



Standard Test Method for Determination of Boron, Silicon, and Technetium in Hydrolyzed Uranium Hexafluoride by Inductively Coupled Plasma—Mass Spectrometer After Removal of Uranium by Solid Phase Extraction¹

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1. Scope

1.1 This test method covers the determination of boron, silicon and technetium in hydrolyzed uranium hexafluoride (UF_6) by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after separation of the uranium by solid phase extraction.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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. Some specific hazards statements are given in Section 7 on Hazards.*

2. Referenced Documents

2.1 *ASTM Standards:*²

C787 Specification for Uranium Hexafluoride for Enrichment

C859 Terminology Relating to Nuclear Materials

C996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % ²³⁵U

C1346 Practice for Dissolution of UF_6 from P-10 Tubes

C1689 Practice for Subsampling of Uranium Hexafluoride

D1193 Specification for Reagent Water

3. Terminology

3.1 *Definitions*—For definitions of other standard terms in this test method, refer to Terminology **C859**.

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 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.

3.2 Definitions:

3.2.1 *internal reference solution, n*—a solution containing non-analyte elements, the signal from which is used to correct for variation in the performance of a measuring instrument through the course of analyzing a batch of samples, thereby improving precision.

3.2.2 *method blank, n*—a solution which in so far as is practical duplicates the sample to be analyzed and passes through the same measurement process but does not initially contain significant quantities of any of the analytes to be measured.

3.2.2.1 *Discussion*—The method blank does not initially contain significant quantities of analyte, hence the value of any analyte measured may be assumed to be due to interference, matrix effects or contamination introduced as a consequence of sample processing. The contribution of such factors to the value measured on the genuine sample may therefore be eliminated by subtracting the measured value for the method blank, typically providing a better estimate for the true value of the quantity of analyte in the sample.

3.2.3 *recovery correction, n*—a factor applied to the measured value of the analyte in the sample to account for losses of analyte during sample processing.

3.2.3.1 *Discussion*—Some of the analyte originally present in a sample is likely to be lost during the process of preparing the sample for instrumental measurement, so that the measured value will typically be subject to negative bias. The proportion of analyte lost may be estimated by repeated measurement of a sample containing a known quantity of the analyte and a correction factor introduced to account for losses. Recovery correction is only required when analyte losses are significant when compared with overall measurement uncertainty.

3.2.4 *spike, n*—a known quantity of analyte added to a sample.

4. Summary of Test Method

4.1 A 4 % by weight solution of UF_6 is initially prepared by reacting a quantity of UF_6 with water. Sub-sampling of UF_6 may be carried out as described in Practice **C1689**. Preparation

of the hydrolyzed solution may be carried out as described in Practice C1346. The laboratory may choose to adopt a simplified version of the standard practices, or to adopt other practices, provided that any additional error thereby introduced is incorporated within precision statements for the method.

4.2 Concentrated nitric acid is added to the uranium solution to give a nitric acid concentration of approximately 1.5 M. The solution is then passed through a diamyl amyolphosphonate (DAAP) resin column which retains the uranium. Boron, silicon and technetium are eluted from the column with 2 M nitric acid and the solution made up to volume with reagent water. The boron, silicon and technetium concentrations are then measured using an ICP-MS. An on-line internal reference solution may be used to correct results for any instrumental drift and results are blank corrected using a prepared method blank.

NOTE 1—The method described in this standard uses a 3 mL sample of 4 % by weight UF₆ solution. The apparatus and the quantities and concentrations of reagents and materials described in the standard are appropriate to this sample size and concentration. The data presented in Section 14 have been generated using samples of this size and concentration. Alternative sample sizes and concentrations may be used but will require that the laboratory adjust apparatus, reagents and materials accordingly and validate the method for the adjusted conditions.

5. Significance and Use

5.1 This method is capable of measuring the concentration of boron, silicon and technetium in UF₆. Limits for these contaminants are set in Specifications C787 and C996.

6. Interferences

6.1 ⁹⁹Tc suffers an isobaric interference with ⁹⁹Ru and a molecular interference due to ⁹⁸MoH⁺ ions; however, the diluted, hydrolyzed UF₆ samples should not give rise to any significant amount of ⁹⁹Ru or ⁹⁸MoH⁺ ions.

7. Apparatus

7.1 Ordinary laboratory apparatus are not listed but are assumed to be present.

7.1.1 ICP-MS controlled by computer and fitted with associated software and peripherals, including an inert sample introduction system.

NOTE 2—A standard quartz sample introduction system is not suitable as it will affect the silicon measurement. A perfluoroalkoxy fluorocarbon plastic (PFA) introduction system with platinum injector has proven acceptable. New equipment may need to be pre-soaked or flushed with a dilute hydrofluoric acid solution, or both, to obtain a stable silicon background.

NOTE 3—It is recommended that an auto sampler with tube racks and plastic sample tubes compatible with the ICP-MS be used.

