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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Isotopic Analysis of Hydrolyzed Uranium Hexafluoride and Uranyl Nitrate Solutions by Thermal Ionization Mass Spectrometry[1]

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}U between 0.1 and 5.0 % mass fraction, abundance of ^{234}U between 0.0055 and 0.05 % mass fraction, and abundance of ^{236}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[2]
C 753 Specification for Nuclear Grade, Sinterable Uranium Dioxide Powder[2]
C 761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride[2]
C 776 Specification for Sintered Uranium Dioxide Pellets[2]
C 787 Specification for Uranium Hexafluoride for Enrichment[2]
C 788 Specification for Nuclear–Grade Uranyl Nitrate Solution[2]
C 996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % ^{235}U[2]
C 1334 Specification for Uranium Oxides with a ^{235}U Content Less Than 5 % for Dissolution Prior to Conversion to Nuclear–Grade Uranium Dioxide[2]
C 1346 Practice for Dissolution of UF_6 from P–10 Tubes[2]
C 1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis[2]
C 1348 Specification for Blended Uranium Oxides with a ^{235}U Content of Less Than 5 % for Direct Hydrogen Reduction to Nuclear–Grade Uranium Dioxide[2]

3. Summary of Test Method

3.1 After dilution of uranyl fluoride or uranyl nitrate solution, approximatively 2 µg 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.

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

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[1] 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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[2] *Annual Book of ASTM Standards*, Vol 12.01.

results. A purification step may be necessary, as described in Specification C 696.

5.2 The type of acid used (HF or HNO_3) 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.[3]

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^{-5} (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^{-6} torr (typically 10^{-7} 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.[4] 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_6 of certified ^{236}U, ^{235}U isotopic composition, such as COG 006, 008, 009, 010, 013, 014, 015.[5]

7.4.2 U_3O_8 of certified isotopic composition, such as NBL CRM U-010, U-020, U-030, U-050, CEA 014.[6]

7.4.3 U_3O_8 from reprocessed origin and of certified ^{236}U composition, such as MIR 1.[6]

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_3(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 ^{187}Re peak and focusing for maximum intensity. The ^{187}Re signal is normally above 0.1 to 0.2×10^{-11} 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 ^{235}U in the 0.1 to 5.0 mass % range and of ^{234}U in the 0.0055 to 0.05 mass % range, four to seven standards should be used (see Table 1). For analysis of ^{236}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_6 Standards—General principles for hydrolysis of UF_6 are described in Test Methods C 761 and Practice C 1346. Hydrolysis should be done in pure water (no HNO_3 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_6 origin, must be transformed to a pure uranyl fluoride solution prior to the analysis. Dissolution of the uranic material can be performed in accordance with Practice C 1347. The solution is then transferred in a platinum crucible to be carefully dried on a heated plate to be transformed to UO_3. The residue is then dissolved with diluted HF (0.05 M) to obtain an uranyl fluoride solution with an uranium concentration of 2 g/L and a fluoride concentration 1 g/L.

9.2.2 Uranyl Nitrate Calibration

9.2.2.1 U_3O_8 Standards—The standards are dissolved in accordance with Practice C 1347. The solutions are evaporated

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[3] 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.

[4] *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.

[5] COGEMA/Service Laboratoire, BP 16, 26701 Pierrelatte Cedex, France.

[6] CEA/CETAMA, BP 171, 30 207 Bagnols sur Cèze, France.

TABLE 1 Mass Ratios to Total Uranium

$^{235}U/U$ (mass fraction, %)

