-024 and those samples that are enriched in <sup>235</sup>U. The second rack contains the UIRM NBL CRM U005-A and those samples at natural level or depleted in <sup>235</sup>U. The plasma is then struck and after a period of 60 minutes (to allow the system to thermally stabilise), a tuning solution of UIRM IRMM-024 is aspirated and the ion beams are optimised. The automatic measurement sequence is then initiated under computer control.

## 14. Calculation

14.1 The measurement software produces three mass bias corrected ratios as follows:

<sup>10</sup> Subsampling of UF<sub>6</sub> is detailed in ASTM Standard Test Method C 761.