



# Standard Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Nitrate Solutions<sup>1</sup>

This standard is issued under the fixed designation C 759; 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 ( $\epsilon$ ) 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 nitrate solutions to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

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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 hazard statements, see Section 6.

<sup>1</sup> 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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<sup>2</sup> Discontinued as of November 15, 1992.

## 2. Referenced Documents

### 2.1 *ASTM Standards:*<sup>3</sup>

- C 697 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets
- 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<sub>2</sub>SO<sub>4</sub> at a Platinum Working Electrode
- C 1206 Test Method for Plutonium by Iron (II)/Chromium (VI) Amperometric Titration
- C 1210 Guide for Establishing a Measurement System Quality Control Program for Analytical Chemistry Laboratories Within the Nuclear Industry
- C 1235 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

<sup>3</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

- C 1307 Test Method for Plutonium Assay by Plutonium(III) Diode Array Spectrophotometry
- C 1415 Test Method for <sup>238</sup>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
- E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals
- E 115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis
- E 116 Practice for Photographic Photometry in Spectrochemical Analysis

### 3. Significance and Use

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

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

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

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

### 4. Committee C-26 Safeguards Statement<sup>4</sup>

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

4.2 When used in conjunction with appropriate Certified Reference Materials (CRMs), these procedures can demonstrate traceability to the national measurement base. However, adherence to these procedures does not automatically guarantee regulatory acceptance of the resulting safeguards measurements. It remains the sole responsibility of the user of these test methods to assure that their application to safeguards has the approval of the proper regulatory authorities.

### 5. Reagents and Materials

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

cal Society, where such specifications are available.<sup>5</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification 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) through (3).<sup>6</sup>

### 7. Sampling

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

7.2 Sample size shall be sufficient to perform the following:

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

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

7.2.3 Referee tests in the event they become necessary.

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

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

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

#### **PLUTONIUM BY CONTROLLED-POTENTIAL COULOMETRY**

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

<sup>4</sup> Based upon Committee C-26 Safeguards Matrix (C 1009, C 1068, C 1128, C 1156, C 1210, C 1297.).

<sup>5</sup> "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."

<sup>6</sup> The boldface numbers in parentheses refer to the list of references at the end of these test methods.

## PLUTONIUM BY AMPEROMETRIC TITRATION WITH IRON(II)

(This test method was discontinued in 1992 and replaced by Test Method C 1206.)

## 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.)

## FREE ACID BY TITRATION IN AN OXALATE SOLUTION

### 8. Scope

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

### 9. Summary of Test Method

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

### 10. Interferences

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

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

### 11. Apparatus

- 11.1 *Magnetic Stirrer.*
- 11.2 *Microburet.*
- 11.3 *Micropipets.*
- 11.4 *pH Meter.*

### 12. Reagents and Materials

12.1 *Ammonium Oxalate Solution*, saturated.

12.2 *Nitric Acid* (3.50 N)—Prepare solution by diluting concentrated nitric acid (HNO<sub>3</sub>, sp gr 1.42) with water. Standardize by titrating 0.500-mL aliquots with 0.100 N NaOH solution.

12.3 *Sodium Hydroxide Solution* (0.100 N)—Prepare and standardize in accordance with Practices E 50.

### 13. Procedure

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

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

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

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

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

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

13.5 Make a daily check of the system by adding 20 μL of 3.50 N HNO<sub>3</sub> to a sample that has already been titrated to the end point and titrate with standard 0.100 N NaOH solution back to the same pH.

### 14. Calculation

14.1 Calculate the free acid (H<sup>+</sup>, N) as follows:

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

where:

A = microlitres of standard NaOH solution required to titrate sample,  
N = normality of NaOH standard solution, and  
V = volume of sample, μL.

### 15. Precision and Bias

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

15.2 *Bias*—99.4 %.

## FREE ACID BY IODATE PRECIPITATION- POTENTIOMETRIC TITRATION TEST METHOD

### 16. Scope

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

### 17. Summary of Test Method

17.1 Free acid is determined by potentiometric titration with standard sodium hydroxide solution after precipitation and subsequent removal of plutonium (up to 50 mg) as plutonium iodate.

### 18. Interferences

18.1 Any hydrolyzable ions that are not precipitated with iodate will interfere.

### 19. Reagents and Materials

19.1 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

19.2 *Nitric Acid* (1 + 14)—Dilute 14 volumes of water with 1 volume of concentrated nitric acid (HNO<sub>3</sub>, sp gr 1.42).

19.3 *Potassium Iodate* (0.3 M)—Dissolve 64.2 g of potassium iodate (KIO<sub>3</sub>) in 900 mL of water, adjust the pH to 4.3 by adding HNO<sub>3</sub> (1 + 14), and dilute to 1 L with water.

19.4 *Sodium Hydroxide* (0.3 M)—Prepare and standardize in accordance with Practices E 50 after making the following alterations: Use 15 mL of the NaOH solution (50 g/50 mL), and in step 42.2, transfer 1.200 g of National Institute for Standards

and Technology (NIST) potassium acid phthalate SRM 84 h or its replacement to a 250-mL Erlenmeyer flask instead of 0.4000 g.

## 20. Procedure

20.1 Pipet 50 mL of  $\text{KIO}_3$  (0.3 M) into a beaker and stir while adding an aliquot of sample solution containing no greater than 50 mg of plutonium.

20.2 After precipitation is complete, filter the solution through either a medium porosity glass frit or a fine textured acid-washed filter paper and collect the filtrate in a beaker.

20.3 Wash the precipitate with two 25-mL portions of 0.3 M  $\text{KIO}_3$  solution, and combine the washings with the filtrate from step 20.2.

20.4 Dissolve the precipitate in  $\text{HNO}_3$  (sp gr 1.42) or HCl (sp gr 1.19) and transfer to a residue bottle.

20.5 Transfer the sample from 20.3 to the titration apparatus, position the electrodes and a magnetic stirring bar in the solution, and start the stirrer.

20.6 Titrate the free acid in the solution by adding the 0.3 M NaOH solution from a 5-mL buret and plot the titration curve (pH versus mL NaOH solution).

20.7 Determine the end point of the titration from the midpoint of the inflection on the titration curve and record the volume of 0.3 M NaOH solutions by the steps given in 20.5 through 20.7 of the procedure.

## 21. Calculation

21.1 Calculate the free acid ( $\text{H}^+$ ,  $N$ ) as follows:

$$\text{H}^+, N = (V_s - V_b)N/S \quad (2)$$

where:

$N$  = normality of NaOH solution,

$V_s$  = millilitres of NaOH solution to titrate sample aliquot,

$V_b$  = millilitres of NaOH solution to titrate reagent blank, and

$S$  = millilitres of sample aliquot.

## 22. Precision and Bias

22.1 The relative standard deviation, based on 49 titrations, is 0.9 % for aliquots of sample containing a minimum of 0.2 milliequivalents of acid.

22.2 Between 99 and 100 % of the free acid in standard plutonium (IV) solutions has been measured by this procedure; however, when the plutonium was in the (III) oxidation state, the results showed a negative bias of as much as 8 % (6).

## URANIUM BY ARSENAZO I SPECTROPHOTOMETRIC TEST METHOD

## 23. Scope

23.1 This test method covers the determination of uranium in the range from 300 to 3000  $\mu\text{g/g}$  of plutonium in plutonium nitrate solutions.

## 24. Summary of Test Method

24.1 Plutonium is reduced to Pu(III) in HCl (1 + 1) solution with hydroxylamine hydrochloride. The uranium and plutonium are then separated by anion exchange, and 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.

## 25. Interference

25.1 Iron at 500  $\mu\text{g/g}$  of plutonium is the most likely interference in this test method.

## 26. Apparatus

26.1 *Columns*, ion exchange, 1 by 10 cm. Columns can be made by sealing a 1-cm diameter filtering tube with a coarse glass frit to the bottom of a 40-mL centrifuge tube and cutting the tube off diagonally just below the frit.

26.2 *Spectrophotometer and 1-cm Matched Cells*.

## 27. Reagents and Materials

27.1 *Ammonium Hydroxide* (1 + 13)—Dilute 1 volume of concentrated ammonium hydroxide ( $\text{NH}_4\text{OH}$ , sp gr 0.90) with 13 volumes of water.

27.2 *Arsenazo I Reagent* (0.500 g/L)—Dissolve 250 mg of the purified reagent [(3-2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid, disodium salt] in water and dilute to 500 mL with water.

NOTE 4—Purify reagents as follows: To a saturated aqueous solution of Arsenazo I, add an equal volume of HCl (sp gr 1.19), filter the orange precipitate, wash with acetonitrile, and dry at 100°C for 1 h.

27.3 *Hydrochloric Acid* (0.1 N)—To prepare, dilute 8.3 mL of hydrochloric acid (HCl, sp gr 1.19) to 1 L with water.

