



Designation: C1165 – 12

Standard Test Method for Determining Plutonium by Controlled-Potential Coulometry in H₂SO₄ at a Platinum Working Electrode¹

This standard is issued under the fixed designation C1165; 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 milligram quantities of plutonium in unirradiated uranium-plutonium mixed oxide having a U/Pu ratio range of 0.1 to 10. This test method is also applicable to plutonium metal, plutonium oxide, uranium-plutonium mixed carbide, various plutonium compounds including fluoride and chloride salts, and plutonium solutions.

1.2 The recommended amount of plutonium for each aliquant in the coulometric analysis is 5 to 10 mg. Precision worsens for lower amounts of plutonium, and elapsed time of electrolysis becomes impractical for higher amounts of plutonium.

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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 8.

2. Referenced Documents

2.1 ASTM Standards:²

C757 Specification for Nuclear-Grade Plutonium Dioxide Powder, Sinterable

C758 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Metal

C759 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of

Nuclear-Grade Plutonium Nitrate Solutions

C833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets

C859 Terminology Relating to Nuclear Materials

C1009 Guide for Establishing and Maintaining a Quality Assurance Program for Analytical 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

C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis

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

C1297 Guide for Qualification of Laboratory Analysts for the Analysis of Nuclear Fuel Cycle Materials

3. Summary of Test Method

3.1 In controlled-potential coulometry, the analyte reacts at an electrode having a maintained potential that precludes reactions of as many impurity components as is feasible. In the electrolysis, current decreases exponentially as the reaction proceeds until a selected background current is reached. The quantity of analyte reacted is calculable by Faraday's law. Detailed discussions of the theory and applications of this technique are presented in Refs (1)³ and (2).

3.2 Plutonium and many impurity element ions are initially reduced in a 0.5 M H₂SO₄ electrolyte at a platinum working electrode (3) maintained at +0.310 V versus a saturated calomel electrode (SCE). Plutonium is then oxidized to Pu(IV) at a potential of +0.670 V. The quantity of plutonium is

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 service@astm.org. 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 the text.

calculated from the number of coulombs required for oxidation according to Faraday's law.

$$Q = \int_0^t i dt = nwF/M \quad (1)$$

Rearrangement to solve for w gives:

$$w = MQ/nF \quad (2)$$

where:

- w = weight of Pu(III) oxidized to Pu(IV), g,
- M = gram-molecular mass of plutonium (adjusted for isotopic composition), grams/equivalent,
- Q = number of coulombs to oxidize Pu(III) to Pu(IV), coulombs,
- n = number of electron change to oxidize Pu(III) to Pu(IV) = 1, and
- F = Faraday constant, coulomb/equivalent.

3.3 An electrolyte of sulfuric acid, that selectively complexes Pu(IV), provides very reproducible electrolysis of Pu(III) to Pu(IV). In a 0.5 M H₂SO₄ electrolyte, the reduction potential of +0.310 V for conversion of Pu(IV and VI) to Pu(III) and the oxidation potential of +0.670 V for conversion of Pu(III) to Pu(IV) accounts for about 99.9 % (as calculated from the Nernst equation) conversion of the total plutonium in solution. There are few interferences at the selected potentials of the metallic impurities usually listed in specifications for fast breeder reactor (FBR) mixed oxide fuel. A chemical calibration of the coulometric system using the selected potentials technique is necessary to correct for the less than 100 % conversions of Pu(III) and Pu(IV).

3.4 Sulfuric acid is a convenient electrolyte since it is used for preliminary fuming of samples to volatilize interfering components (see 5.3 and 5.4). The preliminary fuming with sulfuric acid also serves to depolymerize any polymeric plutonium species, which tend to be electrolytically inactive (3).

4. Significance and Use

4.1 This test method is to be used to ascertain whether or not materials meet specifications for plutonium content or plutonium assay, or both.

4.2 A chemical calibration of the coulometer is necessary for accurate results.

5. Interferences

5.1 Categories of interferences are diverse metal ions that oxidize or reduce at the potential of +0.670 V used for the oxidation of Pu(III) to Pu(IV), organic matter, anions that complex plutonium, and oxygen.