7.1.2 Balance to read to 0.01 g intervals or less.

7.1.3 Appropriately sized, variable volume pipettes such as 1 to 10 mL; 100 to 1200 µL; 20 to 300 µL; 5 to 100 µL used with polyethylene pipette tips.

7.1.4 Appropriately sized plastic, spouted measuring cylinders (for preparing dilute acids).

7.1.5 Plastic beakers, 100 mL size.

7.1.6 Low density polyethylene bottles with leak proof lids, various sizes.

NOTE 4—PFA containers may be used as an alternative and may help to reduce silicon background levels.

7.1.7 Polyfluoroalkoxy fluorocarbon plastic (PFA) bottles, various sizes.

7.1.8 Polyethylene sample tubes with leak proof lids, 25 mL and 50 mL size.

7.1.9 Disposable Gloves—impermeable and powder free to avoid the potential for contamination and to provide protection against toxic and corrosive substances. PVC gloves are suitable.

NOTE 5—The use of glassware must be avoided throughout this method as interaction with acid fluoride solutions will affect the silicon measurement.

8. Reagents and Materials

8.1 The sensitivity of the ICP-MS technique requires the use of ultra high purity reagents in order to be able to obtain low levels of detection and satisfactory precision. All the reagents below are ultra high purity grade unless otherwise stated.

8.1.1 Concentrated nitric acid, specific gravity 1.42, 16 M.

8.1.2 Concentrated hydrochloric acid, specific gravity 1.18, 11.3 M.

8.1.3 Concentrated hydrofluoric acid, 48 % by weight or similar concentration.

8.1.4 Reagent water conforming to Specification D1193.

8.1.5 Nitric acid, 0.32 M (200 mL of concentrated nitric acid diluted to 10 L or equivalent ratio).

8.1.6 Nitric acid, 2 M (125 mL of concentrated nitric acid diluted to 1 L or equivalent ratio).

8.1.7 Nitric acid, 3 M (188 mL of concentrated nitric acid diluted to 1 L or equivalent ratio).

8.1.8 Hydrochloric acid, 0.1 M (8.8 mL of concentrated hydrochloric acid diluted to 1 L or equivalent ratio).

8.1.9 Two independent 10 000 mg/L silicon standards (one for calibration, one for sample spiking and Quality Control).

8.1.10 Two independent 1000 mg/L boron standards (one for calibration, one for sample spiking and Quality Control).

8.1.11 Two independent technetium standards (one for calibration, one for sample spiking and Quality Control). Concentrations at 52.04 Bq/mL (82 µg/L) and 63.24 Bq/mL (100 µg/L) have proven acceptable but other similar values may be used if precisely known.

8.1.12 1000 mg/L indium, scandium and beryllium standards (used for internal reference solutions).

NOTE 6—Alternative elements may be used for the internal reference solution. Care must be taken to ensure consistency between batches of standards where the element chosen has more than one naturally occurring isotope.

8.1.13 Synthetic Pseudo Blank Matrix. 29 mL of 48 % by weight hydrofluoric acid diluted to 1 L or equivalent mixture to produce a 1.3 % by weight fluoride solution (equivalent fluoride concentration to a 4 % by weight UF₆ solution). Store in a PFA bottle and mix thoroughly before use.

8.1.14 Bulked Pseudo Blank Matrix. This is synthetic pseudo blank matrix that has passed through the preparation and solid phase extraction process described in paragraphs 12.1 – 12.10, measured and shown to contain very low levels of

boron, silicon and technetium. It is used to prepare calibration standards and instrument quality control samples.

8.1.15 Pre-packed DAAP resin columns, 2 mL, together with reservoirs and end caps as appropriate.

NOTE 7—New columns may need to be pre-treated before first use to remove trace silicon contamination. Pre-treatment may be carried out by passing sample material that does not require analysis through the column, eluting and regenerating the column as described in Section 12.

8.1.16 Argon gas (carrier gas for the ICP-MS), >99.99 % purity.

9. Hazards

9.1 Adequate laboratory facilities, such as fume hoods and controlled ventilation, along with safe techniques, must be used in this procedure. Extreme care should be exercised in using hydrofluoric and other concentrated acids. Use of chemical resistant gloves and eye protection is recommended. Refer to the laboratory's health and safety arrangements and other applicable guidance for handling chemical and radioactive materials and for the management of radioactive, mixed, and hazardous waste.

9.2 Hydrofluoric acid is a highly corrosive acid that can severely burn skin, eyes, and mucous membranes. Hydrofluoric acid is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid. Hydrofluoric acid differs from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers. Unlike other acids that are rapidly neutralized, hydrofluoric acid reactions with tissue may continue for days if left untreated. Due to the serious consequences of hydrofluoric acid burns, prevention of exposure or injury of personnel is the primary goal. Utilization of appropriate laboratory controls (hoods) and wearing adequate personal protective equipment to protect from skin and eye contact is essential.

