



Standard Test Method for Analysis of Isotopic Composition of Uranium in Nuclear- Grade Fuel Material by Quadrupole Inductively Coupled Plasma-Mass Spectrometry¹

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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): ²³³U, ²³⁴U, ²³⁵U, ²³⁶U, and ²³⁸U. The analysis can be performed on various material matrices after acid dissolution and sample dilution into water or dilute nitric (HNO₃) 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 1344².

1.2 The ²³³U isotope is primarily measured as a qualitative measure of its presence by comparing the ²³³U 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 ²³³U data. A ²³³U 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 ²³³U, ²³⁴U, ²³⁵U, ²³⁶U, and ²³⁸U. 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 ²³⁵U enrichment may be stated as Wt % ²³⁵U or as g ²³⁵U/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 Powder³
- C 776 Specification for Sintered Uranium Dioxide Pellets³
- C 788 Specification for Nuclear-Grade Uranyl Nitrate Solution³
- C 833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets³
- C 859 Terminology Relating to Nuclear Materials³
- C 1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis³
- D 1193 Specification for Reagent Water⁴
- E 135 Terminology Relating to Analytical Chemistry for

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 Policke, T. A., Bolin, R. N., and Harris, T. L., "Uranium Isotope Measurements by Quadrupole 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 *Annual Book of ASTM Standards*, Vol 12.01.

⁴ *Annual Book of ASTM Standards*, Vol 11.01.

Metals, Ores, and Related Materials⁵
 E 456 Terminology Relating to Quality and Statistics⁶
 E 882 Guide for Accountability and Quality Control in the
 Chemical Analysis Laboratory⁷

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 HNO₃ or a HNO₃/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 ²³³U, ²³⁴U, ²³⁵U, ²³⁶U, and ²³⁸U. 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 ²³⁴U intensity/U isotope intensity sum equals the ²³⁴U 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 ²³⁵U peak interfering with the measurement of ²³⁴U and ²³⁶U. 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 ²³⁵U 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*—²³⁵U could interfere with ²³⁶U 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 ²³⁶U 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 ²³⁶U, 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 indicative of general instrument instability or problems with sample uptake and delivery to the plasma.

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.

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 $108 \pm 5^\circ\text{C}$.
- 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.

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.

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. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

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 HNO₃/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 H₂O/HNO₃/HF) may be omitted for material that can be dissolved using only HNO₃, such as U₃O₈. Other sample preparation methods may be used which result in a HNO₃ 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 HNO₃ 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 HNO₃ 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 $108 \pm 3^\circ\text{C}$ 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 HNO₃ to the tube and replace the cap.

11.8 Place the tube back in the oven set at $108 \pm 3^\circ\text{C}$ 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 ²³⁵U or ²³⁸U. 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 ²³⁵U* or ²³⁸U*, for high-enrichment and low-enrichment analyses, respectively. The equations are given as follows:

The HEU analysis equation:

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

The LEU analysis equation:

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

where:

²³³U_{int} = measured ²³³U peak intensity,
²³⁴U_{int} = measured ²³⁴U peak intensity,
²³⁵U_{int} = measured ²³⁵U peak intensity,
²³⁶U_{int} = measured ²³⁶U peak intensity, and
²³⁸U_{int} = measured ²³⁸U peak intensity.

While both equations essentially represent the same summation of all of the uranium isotope intensities, the inference that the sum equals either ²³⁵U or ²³⁸U 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:

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

$$\text{Wt \% } ^{234}\text{U} = ^{234}\text{U}_{\text{int}}/^{235}\text{U}^*$$

$$\text{Wt \% } ^{236}\text{U} = ^{236}\text{U}_{\text{int}}/^{235}\text{U}^*$$

$$\text{Wt \% } ^{238}\text{U} = ^{238}\text{U}_{\text{int}}/^{235}\text{U}^*$$

The LEU analysis calibration standard file:

$$\begin{aligned} \text{Wt \% } ^{233}\text{U} &= ^{233}\text{U}_{\text{int}}/^{238}\text{U}^* \\ \text{Wt \% } ^{234}\text{U} &= ^{234}\text{U}_{\text{int}}/^{238}\text{U}^* \\ \text{Wt \% } ^{235}\text{U} &= ^{235}\text{U}_{\text{int}}/^{238}\text{U}^* \\ \text{Wt \% } ^{236}\text{U} &= ^{236}\text{U}_{\text{int}}/^{238}\text{U}^* \end{aligned} \quad (4)$$