5.2 The major interfering metallic impurity element, of those usually included in specifications for FBR mixed oxide fuel, is iron (4). In the 0.5 M H₂SO₄ electrolyte, the Fe(II) – Fe(III) and Pu(III) – Pu(IV) couples have essentially the same E° value of +0.490 V. The iron interference, therefore, is quantitative and is corrected based on its measured value that can be determined by a spectrophotometric method (5). Alternatively, other techniques such as ICP, DCP, or emission spectrometry can also be used if the iron content is

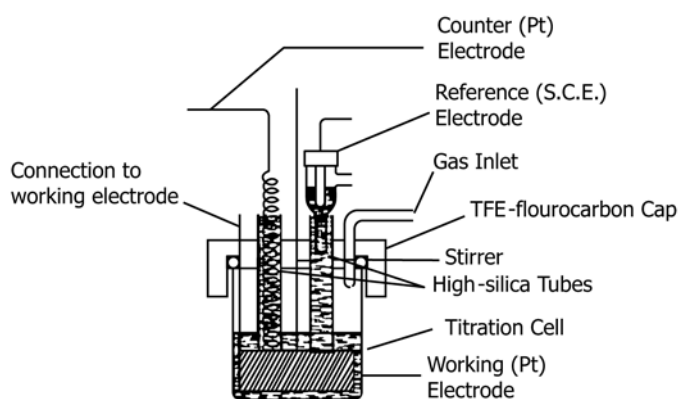


FIG. 1 Example of a Cell Design Used at Los Alamos National Laboratory (LANL)

sufficiently low. When the iron result is <20μ g/g, the lower limit of the spectrophotometric method, no correction is necessary. The best available method for iron determination is recommended since the uncertainty in the iron correction contributes to the uncertainty in the plutonium value.

5.3 Organic matter usually is not present in calcined mixed oxide fuel pellets nor in mixed oxide powder blends prepared using calcined uranium oxide and calcined plutonium oxide. However, it may be introduced as an impurity in reagents. The sulfuric acid fuming of reference material and of samples that precedes the coulometric analysis volatilizes most organic components.

5.4 The sulfuric acid fuming volatilizes nitrate, nitrite, fluoride, and chloride, that are introduced by the use of a nitric-hydrofluoric acid mixture or acid mixtures containing chloride for the dissolution of samples and interfere in the coulometric determination of plutonium.

5.5 Oxygen interferes and must be purged continuously from both the solution and atmosphere in the electrolysis cell with an oxygen-free inert gas before and during the electrolysis.

NOTE 1—The purge gas tube extends through the cell cover and is positioned approximately 1 cm above the sample solution in the cell. The inert gas flow is maintained at a flow rate that causes a dimple to be seen on the surface of the solution with the stirrer off. The inert gas flow rate should be such that no splashing occurs.

5.6 Nitric acid and hydrofluoric acid must be added during the preparation of the plutonium metal to ensure oxidation of the plutonium to Pu(IV) and to match the acid matrix from plutonium oxide dissolution. Plutonium that is dissolved in only hydrochloric acid and then evaporated to dryness in sulfuric acid while in the Pu(III) oxidation state will contain tiny blue crystals within the pink plutonium (IV) sulfate material, and lower recoveries are experienced during the coulometric measurement. Blue crystals are not observed when plutonium oxide materials are dissolved in HNO₃ and HF acids and subsequently fumed to dryness in H₂SO₄.

5.7 Due to a slight overlap between the potential at which Np(VI) reduces to Np(V), +0.660 V, and the potential used in the current method to oxidize Pu(III) to Pu(IV), +0.670 V, a large amount of neptunium will cause the plutonium assay to

be biased high and not accurately reflect the plutonium content of the material being analyzed. Thus, neptunium can only be tolerated up to 1 % in the sample, above that level the neptunium must be removed prior to the sample undergoing the coulometry process.

6. Apparatus

6.1 *Controlled-Potential Coulometer*—A potentiostat having stable potential control at approximately 200 mA and 20 V and an integrator capable of 0.05 % reproducibility are required. The linearity of the integrator should be better than 0.1 % for the selected range.⁴

6.2 *Cell Assembly*—A cell assembly similar to the one described in Ref (5) has been used satisfactorily. Cell design is very critical in controlled-potential coulometry. There are many factors that must be considered in choosing or designing a cell assembly. It is beyond the scope of this test method to describe all of the factors that should be considered. A thorough detailed discussion of electrolysis cell design is presented in Ref (2).

