



# Standard Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets<sup>1</sup>

This standard is issued under the fixed designation C697; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 These test methods cover procedures for the chemical, mass spectrometric, and spectrochemical analysis of nuclear-grade plutonium dioxide powders and pellets to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

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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 and health practices and determine the applica-*

*bility of regulatory limitations prior to use.* For specific precautionary statements, see Sections 6, 16.2.5, 44.7, 51.9 and 92.5.1.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>6</sup>

- C757 Specification for Nuclear-Grade Plutonium Dioxide Powder for Light Water Reactors
- C852 Guide for Design Criteria for Plutonium Gloveboxes
- C859 Terminology Relating to Nuclear Materials
- C1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry
- C1108 Test Method for Plutonium by Controlled-Potential Coulometry
- C1165 Test Method for Determining Plutonium by Controlled-Potential Coulometry in H<sub>2</sub>SO<sub>4</sub> at a Platinum Working Electrode
- C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis
- C1206 Test Method for Plutonium by Iron (II)/Chromium (VI) Amperometric Titration (Withdrawn 2015)<sup>7</sup>
- C1233 Practice for Determining Equivalent Boron Contents of Nuclear Materials
- C1235 Test Method for Plutonium by Titanium(III)/Cerium(IV) Titration (Withdrawn 2005)<sup>7</sup>
- C1268 Test Method for Quantitative Determination of <sup>241</sup>Am in Plutonium by Gamma-Ray Spectrometry
- 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

<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.

<sup>3</sup> Discontinued as of January 1, 2004.

<sup>4</sup> Discontinued as of May 30, 1980.

<sup>5</sup> Discontinued as of June 2016.

<sup>6</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>7</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

**C1625** Test Method for Uranium and Plutonium Concentrations and Isotopic Abundances by Thermal Ionization Mass Spectrometry

**C1637** Test Method for the Determination of Impurities in Plutonium Metal: Acid Digestion and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) Analysis

**C1672** Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer

**D1193** Specification for Reagent Water

**D4327** Test Method for Anions in Water by Suppressed Ion Chromatography

**E60** Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

**E115** Practice for Photographic Processing in Optical Emission Spectrographic Analysis (Withdrawn 2002)<sup>7</sup>

**E116** Practice for Photographic Photometry in Spectrochemical Analysis (Withdrawn 2002)<sup>7</sup>

**E130** Practice for Designation of Shapes and Sizes of Graphite Electrodes (Withdrawn 2013)<sup>7</sup>

### 3. Terminology

3.1 Except as otherwise defined herein, definitions of terms are as given in Terminology **C859**.

### 4. Significance and Use

4.1 Plutonium dioxide is used in mixtures with uranium dioxide as a nuclear-reactor fuel. In order to be suitable for this purpose, the material must meet certain criteria for plutonium content, isotopic composition, and impurity content. These test methods are designed to show whether or not a given material meets the specifications for these items as described in Specification **C757**.

4.1.1 An assay is performed to determine whether the material has the minimum plutonium content specified on a dry weight basis.

4.1.2 Determination of the isotopic content of the plutonium in the plutonium dioxide powder is made to establish whether the effective fissile content is in compliance with the purchaser's specifications.

4.1.3 Impurity content is determined to ensure that the maximum concentration limit of certain impurity elements is not exceeded. Determination of impurities is also required for calculation of the equivalent boron content (EBC) as described in Practice **C1233**.

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.

### 5. Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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>8</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, references to water shall be understood to mean reagent water conforming to Specification **D1193**.

### 6. Safety Precautions

6.1 Since plutonium bearing materials are radioactive and toxic, adequate laboratory facilities, glove boxes, fume hoods, and so forth, along with safe techniques, must be used in handling samples containing these materials. Glove boxes should be fitted with off-gas filters capable of sustained operation with dust-laden atmospheres. A detailed discussion of all the precautions necessary is beyond the scope of these test methods; however, personnel who handle these materials should be familiar with such safe handling practices as are given in Guide **C852** and in Refs **(1-3)**.<sup>9</sup>

6.2 Adequate laboratory facilities, such as fume hoods and controlled ventilation, along with safe techniques, must be used in all procedures in this test method. Extreme care should be exercised in using hydrofluoric acid 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 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. Familiarization and compliance with the Safety Data Sheet is essential.

