



Standard Test Methods for Arsenic in Uranium Hexafluoride¹

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1. Scope

1.1 These test methods are applicable to the determination of total arsenic in uranium hexafluoride (UF₆) 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 µg 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 (UO₂F₂) 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 UO₂F₂ solution prior to measurement of the arsenic by graphite furnace atomic absorption spectrometry.

1.5 Both insoluble and soluble arsenic are measured when UF₆ 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 Hexafluoride²

C 787 Specification for Uranium Hexafluoride for Enrichment²

D 1193 Specification for Reagent Water³

3. Summary of Test Methods

3.1 *Arsine Generation-Atomic Absorption Spectrometry Method*—The sample of UF₆ is hydrolyzed and the UO₂F₂

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 UF₆ is hydrolyzed, and the uranium in the UO₂F₂ 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 UF₆ handling equipment. Arsenic originates as a contaminant in fluor spar (CaF₂) used to produce anhydrous hydrogen fluoride which is used subsequently in the production of UF₆.

4.2 These test methods are used to measure the arsenic content in UO₂F₂ solutions prepared from the hydrolysis of UF₆ for determination of conformance to Specification C 787.

TEST METHOD A—ARSI NE 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 %.⁴

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.

6. Apparatus

6.1 *Atomic Absorption Spectrometer*, equipped with an air-acetylene burner, arsenic hollow cathode lamp and hydride

¹ 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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² *Annual Book of ASTM Standards*, Vol 12.01.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ 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.

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.⁵ 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_2H_2), 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_2O_3) 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_3BO_3).

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_2), 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 ($NaBH_4$) 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_2SO_4).

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_2SO_4 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_6 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_2F_2 solution containing approximately 0.5 g of uranium into a 125-mL Erlenmeyer flask.

9.1.3 Add 0.5 g of H_3BO_3 and 2 mL of concentrated H_2SO_4 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.

9.1.5 Remove sample from hot plate and cool to room temperature.

9.1.6 Quantitatively transfer the sample into a 100-mL volumetric flask and add 10 mL concentrated HCl.

TABLE 1 Atomic Absorption Operating Parameters

Element	arsenic
Wavelength, nm	193.7
Lamp current, mA	10
Slit width, nm	0.5
Gas	C_2H_2 /air
Acetylene, psig	9
Air, psig	40
Argon, psig	50
Fuel flow, L/min	1.5
Oxidant flow, L/min	4.0

⁵ "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."

TABLE 2 Hydride Generator Operating Parameters

Sample flow, mL/min	8
Hydrochloric acid flow, mL/min	1
Sodium borohydride flow, mL/min	1

9.1.7 Add 2 mL of potassium iodide solution (50 % w/v) and dilute to volume with water. Allow a minimum of 75 min at room temperature for the reaction to occur.

9.2 Quality Control:

9.2.1 Prepare one reagent blank with each batch of samples.

9.2.2 Transfer a duplicate aliquot of one sample from each batch into a 125-mL Erlenmeyer flask. Spike this sample with a known amount of arsenic based on the expected concentration of the sample.

9.2.3 Take the reagent blank and the spiked sample through procedure steps 9.1.3-9.1.7.

9.3 Sample Measurement:

9.3.1 Measure the arsenic content in the samples after calibration of the instrument as outlined in Section 8.

9.3.2 Record the concentration for calculation in Section 10. With an instrument which is not microprocessor-controlled, record the absorbance and determine the concentration from the calibration graph.

9.3.3 Use a 30-s water rinse between samples if running several samples. After 10 samples verify the calibration by running the midrange calibration solution again. If the value deviates by more than 5 %, repeat the calibration and measure the samples again.

10. Calculation

10.1 Calculate the arsenic concentration using the following equation:

$$\mu\text{g As/g U} = \frac{A \times B}{C \times D} \times 1000 \quad (1)$$

where:

- A = aliquot concentration (mg As/L) from the calibration curve using the sample absorbance,
- B = dilution volume, mL,
- C = sample aliquot size, mL, and
- D = uranium concentration of sample, g/L.

