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Standard Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Metal[1]

This standard is issued under the fixed designation C758; 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 These test methods cover procedures for the chemical, mass spectrometric, spectrochemical, nuclear, and radiochemical analysis of nuclear-grade plutonium metal to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

	Sections
Dissolution Procedure	[2]
Plutonium by Controlled-Potential Coulometry	[3]
Plutonium by Amperometric Titration with Iron (II)	[2]
Plutonium by Ceric Sulfate Titration Test Method	[3]
Plutonium by Diode Array Spectrophotometry	[3]
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Gamma-Emitting Fission Products, Uranium, and Thorium by Gamma-Ray Spectroscopy	42 – 49
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Tungsten, Niobium (Columbium), and Tantalum by Spectrochemical Test Method	53 – 55
Sample Preparation for Spectrographic Analysis for Trace Impuri ties	56 – 60

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

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 applicability of regulatory limitations prior to use.* For specific safeguard and safety hazards statements, see Section 6.

2. Referenced Documents

2.1 *ASTM Standards:*[4]

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)O_2)

C759 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Nitrate Solutions

C852 Guide for Design Criteria for Plutonium Gloveboxes

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

C1165 Test Method for Determining Plutonium by Controlled-Potential Coulometry in H_2SO_4 at a Platinum Working Electrode

C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis

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[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 February 10, 1998.

[3] Discontinued as of November 15, 1992

[4] 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.

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C1206 Test Method for Plutonium by Iron (II)/Chromium (VI) Amperometric Titration (Withdrawn 2015)[5]
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) Titration (Withdrawn 2005)[5]
C1268 Test Method for Quantitative Determination of ^{241}Am in Plutonium by Gamma-Ray Spectrometry
C1297 Guide for Qualification of Laboratory Analysts for the Analysis of Nuclear Fuel Cycle Materials
C1307 Test Method for Plutonium Assay by Plutonium (III) Diode Array Spectrophotometry
C1415 Test Method for ^{238}Pu 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

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 is made to establish whether the effective fissile content is in compliance with the purchaser's specifications.

3.1.3 Impurity content is verified 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 C-26 Safeguards Statement[6]

4.1 The material (plutonium metal) 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 designed as technically acceptable for generating safeguards accountability measurement data: Plutonium by Controlled-Potential Coulometry; Plutonium by Ceric Sulfate Titration; 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 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.

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. (**1-3**).[8]

7. Sampling

7.1 In the absence of ASTM test methods for sampling plutonium metal, alternative techniques are recommended (**3-6**).

7.2 Cognizance shall be taken of the fact that various impurities can be introduced into samples during the process of sampling. The particular impurities introduced are a function of the method of sampling (for example, iron and alloying elements in drill turning, oxygen or components of cooling oil, or both, from lathe turnings, etc.). It is necessary for the purchaser and the seller to recognize this possibility for contamination during sampling and mutually agree on the most suitable method.

7.3 Sample size shall be sufficient to perform the following:

7.3.1 Quality verification tests at the seller's plant,

7.3.2 Acceptance tests at the purchaser's plant, and

7.3.3 Referee tests in the event these become necessary.

7.4 All samples shall be identified clearly by the seller's button number and by the lot number, and all pieces of metal in that lot shall be identified clearly by the lot number and the piece number.

7.4.1 A lot is defined as a single button, fraction of a button, or multiple castings from a single melt of plutonium metal. Buttons, fractions of buttons, or multiple castings are usually supplied in pieces of not less than 50 g. All pieces shall be identified positively as coming from a particular button, fraction of a button, or casting.

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[5] The last approved version of this historical standard is referenced on www.astm.org.

[6] Based upon Committee C-26 Safeguards Matrix (C1009, C1068, C1128, C1156, C1210, C1297).

[7] *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 *Unites States Pharmacopeia and National Foundary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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

7.4.2 A lot shall normally not be less than 1800 g of plutonium, except as necessary to meet some special requirement. The maximum size of a lot will depend on equipment size of the producer and criticality considerations.

DISSOLUTION PROCEDURE

(This practice is replaced by Standard Practice C1168).

