Designation: C 758 – 04

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 C 758; 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]
Uranium by Arsenazo I Spectrophotometric Test Method	8-10
Thorium by Thorin Spectrophotometric Test Method	11-13
Iron by 1,10-Phenanthroline Spectrophotometric Test Method	14-16
Iron by 2,2′-Bipyridyl Spectrophotometric Test Method	17-23
Impurities by ICP-AES	
Chloride by the Thiocyanate Spectrophotometric Test Method	24-26
Fluoride by Distillation-Spectrophotometric Test Method	27–28
Nitrogen by Distillation-Nessler Reagent Spectrophotometric Test Method	29–30
Carbon by the Direct Combustion-Thermal Conductivity Test Method	31-33
Sulfur by Distillation-Spectrophotometric Test Method	34-36
Isotopic Composition by Mass Spectrometry	37 and 38
Plutonium-238 Isotopic Abundance by Alpha Spectrometry	
Americium-241 by Extraction and Gamma Counting	39-41
Americium-241 by Gamma Counting	[3]
Gamma-Emitting Fission Products, Uranium, and Thorium by Gamma-Ray Spectroscopy	42-49
Rare Earths by Copper Spark Spectrochemical Test Method	50-52
Tungsten, Niobium (Columbium), and Tantalum by Spectrochemical Test Method	53-55
Sample Preparation for Spectrographic Analysis for Trace Impurities	56-60

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 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]

C 697 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets

C 698 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides ($(U, Pu)O_2$)

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

C 852 Guide for Design Criteria for Plutonium Gloveboxes

C 1009 Guide for Establishing a Quality Assurance Program for Analytical Chemistry Laboratories Within the Nuclear Industry

C 1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry

C 1108 Test Method for Plutonium by Controlled-Potential Coulometry

C 1128 Guide for Preparation of Working Reference Materials for Use in the Analysis of Nuclear Fuel Cycle Materials

C 1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials

C 1165 Test Method for Determining Plutonium by Controlled-Potential Coulometry in H_2SO_4 at a Platinum Working Electrode

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

C 1206 Test Method for Plutonium by Iron (II)/Chromium

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[1] These test methods are under the jurisdiction of ASTM Committee C-26 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.

(VI) Amperometric Titration

C 1210 Guide for Establishing a Measurement System Quality Control Program for Analytical Chemistry Laboratories Within the Nuclear Industry

C 1235 Standard Test Method for Plutonium by Titanium(III)/Cerium(IV) Titration

C 1268 Test Method for Quantitative Determination of Americium 241 in Plutonium by Gamma-Ray Spectrometry

C 1297 Guide for Qualification of Laboratory Analysts for the Analysis of Nuclear Fuel Cycle Materials

C 1307 Test Method for Plutonium Assay by Plutonium(III) Diode Array Spectrophotometry

C 1415 Test Method for ^{238}Pu Isotopic Abundance by Alpha Spectrometry

C 1432 Test Method for Determination of Impurities in Plutonium: Acid Dissolution, Ion-Exchange Matrix Separation, and Inductively Coupled Plasma-Atomic Emission Spectroscopic (ICP/AES) Analysis

D 1193 Specification for Reagent Water[3]

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[5]

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.[6] 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 D 1193.

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 C 852 and in Refs. **(1-3)**.[7]

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] Based upon Committee C-26 Safeguards Matrix (C 1009, C 1068, C 1128, C 1156, C 1210, C 1297).

[6] "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."

[7] 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 C 1168).

PLUTONIUM BY CONTROLLED-POTENTIAL COULOMETRY

(This test method was discontinued in 1992 and replaced by Test Method C 1165)

PLUTONIUM BY CONTROLLED-POTENTIAL COULOMETRY

(With appropriate sample preparation, controlled-potential coulometric measurement as described in Test Method C 1108 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 C 1206)

PLUTONIUM BY CERIC SULFATE TITRATION TEST METHOD

(This test method is replaced by Test Method C 1235.)

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

(With appropriate sample preparation, the measurement described in Test Method C 1307 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 C 1168, 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 C 759.

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 C 759:

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

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,

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 C 759.

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 C 759:

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

where:

A, B = constants in the linear calibration equation,

W = sample weight, g,
D = dilution factor = V/E

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 C 759).

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 C 1206.