27.4 *Hydrochloric Acid* (1 + 1)—To prepare, dilute 500 mL of hydrochloric acid (HCl, sp gr 1.19) to 1 L with water.

27.5 *Hydroxylamine Hydrochloride Solution* (100 g/L)—Dissolve 10 g of ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) in water and dilute to 100 mL with water.

27.6 *Nitric Acid* (1 + 2)—Dilute 100 mL of nitric acid ( $\text{HNO}_3$ , sp gr 1.42) to 300 mL with water.

27.7 *Phenolphthalein Solution* (0.25 g/L)—Dissolve 25 mg of phenolphthalein in a water-ethanol (1 + 1) solution and dilute to 100 mL with the water-ethanol solution.

27.8 *Plutonium Matrix Calibration Solution* (7 g/L)—Dissolve approximately 700 mg of plutonium metal, NIST SRM 949e or its replacement, or other metal containing less than 20 ppm of uranium in 5 mL of HCl (1 + 1), and dilute to 100 mL with HCl (1 + 1).

27.9 *Sodium Cyanide Solution* (50 g/L)—Dissolve 5 g of sodium cyanide ( $\text{NaCN}$ ) in water and dilute to 100 mL with water.

27.10 *Resin, Anion Exchange*—Use Dowex 1-X2 anion exchange resin, chloride form, 100 to 200 mesh, or equivalent resin.

27.11 *Stannous Chloride Solution* (700 g/L)—Dissolve 7 g of stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) in hydrochloric acid (HCl, sp gr 1.19) and dilute to 10 mL with HCl (sp gr 1.19). Prepare reagent fresh daily.

27.12 *Sulfuric Acid* (1 + 2)—Dilute 1 volume of sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp gr 1.84) with 2 volumes of water.

27.13 *Sulfuric Acid* (1 + 8)—Dilute 1 volume of sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp gr 1.84) with 8 volumes of water.

27.14 *Triethanolamine Buffer-Ethylenediamine-Tetraacetic Acid Complexing Solution*—Dissolve 74.5 g of triethanolamine

and 72 mg of ethylenediamine-tetraacetic acid, disodium salt (EDTA) in 750 mL of water and 14.0 mL of nitric acid (HNO<sub>3</sub>, sp gr 1.42) and dilute to 1 L with water. Allow solution to stand overnight before using.

27.15 *Uranium Standard Solution* (20 mg/L)—Dissolve 23.60 mg of U<sub>3</sub>O<sub>8</sub> (NIST SRM 950b or its replacement), or uranium oxide of equal purity, in 1 mL of HNO<sub>3</sub>(1 + 2) and dilute to 1 L with H<sub>2</sub>SO<sub>4</sub>(1 + 8).

## 28. Preparation of Ion Exchange Columns

28.1 Wash 250 g of the anion exchange resin alternately with three 350-mL portions of HCl (sp gr 1.19) and three 350-mL portions of water. Allow the resin to remain in each solution for 30 min.

28.2 Fill each column to a height of 10 cm with ion exchange resin and rinse each column with 30 mL of HCl (sp gr 1.19).

NOTE 5—Immediately before each analysis, rinse each column with 30 mL of HCl (sp gr 1.19) and remove any entrapped air from the column.

## 29. Calibration and Standardization

29.1 Pipet ten 10-mL aliquots of plutonium matrix calibration solution (7 g/L) into separate 50-mL beakers and add 2 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 2).

29.2 Add 0.0, 1.0, 4.0, 7.0, and 10.0 mL of uranium standard solution (20 mg/L), respectively, to each of the 5 pairs of solutions prepared in 29.1 and evaporate to dryness.

29.3 Add 4.0 mL of HCl (1 + 1) to each beaker and dissolve the residue.

29.4 Add 3 mL of hydroxylamine hydrochloride solution (NH<sub>2</sub>OH·HCl, 100 g/L) to each beaker and warm the solution under infrared lamps until the plutonium is reduced to Pu(III) as indicated by the blue color. If the solution is not blue, add more NH<sub>2</sub>OH·HCl solution and warm again.

NOTE 6—Plutonium is not adsorbed on the resin if it is in the reduced Pu(III) state.

29.5 Cool the solutions to room temperature and add 3 drops of SnCl<sub>2</sub>·2 H<sub>2</sub>O solution (700 g/L) to each beaker.

NOTE 7—The stannous chloride prevents air oxidation of the Pu(III) during subsequent steps in the procedure.

29.6 Add 13 mL of HCl (sp gr 1.19) to each beaker.

29.7 Transfer each solution to a separate ion exchange column using five 1-mL portions of HCl (sp gr 1.19) to wash each beaker.

29.8 Wash the Pu(III) from each column with six 5-mL portions of HCl (sp gr 1.19).

29.9 Next, elute the uranium from each column by washing each column with six 5-mL portions of 0.1 N HCl. Collect the wash solutions from each column in a 50-mL beaker and evaporate to dryness on a hot plate under infrared lamps.

29.10 Add 3 drops of HCl (sp gr 1.19) to dissolve each residue and wash the sides of the beaker with water.

29.11 Add 4 drops of NaCN solutions (50 g/L) and 2 drops of phenolphthalein solution to each beaker; then add NH<sub>4</sub>OH (1 + 13) until the indicator remains slightly pink.

29.12 Pipet 5 mL of triethanolamine buffer and 3.0 mL of Arsenazo I solution to each beaker.

29.13 Transfer each solution to a 25-mL volumetric flask and dilute to volume with water.

29.14 Allow the solutions to stand 1 h for maximum color development, and then measure the absorbance at 600 nm in 1-cm cells *versus* a reference solution prepared from the reagents starting at 29.11.

29.15 *Calibration Curve:*

29.15.1 Process the results obtained in 29.14 in accordance with the procedure described in 31.1 and 31.2.

29.15.2 Each time samples are analyzed verify the calibration by processing duplicate aliquots of plutonium matrix calibration solutions containing no uranium; also process a set of duplicates that contain 5 mL each of uranium standard (20 mg/L) added to aliquots of plutonium matrix calibration solution by the procedure given in 29.3 through 29.14.

29.15.3 Process the results obtained in 29.15.2 in accordance with the procedure outlined in 31.3. If the individual calibration value disagrees at the 0.05 significance level with the value of the constant obtained from the complete calibration set, investigate and rectify the cause before proceeding with further analyses.

## 30. Procedure

30.1 Prepare duplicate reagent blanks starting with 30.3.

30.2 Transfer a sample aliquot containing approximately 70 mg of plutonium weighed to ±0.1 mg into a 50-mL beaker.

30.3 Add 5 mL of HCl (sp gr 1.19) to the beaker.

30.4 Evaporate the solution to near dryness slowly to avoid loss of sample.

NOTE 8—This eliminates excess nitrate which would prevent reduction of the plutonium.

30.5 Proceed with the analysis as described in 29.3 through 29.14.

30.6 Calculate the concentration of uranium in micrograms per gram of plutonium in accordance with instructions in Section 32.

## 31. Calculation of Calibration Factors

31.1 Calculate the corrected absorbance value for each standard solution as follows:

$$Y = r - s \quad (3)$$

where:

$Y$  = corrected absorbance value for standard,  
 $r$  = absorbance value of standard obtained in 29.14, and  
 $s$  = average absorbance value obtained in 29.14 for the duplicate calibration blanks with no uranium added.

31.2 Use the least squares formulas and the data from 31.1 to calculate values of  $A$  and  $B$  in the linear calibration equation:

$$Y = Ax + B, \text{ that best fits the data} \quad (4)$$

where:

$A, B$  = constants ( $B$  should be approximately zero),  
 $Y$  = corrected absorbance value from 31.1, and  
 $x$  = micrograms of uranium in the standard calibration solution.

31.3 Calculate the individual calibration value for each standard solution processed simultaneously with each set of samples as follows:

$$A' = m/n \quad (5)$$

where:

$A'$  = individual calibration value for each standard solution,

$n$  = micrograms of uranium in the standard solution, and

$m$  = corrected absorbance of standard =  $p - q$

where

$p$  = absorbance for standard solution, and

$q$  = average absorbance obtained from duplicate blank solutions.

31.4 Each individual value of  $A'$  should agree at the 0.05 significance level with the value of  $A$  obtained from the complete calibration set.

### 32. Calibration of Uranium Concentration

32.1 Calculate the uranium concentration in the sample,  $R$ , micrograms per gram Pu, as follows:

$$R = (Y - B)/AWC \quad (6)$$

where:

$R$  = micrograms U per gram plutonium,

$A, B$  = constants in linear calibration equation,

$C$  = grams Pu per gram plutonium nitrate solution in sample,

$W$  = weight of sample aliquot, g, and

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

where:

$a$  = absorbance of sample solution, and

$b$  = average absorbance of duplicate calibration blanks.