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)

PLUTONIUM BY CERIC SULFATE TITRATION TEST METHOD

(This test method is replaced by Test Method C1235.)

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.)

URANIUM BY ARSENAZO I SPECTROPHOTOMETRIC TEST METHOD

8. Scope

8.1 This test method covers the determination of uranium in the range from 300 to 3000 µg/g of plutonium.

9. Summary of Test Method

9.1 Plutonium metal dissolved in 6 *N* HCl is reduced to Pu(III) with hydroxylamine hydrochloride. The uranium and plutonium are separated by anion exchange; then the uranium is determined by measuring the absorbance of the U(VI)-Arsenazo I complex in a 1-cm cell at a wavelength of 600 nm *versus* a reagent blank.

10. Procedure

10.1 Transfer an aliquot of sample solution, prepared in accordance with Practice C1168, that contains approximately 70 mg of plutonium, to a 50-mL beaker and add 1 mL of nitric acid (sp gr 1.42) and heat to boiling. Proceed with the determination of uranium in accordance with the appropriate sections of Test Methods C759.

NOTE 1—Since the sample starts as plutonium metal and is then dissolved in acid and diluted to volume and an aliquot of this solution taken for the uranium determination, the following equation for calculating the uranium concentration must be substituted for the equation given in 28.1 of Test Methods C759:

$$R = (Y - B)D/AW \tag{1}$$

where:

R = micrograms U per gram Pu,
A, B = constants in linear calibration equation,
D = dilution factor = V/E

where:

V = volume in which sample solution was diluted, mL, and
E = volume of aliquot of V used for uranium determination, mL,

where:

W = weight of test portion of Pu metal sample, g, and
Y = $a - b$ = corrected absorbance of sample,

where:

a = absorbance of sample solution, and
b = average absorbance of duplicate calibration blanks.

THORIUM BY THORIN SPECTROPHOTOMETRIC TEST METHOD

11. Scope

11.1 This test method covers the determination of thorium in the range from 10 to 150 µg/g of plutonium in nuclear-grade plutonium metal.

12. Summary of Test Method

12.1 To an acid solution of plutonium metal, lanthanum is added as a carrier and is precipitated along with thorium as insoluble fluoride, while the plutonium remains in solution and is decanted after centrifugation of the sample. The thorium and lanthanum fluoride precipitates are dissolved in perchloric acid and the absorbance of the thorium-Thorin complex is measured at a wavelength of 545 nm *versus* a reference solution. The molar absorptivity of the colored complex is of 15 600 for thorium concentration in the range from 5 to 70 µg Th/10 mL of solution.

13. Procedure

13.1 Transfer an aliquot of solution of plutonium metal, prepared in accordance with Sections 6 and 7 of these test methods, that contains from 10 to 70 µg of thorium and no greater than 500 mg of plutonium, into a 20-mL beaker.

13.2 Determine the thorium concentration in accordance with the appropriate sections of Test Methods C759.

NOTE 2—Since the starting sample is plutonium metal the following equation for calculating the thorium concentration must be substituted for the equation given in 49.3 of Test Methods C759:

$$\text{Th, µg/g of Pu} = (Y - B)D/AW \tag{2}$$

where:

A, B = constants in the linear calibration equation,
W = sample weight, g,
D = dilution factor = V/E

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where:

V = volume to which dissolved plutonium metal is diluted, mL, and
E = volume of aliquot of V taken for determination, mL,

Y = $a - b$ = corrected absorbance of sample solution

where:

a = absorbance of sample solution, and
b = average absorbance from the duplicate reagent blanks (see section 47.2.1 of Test Methods C759).

IRON BY 1,10-PHENANTHROLINE SPECTROPHOTOMETRIC TEST METHOD

14. Scope

14.1 This test method covers the determination of microgram quantities of iron in nuclear-grade plutonium metal.

15. Summary of Test Method

15.1 Ferric iron is reduced to ferrous iron with hydroxylamine hydrochloride. Solutions of 1,10-phenanthroline and acetate buffer are added and the pH adjusted to 3.5 to 4.5. The absorbance of the red-orange complex $[(C_{12}H_8N_2)_3Fe]^{+2}$ is read at 508 nm against a sample blank containing all of the reagents except the 1,10-phenanthroline.