The establishment of a calibration in which the measured intensity ratio (low-abundance isotope-to-intensity sum) is set to equal the weight percent of the given low-abundance isotope, incorporates into the calibration the conversion for atom percent ratio (proportional to intensity ratio) to weight percent ratio. Thus, the bias factors generated from the calibration reflect this conversion.

12.2 Set the instrument operating conditions in accordance with the manufacturer's instructions, or as found to produce optimal results. The following conditions shown in Table 1 have been found to be suitable.¹²

12.2.1 The user may wish to examine the differing signal stability between uptake using the peristaltic pump and natural uptake, that is, with the drain line running through the pump and the uptake line running from the nebulizer directly to the sample. The data presented in this test method were acquired using natural uptake, as it was found to produce optimal stability.

13. Calibration and Standardization

13.1 *Apparatus*—The following preliminary systems checks, with acceptance criteria, are recommended, and were performed for the data presented with this test method.

13.1.1 A mass scale calibration is performed routinely using an appropriately concentrated solution containing, at minimum BE (Beryllium), Co (Cobalt), In (Indium), Ce (Cerium), Bi (Bismuth), and Th (Thorium). The difference between the actual and measured masses shall be less than 0.05 daltons (AMU) and the linear regression coefficient greater than 0.99.

13.1.2 After tuning the lenses while monitoring the high-abundance isotope (either ²³⁵U or ²³⁸U) in a standard solution,

a stability/tuning check is performed daily using an appropriately concentrated solution containing, for example, 10 ug/L of Be, Co, In, Ce, Bi, and Th. The instrument is tuned with a greater emphasis placed on stability for the sake of isotope ratio measurement rather than just sensitivity optimization. The relative standard deviation (RSD) of each isotope from ten trials shall be less than 4 %. Also, a minimum sensitivity response shall be established for each isotope and monitored.

13.1.3 A peak resolution check is performed daily using ²³⁵U. The resolution FWTM shall be within 0.70 ± 0.15 daltons (AMU).

13.1.4 The instrument is normally conditioned for 1 to 2 h with the isotopic calibration or control standard solution (see 8.8 or 8.9) that is to be analyzed. At this time, the concentration of the standard/control materials can be adjusted to achieve the proper intensity. An instrument stability and sensitivity check may also be performed while this solution is being circulated. This check would be run the same as a routine analysis except for having 10 or more trials. Any changes in enrichments to be analyzed require that the instrument system be flushed thoroughly with a 4 % HNO₃/0.5 % HF rinse solution (see 8.11) before this conditioning step; particularly when changing from high-enriched to low-enriched materials or vice versa. The instrument glassware and cones can be changed when changing enrichment levels to improve this transition.

13.1.5 The linear concentration range of the instrument is established in order to determine the maximum intensity that will be allowed with regard to the high-abundance isotope (while continuing to operate in the linear range) as well as the minimum intensity, which will continue to allow adequate intensity above background of the very low-abundance isotopes. The intensity above background for the low-abundance isotopes should be sufficiently large so that any variation in these isotope intensities between samples and the standard are not significantly biased due to the background contribution. To establish the linear concentration range, the ²³⁵U/²³⁸U ratio from a low-enrichment standard is measured as a function of increasing intensity, by increasing the concentration. The data is plotted on a graph; ²³⁵U/²³⁸U as a function of ²³⁸U*. The intensity before the curve begins to be nonlinear is measured from the graph and this is set as the optimum concentration with a ±10 % tolerance range allowed. The concentration that was determined for the instrument that was used to acquire much of the data presented in this test method was 2.0 million cps. Thus, a concentration range from 1.8 to 2.2 million cps was allowed for the calibration standard and controls and they were prepared accordingly, see 8.8 and 8.9. The range limit is also applied to the analysis of the samples. This intensity range and the linear response of the instrument may be checked periodically, depending on the user's quality control (QC) requirements.