### 33. Precision and Bias

33.1 In the range from 300 to 1100  $\mu\text{g}$  U/g Pu the standard deviation is  $\pm 100$   $\mu\text{g}/\text{g}$ ; in the range from 1500 to 3000  $\mu\text{g}$  U/g Pu it is  $\pm 50$   $\mu\text{g}/\text{g}$ .

## THORIUM BY THORIN SPECTROPHOTOMETRIC TEST METHOD

### 34. Scope

34.1 This test method covers the determination of 10 to 150  $\mu\text{g}$  of thorium per gram of plutonium in plutonium nitrate solutions.

### 35. Summary of Test Method

35.1 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 precipitate is 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 15 600 for thorium concentration in the range from 5 to 70  $\mu\text{g}$  Th/10 mL of the solution.

### 36. Interferences

36.1 Cations that form insoluble fluorides and colored complexes with thorin interfere in this test method.

### 37. Apparatus

37.1 *Infrared Heat Lamps*, 250-W, borosilicate glass.

37.2 *Aluminum Heating Block*—Drill a 150-mm high aluminum block to hold 16 12-mL centrifuge tubes and a thermometer. In use the block is heated to 220°C.

37.3 *Platinum Stirring Rod*, 1 mm in diameter by 160 mm long.

37.4 *Spectrophotometer*, with matched cells having 10-mm light path.

37.5 *Vacuum Transfer Device*, approximately 150 mm long with a  $^{10}/_{18}$  standard-taper ground-glass joint that fits a 10-mL volumetric flask.

### 38. Reagents and Materials

38.1 *Ammonium Peroxydisulfate* ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ).

38.2 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

38.3 *Hydrofluoric Acid* (1 + 24)—Dilute 1 volume of concentrated hydrofluoric acid (HF, sp gr 1.15) with 24 volumes of water and store in a polyethylene wash bottle.

38.4 *Hydrogen Peroxide* (30 %)—Concentrated hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).

38.5 *Hydroxylamine Hydrochloride Solution* (250 g/L)—Dissolve 25 g of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) in water and dilute to 100 mL with water.

38.6 *Lanthanum Nitrate Solution* (10 g La/L)—Dissolve 3.12 g of lanthanum nitrate ( $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ ) in water and dilute to 100 mL with water.

38.7 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid ( $\text{HNO}_3$ ).

38.8 *Perchloric Acid* (70 to 72 %)—Concentrated perchloric acid ( $\text{HClO}_4$ ).

38.9 *Silver Nitrate Solution* (2.5 g/L)—Dissolve 250 mg of silver nitrate ( $\text{AgNO}_3$ ) in water and dilute to 100 mL with water. Store solution in an amber bottle.

38.10 *Sulfuric Acid* (1 + 35)—Add 1 volume of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp gr 1.84) to 35 volumes of water.

38.11 *Thorin Solution* (1 g/L)—Dissolve 1 g of thorin *o*-(2-hydroxy-3,6-disulfo-1-naphthylazo) benzenearsonic acid disodium salt in water and dilute to 1 L.

38.12 *Thorium Standard Solution* (20.00 mg/L)—Dissolve 20.00 mg of high-purity thorium as the metal, oxide, or nitrate in HCl (sp gr 1.19) and  $\text{H}_2\text{O}_2$  (30 %). Add 83 mL of  $\text{HClO}_4$  (70 to 72 %) and dilute to 1 L with water.

### 39. Calibration and Standardization

39.1 *Reference Standards and Blanks*:

39.1.1 Pipet 1.00 mL of thorium standard (20 mg/L) into each of two 20-mL beakers, 2.00 mL into each of 2 more beakers and 3.00 mL into each of a third pair of beakers.

39.1.2 To two additional 20-mL beakers and to each of the solutions from 39.1.1, add 1 mL of  $\text{HNO}_3$  (sp gr 1.42) and 2 mL of  $\text{HClO}_4$  (70 to 72 %).

39.1.3 Evaporate each solution to approximately 2 mL on a steam bath; then continue the evaporation to dryness under infrared lamps on a hot plate.

39.1.4 Remove the beakers from the hot plate, and dissolve each residue in approximately 2 mL of  $\text{H}_2\text{SO}_4$  (1 + 35), dispensed from a polyethylene wash bottle.

39.1.5 Transfer each solution to a 12-mL centrifuge tubing using three 2-mL rinses of  $\text{H}_2\text{SO}_4$  (1 + 35).

39.1.6 Add 5 drops of  $\text{La}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$  (10 g/L) solution and 0.1 mL of  $\text{AgNO}_3$  solution (2.5 g/L) and approximately 1 g of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  to each centrifuge tube.

39.1.7 Heat the tubes in a steam bath for 15 min.

39.1.8 Remove the tubes from the steam bath, cool, and add 1 mL of HF (sp gr 1.15). Stir the mixture with a platinum stirring rod; rinse the rod with HF (1 + 24) after each stirring. After 5 min, centrifuge the tubes for 5 min.

39.1.9 Withdraw the supernatant plutonium-containing solution by means of vacuum and transfer to a plutonium residue bottle. Invert the tubes onto a tissue for 1 to 2 min; then draw off to the residue bottle any liquid that has drained down the inner wall of the tubes.

39.1.10 Wash the precipitate by adding 3 mL of HF (1 + 24) and mixing with the platinum rod. Rinse the platinum rod with HF (1 + 24), wait 5 min, and centrifuge for 5 min. Repeat the procedure in 39.1.9 and proceed to step 39.1.11.

39.1.11 Add 1 mL of  $\text{HClO}_4$  (70 to 72 %) to each tube and place the tubes in the heated aluminum heating apparatus for 30 min.

39.1.12 Remove the tubes, cool, and add  $\text{HClO}_4$  (70 to 72 %) to adjust the volume in each tube to 0.5 mL.

39.1.13 Transfer each solution to a 10-mL volumetric flask using the vacuum transfer device with three 2-mL water rinses; then add 0.5 mL of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  solution to each flask.

39.1.14 Prepare a reference solution by adding 0.5 mL of  $\text{HClO}_4$  (70 to 72 %), 0.5 mL of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  solution (250 g/L), and 6 mL of water to a 10-mL volumetric flask.

39.1.15 Place the flasks on a steam bath for 30 min.

39.1.16 Remove the flasks from the steam bath, cool, and add 1 mL of Thorin solution to each flask. Dilute to volume with water, stopper, and shake.

39.1.17 Measure the absorbance of the solutions in 10-mm cells *versus* the reference solution at a wavelength of 545 nm.

39.1.18 Process the data obtained in 39.1.17 in accordance with the procedure described in 41.1.

39.2 *Checking Calibration Curve:*

39.2.1 Each time a set of samples is analyzed verify the procedure and calibration factor by processing two 2-mL thorium standards and two blank solutions (with no thorium added) in accordance with the instructions in 39.1.2 through 39.1.17.

39.2.2 Process the data obtained in 39.2.1 in accordance with the procedures described in 39.2. If an individual calibration value disagrees at the 0.05 significance level with the value of the constant obtained from the complete calibration set, investigate and rectify the cause of the difficulty before proceeding with further analyses.

## 40. Procedure

40.1 Transfer a weighed aliquot of sample containing from 5 to 70  $\mu\text{g}$  of thorium and no greater than 500 mg of plutonium into a 20-mL beaker and proceed with the analysis as described in 39.1.2 through 39.1.17.

40.2 Calculate the thorium concentration in accordance with the procedure described in 41.3.

## 41. Calculation

41.1 *Equation for Calibration Data:*

41.1.1 Calculate the corrected absorbance value for each standard calibration solution as follows:

$$Y = r - s \quad (7)$$

where:

$Y$  = corrected absorbance value for the standard calibration solution,

$r$  = absorbance value obtained in 39.1.17 for the standard calibration solution, and

$s$  = average absorbance value obtained in 39.1.17 for the duplicate calibration blanks.

41.1.2 Use least squares formulas and the data from 41.1.1 to calculate values of  $A$  and  $B$  in the linear calibration equation:

$$Y = Ax + B, \text{ that best fits the data} \quad (8)$$

where:

$A, B$  = constants ( $B$  should be approximately zero),

$Y$  = corrected absorbance from 41.1.1, and

$x$  = micrograms thorium in the standard calibration solution.

41.2 *Individual Calibration Values:*

41.2.1 Calculate the individual calibration value for each standard solution processed with the samples as follows:

$$A' = m/n \quad (9)$$

where:

$A'$  = individual calibration value for each standard solution,

$n$  = micrograms of thorium in standard solution,

$m$  = corrected absorbance value for standard solution  $p - q$

where:

$p$  = absorbance value from standard solution, and

$q$  = average absorbance of duplicate blank solutions from 39.1.17.

41.2.2 Each individual  $A'$  should agree at the 0.05 significance level with the value of  $A$  obtained from the complete calibration set.