16.2 Determine the iron content in accordance with the appropriate sections of Test Methods C 759.

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 C 759 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.[8]

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

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

containing various amounts of iron standard from 5 to 200 µg of iron in accordance with the procedure outlined in 21.1-21.5.

22. Calculation

22.1 Calculate the iron content of the sample as follows:

$$\text{Fe, µg/g} = (A - A_1)F/W \tag{4}$$

where:

A = absorbance for sample,
A_1 = absorbance of reagent blank,
F = micrograms of iron per absorbance unit as determined with calibration standards, and
W = sample weight, g.

23. Precision and Bias

23.1 A relative standard deviation of ±10 % of the amount present has been observed for iron in plutonium in the range from 25 to 500 ppm.

23.2 This test method is unbiased when chemical standardization is used.

IMPURITIES BY ICP-AES

(Cationic impurities may be determined using Test Method C 1432 (Impurities by ICP-AES) with appropriate sample preparation and instrumentation).

CHLORIDE BY THE THIOCYANATE SPECTROPHOTOMETRIC TEST METHOD

24. Scope

24.1 This test method covers the determination of chloride in a nuclear-grade plutonium metal.

25. Summary of Test Method

25.1 An aliquot of plutonium metal sample dissolved in 1.5 *M* sulfuric acid is mixed with a solution containing ferrous ammonium sulfate, sulfamic acid, phosphoric acid, and sulfuric acid, and the chloride is steam distilled at a temperature of 140°C (Note 7). An aliquot of the distillate is mixed with ferric ammonium sulfate and mercuric thiocyanate solutions. Thiocyanate ion is released in direct proportion to the chloride ion concentration. The absorbance of the resulting red-brown ferric thiocyanate complex is read at 460 nm against a reagent blank.

NOTE 7—Save a portion of the distillate to use for the fluoride determination.

26. Procedure

26.1 Dissolve up to 500 mg of plutonium metal in 1.5 *M* sulfuric acid and transfer the solution to a steam distillation flask and proceed with the determination of chloride in accordance with the appropriate section of Test Methods C 759. Use the aliquot of sample from this dissolution of plutonium metal in place of the plutonium nitrate solution described in 64.2 of Test Methods C 759.

26.2 Since the original sample is plutonium metal instead of a solution, omit the term *P* from the equation for calculating the chloride concentration as shown in Section 65 of Test Methods C 759.

FLUORIDE BY DISTILLATION-SPECTROPHOTOMETRIC TEST METHOD

27. Scope

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

28. Procedure

28.1 Use an aliquot of distillate prepared by steam distillation in Section 38 and proceed with the determination in accordance with the appropriate sections of Test Methods C 759.

28.2 Since the original sample is plutonium metal instead of a solution, omit the term *P* from the equation given in Section 73 of Test Methods C 759 for the calculation of the fluoride content of the sample.

NITROGEN BY DISTILLATION-NESSLER REAGENT SPECTROPHOTOMETRIC TEST METHOD

29. Scope

29.1 This test method covers the determination of 5 to 100 µg/g nitride nitrogen in plutonium metal samples.

30. Sample Preparation and Analysis

30.1 Transfer a weighed sample in the range from 1.0 to 1.2 g to a 50-mL beaker and dissolve in HCl (sp gr 1.19).

30.2 Quantitatively transfer the sample solution to a distilling flask and proceed with the analysis in accordance with the appropriate sections of Test Methods C 697.

CARBON BY THE DIRECT COMBUSTION-THERMAL CONDUCTIVITY TEST METHOD

31. Scope

31.1 This test method covers the determination of 10 to 2000 µg of carbon in samples up to 1 g of nuclear-grade plutonium metal.

32. Summary of Test Method

32.1 Samples of plutonium metal are mixed and covered with an accelerator in carbon-free crucibles and burned with oxygen in an induction heating furnace. Traces of sulfur compounds and water vapor are removed from the combustion products by a purification train, and any carbon monoxide is converted to carbon dioxide. The purified carbon dioxide is trapped on a molecular sieve, eluted therefrom with a stream of helium upon application of heat to the trap, and passed through a thermal conductivity cell. The amount of carbon present, being a function of the integrated change in the current of the detector cell, is read directly from a calibrated-digital voltmeter or strip-chart recorder.

