Designation: C697 – 10

Standard Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets[1]

This standard is issued under the fixed designation C697; 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 These test methods cover procedures for the chemical, mass spectrometric, and spectrochemical analysis of nuclear-grade plutonium dioxide powders and pellets to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

	Sections
Plutonium Sample Handling	8 to 10
Plutonium by Controlled-Potential Coulometry	[2]
Plutonium by Ceric Sulfate Titration	[3]
Plutonium by Amperometric Titration with Iron(II)	[2]
Plutonium by Diode Array Spectrophotometry	[3]
Nitrogen by Distillation Spectrophotometry Using Nessler Reagent	11 to 18
Carbon (Total) by Direct Combustion–Thermal Conductivity	19 to 30
Total Chlorine and Fluorine by Pyrohydrolysis	31 to 38
Sulfur by Distillation Spectrophotometry	39 to 47
Plutonium Isotopic Analysis by Mass Spectrometry	[4]
Rare Earth Elements by Spectroscopy	48 to 55
Trace Elements by Carrier–Distillation Spectroscopy	56 to 63
Impurities by ICP-AES	
Impurity Elements by Spark-Source Mass Spectrography	64 to 70
Moisture by the Coulometric Electrolytic Moisture Analyzer	71 to 78
Total Gas in Reactor-Grade Plutonium Dioxide Pellets	79 to 86
Plutonium-238 Isotopic Abundance by Alpha Spectrometry	[3]
Americium-241 in Plutonium by Gamma-Ray Spectrometry	[2]
Rare Earths By Copper Spark-Spectroscopy	87 to 96
Plutonium Isotopic Analysis by Mass Spectrometry	97 to 105
Oxygen-To-Metal Atom Ratio by Gravimetry	106 to 114

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

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.* For specific precautionary statements, see Sections 6, 15, 24, 111, and 52.9 and 101.5.1 .

2. Referenced Documents

2.1 *ASTM Standards:*[5]

C757 Specification for Nuclear-Grade Plutonium Dioxide Powder, Sinterable

C852 Guide for Design Criteria for Plutonium Gloveboxes

C1009 Guide for Establishing a Quality Assurance Program for Analytical Chemistry Laboratories Within the Nuclear Industry

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

C1108 Test Method for Plutonium by Controlled-Potential Coulometry

C1128 Guide for Preparation of Working Reference Materials for Use in Analysis of Nuclear Fuel Cycle Materials

C1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials

C1165 Test Method for Determining Plutonium by Controlled-Potential Coulometry in H_2SO_4 at a Platinum Working Electrode

C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis

C1206 Test Method for Plutonium by Iron (II)/Chromium (VI) Amperometric Titration

C1210 Guide for Establishing a Measurement System Quality Control Program for Analytical Chemistry Laboratories Within the Nuclear Industry

C1235 Test Method for Plutonium by Titanium(III)/Cerium(IV) Titration[6]

[1] These test methods are under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and are the direct responsibility of Subcommittee C26.05 on Methods of Test.

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[2] Discontinued as of November 15, 1992.

[3] Discontinued as of January 1, 2004.

[4] Discontinued as of May 30, 1980.

[5] 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.

[6] Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

C1268 Test Method for Quantitative Determination of Americium 241 in Plutonium by Gamma-Ray Spectrometry
C1297 Guide for Qualification of Laboratory Analysts for the Analysis of Nuclear Fuel Cycle Materials
C1307 Test Method for Plutonium Assay by Plutonium (III) Diode Array Spectrophotometry
C1415 Test Method for ^{238}Pu Isotopic Abundance By Alpha Spectrometry
C1432 Test Method for Determination of Impurities in Plutonium: Acid Dissolution, Ion Exchange Matrix Separation, and Inductively Coupled Plasma-Atomic Emission Spectroscopic (ICP/AES) Analysis
D1193 Specification for Reagent Water
E60 Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry
E115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis[6]
E116 Practice for Photographic Photometry in Spectrochemical Analysis[6]

3. Significance and Use

3.1 Plutonium dioxide is used in mixtures with uranium dioxide as a nuclear-reactor fuel. In order to be suitable for this purpose, the material must meet certain criteria for plutonium content, isotopic composition, and impurity content. These test methods are designed to show whether or not a given material meets the specifications for these items as described in Specification C757.

