



Designation: C1307 – 21

Standard Test Method for Plutonium Assay by Plutonium (III) Diode Array Spectrophotometry¹

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1. Scope

1.1 This test method describes the determination of total plutonium as plutonium(III) in nitrate and chloride solutions. The technique is applicable to solutions resulting from plutonium dioxide powders and pellets (Test Methods C697), nuclear grade mixed oxides (Test Methods C698), plutonium metal (Test Methods C758), and plutonium nitrate solutions (Test Methods C759). Solid samples are dissolved using the appropriate dissolution techniques described in Practice C1168. The use of this technique for other plutonium-bearing materials has been reported (1-6),² but final determination of applicability must be made by the user. The applicable concentration range for plutonium sample solutions is 10 to 200 g Pu/L.

NOTE 1—As directly measured in the spectrophotometer, concentrations will be approximately 0.8 to 4.0 g Pu/L. Sample solutions are diluted to reach this target range. For solid samples, select the sample size and dissolved solution weight to yield sample solutions in the 10 to 30 g Pu/L range. With special preparation and spectral analysis techniques, the method has been applied to nitrate solutions in the 0.1 to 10 g Pu/L range.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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.*

1.4 *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.*

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 The boldface numbers in parentheses refer to a list of references at the end of this standard.

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
- C698 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides ((U, Pu)O₂)
- C757 Specification for Nuclear-Grade Plutonium Dioxide Powder for Light Water Reactors
- 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 for Light Water Reactors
- C859 Terminology Relating to Nuclear Materials
- C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis
- D6122 Practice for Validation of the Performance of Multivariate Online, At-Line, Field and Laboratory Infrared Spectrophotometer, and Raman Spectrometer Based Analyzer Systems
- E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
- E169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis
- E1655 Practices for Infrared Multivariate Quantitative Analysis
- E2617 Practice for Validation of Empirically Derived Multivariate Calibrations

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms related to nuclear materials, refer to Terminology C859.

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.

3.1.2 For definition of terms related to UV-visible spectrophotometry, refer to Practice **E60**.

3.1.3 For definitions of terms related to multivariate calibration, refer to Practices **E1655** and **E2617**.

4. Summary of Method

4.1 The concentration of plutonium in a solution is determined by the spectrophotometric measurement of the absorbance of visible light by plutonium(III).

4.1.1 In a spectrophotometric measurement, the substance being determined absorbs light at wavelengths characteristic of that substance. This characteristic pattern is an absorbance spectrum. The Beer-Lambert Law provides that the magnitude of the absorbance is proportional to the concentration of the absorber. The absorbance spectrum of a solution is equal to the sum of the absorbance spectra of all species in the solution. Where the absorbance spectra of multiple species overlap, accurate measurement of the species of interest requires distinguishing the absorbance of that species from the absorbances of other species. The characteristic wavelengths at which a substance absorbs will depend on the physical and chemical characteristics of the substances.

4.2 Reduction to plutonium(III) is accomplished by the addition of a measured quantity of reductant solution to the sample aliquant

4.2.1 For nitrate solutions, ferrous sulfamate is the recommended reductant. Aliquants (1 mL or less) of the sample solution are diluted with 10 mL of a ferrous reductant/matrix solution to 1 g Pu/L and measured.

4.2.2 For chloride solutions, ascorbic acid is the recommended reductant. Aliquants of the sample solution, each containing 50 to 100 mg of plutonium, are diluted with 2 mL of zirconium solution to complex fluoride ions, 2 mL ascorbic acid reductant solution, and 1.0 M HCl to a total volume of 25 mL, yielding 2 to 4 g Pu/L solutions for measurement.

4.3 Plutonium concentration is determined from absorbance measurements taken on the sample solution from 516 to 640 nm (blue-green region) where a broad doublet band is observed (**7, 8**). Guidelines for the operation and maintenance of ultraviolet-visible spectrophotometers is provided elsewhere (see Practices **E60** and **E169**). Multivariate analysis software is used to calculate the plutonium concentration from measured spectra. The analysis is based on prediction models derived from a set of standard calibration solutions that encompass the range of expected solution conditions (plutonium concentration, potential complexing agents and interferences, etc.). This software is commercially available and in some cases is provided with the spectrophotometer. The users of this procedure are responsible for selecting or customizing, or both, the multivariate analysis (and instrument control) software that best meets their individual measurement methodology and needs. Guidelines for creating and validating multivariate analysis calibrations provided elsewhere (see Practices **E1655** and **E2617**). Guidelines and principles for the creation and maintenance of a spectrophotometer-based analysis method can be found in Practice **D6122**. This procedure is intended to address key measurement requirements and to allow users discretion in establishing appropriate procedural details and

technique variations. The software package selected should include a feature that indicates the quality of the analysis, such as metrics that indicate the similarity of the sample spectrum to those in the calibration set. The user may thereby assess the measurement reliability and the presence of interferences that absorb light or otherwise alter the plutonium(III) spectrum without requiring supplemental measurements.