TEST METHOD B—GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

11. Interferences

11.1 Fluoride interferes with the extraction process and must be removed by evaporation with nitric acid.

11.2 Molecular (nonatomic) absorption interferences are corrected by Zeeman background correction.

11.3 Chlorides may cause loss of arsenic in the drying step.

12. Apparatus

12.1 *Graphite Furnace Atomic Absorption Spectrometer with Zeeman Background Correction:*

12.1.1 *Wavelength Source*, either a hollow cathode lamp or electrodeless discharge lamp to provide arsenic emission lines.

12.1.2 Stabilized temperature platform furnace tubes and platforms.

13. Reagents and Materials

13.1 Reagents:

13.1.1 *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.⁵ 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.

13.1.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

13.1.3 *Arsenic Standard Solution* (0.1 mg/L)—Use 1000 mg/L certified aqueous standard. Dilute 5 mL of 1000 mg/L solution in 500 mL water with 1 mL HNO₃. This solution will be 10 mg/L arsenic. From the 10 mg/L solution, dilute 5 mL into 500 mL water to prepare a 0.1-mg/L solution.

NOTE 3—Prepare 0.1-mg/L solution daily.

13.1.4 *Arsenic Standard Stock Solution* (1000 mg/L)—Certified aqueous standard traceable to NIST primary standards.

13.1.5 *Heptane*, high purity.

13.1.6 *Nickel Nitrate Solution* (5 % Ni w/v)—Dissolve 24.780 g of Ni(NO₃)₂·6H₂O in water and dilute to 100 mL in a volumetric flask.

13.1.7 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO₃).

13.1.8 *Nitric Acid* (1 + 3)—Add one part by volume concentrated HNO₃ to three parts water.

13.1.9 *TEHP-Heptane Solution* (1 + 1)—Mix equal volumes of TEHP and heptane (500 mL each) in a large separatory funnel. Add 100 mL concentrated HNO₃ and shake vigorously to wash the organic layer. Let stand and drain the acid layer. Repeat with rinsewater until the water pH is >3.0.

13.1.10 *Tri(2-ethyl-hexyl)phosphate (TEHP)*—Technical grade.

14. Calibration and Standardization

14.1 *Instrument Parameters*—A set of suggested parameters for the atomic absorption instrument and the graphite furnace is listed in Table 3 and Table 4. The parameters may vary with the type of instrument used and the manufacturer's instructions. Suitable performance may be verified by the analysis of standard solutions.

14.2 Prepare Calibration Standards:

14.2.1 To each of five 10-mL volumetric flasks, add 4 drops of nickel nitrate solution.

TABLE 3 Atomic Absorption Operating Parameters

Element	arsenic
Wavelength, nm	193.7
Lamp power, watts	8
Slit width, nm	0.7
Peak height, time	10 s
Purge gas	argon
Source	EDL
Mode	peak height

TABLE 4 Graphite Furnace Parameters

	Step 1	Step 2	Step 3	Step 4
Temperature, °C	130	600	2400	2500
Ramp time, s	5	5	2	2
Hold time, s	25	25	5	2
Read, s	...	...	-3	...
Record, s	...	...	-5	...
Internal flow, mL	300	300	0	300

14.2.2 Retain one flask as a blank and dilute to volume with water.

14.2.3 Using the 0.1 mg/L arsenic standard solution, add 1, 2, 3, and 5-mL aliquots to the four remaining flasks to produce standard solutions of 0.01, 0.02, 0.03, and 0.05 mg/L As.

14.3 Calibration:

14.3.1 Using the blank and calibration standards, calibrate the instrument automatically in the concentration mode.

14.3.2 Alternatively prepare a calibration curve plotting peak height versus concentration.

14.3.3 A quality control sample is analyzed following the standards. This control must fall within the 95 % confidence range specified by the supplier.

