



Designation: **C759 – 10 C759 – 18**

# 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 C759; 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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Plutonium by Controlled-Potential Coulometry	2
Plutonium by Amperometric Titration with Iron(II)	2
Plutonium by Diode Array Spectrophotometry	
Free Acid by Titration in an Oxalate Solution	8 to 15
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Tungsten, Niobium (Columbium), and Tantalum by Spectrochemical Test Method	106 to 114
Sample Preparation for Spectrographic Analysis for General Impurities	115 to 118

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific safeguard and safety hazard statements, see Section 6.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

<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>

- C697** Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets
- C852/C852M** Guide for Design Criteria for Plutonium Gloveboxes
- C859** Terminology Relating to Nuclear Materials
- C1009** Guide for Establishing and Maintaining a Quality Assurance Program for Analytical Laboratories Within the Nuclear Industry
- C1068** Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry
- C1108** Test Method for Plutonium by Controlled-Potential Coulometry
- C1128** Guide for Preparation of Working Reference Materials for Use in Analysis of Nuclear Fuel Cycle Materials
- C1156** Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials
- C1165** Test Method for Determining Plutonium by Controlled-Potential Coulometry in H<sub>2</sub>SO<sub>4</sub> at a Platinum Working Electrode
- C1206** Test Method for Plutonium by Iron (II)/Chromium (VI) Amperometric Titration (Withdrawn 2015)<sup>4</sup>
- C1210** Guide for Establishing a Measurement System Quality Control Program for Analytical Chemistry Laboratories Within the Nuclear Industry
- C1235** Test Method for Plutonium by Titanium(III)/Cerium(IV) Titration (Withdrawn 2005)<sup>4</sup>
- C1268** Test Method for Quantitative Determination of <sup>241</sup>Am in Plutonium by Gamma-Ray Spectrometry
- C1297** Guide for Qualification of Laboratory Analysts for the Analysis of Nuclear Fuel Cycle Materials
- C1307** Test Method for Plutonium Assay by Plutonium (III) Diode Array Spectrophotometry
- C1415** Test Method for <sup>238</sup>Pu Isotopic Abundance By Alpha Spectrometry
- C1432** Test Method for Determination of Impurities in Plutonium: Acid Dissolution, Ion Exchange Matrix Separation, and Inductively Coupled Plasma-Atomic Emission Spectroscopic (ICP/AES) Analysis
- D1193** Specification for Reagent Water
- E50** Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
- E115** Practice for Photographic Processing in Optical Emission Spectrographic Analysis (Withdrawn 2002)<sup>4</sup>
- E116** Practice for Photographic Photometry in Spectrochemical Analysis (Withdrawn 2002)<sup>4</sup>

## 3. Terminology

- 3.1 For definitions of terms used in this test method but not defined herein, refer to Terminology **C859**.

## 4. Significance and Use

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

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

4.1.2 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.

4.1.3 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).

4.2 Fitness for Purpose of Safeguards and Nuclear Safety Applications—Methods intended for use in safeguards and nuclear safety applications shall meet the requirements specified by Guide **C1068** for use in such applications.

### 4. Committee C26 Safeguards Statement<sup>5</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.

<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

<sup>4</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

## 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.<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 **D1193**.

## 6. Safety Hazards

6.1 Since plutonium bearing materials are radioactive and toxic, adequate laboratory facilities, gloved boxes, fume hoods, etc., along with safe techniques, must be used in handling samples containing these materials. A detailed discussion of all the precautions necessary is beyond the scope of these test methods; however, personnel who handle these materials should be familiar with such safe handling practices as are given in Guide **E852C852/C852M** and in Refs **(1)** through **(2)**.<sup>6</sup>

6.2 Adequate laboratory facilities, such as fume hoods and controlled ventilation, along with safe techniques, must be used in this procedure. Extreme care should be exercised in using hydrofluoric and other hot, concentrated acids. Use of proper gloves is recommended. Refer to the laboratory's chemical hygiene plan and other applicable guidance for handling chemical and radioactive materials and for the management of radioactive, mixed, and hazardous waste.

6.3 Hydrofluoric acid is a highly corrosive acid that can severely burn skin, eyes, and mucous membranes. Hydrofluoric acid is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid. Hydrofluoric acid differs from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers. Unlike other acids that are rapidly neutralized, hydrofluoric acid reactions with tissue may continue for days if left untreated. Due to the serious consequence of hydrofluoric acid burns, prevention of exposure or injury of personnel is the primary goal. Utilization of appropriate laboratory controls (hoods) and wearing adequate personal protective equipment to protect from skin and eye contact is essential.

