



Standard Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides ((U, Pu)O₂)¹

This standard is issued under the fixed designation C 698; 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 mixed oxides, (U, Pu)O₂, powders and pellets to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

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Uranium in the Presence of Pu by Potentiometric Titration	2
Plutonium by Controlled-Potential Coulometry	2
Plutonium by Amperometric Titration with Iron (II)	2
Nitrogen by Distillation Spectrophotometry Using Nessler Reagent	7 to 14
Carbon (Total) by Direct Combustion-Thermal Conductivity	15 to 26
Total Chlorine and Fluorine by Pyrohydrolysis	27 to 34
Sulfur by Distillation-Spectrophotometry	35 to 43
Moisture by the Coulometric, Electrolytic Moisture Analyzer	44 to 51
Isotopic Composition by Mass Spectrometry	3
Rare Earths by Copper Spark Spectroscopy	52 to 59
Trace Impurities by Carrier Distillation Spectroscopy	60 to 69
Impurities by Spark-Source Mass Spectrography	70 to 76
Total Gas in Reactor-Grade Mixed Dioxide Pellets	77 to 84
Tungsten by Dithiol-Spectrophotometry	85 to 93
Rare Earth Elements by Spectroscopy	94 to 97
Plutonium-238 Isotopic Abundance by Alpha Spectrometry	4
Americium-241 in Plutonium by Gamma-Ray Spectrometry	
Uranium and Plutonium Isotopic Analysis by Mass Spectrometry	98 to 106
Oxygen-to-Metal Atom Ratio by Gravimetry	107 to 115

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.* (For specific safeguard and safety precaution statements, see Sections 11, 20, 64, and 112 and 102.6.1.)

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 May 30, 1980.

⁴ Discontinued as of xxxx, 2003.

2. Referenced Documents

2.1 ASTM Standards:⁵

- C 697 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets
- C 833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets
- C 852 Guide for Design Criteria for Plutonium Gloveboxes
- C 1008 Specification for Sintered (uranium-Plutonium) Dioxide Pellets—Fast Reactor Fuel
- C 1009 Guide for Establishing a Quality Assurance Program for Analytical Chemistry Laboratories Within the Nuclear Industry
- C 1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry
- C 1108 Test Method for Plutonium by Controlled-Potential Coulometry
- C 1128 Guide for Preparation of Working Reference Materials for Use in the Analysis of Nuclear Fuel Cycle Materials
- C 1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials
- C 1165 Test Method for Determining Plutonium by Controlled-Potential Coulometry in H₂SO₄ at a Platinum Working Electrode
- C 1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis
- C 1204 Test Method for Uranium in the Presence of Plutonium by Iron (II) Reduction in Phosphoric Acid Followed by Chromium (VI) Titration
- C 1206 Test Method for Plutonium by Iron (II)/Chromium (VI) Amperometric Titration

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.

- C 1210 Guide for Establishing a Measurement System Quality Control Program for Analytical Chemistry Laboratories Within the Nuclear Industry
- C 1268 Test Method for Quantitative Determination of Americium 241 in Plutonium by Gamma-Ray Spectrometry
- C 1297 Guide for Qualification of Laboratory Analysts for the Analysis of Nuclear Fuel Cycle Materials
- C 1415 Test Method for ²³⁸Pu Isotopic Abundance By Alpha Spectrometry
- C 1432 Test Method for Determination of Impurities in Plutonium: Acid Dissolution, Ion Exchange Matrix Separation, and Inductively Coupled Plasma-Atomic Emission Spectroscopic (ICP/AES) Analysis
- D 1193 Specification for Reagent Water
- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals
- E 115 Practices for Photographic Processing in Optical Emission Spectrographic Analysis
- E 116 Practice for Photographic Photometry in Spectrochemical Analysis

3. Significance and Use

3.1 Mixed oxide, a mixture of uranium and plutonium oxides, is used as a nuclear-reactor fuel in the form of pellets. The plutonium content may be up to 10 weight %, and the diluent uranium may be of any ²³⁵U enrichment. In order to be suitable for use as a nuclear fuel, the material must meet certain criteria for combined uranium and plutonium content, effective fissile content, and impurity content as described in Specification C 833.

3.1.1 The material is assayed for uranium and plutonium to determine whether the plutonium content is as specified by the purchaser, and whether the material contains the minimum combined uranium and plutonium contents specified on a dry weight basis.

3.1.2 Determination of the isotopic content of the plutonium and uranium in the mixed oxide 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. Reagents

4.1 *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.⁶ 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.

4.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

5. Safety Precautions

5.1 Since plutonium- and uranium-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 C 852 and in Refs (1) through (3).⁷

5.2 *Committee C-26 Safeguards Statement*.⁸

5.2.1 The materials [nuclear grade mixed oxides (U, Pu)O₂ 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: Uranium by Controlled Potential Coulometry; Plutonium by Controlled-Potential Coulometry; Plutonium by Amperometric Titration with Iron(II); Plutonium-238 Isotopic Abundance by Alpha Spectrometry; and Uranium and Plutonium Isotopic Analysis by Mass Spectrometry.

