



Designation: C 1413 – 99

# Standard Test Method for Isotopic Analysis of Hydrolyzed Uranium Hexafluoride and Uranyl Nitrate Solutions by Thermal Ionization Mass Spectrometry<sup>1</sup>

This standard is issued under the fixed designation C 1413; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This method applies to the determination of isotopic composition in hydrolyzed nuclear grade uranium hexafluoride. It covers isotopic abundance of  $^{235}\text{U}$  between 0.1 and 5.0 % mass fraction, abundance of  $^{234}\text{U}$  between 0.0055 and 0.05 % mass fraction, and abundance of  $^{236}\text{U}$  between 0.0003 and 0.5 % mass fraction. This test method may be applicable to other isotopic abundance providing that corresponding standards are available.

1.2 This test method can apply to uranyl nitrate solutions. This can be achieved either by transforming the uranyl nitrate solution to a uranyl fluoride solution prior to the deposition on the filaments or directly by depositing the uranyl nitrate solution on the filaments. In the latter case, a calibration with uranyl nitrate standards must be performed.

1.3 This test method can also apply to other nuclear grade matrices (for example, uranium oxides) by providing a chemical transformation to uranyl fluoride or uranyl nitrate solution.

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.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

- C 696 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets<sup>2</sup>
- C 753 Specification for Nuclear Grade, Sinterable Uranium Dioxide Powder<sup>2</sup>
- C 761 Test Methods for Chemical, Mass Spectrometric,

Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride<sup>2</sup>

C 776 Specification for Sintered Uranium Dioxide Pellets<sup>2</sup>

C 787 Specification for Uranium Hexafluoride for Enrichment<sup>2</sup>

C 788 Specification for Nuclear-Grade Uranyl Nitrate Solution<sup>2</sup>

C 996 Specification for Uranium Hexafluoride Enriched to Less Than 5 %  $^{235}\text{U}$ <sup>2</sup>

C 1334 Specification for Uranium Oxides with a  $^{235}\text{U}$  Content Less Than 5 % for Dissolution Prior to Conversion to Nuclear-Grade Uranium Dioxide<sup>2</sup>

C 1346 Practice for Dissolution of  $\text{UF}_6$  from P-10 Tubes<sup>2</sup>

C 1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis<sup>2</sup>

C 1348 Specification for Blended Uranium Oxides with a  $^{235}\text{U}$  Content of Less Than 5 % for Direct Hydrogen Reduction to Nuclear-Grade Uranium Dioxide<sup>2</sup>

## 3. Summary of Test Method

3.1 After dilution of uranyl fluoride or uranyl nitrate solution, approximately 2  $\mu\text{g}$  of uranium are deposited on a rhenium filament. Analysis is performed in a thermal ionization mass spectrometer (TIMS), uranium is vaporized and ionized through electrons emitted by a second filament; ions are extracted by an electric field, separated by a magnetic field, and collected by four collectors on mass 234, 235, 236, 238. The collectors are either faraday cups or electron multipliers collectors (ion counting).

3.2 Evaporation sequence and ion counting time are adjusted with the analysis of standard solutions of certified isotopic content. Nitrate and fluoride solutions lead to two different calibrations.

## 4. Significance and Use

4.1 Uranium hexafluoride used to produce nuclear fuel must meet certain criteria for its isotopic composition as described in Specifications C 787 and C 996.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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<sup>2</sup> Annual Book of ASTM Standards, Vol 12.01.

## 5. Interferences

5.1 This test method only applies to nuclear grade uranium matrices (as defined in Specification C 753, C 776, C 787, C 788, C 1334, or C 1348). Large amount of impurities, which are found, for example, in uranium ore concentrates, may bias results. A purification step may be necessary, as described in Specification C 696.

5.2 The type of acid used (HF or HNO<sub>3</sub>) and its concentration will strongly influence the obtained isotopic results (see 9.2).

## 6. Apparatus

6.1 *Thermal Ionization Mass Spectrometer (TIMS)*—Configured with four detectors.<sup>3</sup>

6.1.1 This test method requires a mass spectrometer with a resolution greater than 400 (full width at 1 % of peak height) and an abundance sensitivity of less than 10<sup>-5</sup> (contribution of mass 238 on the mass 237). A typical instrument would have 230 mm radius of curvature, single or double focussing, and single or multiple filament design. The pressure in the ionization chamber should be below 3 × 10<sup>-6</sup> torr (typically 10<sup>-7</sup> torr).

6.2 *Preconditioning Unit for the TIMS*—To dry filament after deposition of uranyl solution.