41.3 Determine the thorium concentration of the sample as follows:

$$\text{Th, } \mu\text{g/g Pu} = R = (Y - B) / AWC \quad (10)$$

where:

$A$  and  $B$  = constants in the linear calibration equation,

$W$  = sample mass, g,

$C$  = grams Pu per gram of sample, and

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

where:

$a$  = absorbance value for sample solution, and

$b$  = average absorbance value from the duplicate reagent blanks described in 39.2.1.

#### 42. Precision and Bias

42.1 The relative standard deviation is less than 2 % at thorium concentrations between 66 and 144  $\mu\text{g/g}$  Pu, 4 % at a concentration of 34  $\mu\text{g/g}$  Pu, and 11 % at a concentration of 10  $\mu\text{g/g}$  Pu.

42.2 The average value for thorium found in 91 measurements of 5 to 70  $\mu\text{g}$  of thorium was  $99 \pm 1 \%$ .

### IRON BY 1,10-PHENANTHROLINE SPECTROPHOTOMETRIC TEST METHOD

#### 43. Scope

43.1 This test method covers the determination of microgram quantities of iron in plutonium nitrate solutions.

#### 44. Summary of Test Method

44.1 Ferric ion is reduced to ferrous ion 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  $[(\text{C}_{12}\text{H}_8\text{N}_2)_3\text{Fe}]^{+2}$  is read at 508 nm against a sample blank containing all of the reagents except the 1,10-phenanthroline (7).

#### 45. Interferences

45.1 Plutonium must be reduced to Pu(III) to avoid causing interference.

45.2 Silver and bismuth form precipitates.

45.3 Tolerance limits for 2  $\mu\text{g/mL}$  Fe for elements that interfere in this determination are as follows (8):

Element	$\mu\text{g/mL}$	Element	$\mu\text{g/mL}$
Cd	50	Mo	100
Hg(I)	10	Zr	10
Zn	10	Cr(VI)	25
W	5	$\text{V}_2\text{O}_5$	50
Ni	2	Mn(II)	200
Co	10	$\text{U}_3\text{O}_8$	400
Cu	10	$\text{P}_2\text{O}_5$	20
Sn(II)	20	F	500
Pu(IV)	300	Np(IV)	100

#### 46. Apparatus

46.1 *Spectrophotometer*, visible range with matched 10-mm cells.

#### 47. Reagents and Materials

47.1 *Acetate Buffer Solution*—Dissolve 410 g of sodium acetate, ( $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ ) in water, add 287 mL of glacial acetic acid, and dilute to 1 L with water.

47.2 *Ammonium Hydroxide* (1 + 9)—Dilute 1 volume of  $\text{NH}_4\text{OH}$  (sp gr 0.9) with 9 volumes of water.

47.3 *Hydrochloric Acid* (1 + 9)—Dilute 1 volume of HCl (sp gr 1.19) with 9 volumes of water.

47.4 *Hydroxylamine Hydrochloride Solution* (104 g/L)—Dissolve 104 g of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) in water and dilute to 1 L with water.

47.5 *Iron Standard* (100  $\mu\text{g}$  Fe/mL)—Carefully dissolve 100 mg of high-purity iron wire in 165 mL of HCl (1 + 1), cool, and dilute to 1 L with water.

47.6 *1,10-Phenanthroline Solution* (0.2 weight/volume %)—Dissolve 2 g of 1,10-phenanthroline in water and dilute to 1 L with water.

#### 48. Procedure

48.1 Transfer an aliquot of sample that contains 5 to 75  $\mu\text{g}$  of iron to a 30-mL beaker and add 10 mL acetate buffer solution and 1 mL of hydroxylamine hydrochloride solution. Let solution stand for 10 min.

48.2 Add 1 mL of 1,10-phenanthroline solution and adjust the pH of the solution to the range from 3.5 to 4.5 with HCl (1 + 9) or  $\text{NH}_4\text{OH}$ .

48.3 Transfer the solution to a 25-mL volumetric flask. Use water to wash the beaker and to dilute to volume. Stopper the flask and mix thoroughly.

48.4 After 10 min, measure the absorbance of the sample aliquot against a sample blank that contains all of the reagents, except 1,10-phenanthroline, at a wavelength of 508 nm.

NOTE 9—For sample aliquots that contain iron in the range of 5  $\mu\text{g}$ , cells of 5-cm length or longer should be used.

48.5 Prepare a calibration curve by adding to separate 30-mL beakers, containing 10 mL of acetate buffer solution and 1 mL of hydroxylamine hydrochloride solution, the following amounts of iron standard: 0, 50, 100, 250, and 500  $\mu\text{L}$  of iron standard solution (100  $\mu\text{g}$  Fe/mL). Follow the steps given in 48.2 through 48.4 of the procedure; then plot the absorbance *versus* the micrograms of iron per 25 mL final volume of the solution.

#### 49. Calculation

49.1 Calculate the iron in micrograms per gram of plutonium as follows:

$$\text{Fe, } \mu\text{g/g Pu} = C / PW \quad (11)$$

where:

$C$  = micrograms of Fe from calibration curve,

$W$  = weight of sample, g, and

$P$  = Pu, g/g of sample.

#### 50. Precision and Bias

50.1 The relative standard deviation is 6 %.

### 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 THIOCYANATE SPECTROPHOTOMETRIC TEST METHOD

#### 51. Scope

51.1 This test method (9) is used to determine chloride in plutonium nitrate solution.

#### 52. Summary of Test Method

52.1 After the sample aliquot is mixed with a solution containing ferrous ammonium sulfate, sulfamic acid, phosphoric acid, and sulfuric acid, the chloride is steam distilled at a temperature of 140°C (Note 10). 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 10—Save a portion of the distillate to use for the fluoride determination.

### 53. Interferences

53.1 Iodide, bromide, cyanide, and thiocyanate ions interfere. Nitrite interference is eliminated by use of sulfamic acid.

### 54. Apparatus

54.1 *Steam Distillation Apparatus*, including a steam generator and heating mantles.

54.2 *Spectrophotometer and Matched 10-mm Cells*.

### 55. Reagents and Materials

55.1 *Chloride Standard Solution* (5 µg Cl/mL)—Prepare a stock solution, A, Cl = 500 µg/mL, by dissolving 824.4 mg of dried NaCl in water and diluting to 1 L. Prepare chloride standard, 5 µg Cl/mL, by diluting 10 mL of stock solution A to 1 L with water.

55.2 *Ferric Ammonium Sulfate Solution* (0.25 M)—Dissolve 12 g FeNH<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>·12 H<sub>2</sub>O in H<sub>2</sub>SO<sub>4</sub>(5 + 95) and dilute to 100 mL with H<sub>2</sub>SO<sub>4</sub>(5 + 95).

55.3 *Ferrous Ammonium Sulfate* (0.2 M) *Sulfamic Acid* (0.5 M) *Solution*—Dissolve 78.4 g of Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6 H<sub>2</sub>O and 48.6 g of NH<sub>2</sub>SO<sub>3</sub>H in H<sub>2</sub>SO<sub>4</sub>(5 + 95) and dilute to 1 L with H<sub>2</sub>SO<sub>4</sub>(5 + 95).

55.4 *Mercuric Thiocyanate Solution* (saturated)—Add Hg(SCN)<sub>2</sub> to 90 % ethyl alcohol until the solution is saturated.

### 56. Procedure

56.1 Transfer 25 mL of acid mixture consisting of 0.2 M ferrous ammonium sulfate-0.5 M sulfamic acid solution, phosphoric acid, and sulfuric acid mixed in the ratio 1 + 1 + 2.5, to a steam distillation flask and steam distill at 140°C until 100 mL of distillate is collected. Retain this solution for use as a reagent blank.

56.2 Transfer an accurately weighed aliquot of plutonium nitrate solution that contains approximately 500 mg of plutonium to a steam distillation flask and add 25 mL of acid mixture as described in 56.1. Steam distill at 140°C until 100 mL of distillate is collected.

56.3 Transfer up to 6 mL of sample distillate, and 6 mL of reagent blank distillate, to separate 10-mL volumetric flasks. To each flask, add 2 mL of 0.25 M ferric ammonium sulfate solution, 2 mL of saturated mercuric thiocyanate solution, and dilute to volume with water solution and mix.

56.4 After 10 min, transfer the solutions to 1-cm cells and measure the absorbance of the sample *versus* the reagent blank at a wavelength of 460 nm.

56.5 Prepare a calibration curve by adding 0, 0.5, 1, 2.5, and 4 mL of the chloride standard (5 µg Cl/mL) to 10-mL volumetric flasks and dilute to about 5 mL with water solution. Add 2 mL of 0.25 M ferric ammonium sulfate solution and 2 mL of mercuric thiocyanate solution, mix, and dilute to volume

with water solution. Mix solutions again and after 10 min transfer the solution to 1-cm absorption cells and read the absorbance *versus* a reagent blank at a wavelength of 460 nm. Plot the micrograms of Cl per 10 mL of solution *versus* the absorbance reading.

