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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Plutonium by Iron (II)/Chromium (VI) Amperometric Titration¹

This standard is issued under the fixed designation C 1206; 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 plutonium in unirradiated nuclear-grade plutonium dioxide, uranium-plutonium mixed oxides with uranium (U)/plutonium (Pu) ratios up to 21, plutonium metal, and plutonium nitrate solutions. Optimum quantities of plutonium to measure are 7 to 15 mg.

1.2 *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.*

2. Referenced Documents

2.1 ASTM Standards:

- C 697 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets²
- C 698 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides ((U, Pu)O₂)²
- C 757 Specification for Nuclear-Grade Plutonium Dioxide Powder, Sinterable²
- C 758 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Metal²
- C 759 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Nitrate Solutions²
- C 833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets²
- C 1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis²

3. Committee C-26 Safeguards Statement

3.1 The materials [nuclear-grade mixed oxides (U, Pu)O₂ powders, pellets, Pu metal, Pu oxides, and Pu nitrates] to which this test method applies, are subject to nuclear safeguards

regulations governing their possession and use. This analytical test method has been designated as technically acceptable for generating safeguards accountability measurement data for plutonium.

3.2 When used in conjunction with appropriate standard reference material this test method can demonstrate traceability to the national measurement base. 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.

4. Summary of Test Method

4.1 Amperometric titrations are based on the measured change in the current flow between two electrodes, held at constant potential, when a titrant is added. The plutonium is first oxidized to the +6 oxidation state in a dilute sulfuric acid solution with argentic oxide. The excess oxidant is destroyed by heating, and the Pu(VI) is then reduced to Pu(IV) by excess Fe(II) during the titration. The excess Fe(II) is titrated by Cr(VI), and the Pu determined by difference from the quantities of the two titrants.

4.2 Oxide and metal samples are prepared to produce final solutions as a soluble sulfate. Plutonium-nitrate solutions can be introduced directly at the beginning of the procedure and are later diluted with sulfuric acid. Chlorides must be removed.

5. Significance and Use

5.1 All plutonium materials covered in this test method are used in the preparation of nuclear-reactor fuels. In order to be suitable for this purpose, the materials must meet specified criteria for plutonium content. This test method is used to verify the plutonium content.

5.2 A primary standard dichromate or a dichromate traceable to a primary standard such as a National Institute of Standards and Technology (NIST) plutonium standard is required for this technique.

6. Interferences

6.1 Interference is caused by ions that are oxidized by argentic oxide and reduced by ferrous ion in sulfuric-acid solution. Elements that may be present in plutonium materials and that will produce quantitative positive errors include

¹ This test method is under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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² *Annual Book of ASTM Standards*, Vol 12.01.

vanadium (V), chromium (Cr), and manganese (Mn). Correction can be made for these elements by calculation when they do not individually exceed 200 µg impurity elements per gram of plutonium.

6.2 Other elements that will cause positive errors include cerium (Ce), ruthenium (Ru), gold (Au), rhodium (Rh), platinum (Pt), lead (Pb), and neptunium (Np). Americium (Am) does not interfere because it is not oxidized to higher valency states during the argentic oxidation.

6.3 Thallium (Tl), selenium (Se), calcium (Ca), and barium (Ba) give low results.

7. Apparatus

7.1 *Weighing Burets*, polyethylene drop-dispenser bottles with polypropylene dropping closure and cap, 30 and 60-mL sizes.³ Squeeze deliveries are made with these burets. They are placed in a secondary, cut-off, slightly larger diameter polyethylene bottle to prevent mass changes from contact with the hands. Burets are transferred to and from the balance using forceps.

7.2 *Digital Voltmeter*, d-c precision, readable to 0.2 mv.⁴

7.3 *Microelectrode*, rotating platinum.⁵

7.4 *Reference Mercury Electrode*, saturated mercurous sulfate.⁶

7.5 *Titratr/Detector*, amperometric (see Fig. 1).

8. Reagents

8.1 *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.⁷ Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

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

8.3 *Argentic Oxide* (AgO).