9.3 The ICP-MS is a source of intense ultra-violet radiation from the radio frequency induced plasma. Protection from radio frequency radiation and UV radiation is provided by the instrument under normal operation.

10. Calibration and Standardization

10.1 The standards and blanks described below are prepared. The laboratory may choose to prepare different volumes of these materials and at different concentrations where appropriate to the requirements of the laboratory and the measurement to be performed.

10.2 *Internal Reference Solution* (50 µg/L In, 100 µg/L Sc and 500 µg/L Be). Add approximately 1.5 L of 0.32 M nitric acid to a 2 L PFA bottle. Pipet 0.1 mL of 1000 mg/L indium standard, 0.2 mL of 1000 mg/L scandium standard and 1.0 mL of 1000 mg/L beryllium standard into the bottle. Fill up to the 2 L mark with 0.32 M nitric acid. Mix thoroughly before use.

10.3 *Boron, Silicon and Technetium Stock Solution*, used for calibration standards (2.5 mg/L B, 100 mg/L Si and 500 ng/L ⁹⁹Tc). Place a labeled 125 mL PFA bottle on to a balance and tare. Add approximately 50 mL of 0.32 M nitric acid to the bottle. Pipet 0.25 mL of 1000 mg/L boron standard, 1.0 mL of

10 000 mg/L silicon standard and 0.61 mL of 82 µg/L technetium standard solution into the bottle. Make up to 101 g (±0.5 g) with 0.32 M nitric acid. Add screw top lid and mix thoroughly.

NOTE 8—The volume of a technetium standard with a different starting concentration should be adjusted to give the required final concentration of 500 ng/L, or any different concentration deemed more appropriate to the requirements of the laboratory (see 10.1).

NOTE 9—The density of 0.32 M nitric acid at 20°C is taken to be 1.009 g/mL.

10.4 *Boron Silicon and Technetium Blank Calibration Standard*. Place a labeled 125 mL PFA bottle on to a balance and tare. Add 101 g (±0.5 g) of Bulk Pseudo Blank Matrix to the bottle. Add screw top lid and mix thoroughly.

10.5 *Boron, Silicon and Technetium Calibration Standard 1* (10 µg/L B, 400 µg/L Si and 2.0 ng/L ⁹⁹Tc). Place a labeled 125 mL PFA bottle on to a balance and tare. Add approximately 50 mL of Bulk Pseudo Blank Matrix to the bottle. Pipet 0.4 mL of Boron, Silicon and Technetium Stock Solution into the bottle and make up to 101 g (±0.5 g) with Bulk Pseudo Blank Matrix. Add screw top lid and mix thoroughly.

10.6 *Boron, Silicon and Technetium Calibration Standard 2* (20 µg/L B, 800 µg/L Si and 4.0 ng/L ⁹⁹Tc). Place a labeled 125 mL PFA bottle on to a balance and tare. Add approximately 50 mL of Bulk Pseudo Blank Matrix to the bottle. Pipet 0.8 mL of Boron, Silicon and Technetium Stock Solution into the bottle and make up to 101 g (±0.5 g) with Bulk Pseudo Blank Matrix. Add screw top lid and mix thoroughly.

10.7 *Boron, Silicon and Technetium Calibration Standard 3* (50 µg/L B, 2.0 mg/L Si and 10 ng/L ⁹⁹Tc). Place a labeled 125 mL PFA bottle on to a balance and tare. Add approximately 50 mL of Bulk Pseudo Blank Matrix to the bottle. Pipet 2.0 mL of Boron, Silicon and Technetium Stock Solution into the bottle and make up to 101 g (±0.5 g) with Bulk Pseudo Blank Matrix. Add screw top lid and mix thoroughly.

10.8 *Boron, Silicon and Technetium Instrument Quality Control Stock/Spike Solution* (12.5 mg/L B, 500 mg/L Si and 2.5 µg /L ⁹⁹Tc). Place a labeled 125 mL PFA bottle on to a balance and tare. Add approximately 50 mL of 0.32 M nitric acid to the bottle. Pipet 1.25 mL of 1000 mg/L boron standard, 5.0 mL of 10 000 mg/L silicon standard and 2.5 mL of 100 µg/L technetium standard into the bottle (see Note 6). Make up to 101 g (±0.5g) with 0.32 M nitric acid. Add screw top lid and mix thoroughly. The standards used for this solution should be different from those used to prepare the Boron, Silicon and Technetium Stock Solution used for preparation of calibration standards.

10.9 *Boron, Silicon and Technetium Instrument Quality Control Sample* (25 µg/L B, 1000 µg/L Si and 5 ng/L ⁹⁹Tc). Place a labeled 125 mL PFA bottle on to a balance and tare. Add approximately 50 mL of Bulk Pseudo Blank Matrix to the bottle. Pipet 0.2 mL of Boron Silicon and Technetium Instrument Quality Control Stock/Spike Solution into the bottle and make up to 101 g (±0.5 g) with Bulk Pseudo Blank Matrix. Add screw top lid and mix thoroughly.