ASTM INTERNATIONAL

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Standard Test Method for
Analysis of Isotopic Composition of Uranium in Nuclear-Grade Fuel Material by Quadrupole Inductively Coupled Plasma-Mass Spectrometry[1]

This standard is issued under the fixed designation C 1474; 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 is applicable to the determination of the isotopic composition of uranium (U) in nuclear-grade fuel material. The following isotopic weight percentages are determined using a quadrupole inductively coupled plasma-mass spectrometer (Q-ICP-MS): ^{233}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U. The analysis can be performed on various material matrices after acid dissolution and sample dilution into water or dilute nitric (HNO_3) acid. These materials include: fuel product, uranium oxide, uranium oxide alloys, uranyl nitrate (UNH) crystals, and solutions. The sample preparation discussed in this test method focuses on fuel product material but may be used for uranium oxide or a uranium oxide alloy. Other preparation techniques may be used and some references are given. Purification of the uranium by anion-exchange extraction is not required for this test method, as it is required by other test methods such as radiochemistry and thermal ionization mass spectroscopy (TIMS). This test method is also described in ASTM STP 1344[2].

1.2 The ^{233}U isotope is primarily measured as a qualitative measure of its presence by comparing the ^{233}U peak intensity to a background point since it is not normally found present in materials. The example data presented in this test method do not contain any ^{233}U data. A ^{233}U enriched standard is given in Section 8, and it may be used as a quantitative spike addition to the other standard materials listed.

1.3 A single standard calibration technique is used. Optimal accuracy (or a low bias) is achieved through the use of a single standard that is closely matched to the enrichment of the samples. The intensity or concentration is also adjusted to within a certain tolerance range to provide good statistical counting precision for the low-abundance isotopes while maintaining a low bias for the high-abundance isotopes, resulting

from high-intensity dead time effects. No blank subtraction or background correction is utilized. Depending upon the standards chosen, enrichments between depleted and 97 % can be quantified. The calibration and measurements are made by measuring the intensity ratios of each low-abundance isotope to the intensity sum of ^{233}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U. The high-abundance isotope is obtained by difference.

1.4 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only. The instrument is calibrated and the samples measured in units of isotopic weight percent (Wt %). For example, the ^{235}U enrichment may be stated as Wt % ^{235}U or as g ^{235}U/100 g of U. Statements regarding dilutions, particularly for ug/g concentrations or lower, are given assuming a solution density of 1.0 since the uranium concentration of a solution is not important when making isotopic ratio measurements other than to maintain a reasonably consistent intensity within a tolerance range.

1.5 *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.* Specific precautionary statements are given in Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*
C 753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder[3]
C 776 Specification for Sintered Uranium Dioxide Pellets[3]
C 788 Specification for Nuclear-Grade Uranyl Nitrate Solution[3]
C 833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets[3]
C 859 Terminology Relating to Nuclear Materials[3]
C 1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis[3]
D 1193 Specification for Reagent Water[4]

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[5]

E 456 Terminology Relating to Quality and Statistics[6]

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory[7]

3. Terminology

3.1 *Definitions*:

3.1.1 For definitions of terms relating to analytical atomic spectroscopy, refer to Terminology E 135.

3.1.2 For definitions of terms relating to statistics, refer to Terminology E 456.

3.1.3 For definitions of terms relating to nuclear materials, refer to Terminology C 859.

3.1.4 For definitions of terms specifically related to Q-IPC-MS in addition to those found in 3.2, refer to Appendix 3 of Jarvis et al.[8]

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *dead time*, *n*—the interval during which the detector and its associated counting electronics are unable to record another event or resolve successive pulses. The instrument signal response becomes nonlinear above a certain count rate due to dead time effects.