5.2.2 When used in conjunction with appropriate certified reference materials (CRMs), these procedures can demonstrate traceability to the national measurements 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.

6. Sampling and Dissolution

6.1 Criteria for sampling this material are given in Specification C 833.

6.2 Samples can be dissolved using the appropriate dissolution techniques described in Practice C 1168.

URANIUM IN THE PRESENCE OF PLUTONIUM BY POTENTIOMETRIC TITRATION

(This test method was discontinued in 1992 and replaced by Test Method C 1204.)

PLUTONIUM BY CONTROLLED POTENTIAL COULOMETRY

(This test method was discontinued in 1992 and replaced by Test Method C 1165.)

⁶ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. 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 Co., Inc., New York, NY, and the "United States Pharmacopeia."

⁷ The boldface numbers in parentheses refer to the list of references at the end of these test methods.

⁸ Based upon Committee C-26 Safeguards Matrix (C 1009, C 1068, C 1128, C 1156, C 1210, C 1297).

PLUTONIUM BY CONTROLLED-POTENTIAL COULOMETRY

(With appropriate sample preparation, controlled-potential coulometric measurement as described in Test Method C 1108 may be used for plutonium determination.)

PLUTONIUM BY AMPEROMETRIC TITRATION WITH IRON(II)

(This test method was discontinued in 1992 and replaced by Test Method C 1206.)

NITROGEN BY DISTILLATION SPECTROPHOTOMETRY USING NESSLER REAGENT

7. Scope

7.1 This test method covers the determination of 5 to 100 µg/g of nitride nitrogen in mixtures of plutonium and uranium oxides in either pellet or powder form.

8. Summary of Test Method

8.1 The sample is dissolved in hydrochloric acid by the sealed tube test 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).

9. Apparatus

- 9.1 *Distillation Apparatus* (see Fig. 1).
- 9.2 *Spectrophotometer*, visible-range.

10. Reagents

- 10.1 *Ammonium Chloride* (NH₄Cl)—Dry the salt for 2 h at 110 to 120°C.
- 10.2 *Boric Acid Solution* (40 g/litre)—Dissolve 40 g of boric acid (H₃BO₃) in 800 mL of hot water. Cool to approximately 20°C and dilute to 1 L.
- 10.3 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).
- 10.4 *Hydrofluoric Acid* (sp gr 1.15)—Concentrated hydrofluoric acid (HF).

10.5 *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 (HgCl₂, 22 g/350 mL) slowly until the first slight precipitate of red mercuric iodide persists. Add 400 mL of 9 N sodium hydroxide (NaOH) and dilute to 1 L with water. Mix, and allow the solution to stand overnight. Decant the supernatant liquid and store in a brown bottle.

10.6 *Nitrogen, Standard Solution* (1 mL = 0.01 mg N)— Dissolve 3.819 g of NH₄Cl 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.

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

10.8 *Sodium Hydroxide Solution* —(50 %)—Dissolve NaOH in an equal weight of ammonia-free water.

10.9 *Water, Ammonia-Free*—To prepare, pass distilled water through a mixed-bed resin demineralizer and store in a tightly stoppered chemical-resistant glass bottle.

11. Precautions

11.1 The use of ammonia or other volatile nitrogenous compounds in the vicinity can lead to serious error. The following precautionary measures should be taken: (1) Clean all glassware and rinse with ammonia-free water immediately prior to use, and (2) avoid contamination of the atmosphere in the vicinity of the test by ammonia or other volatile nitrogenous compounds.

12. Procedure

12.1 *Dissolution of Sample:*

12.1.1 Transfer a weighed sample, in the range from 1.0 to 1.5 g, to a 50-mL beaker.

NOTE 1—Pellet samples should be crushed to a particle size of 1 mm or less with a diamond mortar.

12.1.2 To the sample add 5 mL of HCl (sp gr 1.19) and 3 drops of HF (sp gr 1.15). Heat to put the sample into solution.

NOTE 2—Concentrated phosphoric acid or mixtures of phosphoric acid and hydrofluoric acids or of phosphoric and sulfuric acids may be used for the dissolution of mixed oxide samples. Such acids may require a purification step in order to reduce the nitrogen blank before being used in this procedure.

12.2 *Distillation:*

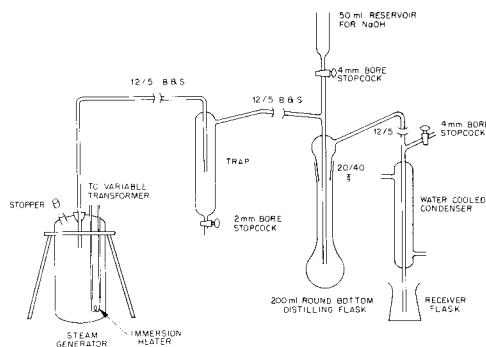


FIG. 1 Distillation Apparatus