Designation: C1502 – 24

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 gram 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder

C776 Specification for Sintered Uranium Dioxide Pellets for Light Water Reactors

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 for Light Water Reactors

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 °C to 1000 °C (**1-4**).[3] 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 determine 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.

[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 www.astm.org/contact. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

6.3 The ionic activities of the chloride and fluoride ions are temperature dependent. Therefore, the standard solutions and sample solutions should be measured at the same temperature.

7. Apparatus

7.1 *Pyrohydrolysis Equipment,* an 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 °C 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 maintaining a temperature of 950 °C ± 25 °C. Combustion tube furnaces with different dimensions may be satisfactory. Temperatures between 900 °C 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 capacity of 10 mL (approx. length of 90 mm to 100 mm, width of 13 mm, and height of 10 mm). 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 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.

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 mol/L)*—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/mL)*—Dissolve 0.165 g of dry sodium chloride (NaCl) in water and dilute to 1 L. Commercially prepared standard solutions may be used.

[4] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

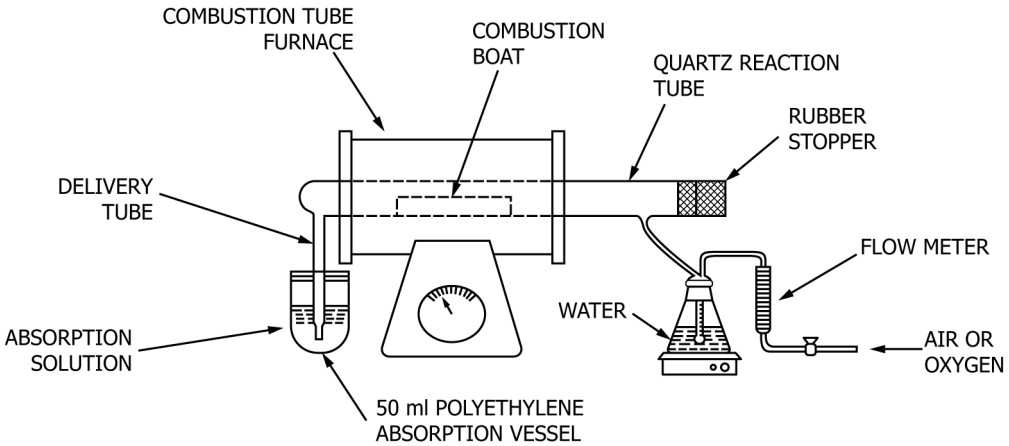

FIG. 1 Pyrohydrolysis Equipment