6.4 Perchloric acid (HClO<sub>4</sub>) forms explosive compounds with organics and many metal salts. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Familiarization and compliance with the Safety Data Sheet is essential. Carry out sample dissolution with perchloric acid in a fume hood with a scrubber unit that is specially designed for use with HClO<sub>4</sub>.

### 7. Sampling and Dissolution

7.1 Criteria for sampling this material are given in Specification **C757**.

7.2 Samples can be dissolved using the appropriate dissolution technique described in Practice **C1168**.

<sup>8</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 *Anal. 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>9</sup> The boldface numbers in parentheses refer to the list of references at the end of these test methods.

## PLUTONIUM SAMPLE HANDLING

### 8. Scope

8.1 This test method covers the conditions necessary to preserve the integrity of plutonium dioxide samples. Conditions listed here are directed toward the analytical chemist. However, they are just as applicable to any group handling the material.

### 9. Summary of Test Method

9.1 Plutonium dioxide is very hygroscopic. In a short time it can sorb sufficient water from an uncontrolled atmosphere to destroy the validity of the most accurate analytical methods. An atmosphere with a dew point of  $-23^{\circ}\text{C}$  has been found adequate to prevent sorption of water, but care must be exercised to use equipment and sample containers known to be dry.

### 10. Sample Handling Conditions

10.1 All sampling and critical weighings are to be performed with consideration of the hygroscopic nature of plutonium and the applicable data quality objectives (DQOs). In some instances an atmosphere with a dew point no greater than  $-23^{\circ}\text{C}$  may be needed to meet DQOs.

10.2 All sampling equipment, including bottles, is to be dried before use. Plastic bottles are not to be used since they cannot be adequately dried. Glass bottles and aluminum foil are to be dried at  $110^{\circ}\text{C}$  for at least 1 h and kept in a desiccator until used.

NOTE 1—It has been shown that plutonium dioxide will sorb water from apparently dry aluminum foil. The foil should be dried at  $110^{\circ}\text{C}$  before use.

10.3 Quantitative methods to correct for moisture absorption, such as drying, must be avoided. The sample will not be representative under these conditions. It is virtually impossible to get equal amounts of moisture in the sample and bulk of the material at the same time.

### 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 CERIC SULFATE TITRATION

(This test method was discontinued in 2003 and replaced by Test Method C1235, which was withdrawn in 2005.)

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

(This test method was discontinued in 1992 and replaced by Test Method C1206, which was withdrawn in 2015.)

## 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.)

## NITROGEN BY DISTILLATION SPECTROPHOTOMETRY USING NESSLER REAGENT

### 11. Scope

11.1 This test method covers the determination of 5 to 100  $\mu\text{g/g}$  of nitride nitrogen in 1-g samples of nuclear-grade plutonium dioxide.

### 12. Summary of Test Method

12.1 The sample is dissolved in hydrochloric acid by the sealed tube method or by phosphoric acid hydrofluoric acid solution, after which the solution is made basic with sodium hydroxide and nitrogen is separated as ammonia by steam distillation. Nessler reagent is added to the distillate to form the yellow ammonium complex and the absorbance of the solution is measured at approximately 430 nm (4, 5).

### 13. Apparatus

13.1 *Distillation Apparatus*, see Fig. 1.

13.2 *Spectrophotometer*, visible range.

### 14. Reagents

14.1 *Ammonium Chloride ( $\text{NH}_4\text{Cl}$ )*—Dry salt for 2 h at  $110$  to  $120^{\circ}\text{C}$ .