16. Procedure

16.1 Dissolve a sample of plutonium metal in HCl as described in Test Method C1206.

16.2 Determine the iron content in accordance with the appropriate sections of Test Methods C759.

NOTE 3—Since the starting sample is plutonium metal, the following equation must be substituted for the equation given in Section 57 of Test Methods C759 in order to calculate the iron concentration of the sample:

$$\text{Fe, µg/g Pu} = CD/W \tag{3}$$

where:

C = micrograms of Fe from calibration curve,
W = sample weight, g, and
D = dilution factor = V/A

where:

V = volume to which dissolved sample is diluted, and
A = aliquot of V that was used for iron determination.

IRON B 2,2′-BIPYRIDYL SPECTROPHOTOMETRIC TEST METHOD

17. Scope

17.1 This test method covers the determination of iron in the concentration range from 20 to 100 µg for samples of nuclear-grade plutonium metal.

18. Summary of Test Method

18.1 The plutonium metal is dissolved in HCl, the solution is buffered with sodium acetate, and the iron(II) as α,α′-dipyridyl complex is extracted into chloroform and the absorbance measured at 520 nm against distilled water.

19. Apparatus

19.1 *Spectrophotometer,* visible range.

19.2 *Extraction Bottles,* glass-stopped, 125-mL volume.

19.3 *Pipets,* 10 and 25-mL, automatic dispensing.

20. Reagents and Materials

20.1 *Chloroform.*

20.2 *2,2′-Bipyridyl Solution,* 2 % aqueous solution.

20.3 *Hydrochloric Acid (1 + 1)*—Add 500 mL of HCl (sp gr 1.19), to 500 mL of water.

20.4 *Iron, Standard Solution (50 µg/mL)*—To prepare, dissolve 1.000 g of pure iron metal in 25 mL of HCl (6 *N*), cool, and dilute to 1 L with water (Note 5). Pipet 25 mL of the iron solution, 1.00 mg/mL, into a 500-mL flask, add 10 mL of 6 *N* HCl, and dilute to volume with water. This solution contains 50 µg of iron/mL.

20.5 *Reagent Composite*—Mix 250 mL of reducing solutions, 250 mL of α,α′-dipyridyl solution, 50 mL of wetting agent, and 500 mL of sodium acetate buffer solutions (Note 4).

20.6 *Reducing Solution*—Dissolve 108 g of hydroxylamine hydrochloride in water, add 600 mL of glacial acetic acid, and dilute to 2 L with water.

20.7 *Sodium Acetate Buffer Solutions*—Dissolve 2270 g (5 lb) of sodium acetate in 8 L of water.

20.8 *Wetting Agent*—Dilute 20 mL of concentrate to 2 L with water.[9]

NOTE 4—This composite solution is stable for 25 h.
NOTE 5—Heat slowly and cover beaker with watchglass to prevent loss of iron during dissolution.

21. Procedure

21.1 Weigh, in duplicate, samples of plutonium metal that contain from 25 to 75 µg of iron, transfer to 125-mL extraction bottles, and dissolve the metal in 1 mL of 6 *N* HCl.

21.2 Add 20 mL of composite reagent, mix thoroughly, and allow 30 min for ferric iron to be reduced.

21.3 Adjust the solution to pH 4.3 with sodium acetate solution.

21.4 Add 25 mL of chloroform from an automatic dispensing pipet. Invert the bottle 20 to 25 times but do not shake vigorously.

NOTE 6—Take care to avoid forming an emulsion.

21.5 Separate the chloroform phase and measure the absorbance against distilled water at a wavelength of 520 nm.

21.6 Determine a reagent blank using all reagents but omitting the sample.

21.7 Prepare a calibration curve, or calculate micrograms of iron per absorbance unit, by processing a series of solutions containing various amounts of iron standard from 5 to 200 µg of iron in accordance with the procedure outlined in 21.1 – 21.5.

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[9] Tergitol, a trademark of Union Carbide Corp., is a satisfactory wetting agent.