Designation: C1502 – 16

Standard Test Method for Determination of Total Chlorine and Fluorine in Uranium Dioxide and Gadolinium Oxide[1]

This standard is issued under the fixed designation C1502; 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 test method covers the determination of chlorine and fluorine in nuclear-grade uranium dioxide (UO_2) powder and pellets, nuclear grade gadolinium oxide (Gd_2O_3) powder and gadolinium oxide-uranium oxide (Gd_2O_3-UO_2) powder and pellets.

1.2 With a 2 gram UO_2 sample size the detection limit of the method is 4 µg/g for chlorine and 2 µg/g for fluorine. The maximum concentration determined with a 2 gram sample is 500 µg/g for both chlorine and fluorine. The sample size used in this test method can vary from 1 to 10 grams resulting in a corresponding change in the detection limits and range.

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

1.4 *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]

C753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder
C776 Specification for Sintered Uranium Dioxide Pellets
C859 Terminology Relating to Nuclear Materials
C888 Specification for Nuclear-Grade Gadolinium Oxide (Gd_2O_3) Powder
C922 Specification for Sintered Gadolinium Oxide-Uranium Dioxide Pellets
D1193 Specification for Reagent Water

3. Terminology

3.1 *Definitions*—Except as otherwise defined herein, definitions of terms are given in Terminology C859.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *accelerator*—a chemical compound or a flux that will decrease the reaction time or prohydrolysis time.

4. Summary of Test Method

4.1 The halogens are separated from the test materials by pyrohydrolysis in a quartz reaction tube with a stream of wet oxygen or air at a temperature of 900 to 1000°C **(1-4)**. Chloride and fluoride are volatilized simultaneously as acids, absorbed in an absorption solution as chloride and fluoride and measured with ion selective electrodes **(4-6)**.

5. Significance and Use

5.1 The method is designed to show whether or not the tested materials meet the specifications as given in either Specification C753, C776, C888 or C922.

6. Interferences

6.1 The absorption solution controls the pH of the measured solution to avoid hydroxide ion interference or the formation of hydrogen complexes with fluoride.

6.2 Bromide, iodide, cyanide and sulfide, if present in the condensate, interfere in the measurement of chloride with ion-selective electrodes, but have very little effect upon the measurement of fluoride with ion-selective electrodes.

6.3 As the ionic activity of the chloride and fluoride ions is temperature dependent, the standard solutions and sample solutions should be measured at the same temperature.

7. Apparatus

7.1 *Pyrohydrolysis Equipment,* the assembly of suitable equipment is shown in Fig. 1.

7.2 *Gas Flow Regulator and Flowmeter.*

7.3 *Hot Plate,* used to warm the water saturating the sparge gas to 50 to 80°C.

7.4 *Combustion Tube Furnace,* having a bore of about 32 mm with a length of about 300 mm and the capability of

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[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.

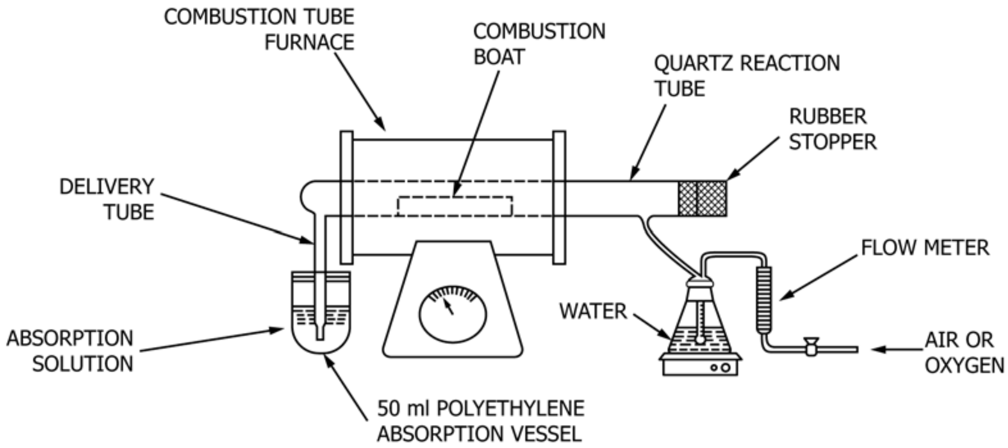


FIG. 1 Pyrohydrolysis Equipment

maintaining a temperature of 950 ± 25°C. Combustion tube furnaces with different dimensions may be satisfactory. Temperatures between 900 and 1000°C have been found to be satisfactory.