14.2 *Boric Acid Solution (40 g/L)*—Dissolve 40 g of boric acid ( $\text{H}_3\text{BO}_3$ ) in 800 mL of hot water. Cool to approximately  $20^{\circ}\text{C}$  and dilute to 1 L.

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

14.4 *Hydrofluoric Acid (48 %)*—Concentrated hydrofluoric acid (HF).

14.5 *Nessler Reagent*—To prepare, dissolve 50 g of potassium iodide (KI) in a minimum of cold ammonia-free water, approximately 35 mL. Add a saturated solution of mercuric chloride ( $\text{HgCl}_2$ , 22 g/350 mL) slowly until the first slight precipitate of red mercuric iodide persists. Add 400 mL of 9 N sodium hydroxide solution and dilute to 1 L with water, mix, and allow the solution to stand overnight. Decant supernatant liquid and store in a brown bottle.

14.6 *Nitrogen Standard Solution (1 mL = 0.01 mg N)*—Dissolve 3.819 g of  $\text{NH}_4\text{Cl}$  in water and dilute to 1 L. Transfer 10 mL of this solution to a 1-L volumetric flask and dilute to volume with ammonia-free water.

14.7 *Sodium Hydroxide (9 N)*—Dissolve 360 g of sodium hydroxide (NaOH) in ammonia-free water and dilute to 1 L.

14.8 *Sodium Hydroxide (50 %)*—Dissolve sodium hydroxide (NaOH) in an equal weight of water.

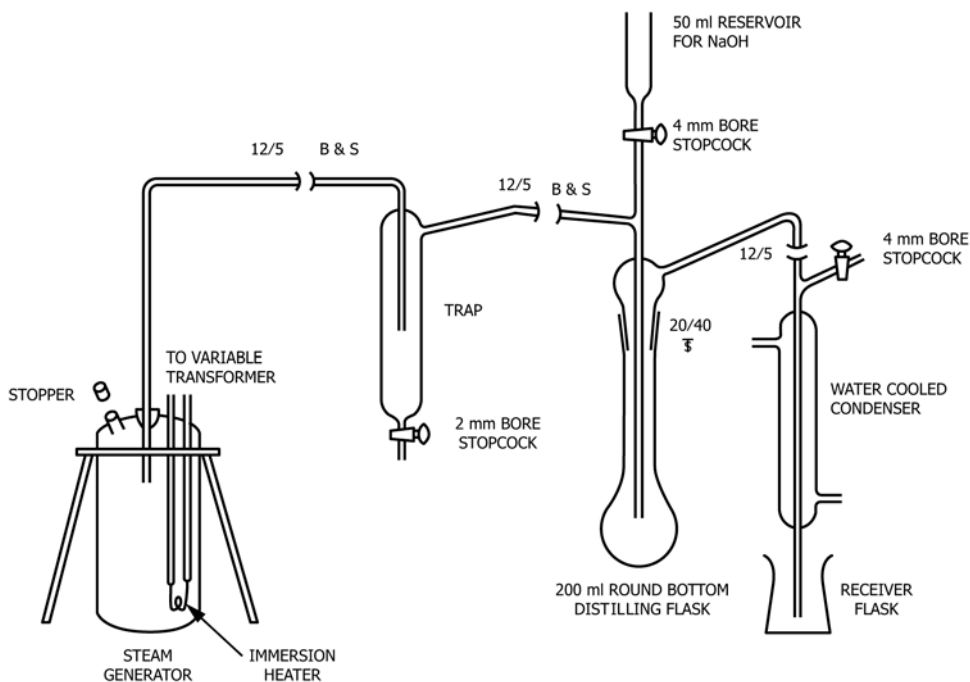


FIG. 1 Distillation Apparatus

14.9 *Water (Ammonia-free)*—To prepare, pass distilled water through a mixed-bed resin demineralizer and store in a tightly stoppered chemical-resistant glass bottle.

## 15. Precautions

15.1 The use of ammonia or other volatile nitrogenous compounds in the vicinity can lead to serious error. The following precautionary measures should be taken: (1) Clean all glassware and rinse with ammonia-free water immediately prior to use, and (2) avoid contamination of the atmosphere in the vicinity of the test by ammonia or other volatile nitrogenous compounds.