4.4 In nitrate solutions, plutonium will form a distribution of complexes with nitrate anions. For plutonium(III), these complexes will be of the form $\text{Pu}(\text{NO}_3)_x^{3-x}$, with x tending to increase at higher nitrate concentration. Each plutonium nitrate complex has a distinct absorbance spectrum, and the total spectrum will be the sum of the spectra of the individual complexes, weighted by their relative concentration in the solution. A similar process occurs in chloride matrices, but the chloride complexes have similar spectra and the overall effect on the total absorbance is less significant.

4.5 The scope of this method is restricted to the spectrophotometric analysis of plutonium in the (III) oxidation state. Other spectrophotometric techniques have been reported to measure Pu in the (IV) or (VI) oxidation state, or for the simultaneous measurement of Pu as a mixture of several oxidation states. (**9, 10**). The user must distinguish the suitability of this method versus another method for the intended application.

5. Significance and Use

5.1 This test method is designed to determine whether a given material meets the purchaser's specification for plutonium content. This method may also be used, with sufficient qualification, for process control or accountability measurements associated with nuclear materials processing.

6. Interferences

6.1 Materials meeting the applicable material specifications of the ASTM standard for which this procedure was developed, when dissolved and diluted without introduction of interfering contaminants as described in Practice **C1168**, will contain no interfering elements or species.

NOTE 2—Fluoride, if present, would interfere if the zirconium, routinely added to the sample solution aliquant for the chloride matrix, were omitted from the procedure. Zirconium may be added to the ferrous sulfamate reductant solution to handle fluorides if present in a nitrate matrix. Zirconium, when used, should be added to all samples, blanks, and standards to obtain a consistent matrix. Refer to Specifications **C833** and **C757**.

6.2 Interferences and measurement biases are caused by: (1) materials that absorb light in the region of the plutonium absorption, (2) undissolved solids that cause light scattering, (3) strong oxidizing or complexing agents that prevent complete reduction of the plutonium to the plutonium(III) oxidation state, (4) anions that competitively form complexes with plutonium and shift the spectrum away from those expected for nitrate or chloride matrices, and (5) variance of other solution conditions (ionic strength, temperature) outside the range(s) encompassed in the calibration model.

6.2.1 Absorption of light in the spectral region of interest by another species is a potential interference. Identification and

inclusion of potentially interfering species in the multivariate analysis calibration set will significantly reduce their effect. At a minimum, sample measurements should be flagged when the higher than normal fitting error occurs, resulting from the presence of unidentified absorbing species. Absorbance limits should be established within the region of interest to ensure that the instrument response remains reliable.

NOTE 3—Specific species of concern will depend on the source of the plutonium and the concentration of the species. For example, nitric acid-based dissolution of stainless steel-clad fuels may lead to significant amounts of Cr^{3+} , Ni^{2+} , and Fe^{3+} . Sample cleanup, as part of the separations process or in the laboratory, can mitigate the effects of these species.

NOTE 4—Care must be taken in the choice of the preprocessing methods (derivatives, mean centering, autoscaling, wavelength selection, or combinations thereof) as these may affect the robustness of the final model, particularly with regard to unknown interferences. Double derivatives of the spectra often ameliorate the effect of interferents. Use of residual analysis will not always detect unknown interferences and results will vary depending on the preprocessing methods and models employed. Even within the calibration set, fit residuals will vary significantly, with correlations to the concentrations of both the plutonium and the interferents. Identification of high fit residuals should prompt the user to further investigate the spectral quality.

NOTE 5—As light intensities approach intrinsic noise and background levels, instrument response will start to become nonlinear. As commonly used multivariate analysis methods based on principal components analysis are intrinsically linear, low light throughput during a measurement will lead to errors in the analysis results.

6.2.2 This spectrophotometric assay method should not be used on turbid (cloudy) solutions or solutions containing undissolved material. In addition to visual or turbidity meter measurements, or both, the presence of undissolved solids may be identified by the resulting shifts in the spectral baseline and by elevated spectral fitting errors.

