



Designation: C1165 – 23

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 mg 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 quantity values stated in SI units are to be regarded as standard. The quantity values with non-SI units are given in parentheses 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 9.

1.5 *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:*²

C859 Terminology Relating to Nuclear Materials

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.

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 Nuclear Industry

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

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

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

4. Summary of Test Method

4.1 In controlled-potential coulometry, the analyte reacts at an electrode having a controlled 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)**.

4.2 Plutonium and many impurity element ions are initially reduced in a 0.5 mol/L (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

³ The boldface numbers in parentheses refer to a list of references at the end of the text.

Pu(IV) at a potential of +0.670 V. The quantity of plutonium, w , is calculated from the number of coulombs, Q , required for oxidation according to Faraday's law:

$$Q = \int_0^t i dt = n w F / M \quad (1)$$

Rearranging to solve for w yields:

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

where:

- w = mass of Pu(III) oxidized to Pu(IV), g,
- M = molar mass of plutonium (adjusted for isotopic composition), g/mol,
- Q = number of coulombs to oxidize Pu(III) to Pu(IV), C,
- n = number of electron change to oxidize Pu(III) to Pu(IV) = 1, and
- F = Faraday constant, C/mol.

4.3 An electrolyte of sulfuric acid, that selectively complexes Pu(IV), provides very reproducible electrolysis of Pu(III) to Pu(IV). In a 0.5 mol/L (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).

4.4 Sulfuric acid is a convenient electrolyte since it is used for preliminary fuming of samples to volatilize interfering components (see 6.4 and 6.5). The preliminary fuming with sulfuric acid also serves to depolymerize any polymeric plutonium species, which tend to be electrolytically inactive (3).

5. Significance and Use

5.1 This test method is used to ascertain whether or not materials meet specifications for plutonium concentration or plutonium mass fraction.

5.1.1 The materials (nuclear grade plutonium nitrate solutions, plutonium metal, plutonium oxide powder, 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. However, adherence to this test method does not automatically guarantee regulatory acceptance of the resulting safeguards measurements. It remains the sole responsibility of the user of this test method to ensure that its application to safeguards has the approval of the proper regulatory authorities.

5.1.2 When used in conjunction with appropriate certified reference materials (CRMs), this test method can demonstrate traceability to the international measurements system (SI).

5.2 *Fitness for Purpose of Safeguards and Nuclear Safety Application*—Methods intended for use in safeguards and nuclear safety applications shall meet the requirements specified by Guide C1068 for use in such applications.

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

6. Interferences

6.1 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.

6.2 The major interfering metallic impurity element, of those usually included in specifications for FBR mixed oxide fuel, is iron (4). In the 0.5 mol/L (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 sufficiently low. When the iron result is <20 µg/g, the lower limit of quantification for 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.

6.3 When iron is present in quantities greater than the nuclear-grade specifications for plutonium metal, oxides, and nitrate solutions, the iron may be removed or substantially reduced by column purification using resins known to be quantitative for plutonium recovery. Guidance and instructions for column purification of plutonium test samples, calibration standards, and quality control (QC) reference materials may be applied as described in C1108.

6.4 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.

6.5 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

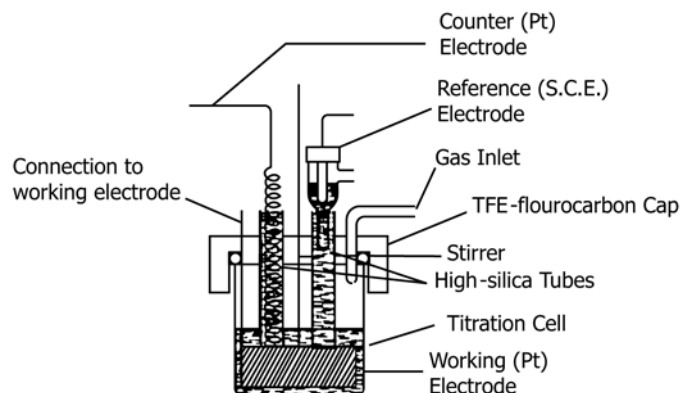


FIG. 1 Example of a Cell Design Used at Los Alamos National Laboratory (LANL)

chloride for the dissolution of samples and interfere in the coulometric determination of plutonium.