3.2.2 *mass bias or fractionation*, *n*—the deviation of the observed or measured isotope ratio from the true ratio as a function of the difference in mass between the two isotopes. This deviation is the result of several different processes. It has been suggested that the Q-ICP-MS ion transmission and focusing device create a dense space charge effect, which can cause a preferential loss of lighter isotopes. The result is an under estimation of the lighter isotopes which can be significant.[9] "Rayleigh fractionation associated with sample evaporation in which lighter isotopes are carried away preferentially" is insignificant with solution nebulization, but with other methods of introduction such as electrothermal vaporization, can be more significant.[9]

4. Summary of Test Method

4.1 A sample of the nuclear-grade material (nominally 0.2 g) is digested in HNO_3 or a HNO_3/HF mixture and diluted in series to a concentration of approximately 0.10 ug of uranium per gram of solution (ug U/g solution or ppm of U). Other dissolution methods may be used. A standard peristaltic pump is used as the means of sample introduction into the plasma. The uranium intensity (that is, concentration), as initially indicated by a ratemeter reading, is adjusted to within a certain tolerance range to provide good precision and a reduced bias for all sample, standard, and control measurements. A calibration standard is run and all sample analyses are bracketed by the analysis of controls. Calculations are performed to measure the intensity ratios of each low-abundance isotope to the intensity sum of ^{233}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U. Mass bias correction factors, which are established using the instrument software and the calibration standard data, are then applied to the sample and control data. The corrected ratio measurement for a low abundance isotope is equal to the abundance of that isotope (for example the ^{234}U intensity/U isotope intensity sum equals the ^{234}U abundance). The high abundance isotope is determined by subtracting the low-abundance isotopes from 100 %.

5. Significance and Use

5.1 Nuclear-grade reactor fuel material must meet certain criteria, such as those described in Specifications C 753, C 776, C 788, and C 833. Included in these criteria is the uranium isotopic composition. This test method is designed to demonstrate whether or not a given material meets an isotopic requirement and whether the effective fissile content is in compliance with the purchaser's specifications.

6. Interferences

6.1 *Adjacent Isotopic Peak Effects*—Interferences can occur from adjacent isotopes of high concentration, such as an intense ^{235}U peak interfering with the measurement of ^{234}U and ^{236}U. This is particularly the case for instruments that provide only nominal unit mass resolution at 10 % of the peak height. For this test method, the Q-ICP-MS peak resolution for ^{235}U was set to within 0.70 ± 0.15 daltons (Atomic Mass Units-AMU) fill-width-tenth-maximum (FWTM) peak height to reduce adjacent peak interference effects.

6.2 *Isobaric Molecular Ion Interferences*—^{235}U could interfere with ^{236}U determinations by forming a UH + ion. Follow the instrument manufacturer's instructions to minimize these molecular ion formations, for example by optimizing the nebulizer gas flow rate. The use of a calibration standard that is similar in isotopic composition and intensity to the samples reduces the potential bias from this interference effect. The bias from the UH^+ interference only becomes significant for the integrated peak intensity of ^{236}U when the sample intensity deviates from the calibration standard intensity and it is very low, that is, near the background intensity contribution. A naturally enriched standard, which contains no ^{236}U, can be used to test the significance of this interference.

6.3 *Memory Interference Effects*—Memory effects or sample carryover can occur from previously run samples. These effects can be detected in several ways. First of all, if the bias factors from the calibration standard are outside of a normal tended range, it can show that the glassware and uptake system is contaminated with another enrichment. Secondly, it can be detected by looking at the standard deviation of the repeat trials from a sample analysis and whether the peak intensity measurements are random between the repeat trials or whether they drift toward increasing or decreasing intensity. Also, the percent standard deviation (% SD) of the intensity ratios should be less than or on the same order of the % SD of the peak intensities. If the peak intensity measurements are higher, then it may be an indication of a memory effect from a sample of a different enrichment level. It could also be

[5] *Annual Book of ASTM Standards*, Vol 03.05

[6] *Annual Book of ASTM Standards*, Vol 14.02.

[7] *Annual Book of ASTM Standards*, Vol 03.06.

