



Designation: C1771 – 19

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

This standard is issued under the fixed designation C1771; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. Some specific hazards statements are given in Section 7 on Hazards.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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

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.

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:*

3.1.1 For definitions of other standard terms in this test method, refer to Terminology C859.

3.2 *Definitions of Terms Specific to This Standard:*

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 UF₆ is initially prepared by reacting a quantity of UF₆ with water. Sub-sampling of UF₆ 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 herein 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 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 UF_6 solution). Store in a PFA bottle and mix thoroughly before use.

8.1.14 Bulk Pseudo Blank Matrix. This is synthetic pseudo blank matrix that has passed through the preparation and solid phase extraction process described in 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 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. Familiarization and compliance with the Safety Data Sheet 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 $\mu\text{g/L}$ In, 100 $\mu\text{g/L}$ Sc and 500 $\mu\text{g/L}$ 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 ^{99}Tc)—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 $\mu\text{g/L}$ technetium standard solution into the bottle. Make up to 101 \pm 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 \pm 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 $\mu\text{g/L}$ B, 400 $\mu\text{g/L}$ Si, and 2.0 ng/L ^{99}Tc)—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 \pm 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 $\mu\text{g/L}$ B, 800 $\mu\text{g/L}$ Si, and 4.0 ng/L ^{99}Tc)—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 \pm 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 $\mu\text{g/L}$ B, 2.0 mg/L Si, and 10 ng/L ^{99}Tc)—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 \pm 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 $\mu\text{g/L}$ ^{99}Tc)—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 $\mu\text{g/L}$ technetium standard into the bottle (see Note 6). Make up to 101 \pm 0.5 g 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 $\mu\text{g/L}$ B, 1000 $\mu\text{g/L}$ Si, and 5 ng/L ^{99}Tc)—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 \pm 0.5 g with Bulk Pseudo Blank Matrix. Add screw top lid and mix thoroughly.

11. Conditioning

11.1 Some types of sample tube may require cleaning before use due to high levels of background silicon contamination. If this is found to be the case then tubes or lids may be cleaned by soaking for at least 1 hr, preferably overnight, in 0.32 M nitric acid. Prior to use the tubes/lids must be rinsed three times with reagent water and any excess liquid shaken off.

11.2 The uranium removal process may use a single DAAP column or a pair of DAAP columns in series depending on the quantity of uranium in the sample. The procedure as described assumes the use of a pair of DAAP columns in series.

11.3 A column pair is required for each sample in a batch, any spiked samples and a method blank. Preparation of Bulk Pseudo Blank Matrix may also be carried out alongside sample analysis and will require additional column pairs.

11.4 Each column pair is prepared and conditioned as follows:

11.4.1 The pair is set up, one above the other in a column rack or other suitable holder. Each column is checked for bubbling or voiding in the resin and for any yellow coloration and discarded if necessary.

11.4.2 A clean, 25 mL reservoir accessory is attached to each column and a plastic beaker is placed under the lower column. The end caps are removed and the column contents allowed to drain into the beakers.

11.4.3 A pipette is used to add 5 mL of 3 M nitric acid to the reservoir fitted to the upper column and allowed to drain through both columns. The contents of the beaker are discarded as waste. The columns are now conditioned and ready for use.

12. Procedure

12.1 Take an appropriate number of 25 mL sample tubes with lids and label with sample details. One tube is required for each sample in a batch, any spiked samples and a method blank. Preparation of Bulk Pseudo Blank Matrix may also be carried out alongside sample analysis and will require additional tubes.

12.2 Pipet 3 mL of Synthetic Pseudo Blank Matrix into the sample tube for the method blank and into any sample tubes that are to be used to generate Bulk Pseudo Blank Matrix.

12.3 Pipet 3 mL of each hydrolyzed UF₆ sample into a separate sample tube. At least one sample should be prepared in duplicate, with the duplicate sample to be spiked.

NOTE 10—3 mL of 4 % by weight of hydrolyzed UF₆ sample solution contains 0.084 g of uranium based on a density of 1.035 g/mL. This value was obtained by repeated weighing of known volumes of solution at 22 °C.

12.4 Pipet 0.1 mL of the Boron, Silicon, and Technetium Instrument Quality Control Stock/Spike Solution into each sample that requires spiking.

12.5 Pipet 0.3 mL of concentrated nitric acid into each sample tube. Screw the lid on to each tube and swirl gently to mix.

12.6 Take an appropriate number of 50 mL sample tubes with lids and label with sample details. One tube is required for each 25 mL sample tube that has been prepared. Place a 50 mL sample tube below each of the pre-conditioned DAAP column pairs (see 11.4.1 – 11.4.3).

12.7 Add the contents of each 25 mL sample tube to the reservoir fitted to the top column of a separate column pair. Use a few mL of 2M nitric acid to rinse the sample tube and lid and also add the rinsing to the reservoir. Allow to drain fully through both columns into the 50 mL sample tube.

12.8 Pipet 5 mL of 2 M nitric acid into the reservoir fitted to the top column of each column pair and allow to drain fully through both columns. Repeat with a second 5 mL aliquot of 2 M nitric acid.

12.9 Once the columns have fully drained make up to 50 mL with reagent water. Screw the lids on to the sample tubes and mix thoroughly.

12.10 Any material intended for use as Bulk Pseudo Blank Matrix is analyzed as a sample. If it is found to have very low levels of boron, silicon, and technetium then it is collected, bulked and used to prepare calibration standards and instrument quality control samples (see 8.1.14). If levels are deemed to be too high then the liquid is discarded alongside other effluents arising from the analysis.

NOTE 11—Upper limits should be set for retention of material as Bulk Pseudo Blank Matrix. If sample analysis is carried out in order to demonstrate conformance with Specifications C787 or C996 then upper limits in the region of 10 % of the relevant limit in the specification are considered appropriate; alternatively, the upper limit may be set as the Limit of Detection for the method as calculated by the laboratory. It is noted that the method blank does not use Bulk Pseudo Blank Matrix so that blank subtraction will tend to correct for any calibration bias that might be introduced through trace quantities of analyte in the calibration standards prepared using the Bulk Pseudo Blank Matrix.

12.11 Place a 100 mL plastic beaker under each pair of columns. Pipet 5 mL of 0.1 M hydrochloric acid into the reservoir fitted to the top column of each column pair and allow to drain fully through both columns. Repeat at least three times until there is no yellow coloration in the resin. Dispose of the content of the beaker in accordance with laboratory procedures for uranium contaminated effluent. This process regenerates the column for repeat use. Replace the end caps on each column and store in reagent water until next required.

12.12 Prepare the ICP-MS for analysis in accordance with the manufacturer's instructions. Conduct any necessary tuning and performance checks.

12.13 It is recommended that the ICP-MS be conditioned by flushing through with previously analyzed sample or Bulk Pseudo Blank Matrix for a minimum of 30 min prior to calibration.

12.14 Fill 50 mL clean sample containers with an appropriate quantity of each of the four calibration solutions described in 10.4 – 10.7. Fill a fifth 50 mL sample container with an appropriate quantity of the instrument quality control sample described in 10.9.

12.15 Provide the instrument with an appropriate quantity of the internal reference solution described in 10.2.