6.6 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 with the stirrer on.

6.7 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.

6.8 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.

7. Apparatus

7.1 *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

7.2 *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—Fig. 1 is an example of a cell design that has been used successfully at the Los Alamos National Laboratory. The electrolysis cell consists of a 50 mL cut off beaker. The working and counter electrodes with a platinum mass fraction of ≥999.5 mg/g (that is, Pt purity of

≥99.95 %) have been used successfully.

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

8. Reagents

8.1 *Purity of Reagents*—ACS ultratrace 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 for ultratrace grade chemicals are available.⁵

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean distilled, deionized water with a conductivity of <0.1 μS (resistance >10 MΩ).

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

8.4 *Hydrochloric Acid (HCl, 10.9 mol/L)*—Concentrated HCl, ACS ultratrace grade.

8.5 *Hydrochloric Acid (HCl, 6 mol/L)*—Add 550 mL of 10.9 mol/L (10.9 M) HCl to less than 400 mL of water and dilute to 1 L with water.

8.6 *Hydrochloric Acid (HCl, 1.0 mol/L)*—Add 92 mL of 10.9 mol/L (10.9 M) HCl to less than 500 mL of water and dilute to 1 L.

8.7 *Hydrofluoric Acid (HF, 29 mol/L)*—Concentrated HF, ACS ultratrace grade.

8.8 *Hydrofluoric Acid (HF, 1.3 mol/L)*—Add 4.5 mL of 29 mol/L (29 M) HF to less than 50 mL of water and dilute to 100 mL.

8.9 *Nitric Acid (HNO₃, 15.9 mol/L)*—Concentrated HNO₃, ACS ultratrace grade.

8.10 *Sulfuric Acid (H₂SO₄, 18.1 mol/L)*—Concentrated H₂SO₄, ACS ultratrace grade.

8.11 *Sulfuric Acid (3 mol/L)*—Add 166 mL of 18.1 mol/L (18.1 M) H₂SO₄ to less than 500 mL of water, while stirring, and dilute to 1 L with water.

8.12 *Sulfuric Acid (0.5 mol/L)*—Add 28 mL of 18.1 mol/L (18.1 M) H₂SO₄ to less than 500 mL of water, while stirring, and dilute to 1 L with water.

8.13 *Plutonium Reference Solution (with desired Pu mass fraction of 5 mg/g)*—Dissolve a weighed quantity (balance capable of weighing to ±0.01 mg) of 0.5 g to 1 g of NBL (Note 4) CRM 126-series of plutonium metal (or its replacement) cleaned in accordance with certificate directions in 6 mol/L (6 M) HCl. Use a sufficient amount of 6 mol/L (6 M) HCl to

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-Cèdre 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 *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

maintain an acid concentration of 1 mol/L to 2 mol/L. Completely transfer the solution with 1.0 mol/L (1.0 M) HCl rinses to a tared container, dilute to 100 g to 200 g with 1.0 mol/L (1.0 M) HCl.

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 test samples containing less than 5 mg of plutonium or greater than 10 mg of plutonium will be measured.

NBL Program Office Certified Reference Materials Catalog (U.S. National Nuclear Security Administration), <https://www.energy.gov/nnsa/nbl-program-office>.

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

8.13.2 Prior to using, add 0.5 mL of 3 mol/L (3 M) H₂SO₄, 1 drop of 1.3 mol/L (1.3 M) HF, and 1 drop of 15.9 mol/L (15.9 M) HNO₃ and fume to dryness.

