



Standard Test Method for Determination of Bromine and Chlorine in UF₆ and Uranyl Nitrate by X-Ray Fluorescence (XRF) Spectroscopy¹

This standard is issued under the fixed designation C1508; 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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This method covers the determination of bromine (Br) and chlorine (Cl) in uranium hexafluoride (UF₆) and uranyl nitrate solution. The method as written covers the determination of bromine in UF₆ over the concentration range of 0.2 to 8 µg/g, uranium basis. The chlorine in UF₆ can be determined over the range of 4 to 160 µg/g, uranium basis. Higher concentrations may be covered by appropriate dilutions. The detection limit for Br is 0.2 µg/g uranium basis and for Cl is 4 µg/g uranium basis.

1.2 *This standard may involve hazardous materials, operations and equipment. 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:²

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

C787 Specification for Uranium Hexafluoride for Enrichment

C788 Specification for Nuclear-Grade Uranyl Nitrate Solution or Crystals

C1118 Guide for Selecting Components for Wavelength-Dispersive X-Ray Fluorescence (XRF) Systems (Withdrawn 2011)³

D1193 Specification for Reagent Water

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.

Current edition approved June 1, 2011. Published June 2011. Originally approved in 2001. Last previous edition approved in 2006 as C1508 – 01(2006). DOI: 10.1520/C1508-01R1.

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 The last approved version of this historical standard is referenced on www.astm.org.

3. Summary of Test Method

3.1 A sample of hydrolyzed UF₆ (uranyl fluoride) or uranyl nitrate solution is treated with sodium nitrite to reduce oxidized forms of bromine and chlorine (bromates and chlorates) to their respective halide ions. Addition of silver nitrate precipitates the silver halides. Spike recoveries can be improved by the addition of potassium iodide causing coprecipitation of the halides. The halides are collected on filter paper and are analyzed by X-ray fluorescence using two different crystal/detector systems.

4. Significance and Use

4.1 The method is designed to show whether or not the tested materials meet the specifications as given in Specifications **C787** and **C788**.

5. Interferences

5.1 Plastic equipment must be used throughout the method for uranyl fluoride as the hydrofluoric acid in the uranyl fluoride leaches chloride from glassware causing a high bias.

5.2 Low recoveries may occur as the precipitate can be difficult to transfer quantitatively to the filter paper. A surfactant can be added (optional step) to minimize the adhesion of the precipitate to the walls of the beakers and the funnel.

6. Apparatus

6.1 *X-Ray Spectrometer*; see Guide **C1118** for the selection of the X-ray Spectrometer.

6.2 *Plastic Vacuum Filtration Apparatus*, for 47 mm diameter filter paper.

6.3 *Filter Paper*, 0.45 micron, 47 mm diameter.⁴

6.4 *Beakers*, polypropylene, 250 mL.

6.5 *Stirring Rods*, plastic or Teflon.

6.6 *X-ray Sample Support, Rings*. Inner diameter approximately 40 mm.

⁴ The filter must be Cl and Br free. Millipore membrane filter type HABP (www.millipore.com) has been successfully used. An alternate is 15A from S.C.B, BP6, RN86, 07130 Soyons France. Any other equivalent is acceptable.



7. Reagents

7.1 *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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type I.

7.3 *Ammonium Hydroxide*, NH_4OH , concentrated, specific gravity 0.90.

7.4 *Ammonium Hydroxide Solution*, 1 + 3 (3.7 M). Dilute 1 part NH_4OH with 3 parts water.

7.5 *Surfactant*, bromine and chlorine free.⁶ (Optional).

7.6 *Surfactant Solution*, 1 + 999. Add 1 mL of surfactant to approximately 1 litre of water. (Optional).

7.7 *Nitric Acid*, HNO_3 , concentrated, specific gravity 1.42.

7.8 *Nitric Acid Solution*, 1 + 999 (0.016 M). Add 1 mL of concentrated HNO_3 to approximately 200 mL of water. Add 1 mL of the surfactant (7.6). (Optional). Dilute to 1 litre.

7.9 *Sodium Nitrite*, NaNO_2 .

7.10 *Sodium Nitrite Solution*, 2 g/L. Dissolve 1 g of sodium nitrite in water and dilute to 500 mL. Prepare fresh immediately before use.