NOTE 6—Plutonium oxides, mixed oxides, and plutonium metals meeting the material specifications for which this test method is intended, will dissolve when procedures in Practice C1168 are followed. Failure to achieve dissolution is an indication that the material does not meet the specifications, and the application of this test method for plutonium assay must be verified by the user. The user and customer are cautioned: when undissolved solids that persist after exhaustive dissolution efforts are to be removed by filtration through filter paper or other inert material of appropriate porosity, the subsequent plutonium assay measurements require close scrutiny. While filtration of undissolved solids may permit the reliable measurement of the concentration of plutonium in the filtrate, the resulting analysis may not be representative of their source material. Solids may indicate incomplete dissolution of the plutonium in the sample material, not necessarily a plutonium-free refractory residue. When this technique is utilized in support of reprocessing operations, process solutions containing solids may be an indication of incomplete dissolution of the plutonium-bearing material being processed or of an error in process operations. In addition to process control considerations, the undissolved solids may represent accountability and criticality control problems.

6.2.3 Strong oxidizing agents and complexing agents in sufficient concentration to prevent complete reduction typically are not present in plutonium nitrate samples. Appreciable concentrations of fluoride and sulfate anions have been found to interfere. The concentration of hydrofluoric acid, added to catalyze dissolution of oxides, may be removed by evaporation prior to measurement to ensure that the zirconium effectively complexes the traces of fluoride ion. Changes in the plutonium spectrum from incomplete reduction due to oxidizing agents

and shifts in the spectrum due to complexing agents are also indicated by increases in the spectral curve fitting error.

6.2.4 The presence of other anions may alter the absorbance spectrum by competitively forming complexes with plutonium (7). This effect may be mitigated by including the expected range of anion identities and concentrations in the multivariate calibration set or by using appropriate spectral fitting features that identify and correct for the effect.

6.2.5 Solution temperature and ionic strength are also known to influence the absorption spectra of actinides, likely through changing the equilibrium of complex formation (11). As with other anions, these effects should be included in multivariate calibration sets.

6.3 A study was conducted at the Los Alamos National Laboratory to determine the immunity of the Pu(III) spectrophotometric assay method to a diverse species of potential interferences. The elements studied were atomic numbers 1, 9, 11 to 13, 17, 19, 22 to 31, 35, 42, 44 to 46, 48, 50, 53, 57, 58, 60, 62, 73, 74, 76, 77, 79, 83, 90, 92, 93, and 95. Potential interferences from nitrate, phosphate, sulfate, and oxalic acid are also documented (12).

7. Apparatus

7.1 *Spectrophotometer*—Wavelength range 190 to 820 nm; wavelength accuracy ± 2 nm; wavelength reproducibility ± 0.05 nm; full dynamic range 0.0022 to 3.3 AU; photometric accuracy at 1 AU with a NBS 931 filter at 512 nm is ± 0.005 AU; baseline flatness < 0.0013 AU; noise at 500 nm is 0.0002 AU RMS; stray light measured with a Hoya O-56 filter at 220 nm < 0.05 %.

NOTE 7—The optical specifications listed in 7.1 are for instruments used in previous reports (2, 3, and 5) and have been found to provide satisfactory results. Instrument resolution should allow for each absorbance feature to be sampled by multiple diode array pixels without interpolation. In addition to these specifications, an acceptable spectrometer system should also provide multivariate analysis and computer control. Optical fiber capabilities will facilitate sample handling in radiological containment. Although the wavelength range for plutonium requires only a fraction of the 190 to 820 nm range specified (plutonium absorption spectrum is measured over the 520 to 634 nm region) spectrophotometers with significantly smaller range would be of little general use to the purchaser.

7.2 *Sample Handling*—Quartz cuvettes with pathlengths from 1 to 4 cm are recommended. The use of a flow-through cuvette 4 eliminates pathlength variability between samples. To that effect, plastic disposable cuvettes should be used with reservation, as pathlength variability can lead to increased measurement uncertainty. Flow systems and operating procedures should ensure complete sample exchange between measurements.

7.3 *Analytical Balance*—Readability of 0.1 mg; linearity 0.1 mg over any 10 g range and 0.2 mg over 160 g full scale.

7.4 *Solution Density Meter*—Readability of 0.1 mg/mL; precision of 0.3 mg/mL; linearity and accuracy 0.5 mg/mL over the range 0 to 2.0 g/mL.

7.5 *Adjustable, Fixed-volume Pipetters*—Calibrated to deliver the desired range of volumes for sample and matrix-reductant solutions.

8. Reagents and Materials

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.⁴ 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.

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

8.3 *Ascorbic Acid-Reductant Solution* ($C_6H_8O_6$, aminoguanidine bicarbonate ($CH_6N_4 \cdot H_2CO_3$), 0.4 M in each reagent)—Prepare fresh daily by dissolving 7 g of ascorbic acid and 5.5 g aminoguanidine bicarbonate in 80 mL of 1 M HCl, then dilute to a final volume of 100 mL 1 M HCl.