13.2 *Reference Standards*—Refer to Guide E 882 for the recommended establishment of quality control charts, guidelines, and corrective actions in case the analysis of a standard is out of control. The quality control standards described as follows are recommended for this test method; however, their usage, frequency, and acceptance criteria levels are at the

¹² A VG PlasmaQuad PQ2+ and a PQS Q-ICP-MS instrument, available from VG Elemental, Inc., 27 Forge Parkway, Franklin, MA 02038, were used for the data presented in this test method.

TABLE 1 Instrument Operating Conditions

Solution pumping rate	sample solution IN: ≈ 0.8 mL/min
ICP incident power	1350 W
ICP reflected power	<5 W
Plasma argon coolant	≈ 14.0 L/min at 80 psig
Plasma argon auxiliary	≈ 0.9 L/min at 80 psig
Plasma argon nebulizer	≈ 0.85 mL/min at 35 psig
Acquisition mode	peak jumping
Points per peak	7 points (1 DAC step each)
Masses detected	²³³ U, ²³⁴ U, ²³⁵ U, ²³⁶ U, ²³⁸ U
Optional background	232, 237, 239, 250, 251 daltons (AMU)
Mass	
rest mass	230 daltons (AMU)
Dwell times	81.92 ms for ²³³ U, ²³⁴ U, and ²³⁶ U; 40.96 ms for ²³⁵ U (LEU) and ²³⁸ U (HEU); 10.24 ms for ²³⁸ U (LEU), ²³⁸ U (HEU), and background masses
Acquisition time per trial	30 s
Number of trials	5
Detector mode	pulse counting

discretion of the user. Refer to the suggested QC protocol given in Appendix X1.

13.2.1 A single standard calibration is performed using a standard solution as listed in 8.8 (see Notes 1 and 2). The standard is run within the intensity range established in 13.1.5. Bias factors are determined for each of the isotopic ratios measured. These factors are applied to the designated set or batch of samples and controls. The background is not subtracted from the spectrum when performing isotopic ratio analysis. The calibration standard is normally run at the beginning, but may be run or reestablished during the middle of the sample batch to better represent the samples due to any instrument drift that may have occurred between the beginning and ending control standards.

13.2.2 The calibration is verified between sample analyses using an initial and continuing control standard solution as listed in 8.9 (see Notes 1 and 2). The control standard is run at a minimum of every ten samples.

13.2.3 A duplicate sample analysis may be run on a single sample within a batch as a means of monitoring the precision of the analysis, as affected by instrumental precision. As indicated in the suggested QC protocol (Appendix X1), each sample may be run in duplicate out of the same final dilution and the two analyses averaged to improve the precision of the result. If the difference between the two analyses is greater than some predetermined value for one or more of the isotopes, then a third analysis can be run and the average of the three reported.

14. Procedure

14.1 Allow the Q-ICP-MS instrument time warm up and reach a stable state of detection.

14.2 Perform any instrument system checks or mass scale calibrations in accordance with 13.1 and the frequencies established.

14.3 With the instrument conditioned for the isotopic enrichment of interest, as described in 13.1.4, place the uptake line into the isotopic calibration standard solution. Based on the ratemeter response (set to monitor the most abundant isotope), adjust or remake the standard solution to achieve the desired intensity (see 13.1.5).

NOTE 4—The ratemeter response will be that of the most abundant isotope and can be used to determine whether a standard, control, or sample solution needs to be diluted or remade. It should be noted, however that the intensity range limit established in 13.1.5 is that of the intensity sum (appearing as ^{235}U or ^{238}U on the results data) and this will differ from the ratemeter response according to enrichment.