## 16. Procedure

### 16.1 Dissolution of Sample:

16.1.1 Transfer a weighed sample in the range from 1.0 to 1.5 g to a 50-mL beaker.

16.1.2 Crush the pellet samples to a particle size of 1 mm or less in a diamond mortar.

16.1.3 To the crushed sample add 5 mL of HCl and 3 drops of HF. Heat to put sample into solution.

NOTE 2—Concentrated phosphoric acid or mixtures of phosphoric acid and hydrofluoric acids or of phosphoric and sulfuric acids may be used for the dissolution of plutonium dioxide. Such acids may require a purification step in order to reduce the nitrogen blank before being used in this procedure.

### 16.2 Distillation:

16.2.1 Quantitatively transfer the sample solution to the distilling flask of the apparatus. Add 20 mL of ammonia-free water; then clamp the flask into place on the distillation apparatus (see Fig. 1).

16.2.2 Turn on the steam generator, but do not close with the stopper.

16.2.3 Add 5 mL of 4 %  $\text{H}_3\text{BO}_3$  solution to a 50-mL graduated flask and position this trap so that the condenser tip is below the surface of the  $\text{H}_3\text{BO}_3$  solution.

16.2.4 Transfer 20 mL of 50 % NaOH solution to the funnel in the distillation head.

16.2.5 When the water begins to boil in the steam generator, replace the stopper and slowly open the stopcock on the distilling flask to allow the NaOH solution to run into the sample solution. (**Warning**—The NaOH solution must be added slowly to avoid a violent reaction, which may lead to a loss of sample.)

16.2.6 Steam distill until 25 mL of distillate has collected in the trap.

16.2.7 Remove the trap containing the distillate from the distillation apparatus and remove the stopper from the steam generator.

16.2.8 Transfer the cooled distillate to a 50-mL volumetric flask.

16.2.9 Prepare a reagent blank solution by following 16.1 through 16.2.8.

### 16.3 Measurement of Nitrogen:

16.3.1 Add 1.0 mL of Nessler reagent to each of the distillates collected in 16.2.8 and 16.2.9 and dilute to volume with ammonia-free water, mix, and let stand 10 min.

16.3.2 Measure the absorbance of the solutions at 430 nm in a 1-cm cell. Use water as the reference.

### 16.4 Calibration Curve:

16.4.1 Add 0, 5, 10, 25, 50, 100, and 150  $\mu\text{g}$  of N from the nitrogen standard solution to separate distilling flasks. Then add 5 mL of HCl and 3 drops of HF plus 20 mL of ammonia-free water to each flask.

16.4.2 Process each solution by the procedure in 16.2 through 16.3 (omit 16.2.9).

16.4.3 Correct for the reagent blank reading and plot the absorbance of each standard against the micrograms of nitrogen per 50 mL of solution.

## 17. Calculation

17.1 From the calibration chart, read the micrograms of nitrogen corresponding to the absorbance of the sample solution.

17.1.1 Calculate the nitrogen content,  $N$ , micrograms per gram, of the sample as follows:

$$N = (A - B)/W \quad (1)$$

where:

$A$  = micrograms of nitrogen from sample plus reagents,  
 $B$  = micrograms of nitrogen in blank, and  
 $W$  = sample mass, g.

## 18. Precision

18.1 The estimated relative standard deviation for a single test measurement by this test method is 20 % for 3 µg of nitrogen and 3 % for 50 to 90 µg of nitrogen.

## CARBON (TOTAL) BY DIRECT COMBUSTION-THERMAL CONDUCTIVITY

## 19. Scope

19.1 This test method covers the determination of 10 to 200 µg of residual carbon in nuclear-grade plutonium dioxide.

## 20. Summary of Test Method

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

## 21. Interferences

21.1 There are no known interferences not eliminated by the purification system.

## 22. Apparatus

22.1 *Commercial Combustion Apparatus*, suitable for the carbon determination, is often modified to facilitate maintenance and operation within the glove box which is required for all work with plutonium materials.

