



Designation: C 1307 – 02

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

This standard is issued under the fixed designation C 1307; 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 describes the determination of total plutonium as plutonium(III) in nitrate and chloride solutions. The technique is applicable to solutions of plutonium dioxide powders and pellets (Test Methods C 697), nuclear grade mixed oxides (Test Methods C 698), plutonium metal (Test Methods C 758), and plutonium nitrate solutions (Test Methods C 759). Solid samples are dissolved using the appropriate dissolution techniques described in Practice C 1168. The use of this technique for other plutonium-bearing materials has been reported (1-5), but final determination of applicability must be made by the user. The applicable concentration range for plutonium sample solutions is 10–200 g Pu/L.²

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 Pellets³

C 698 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides ((U, Pu)O₂)³

C 757 Specification for Nuclear-Grade Plutonium Dioxide Powder, Sinterable³

C 758 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Metal³

C 759 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Nitrate Solutions³

C 833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets³

C 1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis³

3. Summary of Method

3.1 In a diode array spectrophotometric measurement, as in a conventional spectrophotometric measurement, the substance being determined absorbs light at frequencies characteristic of that substance. The amount of light absorbed at each wavelength is directly proportional to the concentration of the species of interest. The absorption is a function of the oxidation state and the complexation obtained in the solution matrix selected for measurement. Beer's Law permits quantifying the species of interest relative to a traceable standard when both solutions are measured under the same conditions. The array of photosensitive diodes permits the (virtually) simultaneous collection of spectral information over the entire range of the instrument, for example, 190–820 nm (or any selected portion of the range). An entire absorption spectrum can be obtained in 0.1 s; however, optimum precision is obtained from multiple spectra collected over a 4-s period.

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

3.2.1 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.

3.2.2 For chloride solutions, ascorbic acid is the recommended reductant. Aliquants of the sample solution, each containing 50–100 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 2–4 g Pu/L solutions for measurement.

3.3 Plutonium concentration is determined from light absorption measurements taken on the sample solution in the blue-green region from 516 to 640 nm where a broad doublet band is observed. Spectral quantifying software capable of

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² For solid samples, select the sample size and dissolved solution weight to yield sample solutions in the 10–30 g Pu/L range. With special preparation and spectral analysis techniques, the method has been applied to nitrate solutions in the 0.1–10 g Pu/L range.

³ *Annual Book of ASTM Standards*, Vol 12.01.

fitting the sample spectrum with spectral information from standard solutions is used to calculate the plutonium concentration. Both commercially available (6) and custom-designed (7-12) spectral fitting software have been developed which may be used for plutonium measurements. The users of this procedure are responsible for selecting or customizing, or both, the spectral fitting (and instrument control) software that best meets their individual measurement methodology and needs. Software selection will dictate many of the procedural specifics not included in this procedure. 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 spectral fit, thereby providing information on the measurement reliability and the presence of interferences that absorb light or otherwise alter the plutonium(III) spectrum without requiring supplemental measurements.

4. Significance and Use

4.1 This test method is designed to determine whether a given material meets the purchaser's specification for plutonium content.

5. Interferences

5.1 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 C 1168, will contain no interfering elements or species.

NOTE 1—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 nitrate matrix. Ferrous-Reductant Solution to handle fluorides if present. Zirconium, when used, should be added to all samples, blanks, and standards to obtain a consistent matrix. Refer to Specifications C 833 and C 757.

5.2 Interferences 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, and 4) anions that shift the spectrum.

5.2.1 Absorption of light in the region of interest by another species is a potential interference. Identification of potentially interfering species and inclusion of their spectra in the spectral curve fitting process 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. Enhancement of the spectral curve fitting capabilities of the DAS can be achieved by taking double derivatives of the spectrum collected. The spectral curve fitting software of the DAS is then used to quantitate the mathematically manipulated spectrum.

NOTE 2—Care must be taken in the choice of the preprocessing methods (derivatives, mean centering, autoscaling and/or channel selection) as these may affect the robustness of the final model, particularly with regard to unknown interferences. Use of residual analysis will not always detect unknown interferences and results will vary depending on the preprocessing methods and models employed.

5.2.2 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 3—Plutonium oxides, mixed oxides, and plutonium metals meeting the material specifications for which this test method is intended, will dissolve when procedures in Practice C 1168 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.

5.2.3 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.

5.2.4 Anion identity and concentration will shift the location and alter the shape of the absorption curve. The system calibration must include the anion shift effect by encompassing the expected range of anion identities and concentrations or by using appropriate spectral fitting features that identify and correct for the effect.

5.3 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 element numbers 1, 9, 11–13, 17, 19, 22–31, 35, 42, 44–46, 48, 50, 53, 57, 58, 60, 62, 73, 74, 76, 77, 79, 83, 90, 92, 93, and 95. Potential interference from nitrate, phosphate, sulfate, and oxalic acid is also documented (13).

6. Apparatus

6.1 *Diode Array Spectrophotometer (DAS)*—wavelength range 190–820 nm; wavelength accuracy ± 2 nm; wavelength reproducibility ± 0.05 nm; full dynamic range 0.0022 to 3.3; photometric accuracy at 1 AU with a NBS 931 filter at 512 nm is ± 0.005 AU; baseline flatness <0.0013 AU/micron at 500 nm.