14.4 Allow the solution sufficient uptake time and then acquire the isotopic ratio data.

NOTE 5—A rinse is not applied between standards, controls, or samples so that a stable conditioning remains. The uptake line is moved directly between each bottle or vial to be analyzed, and sufficient time is given for the signal to stabilize. An acceptable time is established by examining the response on the ratemeter and ultimately judging the response to be sufficient by the standard deviation on the intensity trials and any apparent drift.

14.5 Run the isotopic calibration standard to establish the bias factors (see 13.2.1).

14.6 Run the initial isotopic control standard (see 13.2.2).

14.7 Run the samples, bracketing every ten or less samples by a beginning and ending control standard. Repeat the calibration during the middle of a sample sequence if desired to offset any instrumental drift between the controls and to improve the precision, depending on the control limits established by the user. Run each sample or a given sample in duplicate from the same dilution (see 13.2.3). Follow the instructions on preparing and running each sample dilution for analysis from the sample tube prepared in 11.13.

14.7.1 Dilute the sample from 11.13 into a labeled 14-mL disposable polypropylene tube by taking 300 μL of sample from the tube and diluting to 10 mL with water.

14.7.2 Place the uptake line into the sample tube. Based on the ratemeter response, adjust or remake the sample tube to achieve the desired intensity (see 13.1.5).

14.7.3 Allow the solution sufficient uptake time (see Note 5) and then acquire the isotopic ratio data.

14.7.4 Refer to the suggested QC sample protocol in Appendix X1 or a protocol established by the user to determine the acceptance of the data.

15. Calculation

15.1 The software calculates bias factors for each of the measured ratios by using the calibration standard analysis data and the calibration standard file (see 12.1.2 and 13.2.1). Refer to 3.2.1 for an explanation of mass bias effects.

15.2 The low-abundance isotopic enrichments are obtained directly from the measurement data (see 12.1.2). The high-abundance isotopic enrichment is calculated by difference as follows:

15.2.1 For high-enrichment analysis data, calculate as follows:

$$\text{Wt } \% \text{ } ^{235}\text{U} = 100 \% - \text{Wt } \% \text{ } ^{233}\text{U} - \text{Wt } \% \text{ } ^{234}\text{U} - \text{Wt } \% \text{ } ^{236}\text{U} - \text{Wt } \% \text{ } ^{238}\text{U} \quad (5)$$

15.2.2 For low-enrichment analysis data, calculate as follows:

$$\text{Wt } \% \text{ } ^{238}\text{U} = 100 \% - \text{Wt } \% \text{ } ^{233}\text{U} - \text{Wt } \% \text{ } ^{234}\text{U} - \text{Wt } \% \text{ } ^{235}\text{U} - \text{Wt } \% \text{ } ^{236}\text{U} \quad (6)$$

16. Precision and Bias

16.1 A comparison study was performed between Q-ICP-MS and the more established technique of TIMS analysis. The results, which were acquired in 1997, are presented in Table 2. The TIMS analyses were performed at an independent laboratory. Both data sets for the 97 % U-235 enrichment range provide an indication of the accuracy of Q-ICP-MS analysis. There is good agreement between the two test methods with percent differences ranging from -0.004 to $+0.024$ for the primary isotope of concern, namely U-235.

16.2 Table 3 shows Q-ICP-MS results for ^{234}U , ^{235}U , ^{236}U , and ^{238}U for four blind samples analyzed as part of the New Brunswick Laboratory (NBL) Safeguards Measurement Evaluation Program.¹³ Table 3 provides an indication of both

¹³ Spaletto, M.I., Smith, M.M., Soriano, M.D., "Safeguards Measurement Evaluation Program Uranium Sample Exchange," NBL-348, U.S. Department of Energy, New Brunswick Laboratory, September 1998, p. 27-32.