22.1.1 *Combustion Apparatus*—This apparatus shall consist of an induction furnace suitable for operation at 1600°C, with a purification train, a catalytic furnace, carbon dioxide trap, thermal conductivity cell with appropriate readout equipment, and a regulated supply of oxygen and helium.

22.1.2 *Combustion Tubes*—Quartz combustion tubes with integral baffle shall be used.

22.1.3 *Crucibles*—Expendable alumina or similar refractory crucibles shall be used. The use of crucible covers is optional. Satisfactory operation with covers must be established by analysis of standards. Crucibles and covers (if used) must be ignited at a temperature of 1000°C or higher for a time sufficient to produce constant blank values.

22.1.4 *Accelerators*—Granular tin and tin foil accelerators shall be used as required to obtain satisfactory results. The criterion for satisfactory results is the absence of significant additional carbon release upon re-combustion of the specimen.

22.1.5 *Catalytic Furnace and Tube*—This unit, which is used to ensure complete oxidation of CO to CO<sub>2</sub>, consists of a tube containing copper oxide and maintained at a temperature of 300°C by a small furnace.

22.1.6 *Carbon Dioxide Purifiers*—The purifiers that follow the combustion tube must remove finely divided solid metallic oxides and oxides of sulfur and selenium, dry the gases before they enter the CO<sub>2</sub> trap, and protect the absorber from outside effects. Finely divided solid metal oxides are removed from the gases during their passage through the quartz wool. The SO<sub>2</sub> given off by materials containing sulfur is removed by MnO<sub>2</sub> and any water vapor is absorbed in a tube containing Mg-(ClO<sub>4</sub>)<sub>2</sub>. Hot copper oxide converts carbon monoxide to carbon dioxide. Additional components in the purification train may be required when materials containing very high amounts of sulfur or of halides are being analyzed. The materials used in the purification train must be checked frequently to ensure that their absorbing capacity has not been exhausted.

22.2 *Vibratory Sample Pulverizer Apparatus*, capable of reducing ceramic materials such that 90 % or more of the particles are less than 149 µm (equivalent to a -100-mesh powder). A stainless steel capsule and mixing ball must be used in order to reduce the contamination of the sample with carbon.

## 23. Reagents and Materials

23.1 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) to be used in the oxygen purification train.

23.2 *Quartz Wool*, to use as a dust trap at top of combustion tube.

23.3 *Standard Materials*—Certified reference material standards from a national standards body such as the U.S. National Institute for Standards and Technology (NIST) or equivalent. Certified materials in steel matrices (steel pins, steel rings, steel granules, and steel powder) ranging from 5 µg carbon/g sample to 1500 µg carbon/g sample are available and have been found satisfactory.

## 24. Sampling

24.1 *Sample Size*—The normal sample size for plutonium dioxide fuel materials shall be 1 g. If necessary, this amount shall be altered as required to contain less than 200 µg of carbon.

24.2 *Sample Preparation*—Pellet or particulate samples shall be reduced such that approximately 90 % of the particles

are less than 149  $\mu\text{m}$  (equivalent to approximately a -100-mesh powder) prior to the weighing of the specimens. Exposure of the powdered sample to atmospheric carbon dioxide should be minimized by storage of the powder in a closed vial. Refer to Sections 8 and 10 for guidance in handling plutonium dioxide.

## 25. Preparation of Apparatus

25.1 *Analysis System Purge*—After having properly set the operating controls of the instrument system, condition the apparatus by combustion of several blanks prepared with the sample crucible and accelerator in the amount to be used with the test specimen analyses. Successive blank values should approach a constant value, allowing for normal statistical fluctuations. The instrument should be adjusted for a 2-min combustion period.