7.5 *Quartz Reaction Tube* (Fig. 2)—The exit end should not extend more than 50 mm beyond the furnace with a ground joint connecting to the delivery tube. The delivery tube extends into a polyethylene or Pyrex absorption vessel with a tip capable of giving a stream of very fine bubbles. A second absorption vessel connected in series, may be necessary to ensure complete collection of the fluorine and chlorine from the sample.

7.6 *Combustion Boat,* a ceramic, platinum or quartz boat with a 10 mL capacity (approx. 90 to 100 mm long, 13 mm wide, and 10 mm high). Boats with different dimensions may be satisfactory.

7.7 *Absorption Vessel,* a 50-ml polyethylene graduate or tube is satisfactory.

7.8 *Ion-Selective Electrodes,* fluoride-selective activity electrode, chloride-selective activity electrode. Combination electrodes may be suitable.

7.9 *Double-Junction Reference Electrode,* such as a silver-silver chloride with appropriate filling solutions.

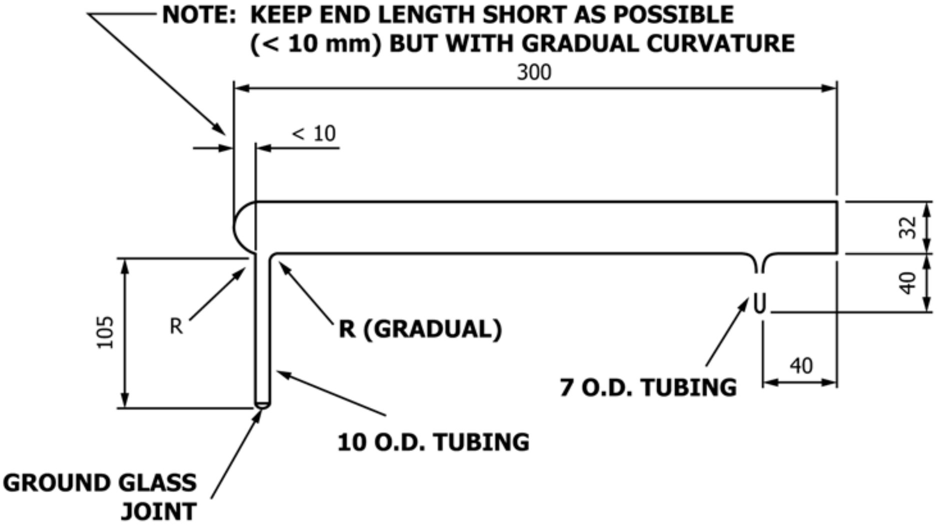
7.10 *pH/mV Meter*—The meter should have minimum resolution of 1 mV.

7.11 *Magnetic Stirrer.*

7.12 *Beakers,* 50 mL polyethylene.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that



Note 1—All dimensions in millimetres.

FIG. 2 Quartz Reaction Tube

all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] 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.

8.2 *Accelerator*—Two accelerators have been investigated for this system, halogen free U_3O_8 and a flux of sodium tungstate and tungsten trioxide (**1**, **2**). Halogen free U_3O_8 requires no special preparation before use but will require a longer pyrohydrolysis period. The flux of sodium tungstate (Na_2WO_4) with tungsten trioxide (WO_3) may reduce the pyrohydrolysis period by half but it requires the following special preparation. Dehydrate 165 g of Na_2WO_4 in a large platinum dish. Transfer the dried material to a mortar, add 116 g of WO_3, and grind the mixture to ensure good mixing. Transfer the mixture into a platinum dish and heat with a burner for 2 h. Cool the melt, transfer the flux to a mortar and grind to a coarse powder. Store the flux in an airtight bottle. Mix about 8 g of flux with each portion of sample to be pyrohydrolyzed.

8.3 *Absorption Solution (0.1 M)*—Dissolve 10 g, potassium acetate ($KC_2H_3O_2$) in water, add 5 mL of acetic acid (CH_3CO_2H, sp gr 1.05), and dilute to 1 L. Other absorption solutions may be satisfactory. It will be necessary to validate the absorption solutions and operating conditions with spike recovery determinations.