TABLE 2 Comparison Uranium Isotopic Data Between TIMS and Q-ICP-MS

Sample I.D.	U-234 TIMS Analysis	U-234 Q-ICP-MS Analysis	U-234 Percent Difference ^A	U-235 TIMS Analysis	U-235 Q-ICP-MS Analysis	U-235 Percent Difference ^A
97-1	1.300	1.289	-0.85	97.658	97.681	+0.024
97-2	1.288	1.286	-0.16	97.656	97.668	+0.012
97-3	1.288	1.291	+0.23	97.664	97.660	-0.004
97-4	1.295	1.298	+0.23	97.659	97.660	+0.001
97-5	1.292	1.291	-0.08	97.663	97.667	+0.004
97-6	1.295	1.292	-0.23	97.655	97.666	+0.011
97-7	1.301	1.300	-0.08	97.661	97.671	+0.010
97-8	1.301	1.303	+0.15	97.664	97.670	+0.006
97-9	1.301	1.302	+0.08	97.661	97.668	+0.007
97-10	1.308	1.301	-0.54	97.658	97.672	+0.014
97-11	1.306	1.305	-0.08	97.660	97.666	+0.006
97-12	1.308	1.304	-0.31	97.659	97.667	+0.008
Mean percent difference			-0.137			0.0082
Mean absolute percent difference			0.252			0.0089
Standard deviation			0.319			0.0070

Sample I.D.	U-236 TIMS Analysis	U-236 Q-ICP-MS Analysis	U-236 Percent Difference ^A	U-238 TIMS Analysis	U-238 Q-ICP-MS Analysis	U-238 Percent Difference ^A
97-1	0.180	0.176	-2.25	0.862	0.854	-0.93
97-2	0.183	0.179	-2.21	0.873	0.867	-0.69
97-3	0.180	0.180	0.00	0.868	0.869	+0.12
97-4	0.179	0.179	0.00	0.867	0.863	-0.46
97-5	0.179	0.178	-0.56	0.866	0.864	-0.23
97-6	0.181	0.179	-1.11	0.869	0.863	-0.69
97-7	0.178	0.178	0.00	0.860	0.851	-1.05
97-8	0.178	0.178	0.00	0.857	0.849	-0.94
97-9	0.180	0.177	-1.68	0.858	0.853	-0.58
97-10	0.178	0.178	0.00	0.856	0.849	-0.82
97-11	0.178	0.177	-0.56	0.856	0.852	-0.47
97-12	0.179	0.178	-0.56	0.854	0.851	-0.35
Mean percent difference			-0.738			-0.59
Mean absolute percent difference			0.738			0.61
Standard deviation			0.859			0.34

^APercent difference = (X2 - X1)/(X1 + X2) · 200 %.

TABLE 3 NBL Blind Round-Robin Evaluation Program Results

Sample No.	Reported Wt% ²³⁴ U	Percent Relative Difference	Reported Wt% ²³⁵ U	Percent Relative Difference	Reported Wt% ²³⁶ U	Percent Relative Difference	Reported Wt% ²³⁸ U	Percent Relative Difference
1-Day 1	0.9508	-0.2604	89.6923	0.0150	0.4002	-1.0310	8.9566	-0.0772
1-Day 2	0.9522	-0.1135	89.6801	0.0014	0.4052	0.2055	8.9625	-0.0114
2-Day 1	0.9471	-0.6485	89.6662	-0.0141	0.4004	-0.9815	8.9862	0.2530
2-Day 2	0.9499	-0.3548	89.6677	-0.0124	0.4040	-0.0913	8.9783	0.1649
3-Day 1	0.9609	0.0370	90.3385	0.0015	0.4052	-0.5627	8.2953	0.0063
3-Day 2	0.9555	-0.5252	90.3436	0.0071	0.4025	-1.2253	8.2983	0.0424
4-Day 1	0.9589	-0.1713	90.3216	-0.0172	0.4057	-0.4400	8.3137	0.2281
4-Day 2	0.9645	0.4118	90.3349	-0.0025	0.4085 ²³⁴ U	0.2471 ²³⁵ U	8.2920 ²³⁶ U	-0.0335 ²³⁸ U
Mean percent difference					-0.203	-0.0026	-0.485	0.0716
Mean absolute percent difference					0.315	0.0089	0.598	0.1021
Standard deviation					0.332	0.0112	0.569	0.1261