NOTE 2—Drawing (see Fig. 1) of a cell design that has been successfully used at the Los Alamos National Laboratory. The titration cell consists of a 50 mL cut off beaker.

6.3 Timer or stopwatch for measuring electrolysis times (capable of measuring in seconds).

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.⁵ 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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean distilled or deionized water.

7.3 *Argon, Oxygen-Free (99.99 %)*—Helium, nitrogen, or other pure inert gas may be used.

7.4 *Hydrochloric Acid (HCl, 10.9 M)*—Concentrated HCl, ACS ultratrace grade.

7.5 *Hydrochloric Acid (HCl, 6 M)*—Add 500 mL of concentrated 10.9 M HCl to less than 500 mL of water and dilute to 1 L with water.

7.6 *Hydrochloric Acid (HCl, 1.0 M)*—Add 82.6 mL of concentrated 10.9 M HCl to water and dilute to 1 L.

7.7 *Hydrofluoric Acid (HF, 29M)*—Concentrated HF, ACS ultratrace grade.

7.8 *Hydrofluoric Acid (HF, 1.3 M)*—Add 4.8 mL of concentrated 29 M HF to water and dilute to 100 mL.

7.9 *Nitric Acid (HNO₃, 15.9 M)*—Concentrated HNO₃, ACS ultratrace grade.

7.10 *Sulfuric Acid (H₂SO₄, 18.1 M)*—Concentrated H₂SO₄, ACS ultratrace grade.

7.11 *Sulfuric Acid (3 M)*—Add 168 mL of concentrated H₂SO₄ to water, while stirring, and dilute to 1 L with water.

7.12 *Sulfuric Acid (0.5 M)*—Add 28 mL of concentrated H₂SO₄ to water, while stirring, and dilute to 1 L with water.

7.13 *Plutonium Reference Solution*—Dissolve a weighed quantity (balance capable of weighing to 0.01 mg) of 0.5 to 1 g of NBL (Note 4) CRM 126 metal (or its replacement) cleaned per certificate directions in 6 M HCl. Use a sufficient amount of 6 M HCl to maintain an acid concentration of 1 to 2 M. Completely transfer the solution with 1.0 M HCl rinses to a tared container, dilute to 100 to 200 g with 1.0 M HCl (to give a plutonium concentration of 5 mg/g), and weigh.

NOTE 3—A tared polyethylene bottle has been used successfully to dispense weighed aliquants.

NOTE 4—To minimize measurement uncertainty, it is recommended that the reference and sample aliquants contain approximately the same amount of plutonium. Users of this standard are responsible for validating method performance if aliquants of standards and/or samples containing less than 5 mg of plutonium or greater than 10 mg of plutonium will be measured.

New Brunswick Laboratory (NBL) Certified Reference Materials Catalog (U.S. Department of Energy), <http://www.nbl.doe.gov>.

7.13.1 Dispense weighed 1 to 2 g aliquants, each containing accurately known 5 to 10 mg quantities of plutonium, to individual electrolysis cells or vials for subsequent use in chemical calibration.

7.13.2 Prior to using, add 0.5 mL of 3 M H₂SO₄, 1 drop of 1.3 M HF and 1 drop of concentrated 15.9 M HNO₃ and fume to dryness.

7.13.3 After cooling, redissolve using a minimal amount of 0.5 M H₂SO₄ and again fume to dryness.

7.13.4 Repeat 7.13.3.

8. Safety Precautions

8.1 Committee C-26 Safeguards Statement⁶:

8.1.1 The materials (nuclear grade plutonium metal, plutonium oxide powder, plutonium nitrate solutions, and mixed oxide and carbide powders and pellets) to which this test method applies, are subject to nuclear safeguards regulations governing their possession and use. This test method has been

⁴ Coulometer suppliers or designers who have reported instrument performances that are consistent with the specification provided in this standard include: the SRNL Coulometer, Savannah River National Laboratory, Aiken, South Carolina, USA; the Mayak Coulometer PIK-200, Ozersk, Russia; and the coulometer at the LAMM Laboratory, CEA Centre de Marcoule, Bagnols-sur-Cèze Cedex, France. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

⁵ *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.

⁶ Based upon Committee C26 Safeguards Matrix (C1009, C1068, C1128, C1156, C1210, and C1297).