33. Procedure

33.1 Transfer a cleaned sample of plutonium metal not to exceed 1 g or of such size as to give not more than 2000 µg of carbon to a tared tin capsule, crimp the capsule, and reweigh to obtain the sample weight.

33.2 Determine the carbon content of the sample as described in the appropriate sections of Test Methods C 698. Use 1 g of iron chip accelerator.

SULFUR BY DISTILLATION-SPECTROPHOTOMETRIC TEST METHOD

34. Scope

34.1 This test method covers the determination of sulfur in the concentration range from 10 to 600 µg/g for samples of nuclear-grade plutonium metal.

35. Summary of Test Method

35.1 Plutonium metal is dissolved in HCl (sp gr 1.19); then higher oxidation states of sulfur are reduced to sulfide by a hypophosphorus-hydriodic acid mixture in a sulfide distillation apparatus. The hydrogen sulfide is distilled into zinc acetate solution, and *p*-phenylenediamine and ferric chloride are added to form Lauth's Violet. The quantity of sulfur is calculated from the measured absorbance at 595 nm and the absorbance per microgram of sulfur obtained for calibration standards of known sulfur content **(4)**.

36. Procedure

36.1 Transfer a weighed sample of plutonium metal, up to 0.500 g, to the distillation flask, insert the reducing-acid delivery tube, and proceed with the determination of sulfur in accordance with the appropriate sections of Test Methods C 698.

NOTE 8—Since the sample is placed in the distillation flask as a solid, omit 68.11 of Test Methods C 698.

NOTE 9—Do not heat the solution in the distillation flask as directed in 68.13 of Test Methods C 698 until the plutonium metal sample has dissolved in the acid mix.

ISOTOPIC COMPOSITION BY MASS SPECTROMETRY

37. Scope

37.1 This test method covers the determination of the isotopic content of nuclear-grade plutonium metal.

38. Sample Preparation and Analysis

38.1 Prepare a solution of plutonium metal sample in accordance with instructions given in Test Method C 1206.

38.2 Transfer an aliquot of the sample solution that does not exceed 50 µL and contains less than 4 mg of plutonium onto the top of a prepared resin column and proceed with the determination of the isotopic composition in accordance with the appropriate sections of Test Methods C 697.

PLUTONIUM-238 ISOTOPIC ABUNDANCE BY ALPHA SPECTROMETRY

(This isotopic abundance may be determined using Test Method C 1415.)

AMERICIUM-241 BY EXTRACTION AND GAMMA COUNTING

39. Scope

39.1 This test method covers the determination of americium-241 in nuclear-grade plutonium metal.

40. Summary of Test Method

40.1 Plutonium metal is dissolved in HCl, diluted with 7 *M* nitric acid, and extracted with trioctylphosphine oxide (TOPO) in cyclohexane. Under these conditions, americium remains in the aqueous phase and is determined by gamma counting the 60 keV photon.

41. Procedure

41.1 Dissolve a weighed sample of plutonium metal, 100 ± 10 mg, in HCl (1 + 1) and dilute to 10 mL with HCl (1 + 1); then proceed with the determination of americium-241 in accordance with the appropriate sections of Test Methods C 759.

NOTE 10—Since the original sample is plutonium metal, delete the *P* term from the equation for calculating the americium-241 content as given in Section 92 of Test Methods C 759.

AMERICIUM-241 BY GAMMA COUNTING

(Test Method C 1268 may be used instead of the method in Sections 39 to 41 if a high-resolution gamma ray counting system is available.)

GAMMA-EMITTING FISSION PRODUCTS, URANIUM, AND THORIUM BY GAMMA-RAY SPECTROSCOPY

42. Scope

42.1 This test method is applicable to the determination of gamma-emitting fission products (for example, ^{95}Zr-^{95}Nb, ^{103}Ru, ^{106}Rh, and ^{137}Cs-^{137m}Ba) and actinide impurities (for example, ^{232}Th, ^{235}U, and ^{238}U) in plutonium metal. The age of the plutonium after the last separation from actinides must be considered in calculating the actinide content.