## 26. Calibration

26.1 *Preparation of Standards for Combustion*—Mix a weighed portion of an accelerator and an accurately weighed portion of approximately 1 g of reference material with a certified carbon value of about 0.005 % in each of three sample crucibles. Repeat with a reference material with a certified carbon value of about 0.5 %, using an accurately weighed portion of approximately 30 to 40 mg.

NOTE 3—These portions represent about 50  $\mu\text{g}$  and 200  $\mu\text{g}$  of carbon, respectively.

26.1.1 Weigh the steel into a tared container, such as a small nickel-sample boat, obtaining the mass to the nearest 0.01 mg. Transfer the chips to a 30-mm square of aluminum foil (previously acetone washed), and fold the foil into a wrapper with the aid of stainless steel tongs and spatulas. The foil should not be touched by the hands. Place the wrapped standard in a numbered glass vial and transfer to the analyzer glove box.

26.2 *Combustion of Standards*—Load and combust the standards and record the results. Adjust the calibration controls in such a way as to produce the correct readout value on the direct readout meter. Combust additional standards as required to produce the correct direct readout. As an alternative, consider the readout digits as arbitrary numbers and prepare a calibration curve of known micrograms of carbon *versus* the readout value. A strip chart recorder connected to present the integrated value of the carbon dioxide response signal is helpful in detecting and correcting for analyzer drift and noise.

## 27. Procedure

27.1 Pulverize the pellet samples for 15 s in the stainless steel capsule of the sample pulverizer.

27.2 Weigh a sample crucible containing the required amount of accelerator to the nearest 0.01 g.

27.3 Transfer the sample powder, not to exceed 1 g or of such size as to give not more than 200  $\mu\text{g}$  of carbon, to the crucible. Weigh the crucible and contents to the nearest 0.01 g and find the specimen mass by difference.

27.4 Mix the specimen powder and the accelerator with a stainless steel spatula.

27.5 Load the sample crucible into the furnace and combust the specimen for 2 min.

27.6 Remove the sample crucible and examine for evidence of incomplete combustion. The crucible contents should be a uniform fused mass.

## 28. Calculation

28.1 Calculate the concentration of carbon in the sample by dividing the net micrograms of carbon found by the sample mass, expressed in grams, as follows:

$$C, \mu\text{g/g} = (C_s - C_b)/W \quad (2)$$

where:

$C_s$  = micrograms of carbon in the sample and reagents,

$C_b$  = micrograms of carbon in reagent blank, and,

$W$  = grams of oxide sample.

## 29. Precision

29.1 The relative standard deviation of this test method is approximately 10 % for a concentration of 30  $\mu\text{g}$  of carbon/g of sample.

## TOTAL CHLORINE AND FLUORINE BY PYROHYDROLYSIS

## 30. Scope

30.1 This test method covers the determination of 5 to 100  $\mu\text{g/g}$  of chlorine and 1 to 100  $\mu\text{g/g}$  of fluorine in 1-g samples of nuclear-grade plutonium dioxide.

## 31. Summary of Test Method

31.1 A 1 to 2-g sample of plutonium dioxide is pyrohydrolyzed at 950°C with a stream of moist air or oxygen. The halogens are volatilized as acids during the pyrohydrolysis and are trapped as chloride and fluoride in a buffered solution. Several procedures are outlined for the measurement of chloride and fluoride in the resultant condensate. Chloride is measured by spectrophotometry, microtitrimetry, or with ion-selective electrodes and fluoride with ion-selective electrodes or spectrophotometry (6, 7).

## 32. Interferences

32.1 Bromide, iodide, cyanide, sulfide, and thiocyanate, if present in the condensate, would interfere with the spectrophotometric and microtitrimetric measurement of chloride. Bromide, iodide, sulfide, and cyanide interfere in the measurement of chloride with ion-selective electrodes, but have very little effect upon the measurement of fluoride with selective electrodes.

## 33. Apparatus (see Fig. 2 and Fig. 3 for examples)

33.1 *Gas Flow Regulator*—A flowmeter and a rate controller to adjust the flow of sparge gas between 1 to 3 L/min.