precision and bias of the measurements. The four samples (1, 2, 3, and 4) are part of a blind round-robin evaluation program, therefore, the inputs values are not given in the evaluation report but instead the percent relative differences are provided by NBL for the data assessment. The four samples are analyzed on two separate days (noted as “Day 1” and “Day 2”). The statistical findings indicate that Samples 1 and 2 are the same, in other words they are duplicates of one another, as well as Samples 3 and 4, thus the data is grouped accordingly. The statistical evaluation of the data shows good precision and no bias. There is no significant difference between the precision and bias of the two days. The results are within the 1993 international target values (for TIMS) for high enrichment (0.02 % for both precision and bias).

16.3 A statistical summary if isotopic control standards data is given in Table 4 for a series of high- and low-enriched certified reference materials (CRM). The data was accumulated over a period of 3 years in a laboratory with two different instruments and four different analysts. All of these standards are available from NBL. The estimate standard deviation, *s*, for the low-abundance isotopes (²³⁴U and ²³⁶U) is between 0.0057 Wt % and 0.0004 Wt %, depending on the level. The estimate standard deviation for the higher abundance level isotopes (²³⁵U and ²³⁸U) varies according to enrichment. At approximately 50 % abundance, the standard deviation is about 0.026 Wt %. At approximately 3 Wt % (or less) abundance or 97 Wt % (or more) abundance, the standard deviation is about 0.006 Wt %. Thus, the precision is good.

TABLE 4 Isotopic Control Data for Certified Reference Materials

Summary Statistics of Measured Values				
Reference	Certified Values $X \pm S_x$	\bar{x}	s	n
²³⁴ U/100 g of U (or Wt % ²³⁴ U)				
CRM U970	1.6582 ± 0.0017	1.6589	0.0057	20
CRM U930	1.0759 ± 0.0020	1.0748	0.0051	20
CRM U900	0.7735 ± 0.0015	0.7741	0.0033	20
CRM U850	0.6399 ± 0.0014	0.6409	0.0023	9
CRM U750	0.5880 ± 0.0009	0.5878	0.0026	20
CRM U500	0.5126 ± 0.0008	0.5131	0.0015	20
CRM U350	0.2467 ± 0.0006	0.2467	0.0011	20
CRM U200	0.1229 ± 0.0003	0.1228	0.0006	17
CRM U050	0.0275 ± 0.0001	0.0275	0.0005	20
CRM U030	0.0187 ± 0.0001	0.0187	0.0006	20
CRM U005A	0.00334 ± 0.00007	0.0033	0.0005	20
²³⁵ U/100 g of U (or Wt % ²³⁵ U)				
Summary Statistics of Measured Values				
Reference	Certified Values $X \pm S_x$	\bar{x}	s	n
CRM U970	97.663 ± 0.003	97.6619	0.0062	20
CRM U930	93.276 ± 0.010	93.2774	0.0123	20
CRM U900	90.098 ± 0.011	90.0984	0.0158	20
CRM U850	84.988 ± 0.017	84.9839	0.0251	9
CRM U750	75.129 ± 0.025	75.1280	0.0242	20
CRM U500	49.383 ± 0.050	49.3824	0.0263	20
CRM U350	34.903 ± 0.035	34.8987	0.0261	20
CRM U200	19.811 ± 0.020	19.8085	0.0218	17
CRM U050	4.949 ± 0.005	4.9507	0.0071	20
CRM U030	3.009 ± 0.003	3.0068	0.0059	20
CRM U005A	0.5000 ± 0.0003	0.5004	0.0043	20
²³⁶ U/100 g of U (or Wt % ²³⁶ U)				
Summary Statistics of Measured Values				
Reference	Certified Values $X \pm S_x$	\bar{x}	s	n
CRM U970	0.1497 ± 0.0005	0.1493	0.0007	20
CRM U930	0.2034 ± 0.0006	0.2041	0.0025	20
CRM U900	0.3337 ± 0.0010	0.3340	0.0015	20
CRM U850	0.3713 ± 0.0011	0.3733	0.0017	9
CRM U750	0.2502 ± 0.0008	0.2507	0.0019	20
CRM U500	0.0754 ± 0.0003	0.0754	0.0008	20
CRM U350	0.1667 ± 0.0005	0.1671	0.0010	20
CRM U200	0.2103 ± 0.0006	0.2100	0.0013	17
CRM U050	0.0476 ± 0.0002	0.0475	0.0006	20
CRM U030	0.0202 ± 0.0001	0.0203	0.0004	20
CRM U005A	0.00117 ± 0.00001	0.0013	0.0004	20
²³⁸ U/100 g of U (or Wt % ²³⁸ U)				
Summary Statistics of Measured Values				
Reference	Certified Values $X \pm S_x$	\bar{x}	s	n
CRM U970	0.5296 ± 0.0006	0.5302	0.0030	20
CRM U930	5.445 ± 0.005	5.4424	0.0113	20
CRM U900	8.795 ± 0.008	8.7935	0.0147	20
CRM U850	14.001 ± 0.014	14.0019	0.0225	9
CRM U750	24.033 ± 0.024	24.0330	0.0251	20
CRM U500	50.029 ± 0.050	50.0293	0.0260	20
CRM U350	64.684 ± 0.036	64.6876	0.0259	20
CRM U200	79.856 ± 0.021	79.8586	0.0223	17
CRM U050	94.975 ± 0.005	94.9744	0.0070	20
CRM U030	96.953 ± 0.003	96.9543	0.0062	20
CRM U005A	99.4955 ± 0.0003	99.4954	0.0041	20