43. Summary of Test Method

43.1 Plutonium metal (0.1 to 0.5 g) is dissolved in HCl (1 + 1), and gamma emissions from test aliquots are measured with a special photon detector. A lithium-drifted germanium detector, [Ge(Li)], is used to detect and measure gamma-emitting nuclides in ^{239}Pu samples. See Fig. 1 for a typical detector-instrumentation configuration, and consult Refs **(5-16)** for gamma-ray energies and branching ratios for actinides, fission products, and plutonium isotopes and other pertinent information. Gamma rays emitted from ^{239}Pu can be used to correct for self-absorption in the matrices being analyzed. The detector signal pulse is electronically shaped and converted from an analog to a digital signal and pulse height is analyzed.

43.2 Counting data are analyzed by manual or machine (computer) techniques following the use of suitable gamma-emitting standards or an energy-calibrated detector. Both calibration methods include the effects of geometry (source position, containment, and shape) as they relate to gamma-ray intensity, branching, and detector response. Discrete gamma rays of some actinides and fission product elements are used while the daughter activities of certain actinides are used with consideration given to appropriate parent-daughter relationships at the time counting data are accumulated.

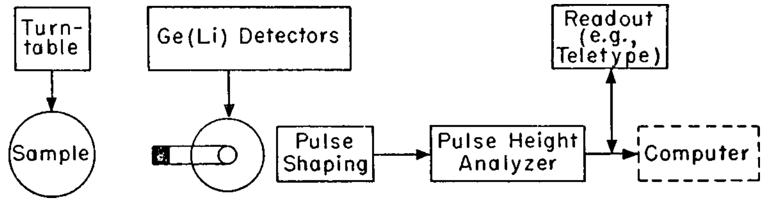

FIG. 1 Plutonium Sample Counting System

44. Interferences

44.1 Aside from self-absorption, gamma-rays from nuclides that are similar in energy or are not resolved from those gamma-rays of nuclides of interest will act as interferences unless standard spectroscopic correction techniques are used.

45. Apparatus

45.1 *Appropriate Sample Disks (28.6 mm) or Vials (15 g, Plastic)*, with appropriate mount holders.

Caution: Give particular attention toward assurance of plutonium containment.

45.2 *Lithium-Drifted Germanium Detector*, [Ge(Li)], with associated cooling and sample support devices.

45.3 *Pulse Height Analyzer* (2000 channels), with type and tape readout.

45.4 *Pipets*, 1-mL to contain.

46. Calibration and Standardization

46.1 Prepare calibration standards for all nuclides of interest using a combination of plutonium chloride matrices with known gamma-emission rates of the subject nuclides. The gamma-emission rates of the sources should be at three or more activity levels that are approximately an order of magnitude different, one from the other. Carefully position these sources near the detector and record the counting data. Make appropriate corrections for self-absorption and parent-daughter state of equilibrium, if needed. Refer to the referenced literature for photon branching, intensities, nuclide half life-specific activity, and spectra analysis techniques currently used. If certain radionuclides are not available, use an energy calibration curve for the detector in use and make appropriate corrections as above.

47. Procedure

47.1 Accurately weigh a sample of plutonium, 100 to 500 mg, dissolved in HCl (1 + 1) and dilute to 25 mL. Pipet 1 mL of the sample solution onto a sample disk and dry slowly under a heat lamp. Alternative source preparation could be as a liquid source in a plastic vial.

47.2 Rinse the pipet and add the rinse to the sample disk or vial. If a vial is used dilute to a prescribed volume.

47.3 Place the sample disk or vial in a source holder and label with sample identification, size, and date.

47.4 Position the sample holder near the thin lead or copper-shielded germanium detector and accumulate counting data for a time sufficient to fulfill the statistical requirements of the analysis.

48. Calculation

48.1 The use of a computer program to analyze the counting data will obviate the need for making further calculations. Frequent checks on the detector system, pulse height analyses, and the computer should be made with calibrated mixtures of plutonium and radionuclides to assure confidence in the program.

48.2 Manual reduction of the counting data will require considerably more calculations and close scrutiny to minimize mathematical errors. When possible, independent determinations should be made on two or more distinct photopeaks for each radionuclide. A typical calculation format is as follows:

$$\text{Element impurity, µg/g of plutonium metal sample} = (A)(F)/(10^{6})/(B)(C)(D)(E)(G)(H)(I)(J) \quad (5)$$

where:

A = total net area under selected photopeaks in counts,
B = branching of gamma-ray, fraction of isotope decay,
C = plutonium metal concentration in sample aliquot, g/mL,
D = specific activity of isotope analyzed, disintegrations $\text{min}^{-1}\ \text{g}^{-1}$,
E = detector efficiency for selected photopeak of impurity element,
F = self-absorption correction, count rate without matrix/count rate with matrix,
G = sample aliquot, mL,
H = parent-daughter equilibrium correction, count rate of daughter at analysis time/count rate of daughter at equilibrium time,
I = counting time to achieve desired statistics, minutes, and
J = fraction of parent decay through daughter analyzed.