Reference	Certified Values[A]	Summary Statistics of Measured Values		
	$\bar{x} \pm s_{\bar{x}}$	$\bar{x}$	s	n
COG 006	0.7112 ± 0.0002	0.7110	0.0004	5
COG 008	0.8676 ± 0.0008	0.8670	0.0004	20
NBL CRM U–010	0.9911 ± 0.0005	0.9918	0.0009	50
COG 009	1.0705 ± 0.0010	1.0696	0.0005	5
COG 010	1.3006 ± 0.0012	1.2995	0.0004	10
NBL U–020	2.0130 ± 0.001	2.0131	0.0009	18
COG 013	2.5959 ± 0.0026	2.5969	0.0005	10
NBL U–030	3.0032 ± 0.0008	3.0042	0.0014	26
COG 014	3.3678 ± 0.0034	3.3663	0.0006	20
CEA 014	3.3678 ± 0.0034	3.3699	0.0010	84
COG 015	4.2960 ± 0.0042	4.2940	0.0011	10
NBL U–050	4.9490 ± 0.0025	4.9449	0.0025	10

$^{234}U/U$ (mass fraction, %)

Reference	Certified Values[A]	Summary Statistics of Measured Values		
	$\bar{x} \pm s_{\bar{x}}$	$\bar{x}$	s	n
NBL CRM U–010	0.0053 ± 0.00002	0.0054	0.0001	50
COG 006	0.0054 ± 0.0001	0.0052	0.0001	5
COG 008	0.0069 ± 0.0001	0.0067	0.0001	20
COG 010	0.0070 ± 0.0001	0.0069	0.0001	10
COG 009	0.0088 ± 0.0001	0.0087	0.0001	5
NBL U–020	0.0123 ± 0.00005	0.0123	0.0001	18
COG 013	0.0224 ± 0.0002	0.0223	0.0001	10
NBL U–050	0.0275 ± 0.00005	0.0273	0.0001	9
CEA 014	0.0288 ± 0.0006	0.0290	0.0001	84
COG 014	0.0325 ± 0.0003	0.0327	0.0002	20
COG 015	0.0378 ± 0.0004	0.0382	0.0001	10

$^{236}U/U$ (mass fraction in %)

Reference	Certified Values[A]	Summary Statistics of Measured Values		
	$\bar{x} \pm s_{\bar{x}}$	$\bar{x}$	s	n
COG 014	0.0006 ± 0.0001	0.0010	0.0001	20
CEA 014	0.0051 ± 0.0001	0.0052	0.0001	84
NBL U–020	0.0164 ± 0.00005	0.0164	0.0001	18
NBL CRM U–010	0.00675 ± 0.00003	0.0070	0.0001	50
NBL U–050	0.0476 ± 0.0002	0.0475	0.0001	9
MIR 1	0.4002 ± 0.0006	0.4006	0.0001	30

[A] Certified values are given with the interval confidence of 1 sigma.

to dryness and the residue is dissolved in 0.1 M HNO_3 to give a solution containing 2 g/L uranium.

9.2.2.2 Hydrolyzed UF_6 Standards—Uranyl fluoride solutions with an uranium concentration of 2 g/L are evaporated to dryness and dissolved in 0.1 M HNO_3 to give an uranyl nitrate solution containing 2 g/L uranium.

9.3 Analysis of the uranyl fluoride or uranyl nitrate standard solutions is performed in accordance with 10.2-10.4.

9.3.1 Calibrate the TIMS in accordance with the manufacturer's recommendations to achieve the user's performance and quality assurance criteria.

9.3.2 The $^{235}U/^{238}U$ mass discrimination factor, B, is calculated as follows:

$$B = (1/\Delta M)\,[(\bar{R}/R_s) - 1] \qquad (1)$$

where:

B = mass discrimination factor,
ΔM = mass difference = (238-235) = 3,
R_s = certified value of $^{235}U/^{238}U$ of standard, and
$\bar{R}$ = average measured value of $^{235}U/^{238}U$ for n different analyses.

B should be below 2×10^{-4}.

9.4 For each batch of routine samples to be analyzed, a verification of the calibration of the acquisition program is recommended. This is done by inserting in the batch a standard with isotopic composition close to that of the samples.

10. Procedure

10.1 Prepare the solution to be analyzed in accordance with 9.2 to obtain either a fluoride or nitrate solution with an uranium concentration of approximately 2 g/L.

10.2 Load 1 µL of solution 10.1 on the filament. Dry and bake the filament with the TIMS preconditioning unit. The heating sequence (electrical current, time applied) must be performed in accordance with the manufacturer's recommendation or user's experience.