7.11 *Silver Nitrate*, AgNO_3 .

7.12 *Silver Nitrate Solution*, 2 g/L. Dissolve 2 g of silver nitrate in water and dilute to 1 litre. Keep away from light in an opaque bottle. The solution should be made fresh weekly. Silver is an RCRA listed hazardous waste. Make up only as much of this solution as required to minimize excess waste.

7.13 *Potassium Bromide*, KBr .

7.14 *Bromide Solution*, 500 mg Br/L. Dissolve 0.1861 g of KBr (dried at 110°C for 1 hour) in water and dilute to 250 mL in a volumetric flask.

7.15 *Sodium Chloride*, NaCl .

7.16 *Sodium Chloride Solution*, 1000 mg Cl/L. Dissolve 1.648 g NaCl (dried at 110°C for 1 hour) in water and dilute to 1 litre in a volumetric flask.

7.17 *Spike Solution*, 5 mg Br/L, 100 mg Cl/L. Transfer 10 mL of 500 mg Br/L solution into a 1 litre volumetric flask by pipette. Transfer 100 mL of 1000 mg Cl/L into the flask by pipette. Dilute to volume.

7.18 *Potassium Iodide*, KI . (Optional).

7.19 *Potassium Iodide Solution*, (Optional), 1g I/L. Dissolve 0.131 g potassium iodide in water and dilute to 100 mL. The solution should be prepared weekly.

8. Standard Preparation

8.1 Pipette the following aliquots of spike solution (from 7.17) into polypropylene beakers. 0 mL, 1 mL, 2 mL, 5 mL, 10 mL. The aliquots represent 0 μg Br, 5 μg Br, 10 μg Br, 25 μg Br, 50 μg Br and 0 μg Cl, 100 μg Cl, 200 μg Cl, 500 μg Cl, 1000 μg Cl.

8.2 Add 70 mL water to each beaker.

8.3 Follow steps 9.3-9.8 at the same time as the samples.

9. Procedure

9.1 Transfer a known aliquot of uranyl fluoride solution (prepared following Test Methods C761) or uranyl nitrate that contains a known amount of uranium, approximately 5 g, with a plastic graduated cylinder into a polypropylene beaker containing 70 mL water.

NOTE 1—Recommend cleaning all laboratory equipment with ammonium hydroxide solution (7.4) prior to use.

9.2 Follow laboratory QA practices and run the necessary duplicates, spikes and controls with the samples. Use the solution prepared in 7.17 for the spikes.

NOTE 2—2 mL and 4 mL spike aliquots were found to be reasonable volumes.

9.3 Add 0.5 mL of potassium iodide solution to each sample and standard. (Optional step).

9.4 Add 4 mL of surfactant solution 7.6. (Optional step).

9.5 Add 10 mL of sodium nitrite solution to each sample and standard. Stir each solution with a dedicated plastic stirring rod and allow to stand for a minimum of 2 minutes.

9.6 Slowly and with stirring add 25 mL of the silver nitrate solution. Remove the plastic stirring rods. Heat the solution in a water bath at approximately $80^\circ\text{C} \pm 10^\circ\text{C}$ for 1½ hours.

9.7 Remove from the bath. Allow the halides to precipitate overnight. A2 hour precipitation time has been found to be successful, but the user must establish precision and bias based on the shorter time. The precision and bias data in this standard were generated using an overnight precipitation.

9.8 Filter using 0.45 micron filter paper. Use a plastic vacuum filtration assembly. Use a plastic rod with a rubber policeman to aid the transfer of precipitate to the filter. Use 1

TABLE 1 Suggested X-Ray Settings

	Bromine	Chlorine
Line	K α	K α
Crystal	LiF 200 (Lithium fluoride)	PE (Tetrakis(hydroxymethyl)-methane)
Detector	Scintillation	Flow
Order	1	1
X-ray tube	Rhodium	Rhodium
Tube voltage (kV)	45	45
Tube Amperage (mA)	45	75
Counting Time (s)	40	40

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 *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.

⁶ Triton X-100, Rohm and Haas, has been successfully used.



+ 999 nitric acid solution to wash the precipitate. Dry the filters before counting in the X-ray.