49. Precision and Bias

49.1 The measurement of many impurities in 0.1 to 0.5-g samples of plutonium metal has been found to have a bias of no greater than 5 %. In practice a standard source should be measured daily to assure the reliability of the counting systems.

49.2 (The precision of this test method is affected by the counting rate of the radionuclide impurity.) Precision of the measurements of impurities in plutonium chloride improves as their concentration increases. Normally, a precision of +5 % at the 95 % confidence level can be realized for a counting period of at least 10-min duration.

RARE EARTHS BY COPPER SPARK SPECTROCHEMICAL TEST METHOD

50. Scope

50.1 This test method covers the determination of rare earths in nuclear-grade plutonium metal in the range from 10 to 200 µg/g.

51. Summary of Test Method

51.1 Rare earths are separated from an acid solution of plutonium metal by solvent extraction into tri-*n*-octylamine, after which the concentration is determined by a copper-spark spectrographic test method.

52. Procedure

52.1 Dissolve a weighed sample of plutonium metal in the range from 600 to 700 mg in 6.7 *M* HCl, and dilute to 25 mL volume with 6.7 *M* HCl.

52.2 Determine the rare earths in accordance with the appropriate sections of Methods C 697.

TUNGSTEN, NIOBIUM (COLUMBIUM), AND TANTALUM BY SPECTROCHEMICAL TEST METHOD

53. Scope

53.1 This test method covers the determination of tungsten, niobium, and tantalum in nuclear-grade plutonium metal.

54. Summary of Test Method

54.1 Plutonium metal is converted to plutonium dioxide under the conditions described in 60.1-60.3. A portion of the plutonium dioxide is blended with 27 % carrier (AgCl), and portions of this blend are weighed into graphite anode caps and excited in a d-c arc. The spectrum is recorded photographically, and the spectral lines of interest are compared visually or photometrically with synthetically prepared standards exposed on the same plate.

55. Procedure

55.1 Convert a weighed sample of plutonium metal to plutonium dioxide in accordance with the procedure described in 60.1-60.3.

55.2 Determine tungsten, niobium, and tantalum in accordance with the appropriate sections of Test Methods C 759.

SAMPLE PREPARATION FOR SPECTROGRAPHIC ANALYSIS FOR TRACE IMPURITIES

56. Scope

56.1 This test method covers the sample preparation for spectrographic analysis of plutonium metal for general metallic impurities by the carrier distillation test method.

57. Summary of Test Method

57.1 A sample of plutonium metal, sufficient to provide 500 mg of plutonium dioxide, is first treated with nitric acid (sp gr 1.42) to remove surface contamination. The plutonium metal is converted to plutonium dioxide at a temperature of 950 ± 25°C. The plutonium dioxide is then analyzed for general metallic impurities in accordance with the appropriate sections of Test Methods C 697.

58. Apparatus

58.1 *Muffle Furnace*, with controls, capable of maintaining a temperature of 950 ± 25°C.

58.2 *Platinum Crucible*.

58.3 *Torsion Balance*, 500-mg capacity.

59. Reagents

59.1 *Nitric Acid* (HNO_3, sp gr 1.42).

60. Procedure

60.1 Weigh sufficient sample to provide 500 mg of plutonium dioxide following oxidation.

60.2 Transfer the sample to a platinum crucible and wash the sample with HNO_3 (sp gr 1.42); then decant the acid solution.

60.3 Transfer the sample to a cold muffle furnace and slowly raise the temperature to 950 ± 25°C and maintain this temperature for 30 min; then cool to 400°C.

NOTE 11—Treatment of the sample affects the performance characteristics in the arc; therefore, the spectrographic equipment must be calibrated for the sample preparation method in use. For highest accuracy the test method for calibration should closely duplicate the test method for analysis of samples.

NOTE 12—An optical pyrometer or an alloy of known melting point should be used to verify the temperature of the muffle furnace.

