Designation: C1907 – 21

Standard Practice for Preparation of Plutonium Materials by Pyrohydrolysis for Determination of Fluoride, Chloride, or Both[1]

This standard is issued under the fixed designation C1907; 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 practice provides a procedure for the preparation of samples of plutonium (Pu) materials, using pyrohydrolysis, for subsequent measurement of fluoride, chloride, or both, by ion chromatography (IC) or ion-selective electrode (ISE).

1.2 This practice utilizes a sample size of 0.3 ± 0.1 g and is therefore suitable when the larger sample size used in Test Methods C697 and C698 is not available.

1.3 Test materials within the scope of this practice include plutonium dioxide powder and mixed (U, Pu) oxide powder. Pellets of plutonium dioxide and mixed (U, Pu) oxide may also be treated after pulverization and with use of an accelerant. Samples of neptunium oxide may also be prepared using this practice.

1.4 Full recovery may not be achieved for levels above 50 µg/g fluoride or 50 µg/g chloride (**1**).[2] At higher levels precipitation may occur in the reaction vessel or condenser, or both. The user should validate suitability of the method above these levels.

1.5 The procedure described in this practice may be applicable to other plutonium materials, such as plutonium compounds and scrap metals. The user must determine the safety and applicability of this practice to such materials.

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

1.8 *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:*[3]

C697 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets

C698 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides ((U, Pu)O_2)

C757 Specification for Nuclear-Grade Plutonium Dioxide Powder for Light Water Reactors

C833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets for Light Water Reactors

C852/C852M Guide for Design Criteria for Plutonium Gloveboxes

C859 Terminology Relating to Nuclear Materials

C1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry

C1502 Test Method for Determination of Total Chlorine and Fluorine in Uranium Dioxide and Gadolinium Oxide

D1193 Specification for Reagent Water

D4327 Test Method for Anions in Water by Suppressed Ion Chromatography

3. Terminology

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

3.2 *Definitions:*

3.2.1 *accelerant, n*—a chemical compound or a flux that will decrease the reaction time or pyrohydrolysis time. **C1502**

3.2.2 *pyrohydrolysis, n*—treatment involving heating of a sample in a stream of moist argon or oxygen at a temperature of 900 to 1000 °C.

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

[3] 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.

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *test material, n*—material being treated by pyrohydrolysis in accordance with this practice.

3.3.1.1 *Discussion*—These materials include plutonium dioxide powder and pellets, and mixed (U, Pu) oxide powder and pellets, and other materials that meet the criteria given in 1.4.

4. Summary of Practice

4.1 A sample of 0.3 ± 0.1 g of test material is treated by pyrohydrolysis in a quartz reaction tube with a stream of moist argon or oxygen at a temperature of 900 to 1000 °C (**2-4**).

NOTE 1—The use of argon or oxygen is recommended, rather than steam or moist air, to purge the pyrohydrolysis system of undesired fluoride compounds (**2**).

4.2 Pellets are pulverized and an accelerant such as tungsten oxide is added.

4.3 Oxides are placed in a stream of moist argon and heated, driving off F and Cl. These analytes are condensed as trace levels of hydrofluoric acid (HF) and hydrochloric acid (HCl), respectively. The distillate is then transferred for quantitative analysis by IC or ISE (see 4.4).

4.4 Fluoride and chloride are measured in the absorption solution using ISE as described in Test Method C1502 or using IC as described in Test Method D4327.

4.5 As stated in Test Methods C697 and C698, fluoride and chloride may also be measured by spectrophotometry, and chloride may also be measured by microtitrimetry (**4, 5**), but these methods typically require a larger sample size. If a method other than ISE or IC is used for the analysis, that method should be qualified as described in Guide C1068.

5. Significance and Use

5.1 This practice provides a means of collecting fluoride and chloride from plutonium test materials for analysis by ISE or IC. The results can be used to determine whether the material meets the requirements of Specifications C757 or C833, or other specification agreed by a supplier and customer, for fluoride or chloride content, or both.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used. 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 quality of the final result.

