



Standard Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Nitrate Solutions¹

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1. Scope

1.1 These test methods cover procedures for the chemical, mass spectrometric, spectrochemical, nuclear, and radiochemical analysis of nuclear-grade plutonium nitrate solutions to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

	Sections
Plutonium by Controlled-Potential Coulometry	²
Plutonium by Amperometric Titration with Iron(II)	²
Plutonium by Diode Array Spectrophotometry	
Free Acid by Titration in an Oxalate Solution	8 to 15
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Sample Preparation for Spectrographic Analysis for General Impurities	115 to 118

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses are 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 and health practices and determine the applica-*

bility of regulatory limitations prior to use. For specific safeguard and safety hazard statements, see Section 6.

2. Referenced Documents

2.1 ASTM Standards:³

- C697 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets
- C852 Guide for Design Criteria for Plutonium Gloveboxes
- C1009 Guide for Establishing a Quality Assurance Program for Analytical Chemistry 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
- C1165 Test Method for Determining Plutonium by Controlled-Potential Coulometry in H₂SO₄ at a Platinum Working Electrode
- C1206 Test Method for Plutonium by Iron (II)/Chromium (VI) Amperometric Titration
- C1210 Guide for Establishing a Measurement System Quality Control Program for Analytical Chemistry Laboratories Within the Nuclear Industry
- C1235 Test Method for Plutonium by Titanium(III)/Cerium(IV) Titration⁴
- C1268 Test Method for Quantitative Determination of Americium 241 in Plutonium by Gamma-Ray Spectrometry
- C1297 Guide for Qualification of Laboratory Analysts for the Analysis of Nuclear Fuel Cycle Materials

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 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.

⁴ Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

C1307 Test Method for Plutonium Assay by Plutonium (III) Diode Array Spectrophotometry

C1415 Test Method for ²³⁸Pu Isotopic Abundance By Alpha Spectrometry

C1432 Test Method for Determination of Impurities in Plutonium: Acid Dissolution, Ion Exchange Matrix Separation, and Inductively Coupled Plasma-Atomic Emission Spectroscopic (ICP/AES) Analysis

D1193 Specification for Reagent Water

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis⁴

E116 Practice for Photographic Photometry in Spectrochemical Analysis⁴

3. Significance and Use

3.1 These test methods are designed to show whether a given material meets the purchaser's specifications.

3.1.1 An assay is performed to determine whether the material has the specified plutonium content.

3.1.2 Determination of the isotopic content of the plutonium in the plutonium-nitrate solution is made to establish whether the effective fissile content is in compliance with the purchaser's specifications.

3.1.3 Impurity content is determined by a variety of methods to ensure that the maximum concentration limit of specified impurities is not exceeded. Determination of impurities is also required for calculation of the equivalent boron content (EBC).

4. Committee C26 Safeguards Statement⁵

4.1 The material (plutonium nitrate) to which these test methods apply is subject to nuclear safeguards regulations governing its possession and use. The following analytical procedures in these test methods have been designated as technically acceptable for generating safeguards accountability measurement data: Plutonium by Controlled-Potential Coulometry; Plutonium by Amperometric Titration with Iron(II); Plutonium by Diode Array Spectrophotometry and Isotopic Composition by Mass Spectrometry.

4.2 When used in conjunction with appropriate Certified Reference Materials (CRMs), these procedures can demonstrate traceability to the national measurement 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 their application to safeguards has the approval of the proper regulatory authorities.

5. Reagents and Materials

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all test methods. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of

⁵ Based upon Committee C26 Safeguards Matrix (C1009, C1068, C1128, C1156, C1210, C1297.).

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.

5.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D1193.

6. Safety Hazards

6.1 Since plutonium 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 C852 and in Refs (1) through (3).⁷

6.2 Adequate laboratory facilities, such as fume hoods and controlled ventilation, along with safe techniques, must be used in this procedure. Extreme care should be exercised in using hydrofluoric and other hot, concentrated acids. Use of proper gloves is recommended. Refer to the laboratory's chemical hygiene plan and other applicable guidance for handling chemical and radioactive materials and for the management of radioactive, mixed, and hazardous waste.

6.3 Hydrofluoric acid is a highly corrosive acid that can severely burn skin, eyes, and mucous membranes. Hydrofluoric acid is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid. Hydrofluoric acid differs from 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. Due to the serious consequence of hydrofluoric acid burns, prevention of exposure or injury of personnel is the primary goal. Utilization of appropriate laboratory controls (hoods) and wearing adequate personal protective equipment to protect from skin and eye contact is essential.