6.3 *Rhenium Filament Loading Assembly for the TIMS*. In this test method, a double filament set up is used.

6.4 *Pipets*—Automatic or equivalent, 1, 20, 50, and 100 µL.

6.5 *Pipets Tips*—In accordance with 6.4.

6.6 *Liquid Dispenser*—2.5 mL.

6.7 *Disposable Polypropylene Vials*.

## 7. Reagents and Materials

7.1 *Purity of Materials*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specification of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>4</sup> Other grades may be used provided it is first ascertained that the reagent is of sufficiently high priority to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Demineralized or distilled water is found acceptable for this uranium isotopic analysis.

7.3 *High Purity Rhenium Filaments (> 99.95 %)*, with geometrical characteristics in accordance with the TIMS manufacturer's recommendations (typically thickness is 0.04 mm and width is 0.70 mm). Some equipment may accept tungsten filaments.

7.4 *Isotopic Uranium Standards*

7.4.1 UF<sub>6</sub> of certified <sup>236</sup>U, <sup>235</sup>U isotopic composition, such as COG 006, 008, 009, 010, 013, 014, 015.<sup>5</sup>

7.4.2 U<sub>3</sub>O<sub>8</sub> of certified isotopic composition, such as NBL CRM U-010, U-020, U-030, U-050, CEA 014.<sup>6</sup>

7.4.3 U<sub>3</sub>O<sub>8</sub> from reprocessed origin and of certified <sup>236</sup>U composition, such as MIR 1.<sup>6</sup>

7.5 *Hydrofluoric Acid (0.05 M)*—Dilute 173 µL of HF solution (sp gr 1.18, 28.9 M) to 100 mL with water.

7.6 *Nitric acid (0.1 M)*—Dilute 0.6 mL of concentrated HNO<sub>3</sub>(sp gr 1.42, 16 M) to 100 mL with water.

## 8. Preparation of Apparatus

8.1 Prepare the thermal ionization mass spectrometer in accordance with the manufacturer's recommendations. A verification of collector yield and an optimisation of the ion beam may be necessary on a daily basis. This can be achieved by heating the ionizing filament, locating the <sup>187</sup>Re peak and focusing for maximum intensity. The <sup>187</sup>Re signal is normally above 0.1 to 0.2 × 10<sup>-11</sup> A.

8.2 A verification of mass calibration is usually performed on a weekly basis in order to optimize the value for the magnetic field.

## 9. Calibration and Standardization

9.1 Because of mass segregation during the evaporation of uranium, it is necessary to adjust the ion acquisition time program with the analysis of uranium standards. The number of standards and the range covered will depend on the instrument used, the evaporation sequence, and the accuracy which is required.

9.1.1 For the analysis of <sup>235</sup>U in the 0.1 to 5.0 mass % range and of <sup>234</sup>U in the 0.0055 to 0.05 mass % range, four to seven standards should be used (see Table 1). For analysis of <sup>236</sup>U in the 0.0003 to 0.5 mass % range, only two standards were used.

9.2 *Preparation of the standards*—Separate calibrations are required for uranyl fluoride solutions and uranyl nitrate solutions.

### 9.2.1 Uranyl Fluoride Calibration

9.2.1.1 UF<sub>6</sub> Standards—General principles for hydrolysis of UF<sub>6</sub> are described in Test Methods C 761 and Practice C 1346. Hydrolysis should be done in pure water (no HNO<sub>3</sub> added). Final concentration is for example 266 g uranium per litre (20 % mass U).

NOTE 1—Other concentrations may be used (for example, 10 % mass U), provided that volumes in 10.2 are adapted to deposit the same uranium amount on the rhenium filament.

NOTE 2—2 µg of uranium are deposited on the filaments. In case of other filament geometries (see 7.3), other uranium amounts may be more adapted (up to 10 µg U).

9.2.1.2 In a polypropylene vial, pour 2.5 mL of water and add 20 µL of solution prepared in 9.2.1.1. Mix the vial content by inverting vigorously to obtain a solution containing approximately 2 g/L uranium.

9.2.1.3 Other Standards—Uranium standard solutions, if not from hydrolyzed UF<sub>6</sub> origin, must be transformed to a pure

<sup>3</sup> A reduced number of detectors may be used which will correspond to a reduced number of isotopes analyzed. For single collector instruments, refer to Specification C 696.

<sup>4</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

<sup>5</sup> COGEMA/Service Laboratoire, BP 16, 26701 Pierrelatte Cedex, France.

<sup>6</sup> CEA/CETAMA, BP 171, 30 207 Bagnols sur Cèze, France.