9.9 Place the filters on X-ray sample support rings and tape or glue in place.

9.10 Analyze using the X-ray.

10. Instrument Calibration

10.1 Follow the manufacturer's instructions for setting up the instrument to achieve an inert gas environment and to obtain the following instrument parameters. (See Table 1).

10.2 Run the standards and construct a calibration curve using the instrument's software or by manually plotting the curve using linear chart paper.

10.3 Run the samples. Determine the weight of Br and Cl present on the filter papers from the calibration curves. Calculate the concentration of Br and Cl in the samples by following Section 11.

11. Calculation

11.1 Calculate the halide content as follows:

$$\text{Halide, } \mu\text{g/g uranium basis} = \frac{A \times 1000}{B \times C}$$

where:

- A = micrograms halide from the calibration curve,
- 1000 = conversion factor, litres to millilitres,
- B = sample aliquot from 9.1, in millilitres, and
- C = uranium concentration of sample solution, in g/L.

TABLE 2 Within Laboratory Precision For UF₆

Laboratory	Halide	Concentration ($\mu\text{g halide/g U}$)	Standard Deviation ($\mu\text{g halide/g U}$)	Number of Determinations
A	Bromine	0.44	0.06	10
A	Bromine	3.1	0.2	9
B	Bromine	5.1	0.7	109
A	Chlorine	2.4	2.1	9
A	Chlorine	66	6	8
A	Chlorine	185	19	9
B	Chlorine	48	5	107

12. Precision and Bias

12.1 Uranium Hexafluoride Data:

12.1.1 *Precision in UF₆ Samples*—The single laboratory precision for the average of multiple determinations is given in Table 2. The data for laboratory A were collected using a rhodium X-ray tube and a LiF200 crystal for bromine and a PE crystal for chlorine. Potassium iodide (optional 9.3) was added to the samples in laboratory A. The results were obtained over a 3 month period by two technicians. The results for laboratory B were obtained by 1 technician over a 1 year period. Potassium iodide was not added to Laboratory B samples. The precision is given in Table 2.

12.1.2 *Bias in UF₆ Samples*—No standard material certified for bromine and chlorine in UF₆ is available. Therefore bias cannot be determined. To determine lower bound bias indications uranyl fluoride solutions were spiked with NIST SRM. The uncertainty of the NIST traceable standard is less than the uncertainty of the procedure. The data for Laboratory A were collected over a 3 month period by two technicians. Potassium iodide was added to laboratory A samples. The result data for Laboratory B were obtained over a 1 year period by 1 technician. No potassium iodide was added to laboratory B samples. The mean minus the prepared values are an indication of the bias. The relative differences are given in Table 3. The relative difference is [(mean-known)/known] \times 100 %.

12.2 Uranyl Nitrate Data:

12.2.1 *Precision in Uranyl Nitrate Samples*—The result data were collected in 1 day by 1 technician. The precision is given in Table 4. No potassium iodide (optional 9.3) was added to the uranyl nitrate samples.

12.2.2 *Bias in Uranyl Nitrate Samples*—The bias should be equivalent to the bias in UF₆ samples.

12.3 The supporting data for Tables 2-4 are available from ASTM headquarters.

13. Keywords

13.1 bromine; chlorine; uranium hexafluoride; X-ray fluorescence; XRF



C1508 – 01 (Reapproved 2011)

TABLE 3 Bias Estimates For UF₆

Laboratory	Halide	Spike Concentration (µg halide/g U)	Spike (µg halide)	Mean (µg halide)	Bias Estimate	Relative Difference	Number of Determinations
A	Bromine	2	10	10.6	+0.6	+6 %	10
A	Bromine	4	20	20.5	+0.5	+2.5 %	10
B	Bromine	5	25	25.5	+0.5	+2 %	109
A	Chlorine	40	200	213	+13	+6.5 %	10
A	Chlorine	80	400	450	+50	+12.5 %	10
B	Chlorine	50	250	238	-12	-6 %	107

TABLE 4 Within Laboratory Precision For Uranyl Nitrate Solutions

Halide	Concentration (µg halide/g U)	Standard Deviation	Number of Determinations
Bromine	10	1.5	3
Bromine	Blank	0.04	3
Chlorine	50	9	3
Chlorine	Blank	0.5	3

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