8.13.3 After cooling, redissolve using a minimal amount of 0.5 mol/L (0.5 M) H₂SO₄ and again fume to dryness.

8.13.4 Repeat 8.13.3.

9. Hazards

9.1 Refer to Safety Data Sheets for hazards and controls for all chemicals and reagent used in this test method.

9.2 **Warning**—Hydrofluoric acid is highly corrosive acid that can severely burn skin, eyes, and mucous membranes. Hydrofluoric acid differs from the 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. Familiarization and compliance with the Safety Data Sheet is essential.

9.3 This standard involves work with nuclear materials. The unique hazards and controls required to conduct the work contained in this standard from a safety, environmental, and security standpoint is the responsibility of the facility operators, in compliance with any applicable regulations. Any information given for handling these types of materials contained herein is meant only as a guide for consideration of the user and not a requirement.

10. Preparation of Apparatus

10.1 Verify proper equipment operation by performing an electrical calibration according to manufacturers' specifications on each day that the instrument is used.

11. Calibration

NOTE 5—All standards (reference material) and samples should be freshly fumed (within 4 h) prior to analysis.

11.1 Perform blank measurements as detailed in 12.1.

11.2 If not done previously as recommended in 8.13.1, completely transfer one of the dispensed aliquants, containing 5 mg to 10 mg of plutonium of the plutonium reference

solution, to an electrolysis cell using 0.5 mol/L (0.5 M) H₂SO₄ rinses and fume to dryness in sulfuric acid.

11.3 Place platinum working electrode in the electrolysis cell. Using 0.5 mol/L (0.5 M) H₂SO₄, completely immerse the working electrode gauze. (See 12.1.2.1.)

11.4 Rinse the exterior surfaces of the counter and reference electrode salt bridges (for example, high-silica tubes) with 0.5 mol/L (0.5 M) H₂SO₄.

11.5 Raise the electrolysis cell into position firmly against the cell cover to ensure a tight fit. Purge the cell atmosphere with flowing argon or other inert gas. (See Note 1.)

11.6 Immediately connect the cell electrodes to the coulometer; begin stirring.

11.7 Reduce Pu(IV) to Pu(III) at +0.310 V until the current decreases to 30 μA.

11.8 Reset the integrator and start timer.

11.9 Oxidize Pu(III) to Pu(IV) at +0.670 V until the current decreases to 30 μA. Record the coulomb accumulation and elapsed time.

11.10 Remove the solution and thoroughly rinse the electrolysis cell and electrodes with 0.5 mol/L (0.5 M) H₂SO₄.

11.11 Repeat 11.2 – 11.10 to attain a desired precision level for the calibration.

NOTE 6—A recommended practice would be to measure one Pu conditioning material, then two calibration standards (reference material) and one QC reference material before measuring the first test sample, and then intersperse standards (reference material) between test samples during the time the analyses are being done.

11.12 Calculate the calibration factor, F , as follows:

$$F = M/(C_c - C_b) \quad (3)$$

where:

F = calibration factor for plutonium, mg/C,

M = mass of plutonium in calibration reference aliquant, mg,

C_c = coulombs measured at 0.670 V electrolysis for calibration reference aliquant, C, and

C_b = coulombs for blank measurement. Use the coulomb value obtained on the blank for the elapsed time (to the nearest minute) as that required for the reference aliquant oxidation time, C.

12. Procedure

12.1 *Blanks*:

12.1.1 Obtain reproducible blank measurements on each individual platinum electrode by following 12.1.2 – 12.1.8.

NOTE 7—Two platinum working electrodes are recommended to increase sample throughput by alternating the electrodes. While one electrode is being used in an electrolysis, the other electrode is being cleaned and conditioned by sitting in a beaker of hot concentrated nitric acid. The electrode that is being cleaned is rinsed thoroughly with water and 0.5 mol/L (0.5 M) sulfuric acid prior to its use.

12.1.2 Add 0.5 mol/L (0.5 M) H₂SO₄ to the electrolysis cell to completely immerse the working electrode gauze.

12.1.2.1 Avoid overfilling the electrolysis cell. Fill only to the top of the platinum gauze of the working electrode.