[8] Jarvis, K.E., Gray, A.L., and Houk, R.S., *Handbook of Inductively Coupled Plasma Mass Spectrometry*, Blackie and Son Ltd., Glasgow and London, or Chapman and Hall, New York, 1992.

[9] Date, A.R., and Gray, A.L., *Applications of Inductively Coupled Plasma Mass Spectrometry*, Blackie and Son Ltd., Glasgow and London, or Chapman and Hall, New York, 1989.

indicative of general instrument instability or problems with sample uptake and delivery to the plasma.

7. Apparatus

7.1 *Balance*, with precision of 0.00001 g.

7.2 *Polytetrafluoroethylene (PTFE) Oak Ridge Tubes*[10], 30 mL, or equivalent.

7.3 *Drying Oven*, controlled at 108 ± 5°C.

7.4 *Polypropylene Sample Bottle*, 125 mL, or equivalent.

7.5 *Disposable Polypropylene Tubes With Snap-on Caps*[10], 14 mL, or equivalent.

7.6 *Q-ICP-MS Instrument*, controlled by computer and fitted with the associated software and peripherals.

7.7 *Peristaltic Pump*.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[11] Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, as defined by Type I of Specification D 1193.

8.3 *Hydrofluoric Acid* (sp gr 1.18)—49 % w/w concentrated hydrofluoric acid (HF).

8.4 *Isotopic Calibration Standard,* 0.10 ug of U per g of solution—Add 100 uL of the appropriate isotopic calibration standard secondary stock solution (see 8.7) to a 125-mL polypropylene sample bottle, and dilute to approximately 84.7 g with water.

8.5 *Isotopic Control Standard,* 0.10 ug of U per g of solution—Add 100 uL of the appropriate isotopic control standard secondary stock solution (see 8.7) to a 125-mL polypropylene sample bottle, and dilute to approximately 84.7 g with water.

Note 1—The concentration of the calibration and control standard solutions are adjusted or remade for a given sample batch analysis to achieve a maximum established uranium intensity measurement. Refer to 13.1.5 for directions on how this intensity level of the uranium isotope sum is determined. The intensity sum was established at 2.0 ± 0.2 million counts per second (cps) for the data presented. The sensitivity, and therefore this concentration, is dependent upon the user's own instrumentation. The 2.0-million cps intensity level is established based on an upper intensity level at which the instrument continues to operate in a linear intensity versus concentration range, and is therefore also instrument

dependent. Intensity levels above this range can become nonlinear as a function of concentration due to dead time effects.

8.6 *Isotopic Enrichment Standard Primary Stock Solutions,* 5000 ug of U_3O_8 per g of solution (4235 ug of U per g of solution)—0.250 g of the appropriate NBL U_3O_8 isotopic standard heated to dissolution with 5 mL of water and 10 mL of concentrated HNO_3, then diluted to 50.0 g of water in a 125-mL polypropylene sample bottle.

8.7 *Isotopic Enrichment Standard Secondary Stock Solutions,* 84.7 ug of U per g of solution—Add 2.0 mL of the appropriate isotopic enrichment standard primary stock solution (see 8.6) to a 125-mL polypropylene sample bottle, add 5 mL of concentrated HNO_3, then dilute to 100.0 g with water.

Note 2—The isotopic calibration standard and analysis control materials should be within 1.0 Wt % of the ^{235}U enrichment to be analyzed in unknown sample materials. Likewise, the low-abundance isotopes (^{234}U and ^{236}U) should be in close agreement between standards and samples. It is recommended that separate primary and secondary stock solutions be made from a separate and preferably an independent source of isotopic enrichment standard (to serve as standard and control stock solutions) if such a source can be found. However, given the limited availability of such standards, the primary and secondary stock solutions may be made from the same enrichment CRM, with separate dissolutions and bottles being designated as standard and control stock solutions.