14.3.4 Verify calibration with an independently prepared check standard every 15 samples, or per run/batch.

15. Procedure

15.1 Sample Preparation:

15.1.1 Hydrolyze the UF₆ according to Test Method C 761.

15.1.2 Pipet duplicate aliquots of the UO₂F₂ solution containing approximately 1 g U into numbered polytetrafluoroethylene (PTFE) dishes.

15.1.3 Add 10 mL of concentrated HNO₃.

15.1.4 Cover with a PTFE cover. Evaporate to near dryness on a hot plate under a fume hood. Remove from heat, cool, and add 10 mL concentrated HNO₃. Replace cover and return to hot plate. Evaporate to near dryness (dryness should occur on cooling).

15.2 Quality Control:

15.2.1 Prepare two reagent blanks with each batch of samples.

15.2.2 Choose one sample of each batch to be spiked. Prepare an additional PTFE dish of this sample for spiking. Add additional spike material based upon expected concentration and dilution factors. Add the same amount of spike material to an empty PTFE dish (extraction process control).

15.2.3 Take the blanks, spiked sample, and extraction process control through steps 15.1.3 and 15.1.4.

15.3 Extraction of Uranium:

15.3.1 Pipet 10 mL of (1 + 3) HNO₃ to each dry sample in PTFE dishes.

15.3.2 After dissolution, transfer to 60-mL separatory funnels.

15.3.3 Add 10 mL of TEHP-heptane mix, stopper, and shake for 2 min. Allow phases to separate.

15.3.4 Drain the aqueous phase into another 60-mL separatory funnel and repeat 15.3.3 twice for a total of three extractions.

15.3.5 Drain the aqueous phase containing the arsenic into a 10-mL volumetric flask containing four drops nickel nitrate solution, stopper, and retain for analysis.

NOTE 4—Nickel nitrate solution must be added at this point if samples are not to be analyzed immediately.

15.4 Measurement:

15.4.1 If expected arsenic concentration is less than 0.5 µg/g, measure the arsenic content in the aqueous phase directly after calibration of the instrument as outlined in Section 14.

15.4.2 If As level is expected to be between 0.5 µg/g and 5 µg As/g U, pipet an aliquot (1 to 5 mL) of aqueous solution into a 10-mL volumetric flask, add sufficient nickel nitrate solution to approximate standard nickel concentration, and dilute to volume with water.

15.4.3 If, upon analysis, samples are out of range of standards, repeat 15.4.2 with a smaller aliquot of aqueous phase.

15.4.4 Record the concentration for calculation in Section 16.

16. Calculation

16.1 Calculate the arsenic concentration using the following equation:

$$\mu\text{g As/g U} = \frac{A \times B}{C \times D} \times 1000 \quad (2)$$

where:

A = measured As concentration × 10, µg/mL,

B = secondary dilution volume, mL,

C = secondary aliquot size, mL, and

D = uranium in sample, g.

17. Precision and Bias

17.1 Precision—The within laboratory precision for Test Method A and Test Method B is shown in Table 5.

17.2 Bias—No standard material certified for As in UF₆ is available. To determine bias estimates for Test Method A and Test Method B, uranyl fluoride solutions were spiked with NIST traceable standard materials. The bias estimates are indicated in Table 6.

18. Keywords

18.1 arsenic; arsine; arsine generation; atomic absorption spectrometry; graphite furnace; uranium hexafluoride; uranyl

TABLE 5 Within Laboratory Precision

Test Method	Concentration, µg As/g U	Standard Deviation	% RSD	Number of Determinations
A	0.43	0.055	12.8	20
	2.00	0.122	6.3	40
	8.90	0.47	5.3	40
B	0.17	0.028	16.5	15
	0.87	0.096	11.0	15
	2.21	0.316	14.3	15
	2.73	0.317	11.6	15
	12.06	1.86	15.4	15

TABLE 6 Bias Estimates

Test Method	µg As/g U	Mean	Bias Estimate	Number of Determinations
A	1.996	1.909	-0.087	20
B	0.10	0.115	0.015	31

fluoride; Zeeman background correction

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