



# Standard Test Method for Determination of Total Chlorine and Fluorine in Uranium Dioxide and Gadolinium Oxide<sup>1</sup>

This standard is issued under the fixed designation C 1502; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 1. Scope

1.1 This test method covers the determination of chlorine and fluorine in nuclear-grade uranium dioxide ( $\text{UO}_2$ ) powder and pellets, nuclear grade gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ) powder and gadolinium oxide-uranium oxide ( $\text{Gd}_2\text{O}_3\text{-UO}_2$ ) powder and pellets.

1.2 With a 2 gram  $\text{UO}_2$  sample size the detection limit of the method is 4  $\mu\text{g/g}$  for chlorine and 2  $\mu\text{g/g}$  for fluorine. The maximum concentration determined with a 2 gram sample is 500  $\mu\text{g/g}$  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 *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 753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder<sup>2</sup>

C 776 Specification for Sintered Uranium Dioxide Pellets<sup>2</sup>

C 888 Specification for Nuclear-Grade Gadolinium Oxide ( $\text{Gd}_2\text{O}_3$ ) Powder

C 922 Specification for Sintered Gadolinium Oxide—Uranium Dioxide Pellets

D 1193 Specification for Reagent Water<sup>3</sup>

## 3. Summary of Test Method

3.1 The halogens are separated from the test materials by pyrohydrolysis in a quartz 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 a buffer solution as chloride and fluoride and measured with ion selective electrodes (4-6).

<sup>1</sup> 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 10, 2001. Published September 2001.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 12.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

## 4. Significance and Use

4.1 The method is designed to show whether or not the tested materials meet the specifications as given in either Specification C 753, C 776, C 888 or C 922.

## 5. Interferences

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

5.2 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.

5.3 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.

## 6. Apparatus

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

6.2 *Gas Flow Regulator and Flowmeter*.

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

6.4 *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  $950 \pm 25^\circ\text{C}$ . Combustion tube furnaces with different dimensions may be satisfactory. Temperatures between 900 and 1000°C have been found to be satisfactory.

6.5 *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.

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

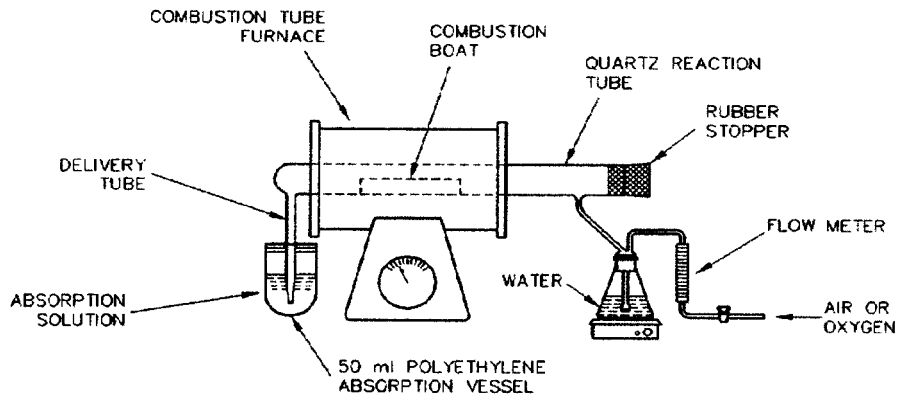


FIG. 1 Pyrohydrolysis Equipment

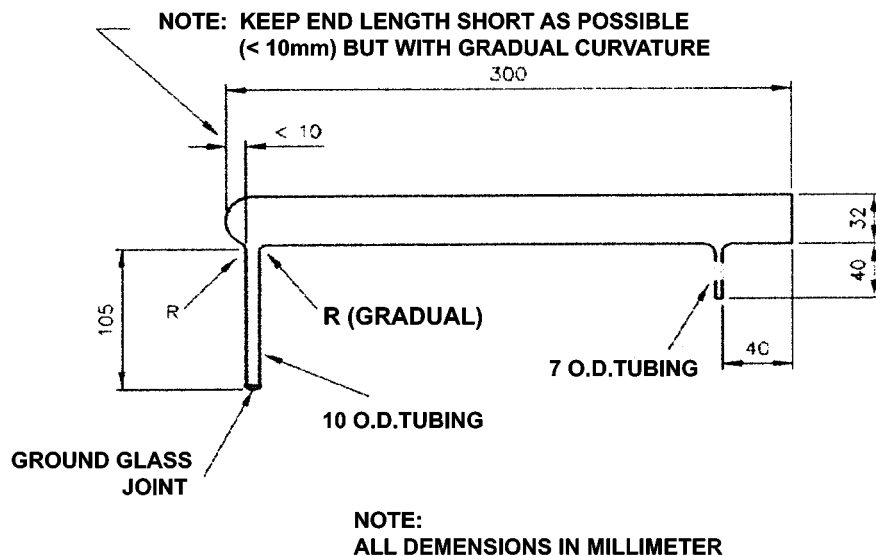


FIG. 2 Quartz Reaction Tube

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

6.8 *Ion-Selective Electrodes*, fluoride-selective activity electrode<sup>4</sup>, chloride-selective activity electrode<sup>5</sup>. Combination electrodes may be suitable.

6.9 *Double-Junction Reference Electrode*<sup>6</sup>, such as a silver-silver chloride with appropriate filling solutions.

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

6.11 *Magnetic Stirrer*.

6.12 *Beakers*, 50 mL polyethylene.

## 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.<sup>7</sup> 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 *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.

<sup>7</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D.C. 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*.

<sup>4</sup> The Orion Model 9409 has been found satisfactory.

<sup>5</sup> The Orion Model 9617 has been found satisfactory.

<sup>6</sup> The Orion Model 9002 has been found satisfactory.