Designation: C1165 – 23

Standard Test Method for Determining Plutonium by Controlled-Potential Coulometry in H_2SO_4 at a Platinum Working Electrode[1]

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

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*) H_2SO_4 electrolyte at a platinum working electrode (**3**) maintained at + 0.310 V versus a saturated calomel electrode (SCE). Plutonium is then oxidized to

[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.

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:

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

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*) H_2SO_4 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*) H_2SO_4 electrolyte, the Fe(II) – Fe(III) and Pu(III) – Pu(IV) couples have essentially the same E^o 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

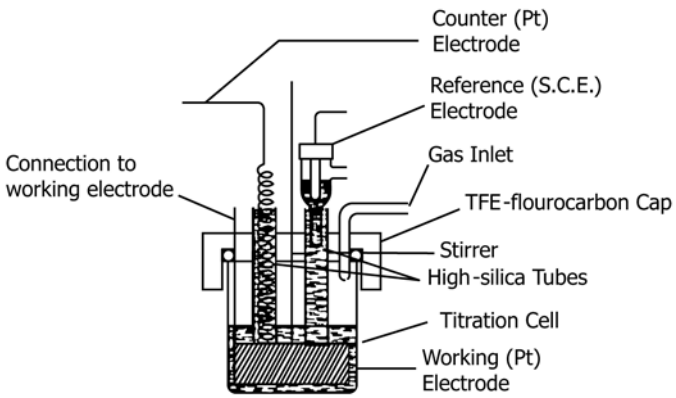

FIG. 1 Example of a Cell Design Used at Los Alamos National Laboratory (LANL)