3.1.1 An assay is performed to determine whether the material has the minimum plutonium content specified on a dry weight basis.

3.1.2 Determination of the isotopic content of the plutonium in the plutonium dioxide powder is made to establish whether the effective fissile content is in compliance with the purchaser's specifications.

3.1.3 Impurity content is determined to ensure that the maximum concentration limit of certain impurity elements is not exceeded. Determination of impurities is also required for calculation of the equivalent boron content (EBC).

4. Committee C26 Safeguards Statement[7]

4.1 The materials (plutonium dioxide powders and pellets) to which these test methods apply are subject to nuclear safeguards regulations governing their possession and use. The following analytical procedures in these test methods have been designated as technically acceptable for generating safeguards accountability measurement data: Plutonium by Controlled-Potential Coulometry; Plutonium by Ceric Sulfate Titration; Plutonium by Amperometric Titration with Iron (II); Plutonium by Diode Array Spectrometry Plutonium-238 Isotopic Abundance by Alpha Spectrometry; and Plutonium Isotopic Analysis by Mass Spectrometry.

4.2 When used in conjunction with appropriate Certified Reference Materials (CRMs), these procedures can demonstrate traceability to the national measurement base. However, adherence to these procedures does not automatically guarantee regulatory acceptance of the resulting safeguards measurements. It remains the sole responsibility of the user of these test methods to assure that its application to safeguards has the approval of the proper regulatory authorities.

5. Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[8] 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.

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

6. Safety Precautions

6.1 Since plutonium bearing materials are radioactive and toxic, adequate laboratory facilities, gloved boxes, fume hoods, etc., along with safe techniques, must be used in handling samples containing these materials. A detailed discussion of all the precautions necessary is beyond the scope of these test methods; however, personnel who handle these materials should be familiar with such safe handling practices as are given in Guide C852 and in Refs (**1**) through (**3**).[9]

6.2 Adequate laboratory facilities, such as fume hoods and controlled ventilation, along with safe techniques, must be used in this procedure. Extreme care should be exercised in using hydrofluoric acid and other hot, concentrated acids. 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.

6.3 Hydrofluoric acid is a highly corrosive acid that can severely burn skin, eyes, and mucous membranes. Hydrofluoric acid is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid. Hydrofluoric acid differs from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers. Unlike other acids that are rapidly neutralized, hydrofluoric acid reactions with tissue may continue for days if left untreated. Due to serious consequences of hydrofluoric acid burns, prevention of exposure or injury of personnel is the primary goal. Utilization of appropriate laboratory controls (hoods) and wearing adequate personal protective equipment to protect from skin and eye contact is essential.

[7] Based upon Committee C26 Safeguards Matrix (C1009, C1068, C1128, C1156, C1210, C1297).

[8] *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.

[9] The boldface numbers in parentheses refer to the list of references at the end of these test methods.

7. Sampling and Dissolution

7.1 Criteria for sampling this material are given in Specification C757.

7.2 Samples can be dissolved using the appropriate dissolution technique described in Practice C1168.

PLUTONIUM SAMPLE HANDLING

8. Scope

8.1 This test method covers the conditions necessary to preserve the integrity of plutonium dioxide samples. Conditions listed here are directed toward the analytical chemist. However, they are just as applicable to any group handling the material.

9. Summary of Test Method

9.1 Plutonium dioxide is very hygroscopic. In a short time it can sorb sufficient water from an uncontrolled atmosphere to destroy the validity of the most accurate analytical methods. An atmosphere with a dew point of −23°C has been found adequate to prevent sorption of water, but care must be exercised to use equipment and sample containers known to be dry.

