Designation: C1477 – 08 (Reapproved 2014)

Standard Test Method for Isotopic Abundance Analysis of Uranium Hexafluoride and Uranyl Nitrate Solutions by Multi-Collector, Inductively Coupled Plasma-Mass Spectrometry[1]

This standard is issued under the fixed designation C1477; 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 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, multicollector, 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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 appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride

C787 Specification for Uranium Hexafluoride for Enrichment

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

D1193 Specification for Reagent Water

2.2 *Other Document:*

STP 1344 Applications of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to Radionuclide Determinations[3]

3. Terminology

3.1 *Acronyms:*

3.1.1 *amu*—atomic mass unit

3.1.2 *ICP-MC-MS*—Inductively Coupled Plasma Multi-Collector Mass Spectrometer

3.1.3 *ICP-MS*—Inductively Coupled Plasma Mass Spectrometer

3.1.4 *UIRM*—Uranium Isotopic Reference Material

4. Summary of Test Method

4.1 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. If required, an internal reference of thorium isotopes can be subsequently added to each diluted sample. As detailed in Section 8, isotope pairs of elements other than thorium could be used for an internal reference.

4.2 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.

4.3 Uranium Isotopic Reference Materials (UIRMs) are used to calibrate the instrument. Each UIRM is prepared in aqueous solution (acidified with nitric acid) and if required spiked with the same internal reference as the samples. This calibration solution is measured and a mass bias parameter is

[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.

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calculated that is stored and subsequently imported into each of the sample measurements[4] to correct the measured uranium isotopic ratios.

4.4 Measurements of isotopic ratios in the calibration solution and the subsequent samples are initiated by customised software. The mass bias factor is computed from the measured isotopic ratios in the calibration solution. This parameter is then exported to correct the measured isotopic ratios of the samples for mass bias. The corrected isotopic abundances are expressed as % atomic and are converted to % mass prior to reporting. Details of the mass bias correction are presented in Appendix X1.

5. Significance and Use

5.1 The test method is capable of measuring uranium isotopic abundances of ^{234}U, ^{235}U, ^{236}U and ^{238}U as required by Specifications C787 and C996.

6. Interferences

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

6.2 *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.

6.3 *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 can be 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 ion beam:[5]

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

where:

$^{236}U_c$ = the corrected ^{236}U ion beam,
$^{236}U_m$ = the measured ^{236}U ion beam,
^{235}U = the measured ^{235}U ion beam,
^{238}UH = the measured ^{238}U hydride ion beam, and
^{238}U = the measured ^{238}U ion beam.

6.4 *Memory Effects:*

6.4.1 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 0.3 M 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.

6.4.2 A background correction is performed during the measurement run by monitoring the analyte signals of the 0.3 M nitric acid rinse solution. The background correction is measured prior to the mass calibration and is re-measured before each subsequent sample.

7. Apparatus

7.1 *Mass Spectrometer:*

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

7.1.2 The mass spectrometer is fully computer controlled using customised software and is equipped with an autosampler.

7.2 *Polypropylene Sample Tubes, Screw-Cap,* 50 mL.

7.3 *Polypropylene Sample Tubes, Screw-Cap,* 10 mL.

7.4 *Positive Displacement Pipette, and Tips to Suit,* 0.01 mL.

7.5 *Positive Displacement Pipette, and Tips to Suit,* 1 mL.

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

8. Reagents and Materials

8.1 *Purity of Water*—Demineralised water as defined by Type I of Specification D1193.

8.2 *High Purity 0.3 M Nitric Acid Solution* (~x 50 dilution of the concentrated acid).

8.3 *Uranium Isotopic Reference Material (UIRMs)*—UIRMs are used to calibrate the instrument for multi-collection measurements. The Institute for Reference Materials and Measurements[7] (IRMM) reference material IRMM-024 is used for enriched samples and the New Brunswick Laboratory[8] 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 0.4 µg/mL of uranium.

8.4 *Optional—Internal Reference Solution* containing ^{230}Th and ^{232}Th isotopes (or isotopes of another suitable element).

8.4.1 It has been found that the stability of the modern ICP-MC-MS can be such that it is not necessary to use an internal reference to monitor variations in mass bias. The data presented in this paper was obtained without the use of an

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

[5] This correction can only be applied to samples which do not contain ^{239}Pu (or any other nuclides with mass 239).

[6] The data presented in the paper was obtained using a 'Nu Plasma' mass spectrometer, manufactured by Nu Instruments (Nu Instruments Ltd, Unit 74 Clywedog Road South, Wrexham LL13 9XS, North Wales, UK). The Nu Plasma was supplied with the (optional) BIG80 vacuum pumping system to achieve optimum sensitivity.

[7] Institute for Reference Materials and Measurement, Retieseweg, B-2440 Geel, Belgium.

[8] New Brunswick Laboratory, D-350, 9800 South Cass Avenue, Argonne, Illinois 60439.