33.2 *Hot Plate*—A heater used to keep the water bubbler temperature between 50 and 90°C.

33.3 *Furnace*—A tube furnace that is capable of maintaining a temperature from 900 to 1000°C. The bore of the furnace should be about 32 mm (1¼ in.) in diameter and about 305 mm (12 in.) in length.

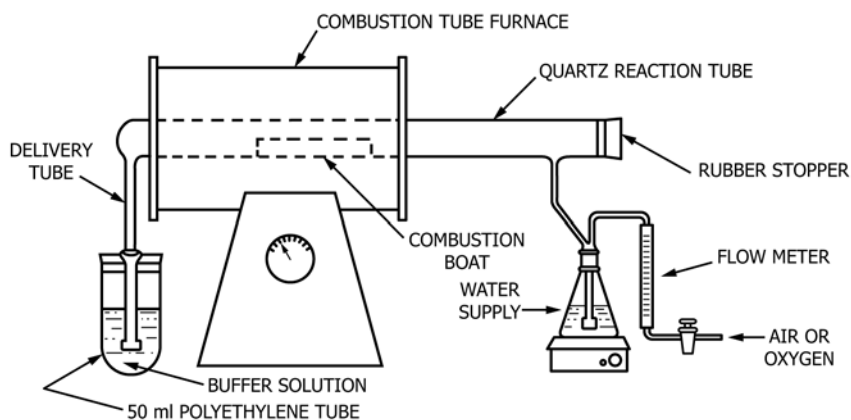


FIG. 2 Pyrohydrolysis Apparatus

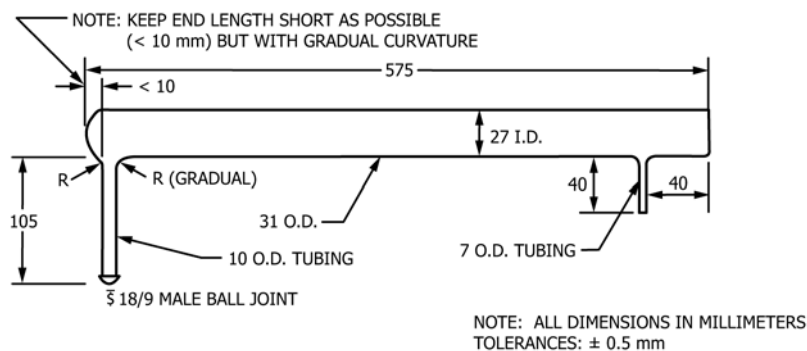


FIG. 3 Quartz Reaction Tube

33.4 *Reactor Tube*, made from fused-silica or platinum. The delivery tube should be a part of the exit end of the reactor tube and be within 51 mm (2 in.) of the furnace (see Fig. 2 for proper tube positioning).

33.5 *Combustion Boats*, made from fused-silica or platinum. A boat about 102 mm (4 in.) long is made by cutting lengthwise a silica tube 20 mm in diameter and flattening one end to provide a handle. A fused-silica inner sleeve for the reactor tube can facilitate the movement of the boat into the tube, prevent spillage, and thus prolong the life of the combustion tube.

33.6 *Collection Vessel*—A plastic graduate or beaker designed to maintain most of the scrubber solution above the tip of the delivery tube.

33.7 *Automatic Chloride Titrator*.

33.8 *Ion-Selective Electrodes*, chloride and fluoride.

33.9 *Reference Electrode*—Use a double-junction type electrode such as mercuric sulfate, sleeve-junction type electrode. Do not use a calomel electrode.

33.10 *Spectrophotometer*, ultraviolet to visible range and absorption cells. For a discussion on spectrophotometers and their use see Practice E60.

33.11 *pH Meter*, with an expanded scale having a sensitivity of 1 mV.

## 34. Reagents

34.1 *Accelerator*—Halogen-free uranium oxide ( $U_3O_8$ ) powder used as a flux to enhance the release of chloride and fluoride.