10. Sample Handling Conditions

10.1 All sampling and critical weighings are to be performed in an atmosphere with a dew point no greater than −23°C.

10.2 All sampling equipment, including bottles, is to be dried before use. Plastic bottles are not to be used since they cannot be adequately dried. Glass bottles and aluminum foil are to be dried at 110°C for at least 1 h and kept in a desiccator until used.

NOTE 1—It has been shown that plutonium dioxide will sorb water from apparently dry aluminum foil. The foil should be dried at 110°C before use.

10.3 Quantitative methods to correct for moisture absorption, such as drying, must be avoided. The sample will not be representative under these conditions. It is virtually impossible to get equal amounts of moisture in the sample and bulk of the material at the same time.

PLUTONIUM BY CONTROLLED-POTENTIAL COULOMETRY

(This test method was discontinued in 1992 and replaced by Test Method C1165.)

PLUTONIUM BY CONTROLLED-POTENTIAL COULOMETRY

(With appropriate sample preparation, controlled-potential coulometric measurement as described in Test Method C1108 may be used for plutonium determination.)

PLUTONIUM BY CERIC SULFATE TITRATION

(This test method was discontinued in 2003 and replaced by Test Method C1235.)

PLUTONIUM BY AMPEROMETRIC TITRATION WITH IRON (II)

(This test method was discontinued in 1992 and replaced by Test Method C1206.)

STANDARD TEST METHOD FOR PLUTONIUM ASSAY BY PLUTONIUM(III) DIODE ARRAY SPECTROPHOTOMETRY

(With appropriate sample preparation, the measurement described in Test Method C1307 may be used for plutonium determination.)

NITROGEN BY DISTILLATION SPECTROPHOTOMETRY USING NESSLER REAGENT

11. Scope

11.1 This test method covers the determination of 5 to 100 µg/g of nitride nitrogen in 1-g samples of nuclear-grade plutonium dioxide.

12. Summary of Test Method

12.1 The sample is dissolved in hydrochloric acid by the sealed tube method or by phosphoric acid hydrofluoric acid solution, after which the solution is made basic with sodium hydroxide and nitrogen is separated as ammonia by steam distillation. Nessler reagent is added to the distillate to form the yellow ammonium complex and the absorbance of the solution is measured at approximately 430 nm **(4,5).**

13. Apparatus

13.1 *Distillation Apparatus*, see Fig. 1.

13.2 *Spectrophotometer*, visible range.

14. Reagents

14.1 *Ammonium Chloride (NH_4Cl)*—Dry salt for 2 h at 110 to 120°C.

14.2 *Boric Acid Solution (40 g/L)*—Dissolve 40 g of boric acid (H_3BO_3) in 800 mL of hot water. Cool to approximately 20°C and dilute to 1 L.

14.3 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

14.4 *Hydrofluoric Acid (48 %)*—Concentrated hydrofluoric acid (HF).

14.5 *Nessler Reagent*—To prepare, dissolve 50 g of potassium iodide (KI) in a minimum of cold ammonia-free water, approximately 35 mL. Add a saturated solution of mercuric chloride ($HgCl_2$, 22 g/350 mL) slowly until the first slight precipitate of red mercuric iodide persists. Add 400 mL of 9 *N* sodium hydroxide solution and dilute to 1 L with water, mix, and allow the solution to stand overnight. Decant supernatant liquid and store in a brown bottle.

14.6 *Nitrogen Standard Solution* (1 mL = 0.01 mg *N*)—Dissolve 3.819 g of NH_4Cl in water and dilute to 1 L. Transfer 10 mL of this solution to a 1-L volumetric flask and dilute to volume with ammonia-free water.

14.7 *Sodium Hydroxide (9 N)*—Dissolve 360 g of sodium hydroxide (NaOH) in ammonia-free water and dilute to 1 L.