8.4 *Chloride, Standard Solution (100 µg Cl/mL)*—Dissolve 0.165 g of dry sodium chloride (NaCl) in water and dilute to 1 L. Commercially prepared standard solutions may be used.

8.5 *Fluoride, Standard Solution (50 µg F/mL)*—Dissolve 0.111 g of dried sodium fluoride (NaF) in water and dilute to 1 L. Store the solution in a polyethylene bottle. Commercially prepared standard solutions may be used.

8.6 *Compressed Oxygen or Air.*

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

9. Procedure

9.1 Adjust the pyrohydrolysis system to operating condition as follows:

9.1.1 Heat the furnace to 950 ± 25°C. (See 7.4).

9.1.2 Fill the water reservoir and heat to 50 to 80°C.

9.1.3 Adjust the gas flow to 1 to 2 L/min.

9.1.3.1 The furnace temperature, the gas flow, and the dimensions of the delivery tube tip are critical variables that will affect the spike recovery of the method.

9.2 Flush the quartz reaction tube and boat with moist oxygen.

9.3 Run a pyrohydrolysis blank using a halogen-free uranium oxide or gadolinium oxide according to the procedure in 9.5.

9.3.1 Alternatively an empty combustion boat can be used for the pyrohydrolysis blank.

9.3.2 A blank run should be made each day and after any sample that contains abnormally high levels of chlorine or fluorine.

9.4 Run samples, controls, duplicates and spikes in accordance with the user's quality assurance control plan and requirements.

9.5 *Sample Pyrohydrolysis:*

9.5.1 Pellets should be crushed prior to analysis.

9.5.2 Weigh 1 to 10 g of sample and spread in the combustion boat. If an accelerator is desired, mix 4 g of U_3O_8 accelerator or 8 g of the tungstate flux with the sample before spreading in the boat. A flux to sample ratio of 1 has been found to work satisfactorily. Other ratios may be applicable as determined by the analyst.

9.5.3 Place 15 mL of absorption solution in the polyethylene absorption vessel and submerge the delivery tip in the solution.

9.5.4 Remove the stopper from the entrance of the quartz reaction tube and insert the boat into the hot area of the furnace. Quickly stopper the quartz reaction tube.

9.5.5 Check the gas flow and adjust to 1 to 2 L/min.

9.5.6 Continue the reaction for 1 hour. Thirty minutes may be sufficient with the tungstate flux.

NOTE 1—The time required to complete the pyrohydrolysis will vary with differences in accelerator type, equipment and sample type. To establish the total time required for complete pyrohydrolysis, replace the absorption solution at 15 to 30 minute intervals and continue the reaction until complete.

9.5.7 When the pyrohydrolysis is completed, transfer the absorption solution to a 25-mL volumetric flask. Rinse the delivery tube (including inside) and the polyethylene absorption vessel with a minimum of absorption solution. Make up to volume with the absorption solution.

9.6 *Chloride and Fluoride Measurement:*

9.6.1 Assemble the mV meter and ion selective electrode and take the meter readings in accordance with the manufacturer's instructions.

9.6.2 Add 0, 0.1, 0.2, 0.4, 0.8, 1, 2, 4 and 10 mL of the chloride standard solution and the fluoride standard solution prepared in 8.4 and 8.5 to separate 25 mL flasks. Dilute each with absorption solution. Prepare calibration curves by plotting the millivolt readings of the standards versus the concentration in micrograms per 25 mL on semi-log paper. The concentration of chloride covers 10 µg/25 mL to 1000 µg/25 mL and the fluoride from 5 µg/25 mL to 500 µg/25 mL.

9.6.3 Use one half of the diluted sample from 9.5.7 for each of the halide determinations. Read the concentrations from the calibration curves. Alternatively the spike addition technique may be applicable as determined by the analyst.

NOTE 2—The chloride and fluoride measurements may be determined using ion chromatography. Appropriate absorption solutions that are compatible with ion chromatography, will be necessary. The solutions will require spike recovery test work.

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[3] *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.

10. Calculations

10.1 *Chlorine*—Calculate as follows:

$$Cl, \mu g/g = \frac{(C - B)}{W} \tag{1}$$

where:

C = micrograms of total chlorine in absorption solution,
B = micrograms of total chlorine in the pyrohydrolysis blank, and
W = sample weight in grams.

