



Designation: C 1219 – 92 (Reapproved 1997)

## Standard Test Methods for Arsenic in Uranium Hexafluoride<sup>1</sup>

This standard is issued under the fixed designation C 1219; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 These test methods are applicable to the determination of total arsenic in uranium hexafluoride ( $UF_6$ ) by atomic absorption spectrometry. Two test methods are given: Test Method A—Arsine Generation-Atomic Absorption (Sections 5-10), and Test Method B—Graphite Furnace Atomic Absorption (Sections 11-16).

1.2 The test methods are equivalent. The limit of detection for each test method is 0.1  $\mu g$  As/g U when using a sample containing 0.5 to 1.0 g U.

1.3 Test Method A covers the measurement of arsenic in uranyl fluoride ( $UO_2F_2$ ) solutions by converting arsenic to arsine and measuring the arsine vapor by flame atomic absorption spectrometry.

1.4 Test Method B utilizes a solvent extraction to remove the uranium from the  $UO_2F_2$  solution prior to measurement of the arsenic by graphite furnace atomic absorption spectrometry.

1.5 Both insoluble and soluble arsenic are measured when  $UF_6$  is prepared according to Test Method C 761.

1.6 *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.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

C 761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride<sup>2</sup>

C 787 Specification for Uranium Hexafluoride for Enrichment<sup>2</sup>

D 1193 Specification for Reagent Water<sup>3</sup>

### 3. Summary of Test Methods

3.1 *Arsine Generation-Atomic Absorption Spectrometry Method*—The sample of  $UF_6$  is hydrolyzed and the  $UO_2F_2$

solution is fumed with sulfuric acid in the presence of boric acid to complex the fluoride. Potassium iodide is used to reduce arsenic(V) to arsenic(III). Sodium borohydride is used to generate arsine vapor in a hydride generator with subsequent measurement by flame atomic absorption spectrometry.

3.2 *Graphite Furnace Atomic Absorption Spectrometry Method*—The sample of  $UF_6$  is hydrolyzed, and the uranium in the  $UO_2F_2$  solution is removed by extraction with tri(2-ethylhexyl)phosphate/heptane. The aqueous phase containing the arsenic is analyzed by graphite furnace atomic absorption.

### 4. Significance and Use

4.1 Arsenic compounds are suspected to cause corrosion in some materials used in  $UF_6$  handling equipment. Arsenic originates as a contaminant in fluorspar ( $CaF_2$ ) used to produce anhydrous hydrogen fluoride which is used subsequently in the production of  $UF_6$ .

4.2 These test methods are used to measure the arsenic content in  $UO_2F_2$  solutions prepared from the hydrolysis of  $UF_6$  for determination of conformance to Specification C 787.

### TEST METHOD A—ARSINE GENERATION-ATOMIC ABSORPTION SPECTROMETRY

#### 5. Interferences

5.1 The presence of hydrofluoric acid in the sample suppresses arsine generation when using sodium borohydride. Boric acid is added to complex the fluoride present at a molar excess of 250 %.<sup>4</sup>

5.2 Arsenic(V) must be reduced to arsenic(III) otherwise arsine will not be generated using sodium borohydride and hydrochloric acid.

5.3 The reduction of arsenic(V) by potassium iodide is time dependent at room temperature requiring strict adherence to the procedure.

5.4 Do not use platinum labware.

<sup>1</sup> This test methods are under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and are the direct responsibility of Subcommittee C26.05 on Methods of Tests.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 12.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> Petrik, K., and Krivan, V., "Radiotracer Investigation of the Interference of Hydrofluoric Acid in the Determination of Arsenic and Antimony by Hydride Generation Atomic Absorption Spectroscopy," *Analytical Chemistry*, Vol 59, No. 20 (1987), pp. 2426–2427.

## 6. Apparatus

6.1 *Atomic Absorption Spectrometer*, equipped with an air-acetylene burner, arsenic hollow cathode lamp and hydride generator, gas/liquid separator, and hydride absorption cell.

6.2 *Hot Plate*, capable of reaching a surface temperature of 500°C.

## 7. Reagents and Materials

### 7.1 Reagents:

7.1.1 *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.<sup>5</sup> 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.

7.1.2 *Purity of Water*— Unless otherwise indicated, references to water shall mean reagent water Type II conforming to Specification D 1193.

7.1.3 *Acetylene* (C<sub>2</sub>H<sub>2</sub>), 99.6 % minimum purity.

7.1.4 *Air*—compressed breathing air or equivalent.