## 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.

<sup>5</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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

**PLUTONIUM BY CONTROLLED-POTENTIAL COULOMETRY**

(This test method was discontinued in 1992 and replaced by Test Method **C1165**.)

**PLUTONIUM BY CONTROLLED-POTENTIAL COULOMETRY**

(With appropriate sample preparation, controlled-potential coulometric measurement as described in Test Method **C1108** may be used for plutonium determination.)

**PLUTONIUM BY AMPEROMETRIC TITRATION WITH IRON(II)**

(This test method was discontinued in 1992 and replaced by Test Method **C1206**.)

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

(With appropriate sample preparation, the measurement described in Test Method **C1307** may be used for plutonium determination.)

**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 **(3, 4)**.

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**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 **E50**.

**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 ( $H^+$ ,  $N$ ) 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,  $\mu\text{L}$ .

## 15. Precision and Bias

15.1 *Precision*—Of individual results,  $\pm 5\%$  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.~~

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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 ( $\text{HNO}_3$ , sp gr 1.42).

19.3 *Potassium Iodate (0.3 M)*—Dissolve 64.2 g of potassium iodate ( $\text{KIO}_3$ ) in 900 mL of water, adjust the pH to 4.3 by adding  $\text{HNO}_3$  (1 + 14), and dilute to 1 L with water.

19.4 *Sodium Hydroxide (0.3 M)*—Prepare and standardize in accordance with Practices **E50** 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 ( $H^+$ ,  $N$ ) as follows:

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

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 % (5).

## 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.

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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 ( $\text{HNO}_3$ , 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  $\text{U}_3\text{O}_8$  (NIST SRM 950b or its replacement), or uranium oxide of equal purity, in 1 mL of  $\text{HNO}_3$  (1 + 2) and dilute to 1 L with  $\text{H}_2\text{SO}_4$  (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  $\text{H}_2\text{SO}_4$  (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 ( $\text{NH}_2\text{OH} \cdot \text{HCl}$ , 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  $\text{NH}_2\text{OH} \cdot \text{HCl}$  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  $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$  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  $\text{NH}_4 \text{OH}$  (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  $\pm 0.1$  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 µg U/g Pu the standard deviation is ±100 µg/g; in the range from 1500 to 3000 µg U/g Pu it is ±50 µg/g.

## THORIUM BY THORIN SPECTROPHOTOMETRIC TEST METHOD

### 34. Scope

~~34.1 This test method covers the determination of 10 to 150 µg of thorium per gram of plutonium in plutonium nitrate solutions.~~

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### 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 µg 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 19/18 standard-taper ground-glass joint that fits a 10-mL volumetric flask.

### 38. Reagents and Materials

38.1 *Ammonium Peroxydisulfate* ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>).

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 (H<sub>2</sub>O<sub>2</sub>).

38.5 *Hydroxylamine Hydrochloride Solution (250 g/L)*—Dissolve 25 g of hydroxylamine hydrochloride (NH<sub>2</sub>OH·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 (La(NO<sub>3</sub>)<sub>3</sub>·6 H<sub>2</sub>O) in water and dilute to 100 mL with water.

38.7 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO<sub>3</sub>).

38.8 *Perchloric Acid (70 to 72 %)*—Concentrated perchloric acid (HClO<sub>4</sub>).

38.9 *Silver Nitrate Solution (2.5 g/L)*—Dissolve 250 mg of silver nitrate (AgNO<sub>3</sub>) 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 (H<sub>2</sub> SO<sub>4</sub>, 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 H<sub>2</sub>O<sub>2</sub> (30 %). Add 83 mL of HClO<sub>4</sub> (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 HNO<sub>3</sub> (sp gr 1.42) and 2 mL of HClO<sub>4</sub> (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 H<sub>2</sub>SO<sub>4</sub> (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 H<sub>2</sub>SO<sub>4</sub> (1 + 35).

39.1.6 Add 5 drops of La(NO<sub>3</sub>)<sub>3</sub>·6 H<sub>2</sub>O (10 g/L) solution and 0.1 mL of AgNO<sub>3</sub> solution (2.5 g/L) and approximately 1 g of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 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 HClO<sub>4</sub> (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 HClO<sub>4</sub> (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 NH<sub>2</sub>OH·HCl solution to each flask.

39.1.14 Prepare a reference solution by adding 0.5 mL of HClO<sub>4</sub> (70 to 72 %), 0.5 mL of NH<sub>2</sub> OH·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 µg 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),