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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 (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 (Appendix X1).

1.2 The test methods are equivalent. The limit of detection for each test method is 0.1 $\mu\text{g As/g U}$ when using a sample containing 0.5 to 1.0 g U. Test Method B does not have the complete collection details for precision and bias data thus the method appears as an appendix.

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 C761.

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

1.7 *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 appro-*

priate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 *ASTM Standards:*²

C761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride

C787 Specification for Uranium Hexafluoride for Enrichment

D1193 Specification for Reagent Water

3. Summary of Test Method

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 .

¹ This test methods are under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and are 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.

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 C787.

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 %.³

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 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.⁴ 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 D1193.

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.

³ 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.

⁴ *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

TABLE 1 Atomic Absorption Operating Parameters

Element	arsenic
Wavelength, nm	193.7
Lamp current, mA	10
Slit width, nm	0.5
Gas	$\text{C}_2\text{H}_2/\text{air}$
Acetylene, psig	9
Air, psig	40
Argon, psig	50
Fuel flow, L/min	1.5
Oxidant flow, L/min	4.0

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 Tables 1 and 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:

TABLE 2 Hydride Generator Operating Parameters

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

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 UF₆ solution within a concentration range of 50 to 250 g/L U using the appropriate sections of Test Method C761.

9.1.2 Transfer an aliquot of UO₂F₂ solution containing approximately 0.5 g of uranium into a 125-mL Erlenmeyer flask.

9.1.3 Add 0.5 g of H₃BO₃ and 2 mL of concentrated H₂SO₄ 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.

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.

TABLE 3 Within Laboratory Precision

Test Method	Concentration, µg As/g U	Standard Deviation	% RSD	Number of Determinations
A	0.35	0.033	9.4	30
	3.76	0.23	6.1	30
	13.60	0.69	5.0	30

TABLE 4 Bias Estimates

Test Method	µg As/g U	Mean	Bias Estimate	Number of Determinations
A	1.996	1.909	-0.087	20

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.

11. Precision and Bias

11.1 *Precision*—The within laboratory precision for Test Method A is shown in Table 3. The data for Test Method A was collected over a 10 month period in one laboratory by 4 technicians. The samples were taken through the entire Test Method A.

11.2 *Bias*—No standard material certified for As in UF₆ is available. To determine bias estimates for Test Method A, uranyl fluoride solutions were spiked with NIST traceable standard materials. The bias estimates are indicated in Table 4.

12. Keywords

12.1 arsenic; arsine; arsine generation; atomic absorption spectrometry; graphite furnace; uranium hexafluoride; uranyl fluoride; Zeeman background correction



APPENDIX

(Nonmandatory Information)

X1. TEST METHOD B—GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

X1.1 Interferences

X1.1.1 Fluoride interferes with the extraction process and must be removed by evaporation with nitric acid.

X1.1.2 Molecular (nonatomic) absorption interferences are corrected by Zeeman background correction.

X1.1.3 Chlorides may cause loss of arsenic in the drying step.

X1.2 Apparatus

X1.2.1 *Graphite Furnace Atomic Absorption Spectrometer with Zeeman Background Correction:*

X1.2.1.1 *Wavelength Source*, either a hollow cathode lamp or electrodeless discharge lamp to provide arsenic emission lines.

X1.2.1.2 Stabilized temperature platform furnace tubes and platforms.

X1.3 Reagents and Materials

X1.3.1 *Reagents:*

X1.3.1.1 *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.⁴ 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.

X1.3.1.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification **D1193**.

X1.3.1.3 *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 X1.1—Prepare 0.1-mg/L solution daily.

X1.3.1.4 *Arsenic Standard Stock Solution* (1000 mg/L)—Certified aqueous standard traceable to NIST primary standards.

X1.3.1.5 *Heptane*, high purity.

X1.3.1.6 *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.

X1.3.1.7 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO₃).

X1.3.1.8 *Nitric Acid* (1 + 3)—Add one part by volume concentrated HNO₃ to three parts water.

X1.3.1.9 *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

TABLE X1.1 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

to wash the organic layer. Let stand and drain the acid layer. Repeat with rinsewater until the water pH is >3.0.