7.1.5 *Arsenic Standard Stock Solution* (1000 mg As/L)—Dissolve 1.320 g of arsenic trioxide (As<sub>2</sub>O<sub>3</sub>) in 100 mL of hydrochloric acid (1 + 2) and dilute to 1 L. Commercially available stock solutions traceable to NIST primary standards may be used.

7.1.6 *Arsenic Standard Solution* (0.10 mg As/L)—Pipet 10 mL of 1000 mg/L arsenic stock solution into a 1-L volumetric flask containing 500 mL of water. Add 20 mL of concentrated hydrochloric acid, dilute to volume with water and mix. This (10 mg/L) solution should be kept no longer than one month. Pipet 2 mL of the 10 mg/L arsenic solution into a 200-mL volumetric flask containing 100 mL of water. Add 4 mL of concentrated hydrochloric acid and dilute to volume with water.

NOTE 1—The 0.10-mg As/L solution must not be kept longer than one day.

7.1.7 *Boric Acid* (H<sub>3</sub>BO<sub>3</sub>).

7.1.8 *Hydrochloric Acid* (sp gr 1.18)—Concentrated hydrochloric acid (HCl).

7.1.9 *Hydrochloric Acid* (1 + 1)—Add one volume of concentrated hydrochloric acid to one volume of water.

7.1.10 *Hydrochloric Acid* (1 + 2)—Add one volume of concentrated hydrochloric acid to two volumes of water.

7.1.11 *Nitrogen* (N<sub>2</sub>), 99.9 % minimum purity.

7.1.12 *Potassium Iodide Solution* (50 % w/v)—Dissolve 50 g of potassium iodide in water and dilute to 100 mL in a volumetric flask. Store in a brown bottle.

NOTE 2—The colorless solution is stable for two days. A yellow tinge indicates the solution has deteriorated.

7.1.13 *Sodium Borohydride Solution* (6.0 g/L)—Dissolve 3.0 g of sodium borohydride (NaBH<sub>4</sub>) and 2.5 g of sodium hydroxide (NaOH) in water and dilute to 500 mL in a volumetric flask. This solution should be prepared weekly.

7.1.14 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).

## 8. Calibration and Standardization

8.1 *Instrument Parameters*—A set of suggested atomic absorption operating parameters is listed in Table 1 and Table 2. The parameters may vary with the type of instrument used and the manufacturer's instructions.

### 8.2 Preparation of Calibration Solutions:

8.2.1 Aliquot 0, 2, 5, 10, 20, and 30 mL of the 0.10 mg As/L solution into 100-mL volumetric flasks. Add 2 mL concentrated H<sub>2</sub>SO<sub>4</sub> and 10 mL concentrated HCl to each flask.

8.2.2 Add 2 mL of 50 % potassium iodide solution and dilute to volume with water 75 min before running the calibration solutions.

### 8.3 Calibration:

8.3.1 Follow the manufacturer's directions to calibrate the instrument. Use the following arsenic calibration solutions with a 30-s water rinse between each solution: 0, 0.002, 0.005, 0.010, 0.020, and 0.030 mg As/L. If the AA is manually controlled, record the absorbances.

8.3.2 With a microprocessor-controlled instrument, generate the calibration curve using the manufacturer's directions. The calibration curve can also be generated manually by graphing the absorbance of the calibration solutions on the ordinate and the corresponding concentration on the abscissa.

8.3.3 Verify the calibration by running the mid-range 0.010 mg As/L calibration solution. If the value differs by more than 5 %, repeat the calibration.

## 9. Procedure

### 9.1 Sample Preparation:

9.1.1 Prepare a hydrolyzed UF<sub>6</sub> solution within a concentration range of 50 to 250 g/L U using the appropriate sections of Test Method C 761.

9.1.2 Transfer an aliquot of UO<sub>2</sub>F<sub>2</sub> solution containing approximately 0.5 g of uranium into a 125-mL Erlenmeyer flask.

9.1.3 Add 0.5 g of H<sub>3</sub>BO<sub>3</sub> and 2 mL of concentrated H<sub>2</sub>SO<sub>4</sub> to the sample.

9.1.4 Heat the sample at 325°C until the acid starts to fume. Increase the hot plate temperature to 385°C. When the sample fumes vigorously, increase the temperature to 500°C and heat until the acid fumes lift above the solution.

**TABLE 1 Atomic Absorption Operating Parameters**

Element	arsenic
Wavelength, nm	193.7
Lamp current, mA	10
Slit width, nm	0.5
Gas	C <sub>2</sub> H <sub>2</sub> /air
Acetylene, psig	9
Air, psig	40
Argon, psig	50
Fuel flow, L/min	1.5
Oxidant flow, L/min	4.0

<sup>5</sup> "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 "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Company, Inc., New York, New York, and the "United States Pharmacopeia."