8.4 *Ferrous Ammonium Sulfate Solution, Iron (II) Titrant*—Dissolve 19.6 g of Fe(NH₄)₂(SO₄)₂·6 H₂O in 500 mL of cold 1 N H₂SO₄ and dilute to 1 L with 1 N H₂SO₄. The solution is standardized daily or before beginning a series of plutonium standard and sample titrations, or both.

8.5 *Potassium Dichromate Solution*—Use NIST SRM

³ Nalgene drop-dispenser bottles, Nos. 2411-0030 and 2411-0060 have been found satisfactory.

⁴ Both Ealing Pye Scalamp Microammeter No. 29-222 and Keithley Model 197 Digital Multimeter have been found satisfactory.

⁵ Both Sargent & Co. No. S-30420 with No. S-76485 synchronous rotator and Brinkmann Model 2.628.0010 (628-10, 68-50) have been found satisfactory.

⁶ Brinkmann Model EA 406 has been found satisfactory.

⁷ "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."

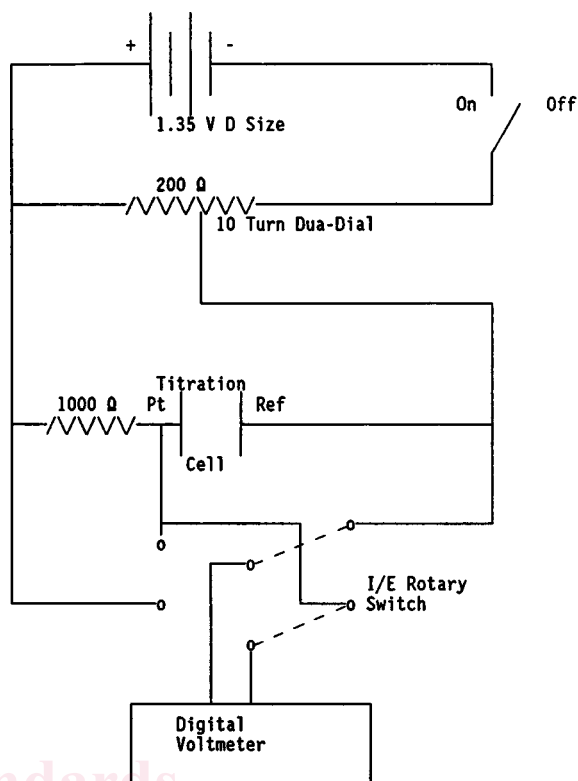


FIG. 1 Amperometric Detector Circuit

136e⁸ or equivalent. Weigh approximately 4.9 g to nearest 0.0001 g of potassium dichromate (K₂Cr₂O₇) and dissolve in water. Transfer to a tared 2-L volumetric flask. Dilute to volume with water. Weigh the flask and contents. Make the buoyancy correction and determine the mass of the solution. Express the oxidizing strength as milliequivalents per gram of solution (C1).

$$C1 = \frac{K \times P \times B}{E \times S} \quad (1)$$

where:

C1 = K₂Cr₂O₇ concentration, milliequivalents per gram,

K = weight, mg, K₂Cr₂O₇,

P = purity of K₂Cr₂O₇,

B = buoyancy correction for K₂Cr₂O₇, 1.00031 (use only if significant),

E = equivalent weight of K₂Cr₂O₇, 49.0320, and

S = weight of solution, g.

8.6 *Sulfuric Acid (0.5 N)*—Prepare by adding 14 mL of sulfuric acid (H₂SO₄, sp gr 1.84) to water with stirring and dilute to 1 L.

8.7 *Sulfuric Acid (1 N)*—Prepare by adding 28 mL of H₂SO₄ (sp gr 1.84) to water with stirring and dilute to 1 L.

8.8 *Sulfuric Acid (18 N)*—Prepare by carefully adding (with continuous stirring) 500 mL of H₂SO₄ (sp gr 1.84) slowly to 450 mL water, cool, and dilute to 1 L.

9. Standardization of Iron (II) Titrant

9.1 Transfer 20 mL water and 10 mL of 18 N H₂SO₄ to a

⁸ Available from National Institute of Standards and Technology, Gaithersburg, MD 20899.