8.8 *Isotopic Enrichment U_3O_8 Standards*—New Brunswick Laboratory (NBL) Certified Reference Materials (CRMs), depending on the enrichment level to be analyzed: for example, CRM U-010, CRM U-030, CRM U-030A, CRM U-050, CRM U-200, CRM U-350, CRM U-500, CRM U-750, CRM U-850, CRM U-900, CRM U-930, and CRM U-970.

8.9 *Nitric Acid* (sp gr 1.42)—70 % w/w concentrated nitric acid (HNO_3).

8.10 ^{233}U *Isotopic Enrichment Spike Standard*—New Brunswick Laboratory (NBL) CRM 111A, used as a spike addition. This standard is listed for optional use by the user as a spike addition to the other standards previously given, if ^{233}U is found to be present in measurable quantities for the sample materials (see 1.2)

8.11 *Nitric/Hydrofluoric Acid Rinse Solution* (4 % HNO_3 v/v and 0.5 % HF v/v)—Add approximately 6.0 mL of concentrated HNO_3 and 1.0 mL of concentrated HF to water, dilute to 100 mL, and mix.

9. Hazards

9.1 The plasma or ICP of the instrument is at a very high temperature and emits ozone and intense ultraviolet light. Protection from such radiation and emissions are provided by the instrument shields and covers along with adequate ventilation of the chamber exhaust.

9.2 Since uranium-bearing materials are radioactive and toxic, adequate laboratory facilities and fume hoods along with safe handling techniques must be used. A detailed discussion of all safety precautions needed is beyond the scope of this test method. Follow site- and facility-specific radiation protection and chemical hygiene plans.

9.3 Acute exposure to HF can cause painful and severe burns upon skin contact that require special medical attention. Chronic or prolonged exposure to low levels on the skin may cause fluorosis.

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[10] PTFE Oak Ridge Tubes (30 mL) and 14-mL disposable polypropylene tubes with snap-on caps are available from Fisher Scientific or other major laboratory supply house.

[11] *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 *Annular Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmacepeial Convention, Inc. (USPC), Rockville, MD.

10. Sampling, Test Specimens, and Test Units

10.1 Criteria for material sampling are given in Specifications C 753 and C 776 for the material types that they address and can also be used as a guidance for other material types. Generally, only about 0.2 g of material is used during sample digestion and it is then diluted to a proper concentration level. Because so little material is actually used (about 2 ug), often times the remainder portion of the sample from some other analysis, such as uranium titration, is taken and diluted appropriately. Since the analysis is performed at a very low concentration level, the dilutions are easily subject to contamination, therefore, disposable plastic ware is used whenever possible.

11. Sample Preparation

NOTE 3—The sample preparation discussed as follows is designed for the dissolution of fuel product material or other material types that require a HNO_3/HF acid dissolution. It provides a complete dissolution of the material that may then be used for other analyses. A simple acid leach followed by dilution may be adequate for the user's needs. The initial stage of the dissolution (using H_2O/HNO_3/HF) may be omitted for material that can be dissolved using only HNO_3, such as U_3O_8. Other sample preparation methods may be used which result in a HNO_3 matrix (about 1 to 2 % w/v) which may have a trace presence of HF (less than 1 % w/v) after dilution to a concentration of about 0.10 ug of Uranium per gram of solution for analysis. Refer to Practice C 1347. The UNH crystals are prepared in water and diluted to the appropriate concentration.

11.1 Weigh out approximately 0.18 ± 0.02 g of material into a 30-mL PTFE Oak Ridge tube.

11.2 If the material type is known to be digested using HNO_3 alone, then add 0.5 mL of water to the tube and proceed to 11.7.

11.3 Add 100 uL of water and 100 uL of concentrated HNO_3 to the tube. Add 100 uL of concentrated HF to the tube and immediately cap the tube tightly before any reaction fully develops. Shake or swirl it to mix the material thoroughly.

11.4 Place the tube in a small beaker or container to hold it upright and place it in the oven set at $108 \pm 3°C$ for 45 min.