16.4 The bias is insignificant since all of the means are within one standard deviation from the certified value except for the ²³⁶U data for CRM U850 which is right at the 1 standard deviation difference and is based on fewer data points. Much of the CRM U030 and U050 data was generated during the support of a production process to generate 4 % enriched product material, and some of the CRM U030 data points were generated with a calibration on CRM U050. Thus, this particu-

lar data provides an indication of the linearity of the use of the single standard across a range of ±2 % enrichment. As indicated in Section 1, the background is not subtracted from the data, and, in the cases in which the abundance is less than approximately 0.020 %, it can become appreciable and this will be indicated in the bias factors. This background effect can be adjusted by changing the background discriminator setting in most instruments. So the selection of an appropriate standard

can be important, depending on the level of accuracy required. MS); isotopic ratio; uranium

17. Keywords

17.1 inductively coupled plasma-mass spectrometry (ICP-

APPENDIX

(Nonmandatory Information)

X1. QUALITY ASSURANCE AND QUALITY CONTROL

X1.1 The following quality control practices are recommended for the uranium isotonic analyses and data acceptance. This information is in addition to the standardization and control checks given in 13.2.

X1.1.1 The intensity measurements for ^{235}U and ^{238}U shall have a RSD of less than 3 % for the 5 trials.

X1.1.2 The ratio measurement of $^{235}\text{U}/^{238}\text{U}$ or $^{238}\text{U}/^{235}\text{U}$ shall have a RSD of less than 1 % for the 5 trials.

X1.1.3 Each sample shall be run in duplicate from the same 14-mL disposable tube, and if the difference in the high-

abundance isotope is greater than 0.05 Wt % then a third run is performed. The average of the runs is reported as the final result. Trials from a given run are excluded only under known upset conditions like an air bubble or sample loss.

X1.1.4 The bias factors will be reasonably constant for a given instrument from one day to another, and the user may want to set up trend tables or charts. Any factor that is outside of the normal trended range may indicate a system contamination problem from different enrichment materials recently run and would indicate the need to clean the system.

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