NOTE 8—The ascorbic acid is stabilized by the addition of aminoguanidine (Guanylhiazine:HN:C(NH₂)NHNH₂). The stabilized reductant solution has been found to be effective when ascorbic acid stability problems are encountered.

8.4 *Ferrous-reductant Solution* (ferrous sulfamate, 0.05 M; sulfamic acid, 0.25 M; nitric acid, 1.0 M)—Prepare fresh weekly by adding 12 mL of freshly prepared ferrous sulfamate (2 M) to 90 mL of sulfamic acid (1.5 M). Stir, then add 175 mL of nitric acid (3.0 M) and dilute to 500 mL with water.

8.5 *Ferrous Sulfamate* ($Fe(NH_2SO_3)_2$, 2.0 M)—Prepare fresh for the preparation of the ferrous-reductant solution. Add 220 g of solid sulfamic acid to 450 mL of water, stir, and heat at 70 to 80 °C until dissolved. Continue stirring and heating, while adding approximately 0.5 g portions of iron metal powder (Fe^0) until 56 g of iron have been dissolved in the heated sulfamic acid. Filter the solution while hot; allow to cool; then dilute to a final volume of 50 mL.

NOTE 9—The dissolution of the sulfamic acid need not be quantitative before beginning the addition of the iron powder. Excessive heating beyond the time required to achieve the dissolution of the sulfamic acid/iron powder or at temperatures above 80 °C will cause excessive decomposition of the sulfamic acid.

8.6 *Hydrochloric Acid* (HCl, 12 M)—Concentrated, sp gr 1.19.

8.7 *Hydrochloric Acid* (HCl, 1.0 M)—Add 84 mL of hydrochloric acid (sp gr 1.19) to approximately 500 mL of water. Stir, then dilute to a final volume of 1 L.

8.8 *Nitric Acid* (HNO₃, 15.8 M)—Concentrated, sp gr 1.42.

8.9 *Nitric Acid* (1.0 M)—Add 63 mL of nitric acid (sp gr 1.42) to approximately 500 mL of water. Stir, then dilute to a final volume of 1 L.

8.10 *Nitric Acid* (3.0 M)—Add 190 mL of nitric acid (sp gr 1.42) to approximately 500 mL of water. Stir, then dilute to a final volume of 1 L.

8.11 *Plutonium Standard Solutions*—Prepare standards traceable to a national measurement system, which cover the range of concentrations over which sample measurements will be performed.

8.12 *Sulfamic Acid* (NH_2SO_3H , 1.5 M)—Dissolve 145 g of solid sulfamic acid in 900 mL of water with stirring. Filter, then dilute with water to a final volume of 1 L.

8.13 *Zirconium Reagent* ($ZrOCl_2 \cdot 8H_2O$, 0.75 M)—Dissolve 120.5 g zirconium chloride octahydrate in 450 mL of 1.0 M HCl; dilute to a final volume of 500 mL of 1.0 M HCl.

9. Quality Control

9.1 Perform quality control checks of the system prior to each use. To perform these checks, prepare several aliquants of at least two different plutonium standard solutions in the same concentration range as the samples to be measured in accordance with the preparation procedure described in Section 10. The aliquants should also be representative of the matrix conditions of the samples. The standard solutions should be prepared independently of any solutions used to generate the multivariate calibration.

9.2 Following spectral referencing, measure each of the aliquants from one or more of the standard solutions. Quantitate each of the resulting spectra using appropriate multivariate analysis routines and establish that all results and parameters meet the control limits previously established by the user.

9.3 Blank solutions may also be required for quality control purposes.

9.4 Sample results should only be adjusted based on the results of a regularly maintained control program that takes into account method uncertainties and can identify long term biases. One-time or daily correction factors should not be applied to the sample results.

10. Procedure

10.1 Sample Preparation:

10.1.1 Dissolve all solid samples in accordance with Practices C1168 or equivalent practices.

10.1.2 Dissolve metal with hydrochloric acid.

10.1.3 Dissolve all oxides by acid digestion in either sealed reflux tubes or in beakers. If hydrofluoric acid was added for dissolution, convert the dissolved sample solution to either a nitrate or chloride matrix by evaporation, ensuring removal of hydrofluoric acid.

10.1.4 Plutonium nitrate sample solutions are measured directly.

10.1.5 Inspect all solutions to be measured for unusual appearance or properties.

10.2 Preparation of Samples and Standards for Spectroscopic Measurement:

10.2.1 For solutions with a nitrate/sulfamate matrix, take aliquants of the sample solution, each containing 7 to 13 mg of

⁴ *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.