10.2 If a second sample solution was generated in a secondary absorption vessel as described in 7.5 calculate the result of the second absorption vessel in the same manner as 10.1. The total micrograms of chlorine in the sample is the sum of both impingers.

10.3 *Fluorine*—Calculate as follows:

$$F, \mu g/g = \frac{(F - B)}{W} \tag{2}$$

where:

F = micrograms of total fluorine in absorber solution,
B = micrograms of total fluorine in the pyrohydrolysis blank, and
W = sample weight in grams.

10.4 If a second sample solution was generated in a secondary absorption vessel as described in 7.5 calculate the result of the second absorption vessel in the same manner as 10.3. The total micrograms of fluorine in the sample is the sum of both absorption vessels.

11. Precision and Bias

11.1 *Uranium Dioxide:*

11.1.1 *Precision*—The standard deviation for the method is given in Table 1. The data were obtained over several months by different analysts in laboratory A.

11.1.2 *Bias*—There is no accepted reference material available. The bias of the method was evaluated by spiking 4 gram samples of uranium oxide powder. The powder was prepared by furnace oxidation of UO_2 at 950°C. The spiking solution was added directly to the sample in the combustion boat. The sample was dried at 110°C for 30 min. before pyrohydrolysis. The data in Table 3 were obtained during a five week period using one furnace by one analyst in Laboratory A.

TABLE 1 Standard Deviation—Uranium Dioxide

Sample Type	Element	Concentration (µg/g)	Standard Deviation (µg/g)	Determinations
UO_2 powderA	Fluorine	28	2	20
UO_2 powderA	Chlorine	38	4	20
UO_2 powderB	Fluorine	18	2	20

TABLE 2 Standard Deviation—Gadolinium Oxide

Sample Type	Element	Spike (µg)	Mean (µg)	Standard Deviation	Bias Estimate	Number of Determinations
Gd_2O_3-UO_2 pellets	Fluorine	50	49	4	−1	31
Gd_2O_3-UO_2 pellets	Chlorine	50	50	5	0	31

11.1.3 The supporting data for Table 1 are available from ASTM headquarters.

11.2 *Gadolinium Oxide:*

11.2.1 *Precision*—The standard deviation for the method is shown in Table 2. The data were obtained during a one month period using three different furnaces.

11.2.2 *Bias*—There is no accepted reference material available. The bias of the method was evaluated by spiking a sample of Gd_2O_3-UO_2 pellets. The data in Table 2 were obtained during a one month period using three different furnaces at laboratory B.

11.2.3 The supporting data for Table 2 are available from ASTM headquarters.

12. Keywords

12.1 chlorine; fluorine; gadolinium oxide; uranium dioxide

TABLE 3 Standard Deviation and Bias—Uranium Oxide

Sample Type	Element	Spike (ug/gU)	Mean (ug/gU)	Standard Deviation (ug/gU)	Bias Estimate (Difference) (ug/gU)	Number of Determinations
U_3O_8	Fluorine	73.7	78.1	9.7	+4.4	8
U_3O_8	Chlorine	73.7	71.8	8.0	– 1.9	16
U_3O_8	Fluorine	14.7	14.5	1.4	– 0.2	8

REFERENCES

(1) American Standards Association, Inc., "Referee Methods for the Chemical Analysis of Nuclear Fuels," ASA N5.7, 1965, p. 37.

(2) Powell, R.H., and Menis, O., "Separation of Fluoride from Inorganic Compounds by Pyrolysis," Analytical Chemistry, ANCHA, Vol 30, 1958, p. 1546.

(3) Warf, J.C., Cline, W.E., and Tevebaugh, R.D., "Pyrohydrolysis in the Determination of Fluoride and Other Halides," Analytical Chemistry, ANCHA, Vol 26, 1954, p. 342.

(4) Plucinski, C.E., "Determination of Microgram Quantities of Fluoride in Metal Oxides," USAEC Document BNWL-601, AEROB, 1968.

(5) Frant, M.S., and Ross, J.W., Jr., "Electrode for Sensing Fluoride Ion Activity in Solution," Science, KAGTA, Vol 154, 1966, p. 1553.

(6) Rechnitz, G.A., "Ion-Selective Electrodes," Chemical and Engineering News, CENEA, Vol 25, 1967, p. 1946.

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