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

6.3 *Uranium Oxide* (U_3O_8)—Halogen-free powder used as a blank and as the medium for pyrohydrolyzing the chloride standard solution (6.6) and the fluoride standard solution (6.9). The U_3O_8 serves as an accelerant for the reaction.

6.4 *Tungsten Oxide* (WO_3)—Accelerant utilized when preparing pellets for analysis.

6.5 *Sodium Chloride* (NaCl).

6.6 *Chloride Standard Solution* (1 mL = 1 mg Cl)—Dissolve 1.65 g of NaCl in water and dilute to 1 L.

6.7 *Chloride Standard Solution* (1 mL = 0.4 mg Cl)—Dilute 40 mL of chloride standard solution (1 mL = 1 mg Cl) to 100 mL with water.

6.8 *Sodium Fluoride* (NaF).

6.9 *Fluoride Standard Solution* (1 mL = 1 mg F)—Dissolve 2.21 g of NaF in water and dilute to 1L.

6.10 *Fluoride Standard Solution* (1 mL = 0.4 mg F)—Dilute 40 mL of fluoride standard solution (1 mL = 1 mg F) to 100 mL with water.

6.11 *Argon (if Used as Carrier Gas)*—Greater than 99.99 % purity.

6.12 *Oxygen (if Used as Carrier Gas)*—Greater than 99.5 % purity.

7. Apparatus

7.1 See Figs. 1 and 2 for examples of apparatus described below.

7.2 *Gas Flow Meter*—A flowmeter and a rate controller to adjust the flow of gas to 60 ± 2 mL/min.

7.3 *Heat Source*—Heating mantle or hot plate used to generate steam to moisten the argon or oxygen.

7.4 *Closure,* such as a rubber or ground glass stopper or rubber clamps, sufficient to ensure that the reaction tube is leak tight.

7.5 *Furnace Temperature Gauge,* capable of reading to at least 1200 °C.

NOTE 2—A calibrated thermocouple may be used in lieu of a temperature gauge. Traceability of the calibration to a national reference system such as the U.S. National Institute of Standards and Technology (NIST) is recommended.

7.6 *Collection Vessel*—Plastic or glass container (graduated cylinder, graduated vial, test tube, or beaker).

7.7 *Condenser Tube*—Glass tube with water jacket to condense the gases containing chloride and fluoride for collection in the collection vessel (7.6).

7.8 *Tube Furnace*—A tube furnace capable of maintaining a temperature from 900 to 1000 °C. The bore of the furnace should be about 32 mm in diameter and about 300 mm in length.

7.9 *Combustion Boat,* made from quartz (fused-silica) or platinum. A boat about 100 mm long is made by cutting lengthwise a silica tube 20 mm in diameter and flattening one end to provide a handle. A quartz inner sleeve for the reactor

[4] Reagent Chemicals, American Chemistry 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.