### 57. Calculation

57.1 Calculate the micrograms of Cl per gram of plutonium as follows:

$$\text{Cl, } \mu\text{g/g Pu} = CD / WP \quad (12)$$

where:

*C* = micrograms Cl from calibration curve,

*D* = dilution factor = distillate, mL/aliquot of distillate, mL,

*W* = weight of sample, g, and

*P* = Pu, g/g of sample.

### 58. Precision and Bias

58.1 The precision and bias of this test method is 100 ± 5 % with a sodium chloride matrix. No plutonium standard is available.

## FLUORIDE BY DISTILLATION-SPECTROPHOTOMETRIC TEST METHOD

### 59. Scope

59.1 This test method covers the determination of microquantities of fluoride in plutonium nitrate solutions.

### 60. Summary of Test Method

60.1 Fluoride is separated from the plutonium nitrate dissolved in a mixture of phosphoric and sulfuric acid by steam distillation at 140 ± 5°C (Note 11). The fluoride, in an aliquot of the distillate, is complexed with Amadac F<sup>7</sup> and the absorbance of the blue-colored complex is read in 1-cm cells *versus* a reagent blank at a wavelength of 620 nm.

NOTE 11—An aliquot of the distillate from the test method for the determination of chloride (see 52.1) can also be used to determine fluoride.

### 61. Interferences

61.1 Sulfate or phosphate ions, which may be carried over by bumping or steam distillation at too high a temperature, cause low absorbance reading by bleaching the colored complex. The formation of the colored complex is sensitive to pH range and high salt concentration.

### 62. Apparatus

62.1 See Section 54.

### 63. Reagents and Materials

63.1 *Amadac F Solution* (0.1 g/mL)<sup>9</sup>—Dissolve 10 g of Amadac F reagent in 60 % isopropyl alcohol in a 100-mL volumetric flask and dilute to volume with 60 % isopropyl alcohol.

<sup>7</sup> Amadac F is a proprietary reagent, available from Burdick and Jackson Laboratories, Inc., Muskegon, MI (see Amadac F Data Sheet).

63.2 *Fluoride Standard Solution* (10 µg F/mL)—Prepare a stock solution, 1.000 mg F/mL, by dissolving 2.210 g of dry NaF in water and diluting to 1 L. Pipet 10 mL of stock solution, 1.000 mg F/mL, into a 1-L volumetric flask and dilute to volume with water to prepare the fluoride standard, 10 µg F/mL.

#### 64. Procedure

64.1 Transfer 20-mL aliquots of the sample and of the reagent blank distillates, which were prepared during the determination of chloride, to 50-mL beakers and adjust the pH to 5.0 to 5.2 by the addition of fluoride-free NaOH solution or HCl. Dilute these solutions to 25 mL.

64.2 Transfer 8-mL aliquots of the solutions prepared in 64.1 to 10-mL flasks and add 2 mL of Amadac F reagent (0.1 g/L) to each solution and mix.

64.3 Allow the solutions to stand 1 h; then measure the absorbance of the blue-colored complex in the sample *versus* the reagent blank solution at a wavelength of 620 nm in 1-cm cells.

64.4 To prepare a calibration curve, pipet 0, 50, 100, 200, 500, and 1000-µL aliquots of the fluoride standard solution (10 µg F/mL) into separate 10-mL volumetric flasks. Add 2 mL of Amadac F solution (0.1 g/L) to each flask and dilute to volume. Mix, allow solutions to stand in the dark for 1 h, and measure the absorbance of each in 1-cm cells *versus* a reagent blank at a wavelength of 620 nm. Plot the micrograms of fluoride in the 10-mL volume of solution *versus* the absorbance.

#### 65. Calculation

65.1 Calculate the fluoride in micrograms per gram of plutonium as follows:

$$F, \mu\text{g/g Pu} = CD / WP \quad (13)$$

where:

$C$  = micrograms of F from calibration curve,

$D$  = dilution factor =  $V_1V_2/A_1A_2$

where:

$V_1$  = volume of distillate,

$A_1$  = aliquot from  $V_1$ , mL,

$V_2$  = volume to which  $A_1$  is diluted, mL, and

$A_2$  = aliquot of  $V_2$  taken for analysis, mL,

$W$  = weight or original sample aliquot, g, and

$P$  = Pu, g/g of sample.

#### 66. Precision and Bias

66.1 Precision and bias of the analysis is  $100 \pm 5\%$  with a sodium fluoride matrix. No plutonium matrix standard is available.

### SULFATE BY BARIUM SULFATE TURBIDIMETRIC TEST METHOD

#### 67. Scope

67.1 This test procedure covers the determination of the sulfate concentration in plutonium nitrate solutions in the range from 50 to 700 µg/g of plutonium.

#### 68. Summary of Test Method

68.1 In plutonium nitrate solutions plutonium is removed by extraction with tributylphosphate, TBP. The sulfate in the sample is precipitated as barium sulfate in the presence of excess salt and acid and is held in suspension in a glycerin matrix. Sulfate is determined turbidimetrically using a spectrophotometer (10, 11).

#### 69. Interferences

69.1 The reproducibility of this test method depends on careful control of many variables. Some parameters that are known to cause variances are: particle size of the  $\text{BaCl}_2$ , particle size of the  $\text{BaSO}_4$  formed, total ionic concentration of the final solution, degree of mixing of sample and reagents (number of times the flask is inverted), concentration of hydrogen ion in the final solution, and the length of time of standing of the supernatant before the absorbance is measured.

69.2 Any anions that form insoluble precipitates with barium, such as phosphate, oxalate, and chromate, will interfere.

#### 70. Apparatus

70.1 *Spectrophotometer*, visible range equipped with 50-mm cells.

#### 71. Reagents and Materials

71.1 *Barium Chloride* ( $\text{BaCl}_2$ )—Sift the salt and use only the portion that passes through a 28-mesh screen and is retained on a 35-mesh screen.

71.2 *Potassium Sulfate Standard Solution* (600 µg  $\text{SO}_4^{=}$ /mL)—Dissolve 1.088 g of dried potassium sulfate ( $\text{K}_2\text{SO}_4$ ) in water and dilute to 1 L with water.

71.3 *Sodium Chloride-Glycerin Solution*—Dissolve 40 g of sodium chloride in 60 mL of HCl (sp gr 1.19). Add 833 mL of glycerin and dilute to 2.5 L with water.

71.4 *Tributyl Phosphate* (TBP), (30 volume %)—Dilute 300 mL of TBP to 1 L with a *n*-paraffin diluent (kerosine) and pre-equilibrate with 8 M nitric acid.

#### 72. Procedure

72.1 Transfer a weighed aliquot of sample that contains approximately 1 g of Pu to an extraction funnel, and adjust the nitric acid concentration to 4 to 5 M and the volume to 5 mL.

72.2 Add 10 mL of TBP (30 volume %) reagent and equilibrate the solutions.

72.3 Allow the phases to separate and transfer the aqueous phase to a 50-mL volumetric flask containing 30 mL of distilled water. Use a minimum volume of 1 N  $\text{HNO}_3$  wash solution to ensure quantitative transfer of the aqueous phase to the 50-mL flask.

72.4 Pipet 10 mL of sodium chloride-glycerin solution into the 50-mL flask and dilute to volume with water.

72.5 Add 0.50 g of  $\text{BaCl}_2$  (see 71.3), stopper the flask, and invert the solution 20 times to dissolve the  $\text{BaCl}_2$ .

NOTE 12—The conditions of mixing and the time of standing prior to measuring the absorbance must be the same for samples and standards.

72.6 After the solution stands  $60 \pm 5$  min, measure the absorbance at 450 nm against a blank containing all of the reagents but no sample.

72.7 To prepare a calibration curve, transfer 0.100, 0.200, 0.500, 0.750, and 1.000-mL aliquots of the standard sulfate solution ( $600 \mu\text{g SO}_4/\text{mL}$ ) into separate extraction funnels that contain 5 mL of 4 to 5 M  $\text{HNO}_3$  and process in accordance with 72.2 through 72.6.

### 73. Calculation

73.1 Calculate the sulfate content ( $\text{SO}_4^{=}$ ), in micrograms per gram of plutonium, as follows:

$$\text{SO}_4^{=}, \mu\text{g/g Pu} = \mu\text{g of SO}_4^{=} \text{ (from calibration curve)} / \text{sample mass, g} \times \text{Pu/g solution} \quad (14)$$

### 74. Precision and Bias

74.1 The precision is  $\pm 3\%$  at the 95 % confidence level.

74.2 The bias of this test method is 4.4 %.

## ISOTOPIC COMPOSITION BY MASS SPECTROMETRY

### 75. Scope

75.1 This test method covers the determination of the isotopic content of nuclear-grade plutonium nitrate solutions.

### 76. Sample Preparation

76.1 Transfer an aliquot of the samples that contains not over 4 mg of Pu to an anion exchange column prepared as described in the appropriate sections of Test Methods C 697.