NOTE 13—Following calcination of the sample, the furnace should be cooled to 400°C before opening to avoid excessive heat load inside the glove box.

60.4 Cool the furnace to room temperature and remove the sample. Proceed with the analysis for trace metal impurities in accordance with the appropriate sections of Test Methods C 697.

NOTE 14—Although sodium and lithium do not appear in the list of elements in Table 2 of Test Methods C 697, these elements can also be determined using AgCl carrier. The wavelength and the concentration range for each element are as follows:

Element	Wavelength, Å	Concentration Range, µg/g
Na	5859.95	1 to 1000
	5895.92	
Li	6707.84	1 to 1000
	6103.64	

61. Keywords

61.1 impurity content; isotopic composition; plutonium content; plutonium metal

REFERENCES

(**1**) American Standards Association Sectional Committee N6 and American Nuclear Society Standards Committee, “Nuclear Safety Guide,” *USAEC Report TID-7016* (Rev. 1), AERDB, Goodyear Atomic Corp., 1961.

(**2**) Metz, C. F.,“ Analytical Chemical Laboratories for the Handling of Plutonium,” *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy*, Geneva, Vol 17, 1958, pp. 681–690, United Nations, NY, 1959.

(**3**) Wick, O. J., Ed., *Plutonium Handbook*, Vol II, Gordon and Beach Science Publishers, 1967.

(**4**) Rein, J. E., Matlack, G. M., Waterbury, G. R., Phelps, R. T., and Metz, C. F., Eds., “Methods of Chemical Analysis for FBR Uranium-Plutonium Oxide Fuel and Source Materials,” *USAEC Document LA-4622*, AERDB, 1971, pp. 95–99.

(**5**) Zimmer, W. H. and Campbell, M. H., “The Detection and Analysis of Actinide Contaminants in Plutonium-239,” *ARH-SA-106*, Atlantic Richfield Hanford Company, Richland, WA, August 1971.

(**6**) Adopted Value, Nuclear Data Sheets (Nuclear Data Group, Oak Ridge National Laboratory, Eds.), Academic Press, New York and London.

(**7**) Rosetling, P. B., Ganley, W. P., and Klaiber, G. S. “The Decay of Lead 212,” *Nuclear Physics*, Vol 20, 1960, p. 347.

(**8**) Wright, H. W., Wyatt, E. I., Reynolds, S. A., Lyon, S. W., and Handley, T. H., “Half-Lives of Radionuclides II,” *Nuclear Science and Engineering*, NSENA, Vol 2, 1957, p. 427.

(**9**) Clin, J. E., “Gamma Rays Emitted by the Fissionable Nuclides and Associated Isotopes,” *USAEC Report IN-1448*, 1970.

(**10**) Wapstra, A. H., “The Decays of^{234}Np and^{243m}iPa(UX),” *Nuclear Physics*, A97, 1967, p. 641.

(**11**) Hyde, E. K., Perlman, I., and Senborg, G. T., Eds., *The Nuclear Properties of the Heavy Elements*, Vol II, Prentice Hall, Inc., Englewood Cliffs, NJ, 1964, pp. 541–547, 629–632, 726–733, 1062.

(**12**) Wagner, F., Jr., Freedman, M. S. Englkemier, D. W., and Hunizenga, J. R.,“ Radiation of 6.7 Day Uranium 237,” *Physical Review*, Vol 89, 1953, p. 502.

(**13**) Chart of the Nuclides, Pacific Northwest Laboratory, Richland, WA, 1970.

(**14**) Zimmer, W. H., “Detection and Analysis of Actinide Contaminants in Plutonium 239,” *IA-EA-SM-149/28*, *Analytical Methods in the Nuclear Fuel Cycle*, International Atomic Energy Agency, Vienna, 1972.

(**15**) Gunnink, R., and Tinney, J. F., “Total Fissile Content and Isotopic Analysis of Nuclear Materials by Gamma-Ray Spectrometry,” *UCRL-73274*, Lawrence Radiation Laboratory, Livermore, CA, Oct. 19, 1971.

(**16**) Zimmer, W. H., “A Systematic Peak Reduction Method for Semiconductor Detector Spectra,” *USAEC Report ARH-1877*, Atlantic Richfield Hanford Co., Richland, WA, January 1971.