7. Sampling

7.1 A sample representative of the lot shall be taken from each lot into a container or multiple containers that are of such composition that corrosion, chemical change, radiolytic decomposition products, and method of loading or sealing will not disturb the chemical or physical properties of the sample. (A flame-sealed quartz vial that is suitable for accommodating pressure resulting from radiolytic decomposition is generally considered to be an acceptable sample container.)

⁶ *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.

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

7.2 Sample size shall be sufficient to perform the following:

7.2.1 Assay and acceptance tests at the seller's plant,

7.2.2 Assay and acceptance tests at the purchaser's plant, and

7.2.3 Referee tests in the event they become necessary.

7.3 All samples shall be identified clearly, including the seller's lot number.

7.3.1 A lot is defined as any quantity of aqueous plutonium nitrate solution that is uniform in isotopic, chemical, and physical characteristics by virtue of having been mixed in such a manner as to be thoroughly homogeneous.

7.3.2 All containers used for a lot shall be identified positively as containing material from a particular homogeneous solution.

PLUTONIUM BY CONTROLLED-POTENTIAL COULOMETRY

(This test method was discontinued in 1992 and replaced by Test Method **C1165**.)

PLUTONIUM BY CONTROLLED-POTENTIAL COULOMETRY

(With appropriate sample preparation, controlled-potential coulometric measurement as described in Test Method **C1108** 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 **C1206**.)

TEST METHOD FOR PLUTONIUM ASSAY BY PLUTONIUM(III) DIODE ARRAY SPECTROPHOTOMETRY

(With appropriate sample preparation, the measurement described in Test Method **C1307** may be used for plutonium determination.)

FREE ACID BY TITRATION IN AN OXALATE SOLUTION

8. Scope

8.1 This test method covers the determination of free acid in plutonium nitrate solutions (**4, 5**).

9. Summary of Test Method

9.1 Free acid is determined by titrating an aliquot of sample, which contains an excess of ammonium oxalate added to complex the plutonium, back to the original pH of the ammonium oxalate solution with standard sodium hydroxide solution. Micropipets and microburets are required to measure the small volume of sample and titrant used.

10. Interferences

10.1 Any metal ions not complexed by oxalate which form precipitates at the pH of the end point of the titration will cause interference in this test method.

NOTE 1—A "rule of thumb" is that 1 mL of saturated ammonium oxalate solution will complex 6.4 mg of plutonium.

11. Apparatus

11.1 *Magnetic Stirrer.*

11.2 *Microburet.*

11.3 *Micropipets.*

11.4 *pH Meter.*

12. Reagents and Materials

12.1 *Ammonium Oxalate Solution*, saturated.

12.2 *Nitric Acid (3.50 N)*—Prepare solution by diluting concentrated nitric acid (HNO_3 , sp gr 1.42) with water. Standardize by titrating 0.500-mL aliquots with 0.100 *N* NaOH solution.

12.3 *Sodium Hydroxide Solution (0.100 N)*—Prepare and standardize in accordance with Practices **E50**.

13. Procedure

13.1 Transfer 1.0 mL of saturated ammonium oxalate solution to a small vial and dilute to about 2 mL with water.

13.2 Add a stirring bar and insert the electrodes and start stirrer. When the pH value becomes stable, record the value as the pH of reagent.

NOTE 2—Normally, the pH value for the saturated solution is approximately 6.4.

13.3 Add 20 μL of sample to the vial, rinse the pipet thoroughly with water, and stir the solution for 1 min.

13.4 Titrate with 0.100 *N* NaOH solution to within one pH unit of the end point; then, by adding successively smaller increments, titrate to the pH of the ammonium oxalate reagent and record the volume of titrant.

NOTE 3—Allow time for the pH reading to stabilize between additions of titrant as the end point is approached.

13.5 Make a daily check of the system by adding 20 μL of 3.50 *N* HNO_3 to a sample that has already been titrated to the end point and titrate with standard 0.100 *N* NaOH solution back to the same pH.

14. Calculation

14.1 Calculate the free acid (H^+ , *N*) as follows:

$$\text{H}^+, N = (A \times N)/V \quad (1)$$

where:

A = microlitres of standard NaOH solution required to titrate sample,

N = normality of NaOH standard solution, and

V = volume of sample, μL .

15. Precision and Bias

15.1 *Precision*—Of individual results, $\pm 5\%$ at the 95% confidence level.

15.2 *Bias*—99.4%.

FREE ACID BY IODATE PRECIPITATION-POTENTIOMETRIC TITRATION TEST METHOD

16. Scope

16.1 This test method covers the determination of free acid in strong acid solutions of plutonium nitrate.