NOTE 13—The original sample can be diluted with 7.2 M  $\text{HNO}_3$  to reduce the Pu concentration and an aliquot of the diluted solution used for analysis.

76.2 Determine the isotopic composition of the sample in accordance with the procedure outlined in the appropriate sections of Test Methods C 697.

## PLUTONIUM-238 ISOTOPIC ABUNDANCE BY ALPHA SPECTROMETRY

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

## AMERICIUM-241 BY EXTRACTION AND GAMMA COUNTING

### 77. Scope

77.1 This test method covers the determination of americium-241 in plutonium nitrate solutions.

### 78. Summary of Test Method

78.1 Plutonium is extracted from a nitric acid solution (1 + 1) 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.

### 79. Interferences

79.1 Gamma emitting impurities, other than americium, that are not extracted with TOPO will interfere.

### 80. Apparatus

80.1 *Mixer.*

80.2 *Gamma Counter.*

80.3 *Scintillation Detector-Sodium Iodide (Thallium Activated), well-type.*

### 81. Reagents and Materials

81.1 *Nitric Acid (1 + 1)*—Dilute 100 mL of  $\text{HNO}_3$ (sp gr 1.42) to 200 mL with water.

81.2 *Nitric Acid (1 + 7)*—Dilute 25 mL of  $\text{HNO}_3$ (sp gr 1.42) to 200 mL with water.

81.3 *Trioctyl Phosphine Oxide (TOPO) (0.1 M)*—Weigh 38.0 g of TOPO and dilute to a litre with cyclohexane.

### 82. Calibration and Standardization

82.1 Weigh at least 10 mg of americium as the metal or oxide with a semi-micro balance.

82.2 Dissolve the americium metal or oxide with  $\text{HNO}_3$  in a clean platinum dish.

82.3 Transfer the dissolved americium to a weighed quartz reagent bottle; then rinse the platinum dish and add the rinse to the solution in the bottle. Reweigh the bottle with the americium solution.

82.4 Verify the americium concentration by mass analysis, gamma analysis, and alphanetric measurements.

82.5 Determine the density of the standard solution with a certified pycnometer.

82.6 Prepare known dilutions and transfer 1-mL aliquots to the same size test tubes to be used for sample measurements.

82.7 Determine by gamma counting the gamma ray emission rate relative to the amount of americium in the 1-mL aliquot.

### 83. Procedure

83.1 Transfer a weighed aliquot of plutonium nitrate sample that contains  $100 \pm 10$  mg of plutonium to a 10-mL volumetric flask and dilute to 10 mL with  $\text{HNO}_3$ (1 + 1) and mix.

83.2 Transfer 100  $\mu\text{L}$  of the diluted plutonium nitrate solution from 83.1 to a 40-dram vial containing 4.9 mL of  $\text{HNO}_3$ (1 + 1).

83.3 Add 5 mL of 0.1 M TOPO to the vial and mix the solutions.

83.4 Remove the organic phase; then pipet 1 mL of the aqueous phase and deliver it to a test tube. Stopper the tube and measure the emission rate of the 60-keV photon.

NOTE 14—If the count rate is too high, dilute the solution before counting; if too low, return to 83.2 and use a larger aliquot of the diluted plutonium nitrate solution; then continue through 83.4 of the procedure.

### 84. Calculation

84.1 Calculate the americium content in micrograms per gram of plutonium, as follows:

$$\text{Am, } \mu\text{g/g Pu} = [B + (A - B)(F - D)/C - D]E / WP \quad (15)$$

where:

A = concentration of americium standard that has a count rate just higher than the sample,  $\mu\text{g/mL}$ ,

- B* = concentration of americium standard that has a count rate just lower than the sample,  $\mu\text{g/mL}$ ,  
*C* = gamma count of standard that counts just higher than the sample,  
*D* = gamma count of standard that counts just lower than the sample,  
*F* = gamma count of sample,  
*P* = grams of Pu per gram of plutonium nitrate sample,  
*W* = weight of sample aliquot, g, and  
*E* = dilution factor =  $5v_1/a_1$

where:

- $V_1$  = volume to which sample, *W*, is diluted, mL, and  
 $A_1$  = aliquot of  $v_1$  taken for dilution to 5 mL prior to the extraction noted in 83.3.

## 85. Precision

85.1 Relative standard deviation is 4 %.

### AMERICIUM-241 BY GAMMA COUNTING

(Test Method C 1268 may be used instead of this method if a high-resolution gamma ray counting system is available.)

## 86. Scope

86.1 This test method covers the determination of americium-241 in plutonium nitrate solutions that do not contain significant amounts of other radioactive fission products or high specific-activity gamma emitters.

## 87. Summary of Test Method

87.1 An aliquot of sample that contains 1 to 50 ng of americium-241 is transferred to a well-type sodium iodide, NaI(Tl), detector, and the 60-keV photon of americium-241 is measured. Since a correction is made for the small contribution to the gamma activity by plutonium, it is not necessary to make a chemical separation of the americium and plutonium.

## 88. Interferences

88.1 Gamma-emitting fission products and other high-specific activity gamma emitters will interfere.

## 89. Apparatus

89.1 *Gamma Counter*—The recommended detector is a well-type NaI (Tl) crystal, 51 mm in diameter with a 17-mm diameter by 40-mm-deep well, coupled to a 50-mm-diameter multiplier phototube. The detector with associated power supply is connected to an amplifier and scaler capable of accepting counts at a rate of  $2 \times 10^3$  counts per second with less than 2 % coincidence loss. The detector is surrounded by lead shielding having a thickness of 50 mm or more.

89.2 *Test Tubes*, 13 by 100-mm.

## 90. Reagents and Materials

90.1 *Americium-241 Standard Solution* (5 ng/mL)—Dissolve an accurately weighed portion of americium oxide ( $^{241}\text{AmO}_2$ )<sup>8</sup> in hot  $\text{HNO}_3(1+1)$ . Dilute with  $\text{HNO}_3(1+15)$  until the americium concentration is approximately 5 ng/mL.

90.2 *Nitric Acid* (1 + 1)—Dilute 100 mL of concentrated nitric acid ( $\text{HNO}_3$  sp gr 1.42) with 100 mL of water.

90.3 *Nitric Acid* (1 + 15)—Dilute 10 mL of  $\text{HNO}_3$ (sp gr 1.42) with 150 mL of water.

90.4 *Plutonium Standard Solution* (100  $\mu\text{g/mL}$ )—Purify 10 mg of plutonium by ion exchange as described in Test Methods C 697. Dilute the purified plutonium solution with  $\text{HNO}_3(1+15)$  to 100 mL. To avoid error due to in-growth of americium-241, count the “pure” plutonium solution within 6 h after purification.

## 91. Calibration and Standardization

91.1 Transfer 2.00 mL of the americium-241 standard solution (5 ng/mL) to a 13 by 100-mm test tube, and close the tube with a stopper to prevent evaporation.

91.2 Place the tube in the detector cell.

91.3 Turn on the counter and adjust the high voltage to the point that the count rate begins to increase rapidly with increasing voltage.

91.4 Count the sample for 600 s and record the count rate.

91.5 Increase the high voltage by 10 V, and repeat 91.4.

91.6 Repeat 91.5 until the count rate remains constant at 5 to 10 successive voltages.

91.7 Plot the difference between successive count rates (*y* coordinate) as a function of the voltage (*x* coordinate), and locate the peak corresponding to 59.6 keV ( $9.55 \times 10^{-15}$  J or 9.55 fJ).

91.8 Locate the voltage on the higher side of the peak at which successive differences in count rate are small, and adjust the power supply to this voltage to accept the 9.55-fJ pulses from americium-241 but to reject the weaker *L X* rays from plutonium.

91.9 Transfer 2.00 mL of plutonium standard solution (100  $\mu\text{g/mL}$ ) to a test tube, seal with a stopper, and place the tube in the detector well.

91.10 Count the plutonium solution at the operating voltage determined in 91.8, subtract the detector background and record the net count rate as  $R_{\text{Pu}}$ . Obtain at least  $10^6$  counts to ensure a counting precision of 0.1 % relative standard deviation.

91.11 Count the americium standard solution (5 ng/mL) at the operating voltage determined in 91.8, subtract the detector background, and record the net count rate as  $R_{\text{Am}}$ . Count at least  $10^6$  counts to ensure a counting precision of 0.1 % relative standard deviation.

91.12 Remove the stopper from the tube containing the americium-241 calibration solution and seal the tube with a hot flame.

91.13 Calibrate each gamma counter with the americium-241 calibration solution at the beginning of each shift. Adjust the operating voltage of the counter slightly to produce the count rate originally obtained in 91.11.