NOTE 3—For uranyl fluoride solutions, temperatures significantly greater than 600°C must be avoided. The temperature of the filament during the final stages of sample mounting is a critical parameter and can produce a significant bias between runs if not carefully controlled.

10.3 Insert the filaments assembly into the mass spectrometer and obtain a pressure of less than 3×10^{-6} torr.

10.4 Analysis in accordance with the user's standard operating procedure for TIMS analysis.

NOTE 4—The heating pattern for the filaments and the mass spectrometer ratio measurements may slightly vary depending on the instrument.

10.4.1 Heat the ionization filament to 5 A.

10.4.2 Heat the evaporation filament to 1 A.

10.4.3 Heat the ionization filament until a signal of 0.08×10^{-11} A is obtained, locate the ^{187}Re peak and adjust the focus for maximum intensity. Heat the ionization filament until a signal of 0.2×10^{-11} A is obtained on the ^{187}Re peak.

10.4.4 Heat the evaporation filament until a signal of 10^{-11} A is obtained on the ^{238}U peak, focus for maximum intensity. Heat the evaporation filament until a signal of 7×10^{-11} A is obtained.

10.4.5 Start the ratio measurement (this should correspond to approximately 30 minutes after step 10.4.1).

10.4.5.1 Determine the baseline at mass 233.5.

10.4.5.2 During a 32–second scan, acquire the ^{234}U, ^{235}U, ^{236}U, ^{238}U signal on the four collectors. Calculate the ratio $^{234}U/^{238}U$, $^{235}U/^{238}U$, $^{236}U/^{238}U$, corrected from baseline.

10.4.5.3 Repeat step 10.4.5.2 ten times. Calculate the average ratio together with the estimated standard deviation. Perform a Dixon test to eliminate anomalous points.

10.4.5.4 Repeat steps 10.4.5.1-10.4.5.3 so that the total acquisition time corresponds to that obtained during the calibration (see 9.1).

11. Calculation

11.1 Calculate the average isotope ratio obtained from section 10.4.5.4.

11.2 The final isotopic ratio may be corrected from mass discrimination as follows:

$$R' = [R/(1 + \Delta M\, B)] \qquad (2)$$

where:

R' = final isotopic ratio,

R = average raw ratio,
ΔM = mass difference, and
B = mass discrimination factor, obtained in 9.3.

This correction is not always necessary, depending on B.

11.3 Calculate the atom and mass percent for all the isotopes as follows:

$$A_i = \frac{R_{i,\,238} \times 100}{1 + \sum_{j=234}^{236} \mathrm{R}_{j,\,238}} \tag{3}$$

$$W_i = \frac{A_i\ M_i \times 100}{\sum_{j=134}^{238} A_j\ M_j} \tag{4}$$

where:
A_i = atom percent of isotope i,
W_i = mass percent of isotope i,
$R_{i,\,238}$ = isotopic ratio of isotope i to 238 obtained in 11.2, and
M_i = nuclidic mass of isotope i.

12. Precision and Bias

12.1 Isotopic uranium standards have been analysed over a four year period in three laboratories. Results, obtained for ^{235}U, ^{234}U, ^{236}U mass ratios to total uranium, are listed in Table 1. For each standard, the average measured value, $\bar{x}$, is given together with the estimated standard deviation, *s*, obtained for n experiments. COG standards were analysed with the fluoride calibration. NBL and MIR standards were analysed with the nitrate calibration.

12.2 *Precision*—The estimated standard deviation, *s*, for ^{235}U is between 0.0004 and 0.0011 %, depending on the ^{235}U level. The estimated standard deviation for ^{234}U and ^{236}U are usually below 0.0002 %.

12.3 *Bias*—^{235}U and ^{234}U, all average measured values are within the certified interval, which depend on the isotope level. For ^{236}U, a slight bias (0.0004 %) is found for low ^{236}U concentration.

13. Keywords

13.1 isotopes; thermal ionization mass spectrometry; uranium hexafluoride; uranyl nitrate solutions