X1.3.1.10 *Tri(2-ethyl-hexyl)phosphate (TEHP)*—Technical grade.

X1.4 Calibration and Standardization

X1.4.1 *Instrument Parameters*—A set of suggested parameters for the atomic absorption instrument and the graphite furnace is listed in **Tables X1.1 and X1.2**. 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.

X1.4.2 *Prepare Calibration Standards:*

X1.4.2.1 To each of five 10-mL volumetric flasks, add 4 drops of nickel nitrate solution.

X1.4.2.2 Retain one flask as a blank and dilute to volume with water.

X1.4.2.3 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.

X1.4.3 *Calibration:*

X1.4.3.1 Using the blank and calibration standards, calibrate the instrument automatically in the concentration mode.

X1.4.3.2 Alternatively prepare a calibration curve plotting peak height versus concentration.

X1.4.3.3 A quality control sample is analyzed following the standards. This control must fall within the 95 % confidence range specified by the supplier.

X1.4.3.4 Verify calibration with an independently prepared check standard every 15 samples, or per run/batch.

X1.5 Procedure

X1.5.1 *Sample Preparation:*

X1.5.1.1 Hydrolyze the UF₆ according to Test Method **C761**.

X1.5.1.2 Pipet duplicate aliquots of the UO₂F₂ solution containing approximately 1 g U into numbered polytetrafluoroethylene (PTFE) dishes.

X1.5.1.3 Add 10 mL of concentrated HNO₃.

X1.5.1.4 Cover with a PTFE cover. Evaporate to near dryness on a hot plate under a fume hood. Remove from heat,

TABLE X1.2 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

cool, and add 10 mL concentrated HNO₃. Replace cover and return to hot plate. Evaporate to near dryness (dryness should occur on cooling).

X1.5.2 Quality Control:

X1.5.2.1 Prepare two reagent blanks with each batch of samples.

X1.5.2.2 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).

X1.5.2.3 Take the blanks, spiked sample, and extraction process control through steps X1.5.1.3 and X1.5.1.4.

X1.5.3 Extraction of Uranium:

X1.5.3.1 Pipet 10 mL of (1 + 3) HNO₃ to each dry sample in PTFE dishes.

X1.5.3.2 After dissolution, transfer to 60-mL separatory funnels.

X1.5.3.3 Add 10 mL of TEHP-heptane mix, stopper, and shake for 2 min. Allow phases to separate.

X1.5.3.4 Drain the aqueous phase into another 60-mL separatory funnel and repeat X1.5.3.3 twice for a total of three extractions.

X1.5.3.5 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 X1.2—Nickel nitrate solution must be added at this point if samples are not to be analyzed immediately.

X1.5.4 Measurement:

X1.5.4.1 If expected arsenic concentration is less than 0.5 mg/g, measure the arsenic content in the aqueous phase directly after calibration of the instrument as outlined in Section X1.4.

X1.5.4.2 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.

X1.5.4.3 If, upon analysis, samples are out of range of standards, repeat X1.5.4.2 with a smaller aliquot of aqueous phase.

X1.5.4.4 Record the concentration for calculation in Section X1.6.

TABLE X1.3 Within Laboratory Precision

Test Method	Concentration,	Standard Deviation	% RSD	Number of Determinations
B	0.17	0.28	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 X1.4 Bias Estimates

Test Method	µg As/g U	Mean	Bias Estimate	Number of Determinations
B	0.10	0.115	0.015	31

X1.6 Calculation

X1.6.1 Calculate the arsenic concentration using the following equation:

$$\mu\text{g As/g U} = \frac{A \times B}{C \times D} \times 1000 \quad (\text{X1.1})$$

where:

- A = measured As concentration × 10, µg/mL,
- B = secondary dilution volume, mL,
- C = secondary aliquot size, mL, and
- D = uranium in sample, g.

X1.7 Precision and Bias

X1.7.1 *Precision*—The within laboratory precision for Test Method B is shown in Table X1.3. Information about the collection details for data for Test Method B is unavailable from laboratory B.

X1.7.2 *Bias*—No standard material certified for As in UF₆ is available. To determine bias estimates for Test Method B, uranyl fluoride solutions were spiked with NIST traceable standard materials. The bias estimates are indicated in Table X1.4.

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