## 92. Procedure

92.1 Transfer an accurately weighed aliquot of plutonium nitrate solution that contains about 200 mg of plutonium to a weighed, heavy-walled polyethylene container and add  $\text{HNO}_3(1+15)$  to bring the solution weight to about 35 g and mix the solution thoroughly.

<sup>8</sup> Americium-241 oxide may be obtained from Isotopes Division, ORNL, Oak Ridge, TN 37830.

92.2 Transfer a weighed aliquot, about 25 mg, of the solution from 92.1 to a 50-mL volumetric flask, dilute to volume with HNO<sub>3</sub>(1 + 1), and mix thoroughly.

92.3 Pipet 2.00 mL of the diluted solution from 100.2 into a 13 by 100-mm test tube and stopper the tube.

92.4 Place the tube in the gamma detector and count until a total of at least 10<sup>5</sup> counts are accumulated. After correcting for background, record the count rate as R<sub>S</sub>.

**93. Calculation**

93.1 Calculate the americium-241 calibration factor as follows:

$$F_A = R_{A_m}/W_A \tag{16}$$

where:

F<sub>A</sub> = counts per second per microgram of americium-241,

R<sub>A<sub>m</sub></sub> = counts per second in the calibration solution, and

W<sub>A</sub> = weight, μg, of americium-241 in the calibration solution.

93.2 Calculate the plutonium calibration factor, F<sub>P<sub>u</sub></sub>, as follows:

$$F_{P_u} = R_{P_u}/W_{P_u} \tag{17}$$

where:

F<sub>P<sub>u</sub></sub> = counts per second per microgram of plutonium,

R<sub>P<sub>u</sub></sub> = counts per second for the calibration sample, and

W<sub>P<sub>u</sub></sub> = weight of plutonium in calibration sample, μg.

93.3 Calculate the americium-241 in the sample as follows:

$$R_1 = 10^6[R_S - F_{P_u}W_S]/F_AW_S \tag{18}$$

where:

R<sub>1</sub> = americium-241 in micrograms per gram of plutonium,

R<sub>S</sub> = counts per second for sample,

F<sub>P<sub>u</sub></sub> = plutonium calibration factor,

F<sub>A</sub> = americium-241 calibration factor, and

W<sub>S</sub> = weight of plutonium in the sample counting tube, μg.

**94. Precision and Bias**

94.1 *Precision*—The pooled relative standard deviation for several hundred plutonium samples has been less than 1 % when the counted aliquot contained 5 ng of americium-241. For aliquots containing 1 ng or less the relative standard deviation has been 2 to 5 %.

94.2 *Bias*—When suitable calibration materials are used properly this test method is not biased.

NOTE 15—NBL plutonium metal, CRM 126or its replacement, and americium oxide containing less than 10 weight % plutonium are

recommended for calibration.

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

**95. Scope**

95.1 This test method covers the determination of gamma-emitting fission products (for example, <sup>95</sup>Zr-<sup>95</sup>Nb, <sup>103</sup>Ru, <sup>106</sup>Rh, and <sup>137</sup>Cs-<sup>137m</sup>Ba) and actinide impurities (<sup>232</sup>Th, <sup>235</sup>U, and <sup>238</sup>U) in plutonium nitrate. Test portions of plutonium nitrate are prepared to contain from 0.1 to 1.0 g of plutonium. The age of the plutonium after the last separation from actinides must be considered in calculating the actinide contents.

**96. Summary of Test Method**

96.1 A lithium-drifted germanium detector, Ge(Li), is used to detect and measure gamma-emitting nuclides in plutonium-239 samples. See Fig. 1 for a typical detector-instrumentation configuration, and consult Refs (12-23) for gamma-ray energies, branching ratios for actinides, fission products, plutonium isotopes, and other pertinent information. Gamma rays emitted from <sup>239</sup>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.

96.2 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.

**97. Interferences**

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

**98. Apparatus**

98.1 *Stainless-Steel Sample Disks* (28.6 mm) or appropriate vials (for example, 15-g plastic) with appropriate mount holders.

**Caution:** Give particular attention toward assurance of plutonium containment.

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

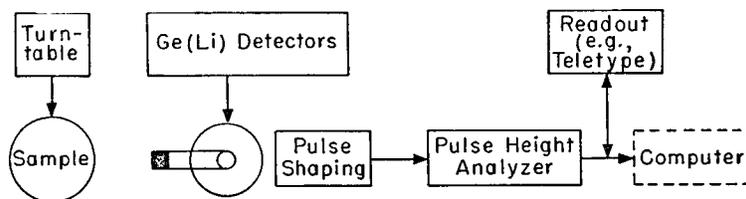


FIG. 1 Plutonium Sample Counting System

98.3 *Pulse-Height Analyzer* (2000 channels), with type or tape readout, or both.

## 99. Calibration and Standardization

99.1 Prepare calibration standards for all nuclides of interest using a combination of plutonium nitrate 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.

## 100. Procedure

100.1 Pipet a measured aliquot of the sample onto a 19.6-mm stainless steel sample disk and dry slowly under a heat lamp. Alternative source preparation could be as a liquid source in a plastic vial.

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

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

100.4 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.

## 101. Calculation

101.1 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.

101.2 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 such radionuclides. A typical calculation format is as follows:

$$\begin{aligned} & \text{Element impurity, } \mu\text{g/g of plutonium nitrate sample} \\ & = (A)(F)(10^6)/(B)(C)(D)(E)(G)(H)(I)(J) \end{aligned} \quad (19)$$

where:

- A* = total net area under selected photopeaks in counts,
- B* = branching of gamma-ray, fraction of isotope decay,
- C* = plutonium nitrate concentration in sample aliquot, g/mL,
- D* = specific activity of isotope analyzed, disintegrations  $\text{min}^{-1} \text{ gram}^{-1}$ ,
- 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.

## 102. Precision and Bias

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

102.2 The bias for the measurement of many impurities in 0.1 to 1.0-g samples of plutonium nitrate has been found to be  $100 \pm 5\%$ . In practice, a standard source should be measured daily to assure the reliability of the counting systems.

## RARE EARTHS BY COPPER SPARK SPECTROCHEMICAL TEST METHOD

### 103. Scope

103.1 This test method covers the determination of rare earths in plutonium nitrate solutions in the range from 10 to 200  $\mu\text{g/g}$  of plutonium.

### 104. Summary of Test Method

104.1 Rare earths are separated from plutonium by solvent extraction, after which the concentration is determined by a copper-spark spectrographic test method.

### 105. Procedure

105.1 Transfer an accurately weighed aliquot of sample that contains 0.5 g of Pu to a 25-mL volumetric flask and dilute to volume with 6.7 *M* HCl and mix thoroughly.

105.2 Transfer a 10-mL aliquot of the solution to a 35-mL vial containing 10 mL of TOA, 4 mL of internal standard solution, 5 mg of  $\text{H}_3\text{BO}_3$  crystals, and a magnetic stirring bar.

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

NOTE 16—In making the calculations multiply the weight of the sample aliquot by the ratio, grams Pu per gram of sample, and report micrograms of rare earth per gram of Pu in the plutonium nitrate solution.

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

### 106. Scope

106.1 This test method covers the determination of tungsten, niobium, and tantalum in plutonium nitrate solutions.

### 107. Summary of Test Method

107.1 The sample is dried under a heat lamp, ignited in a muffle furnace at 600°C, and blended with 27% carrier

(AgCl). 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.

**108. Apparatus**

108.1 *Spectrograph*—A spectrograph with sufficient resolving power and linear dispersion to separate the analytical lines from other lines in the spectrum of the sample in the spectral region from 2200 to 5000 Å. Instruments with a reciprocal linear dispersion of approximately 3 Å/mm or less are satisfactory.

108.2 *Excitation Source*—A continuous d-c arc source capable of providing a 14-A d-c arc (short circuit).

108.3 *Excitation Stand*—Conventional type with adjustable water-cooled electrode holders.

108.4 *Developing Equipment*—Developing, fixing, washing, and drying equipment conforming to the requirements of Practices E 115.

108.5 *Microphotometer*—Photometric microphotometer or comparator capable of projecting the spectrum for visual comparison of samples and standards.

108.6 *Mixer Mill*.<sup>9</sup>

108.7 *Venting Tool*—See Fig. 2 for diagram.

108.8 *Muffle Furnace*, with suitable temperature control to sustain  $600 \pm 50^\circ\text{C}$ .

108.9 *Electrode Forceps*, with each V-tip bent to form a semicircular grasp around the electrodes.

108.10 *Balance, Torsion Type*—A balance with a capacity up to 1 g and capable of weighing to  $\pm 1.0$  mg is suitable.

108.11 *Agate Mortars*.

108.12 *Electrodes*.

108.13 *Anode Cap*—Ultra Carbon Corporation Type 7010 (see Fig. 3).<sup>10</sup>

108.14 *Pedestal*—ASTM Type S-1.

