Designation: C1474 – 00 (Reapproved 2011)

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 C1474; 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:*[3]

C753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder

C776 Specification for Sintered Uranium Dioxide Pellets

C778 Specification for Sand

C833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets

C859 Terminology Relating to Nuclear Materials

[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.

Current edition approved June 1, 2011. Published June 2011. Originally approved in 2000. Last previous edition approved in 2006 as C1474 – 00(2006)$^{\varepsilon 1}$. DOI: 10.1520/C1474-00R11.

[2] Policke, T. A., Bolin, R. N., and Harris, T. L., "Uranium Isotope Measurements by Quqdrupole ICP-MS for Process Monitoring of Enrichment," *Symposium on Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations: Second Volume, ASTM STP 1344*, ASTM, 1998, p. 3.

[3] 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.

C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis
D1193 Specification for Reagent Water
E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
E456 Terminology Relating to Quality and Statistics
E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms relating to analytical atomic spectroscopy, refer to Terminology E135.

3.1.2 For definitions of terms relating to statistics, refer to Terminology E456.

3.1.3 For definitions of terms relating to nuclear materials, refer to Terminology C859.

3.1.4 For definitions of terms specifically related to Q-ICP-MS in addition to those found in 3.2, refer to Appendix 3 of Jarvis et al.[4]

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.[5] "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.[5]

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 C753, C776, C778, and C833. 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) full-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

[4] 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* .

[5] 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.*