11.5 Remove the tube from the oven and allow it to cool to or below room temperature. The sample may be placed under a cool water flow or in a refrigerator for 5 min to aid in the cooling.

11.6 Open the sample tube and add about 10 mL of water. Replace the cap to shake or swirl the tube and then, after letting any solids settle to the bottom, decant off the liquid into a tare weighed 125-mL sample bottle. Repeat the water addition and decanting a second time.

11.7 With about 0.5 mL of water placed in the tube or remaining from the decanting process, add 1.0 mL of concentrated HNO_3 to the tube and replace the cap.

11.8 Place the tube back in the oven set at $108 \pm 3°C$ for 20 to 60 min. If all of the undissolved material goes into solution, the tube may be removed from the oven before the 60-min time period, otherwise remove it after 60 min.

11.9 Allow the tube to cool to or below room temperature as described in 11.5.

11.10 Open the sample tube and add about 10 mL of water. Replace the cap to shake or swirl the tube. If any solids remain in the tube, let them settle to the bottom, then decant off the liquid into the 125-mL sample bottle. Repeat the water addition and decanting a second time.

11.11 If solids remain in the tube, return to 11.3 to repeat the acid dissolution. Once the sample is completely dissolved, thoroughly rinse the tube into the sample bottle.

11.12 Dilute the sample in the bottle to approximately 100 g or a dilution factor of about 500:100-g solution/0.20-g sample = 500.

11.13 Dilute the sample into a labelled 14-mL disposable polypropylene tube by taking 200 uL of sample from the sample bottle and diluting to 10 mL with water.

12. Preparation of Apparatus

12.1 Set up the necessary instrument software files for data acquisition, calculation, archival, and so forth. The instrument software of many instruments can establish and apply the appropriate equations discussed as follows which represent the sum of the uranium isotopes as either ^{235}U or ^{238}U. If the instrument does not have this ability, the data manipulation can be performed using an external software program.

12.1.1 Two separate equations are set up for use in the data manipulation, one for high-enriched uranium (HEU) isotopic measurements and one for low-enriched uranium (LEU) isotopic analyses. In each case, the high-abundance isotope intensity is set to equal the sum of all of the uranium isotope intensities, then redefined as either ^{235}U* or ^{238}U*, for high-enrichment and low-enrichment analyses, respectively. The equations are given as follows:

The HEU analysis equation:

$$^{235}U^* = {}^{233}Uint + {}^{234}Uint + {}^{235}Uint + {}^{236}Uint + {}^{238}Uint \quad (1)$$

The LEU analysis equation:

$$^{238}U^* = {}^{233}Uint + {}^{234}Uint + {}^{235}Uint + {}^{236}Uint + {}^{238}Uint \quad (2)$$

where:

^{233}Uint = measured ^{233}U peak intensity,
^{234}Uint = measured ^{234}U peak intensity,
^{235}Uint = measured ^{235}U peak intensity,
^{236}Uint = measured ^{236}U peak intensity, and
^{238}Uint = measured ^{238}U peak intensity.

While both equations essentially represent the same summation of all of the uranium isotope intensities, the inference that the sum equals either ^{235}U or ^{238}U for the instrument software allows many of the instruments to ratio the low-abundance isotope intensities to this intensity sum, thereby directly producing the percent abundance of that isotope reading. The high-abundance isotope is then determined by difference from 100 % (see 1.3 and 15.2). If this data manipulation is performed external to the instrument software with the intensities entered, there only needs to be one equation that equals the isotope sum.

12.1.2 A calibration standard file is set up for the NBL CRM that is to be used. The isotopic weight percents (Wt %) of each isotope is obtained from the certificate of analysis and entered into a calibration standard file as a ratio of each low-abundance isotope to the intensity sum previously defined. Refer to the following equations:

The HEU analysis calibration standard file:

$$Wt \% {}^{233}U = {}^{233}Uint/{}^{235}U^* \quad (3)$$

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