108.15 *Counter Electrode*—ASTM Type C-1.

108.16 *Mixing Vial*, plastic, 12.7-mm ( $\frac{1}{2}$ -in.) diameter, 25 mm (1 in.) long with cap, and 9.5-mm ( $\frac{3}{8}$ -in.) diameter plastic ball.

108.17 *High-Silica Crucible*, 10-mL capacity.

108.18 *Heat Lamp*.

**109. Reagents and Materials**

109.1 *Carrier*—Silver chloride, spectrographic-grade or equivalent purity and texture.

109.2 *Photographic Processing Solutions*— Prepare solutions as noted in Practices E 115.

**110. Standards**

110.1 Standards can be synthesized by blending oxides of tungsten, tantalum, and columbium with ignited high-purity  $\text{PuO}_2$ . A stock standard of 2000  $\mu\text{g/g}$  each of W, Ta, and Nb is first prepared, which is subsequently diluted with high purity  $\text{PuO}_2$  ignited at  $600 \pm 50^\circ\text{C}$ . The mixed oxide matrix should be as similar as possible to the sample in bulk density.

**111. Procedure**

111.1 Place a quantity of  $\text{Pu}(\text{NO}_3)_4$  solution, estimated to contain 1 g of plutonium, in a high-silica crucible and evaporate to dryness under a heat lamp.

<sup>9</sup> The Spex Industries Mixer Mill Model 5100 is satisfactory for small quantities.

<sup>10</sup> Ultra Carbon Corp. Type 7010 Electrode has been found satisfactory for this application.

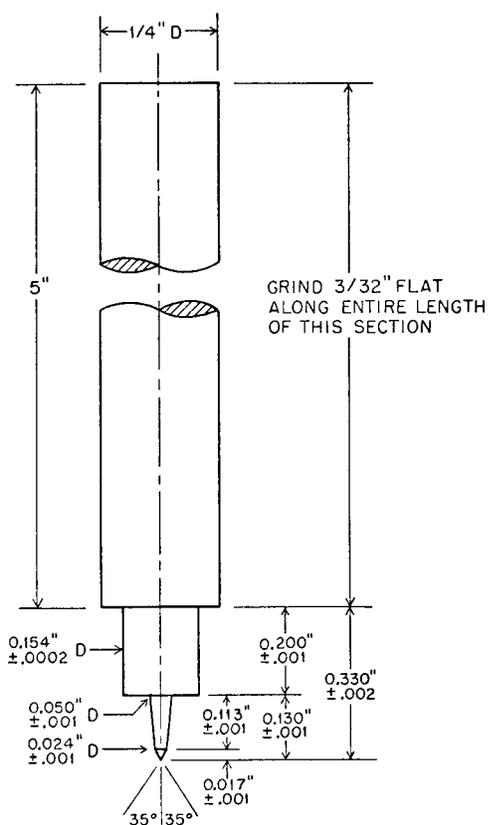


FIG. 2 Venting Tool

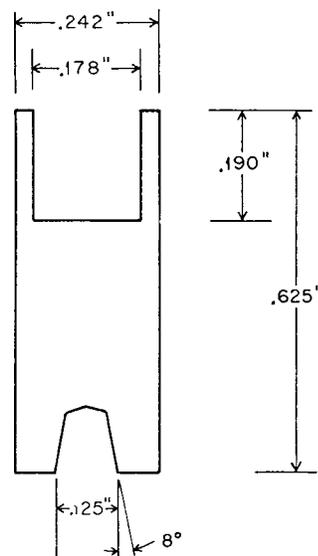


FIG. 3 Anode Cap<sup>10</sup>

111.2 Ignite the sample in a muffle furnace at  $600 \pm 50^\circ\text{C}$  for 4 h.

111.3 Remove from furnace and cool to room temperature.

111.4 Utilizing a mixer mill, blend 160 mg of sample with 60 mg of carrier (AgCl) for 30 s.

111.5 Weigh duplicate 50 mg charges of samples into Ultra Type 7010 electrodes.

111.6 Tap pack and vent the charge before excitation.

111.7 Excite the samples and standards under the following conditions:

111.7.1 *Excitation*—10 A d-c arc.

111.7.2 *Preburn*—0 s.

111.7.3 *Exposure*—35 s.

111.7.4 *Slit Width*—10  $\mu\text{m}$ .

111.7.5 *Slit Height*—2.5 mm.

111.7.6 *Rock*—3.0 mm.

111.7.7 *Wavelength Range*—2100 to 4400  $\text{\AA}$ , first order.

111.7.8 *Light Transmission*—Total filter: 25 % T; split field filter: 100/25 % T.

111.7.8.1 *Emulsion*—SA No. 1.

111.7.9 *Electrode Gap*—3 mm.

## 112. Photographic Processing

112.1 Process the photographic plate in accordance with the conditions in Practices E 115.

## 113. Calculation

113.1 *Analytical Lines:*

W	2681.41 $\text{\AA}$	25 to 500 $\mu\text{g/g}$
	4008.75 $\text{\AA}$	10 to 300 $\mu\text{g/g}$
Nb	3358.42 $\text{\AA}$	25 to 500 $\mu\text{g/g}$
	4100.9 $\text{\AA}$	5 to 300 $\mu\text{g/g}$
Ta	2647.42 $\text{\AA}$	50 to 500 $\mu\text{g/g}$
	2653.27 $\text{\AA}$	50 to 500 $\mu\text{g/g}$
	3311.16 $\text{\AA}$	100 to 1000 $\mu\text{g/g}$

113.2 *Visual Comparative Analysis*—Visually compare the density of the sample impurity spectral line with the corresponding line in the standard spectrum. Estimate the impurity concentration using the lines listed in 111.1.

113.3 *Photometric Analysis:*

113.3.1 *Emulsion Calibration*—Calibrate the emulsion in accordance with Practice E 116.

113.3.2 *Preparation of Analytical Curves*—Prepare analytical curves by converting the transmittance readings of the analytical lines to intensities using the emulsion calibration curve, and plot the log of the intensity *versus* the log of the concentration for each element.

113.3.3 *Determination of Impurity Concentration*—Determine the log intensity for each analytical line from the emulsion calibration curve, and obtain sample impurity concentrations from the appropriate analytical curve.

## 114. Precision and Bias

114.1 *Precision*—For photometric measurements, an overall relative standard deviation of  $\pm 25\%$  has been obtained. For visual estimates, the method has been found to be reliable to within a factor of two (that is,  $-\frac{1}{2}$  to  $+2$ ).

114.2 *Bias*—The bias of this test method is estimated to be comparable to the precision.

## SAMPLE PREPARATION FOR SPECTROGRAPHIC ANALYSIS FOR GENERAL IMPURITIES

### 115. Scope

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

### 116. Summary of Test Method

116.1 An aliquot of plutonium nitrate solution is transferred to a platinum crucible and dried at temperatures that start at room temperature and reach a maximum of  $125^\circ\text{C}$ . The dried salt is then calcined to plutonium dioxide in a muffle furnace as the temperature is slowly increased from 100 to  $800 \pm 25^\circ\text{C}$ . After the oxide is cooled to room temperature it is analyzed for trace elements in accordance with the appropriate sections of Test Methods C 697.

### 117. Apparatus

117.1 *Muffle Furnace*, with controls, capable of maintaining a temperature of  $800 \pm 25^\circ\text{C}$ .

117.2 *Platinum Crucible*.

117.3 *Transite Sheets*,  $\frac{1}{4}$  in. (6.35 mm) thick.

### 118. Procedure

118.1 Transfer sufficient sample to a platinum crucible to provide 500 mg of plutonium dioxide following calcination of the sample.

118.2 Place the crucible on a cold hot plate and slowly raise the temperature to  $125^\circ\text{C}$  until the sample has dried.

NOTE 17—To provide uniform heating of the plutonium nitrate solution Transite sheeting is used as a barrier between the hot plate and the crucible.

118.3 Transfer the dried sample and crucible to a cold muffle furnace, heat slowly to  $800^\circ\text{C}$ , and maintain this temperature for 30 min; then cool to  $400^\circ\text{C}$ .

NOTE 18—Following calcination of the sample the furnace is cooled to  $400^\circ\text{C}$  before opening to avoid excess heat load inside the glove box.

118.4 Cool the muffle furnace to room temperature and remove the sample.

118.5 Analyze the sample for trace elements in accordance with the appropriate sections of Test Methods C 697.

NOTE 19—Treatment of the sample affects the performance characteristics in the arc; therefore, the spectrographic equipment must be calibrated for the sample preparation method used. For highest accuracy, the calibration test method should closely duplicate the sample analysis test method.

NOTE 20—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, $\text{\AA}$	Concentration Range, ppm
Na	5859.95	1–1000
	5895.92	
Li	6707.84	1–1000
	6103.64	

## 119. Keywords

119.1 impurity content; isotopic composition; plutonium content; plutonium nitrate

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