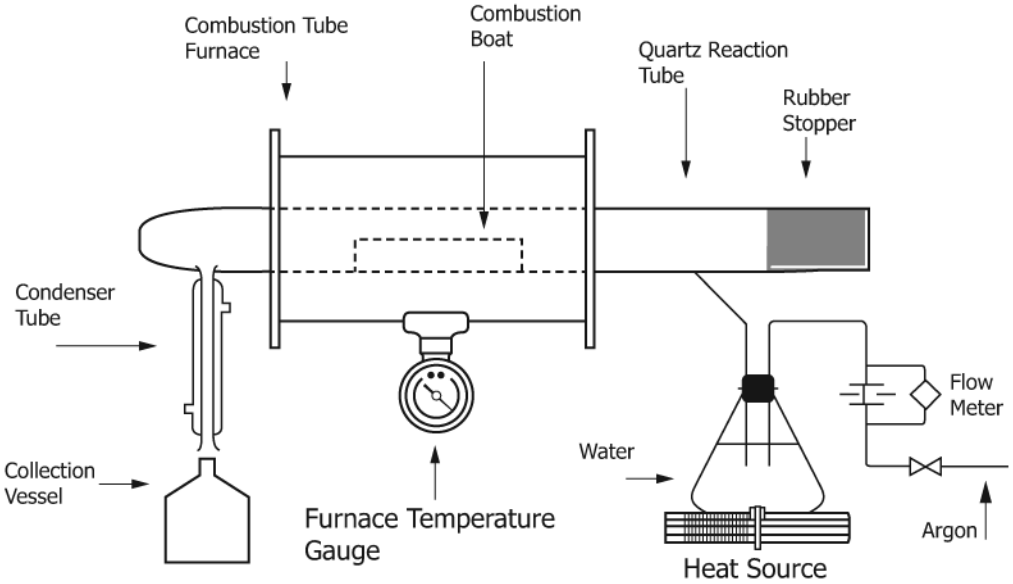

FIG. 1 Example Pyrohydrolysis Apparatus

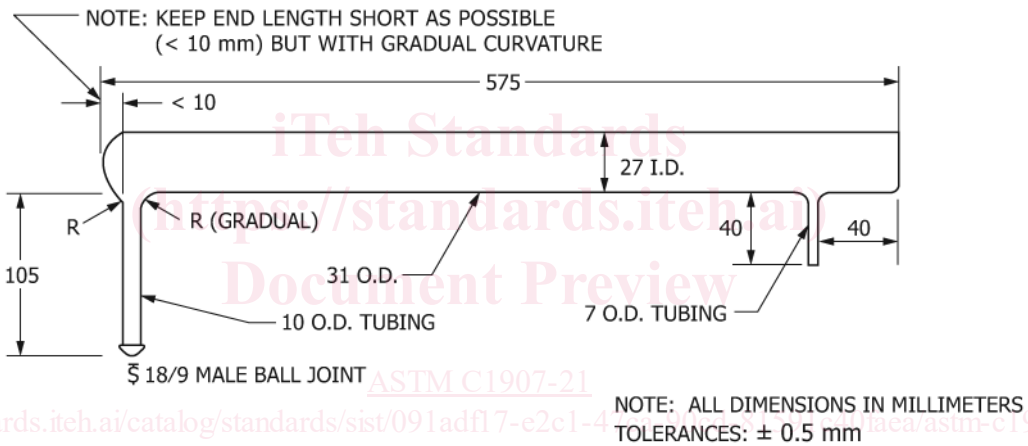

FIG. 2 Example Quartz Reaction Tube

tube can facilitate the movement of the boat into the tube, prevent spillage, and thus prolong the life of the combustion tube.

7.10 *Reaction Tube,* made from quartz or platinum. The delivery tube should be a part of the exit end of the reaction tube and be within 50 mm of the furnace (see Fig. 1 for proper tube positioning).

7.11 *Centrifuge Tubes,* 50 mL, plastic, with caps

NOTE 3—Plastic test tubes of similar size may also be used.

7.12 *Tongs,* for removing combustion boats from the furnace.

7.13 *Pipets,* calibrated, for pipetting 50 µL and 10 mL aliquots.

7.14 *Analytical Balance,* capable of measuring to the nearest 0.1 mg.

8. Safety Precautions

8.1 Since plutonium bearing materials are radioactive and toxic, adequate laboratory facilities, glove boxes, fume hoods, and so forth, along with safe techniques, must be used in handling samples containing these materials. Glove boxes should be fitted with off-gas filters capable of sustained operation with dust-laden atmospheres. A detailed discussion of all the precautions necessary is beyond the scope of this practice; however, personnel who handle these materials should be familiar with such safe handling practices as are given in Guide C852/C852M and in Refs (**5**, **6**).

8.2 Adequate laboratory facilities, such as fume hoods and controlled ventilation, along with safe techniques, must be used in this practice. Use of proper gloves is recommended. Refer to the laboratory's chemical hygiene plan and other applicable guidance for handling chemical and radioactive materials and for the management of radioactive, mixed, and hazardous waste.

9. Procedure

9.1 Prepare the pyrohydrolysis apparatus for use as follows:

9.1.1 Regulate the gas flow to 60 ± 2 mL/min.