34.2 *Air or Oxygen*, compressed.

34.3 *Buffer Solution* (0.001 N)—Prepare by adding 50  $\mu$ L of concentrated glacial acetic acid ( $CH_3CO_2H$ , sp gr 1.05) and 0.1 g of potassium acetate ( $KC_2H_3O_2$ ) to 1 L of water.

34.4 *Chloride Standard Solution* (1 mL = 1 mg Cl)—Dissolve 1.65 g of sodium chloride (NaCl) in water and dilute to 1 L.

34.5 *Chloride, Standard Solution* (1 mL = 5  $\mu$ g Cl)—Prepare by diluting 5 mL of chloride solution (1 mL = 1 mg Cl) to 1 L with water.

34.6 *Ferric Ammonium Sulfate Solution* (0.25 M in 9 M nitric acid)—Dissolve 12 g of ferric ammonium sulfate ( $Fe(NH_4)(SO_4)_2 \cdot 12 H_2O$ ) in 58 mL of concentrated nitric acid ( $HNO_3$ , sp gr 1.42) and dilute to 100 mL with water.

34.7 *Fluoride, Standard Solution* (1 mL = 1 mg F)—Dissolve 2.21 g of sodium fluoride (NaF) in water and dilute to 1 L.

34.8 *Fluoride, Standard Solution* (1 mL = 10  $\mu$ g F)—Dilute 10 mL of fluoride solution (1 mL = 1 mg F) to 1 L with water.

34.9 *Gelatin Solution*—Add 6.2 g of dry gelatin mixture (60 parts of dry gelatin + 1 part of thymol blue + 1 part of thymol) to 1 L of hot water and heat with stirring until solution is clear.

34.10 *Lanthanum-Alizarin Complexone*—Dissolve 0.048 g of alizarin complexone (3-aminomethylalizarin-*N*, *N*-diacetic acid) in 100  $\mu\text{L}$  of concentrated ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), 1 mL of an ammonium acetate solution ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , 20 mass %), and 5 mL of water. Filter the solution through a high-grade, rapid-filtering, qualitative filter paper. Wash the paper with a small volume of water, and add 8.2 g of anhydrous sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2$ ) and 6 mL of concentrated glacial acetic acid ( $\text{CH}_3\text{CO}_2\text{H}$ , sp gr 1.05) to the filtrate. Add 100 mL of acetone while swirling the filtrate. Add 0.040 g of lanthanum oxide ( $\text{La}_2\text{O}_3$ ) dissolved in 2.5 mL of warm 2 *N* HCl. Mix the two solutions and dilute to 200 mL. After 30 min readjust the solution volume.

NOTE 4—A 0.1-g/L solution is prepared by dissolving 100 mg of the reagent in water and diluting with isopropyl alcohol to obtain a 60 % alcoholic medium.

34.11 *Mercuric Thiocyanate Solution*—Prepare a saturated solution by adding 0.3 g of mercuric thiocyanate ( $\text{Hg}(\text{SCN})_2$ ) to 100 mL of 95 % ethanol. Shake the mixture thoroughly for maximum dissolution of the solid. Filter the solution.

34.12 *Nitric Acid-Acetic Acid Solution* (1 *N* Nitric Acid and 4 *N* Acetic Acid)—Prepare by adding 64 mL of nitric acid ( $\text{HNO}_3$ , sp gr 1.42) to a 1-L volumetric flask which contains 500 mL of water. Swirl the solution in the flask and add 230 mL of acetic acid ( $\text{CH}_3\text{CO}_2\text{H}$ , sp gr 1.05). Dilute the solution with water to 1 L.

## 35. Pyrohydrolysis Procedure

35.1 Prepare the pyrohydrolysis apparatus for use as follows:

35.1.1 Regulate the gas flow between 1 and 3 L/min.

35.1.2 Adjust the temperature of the hot plate to heat the water to approximately 90°C.

35.1.3 Adjust the temperature of the furnace to  $950 \pm 50^\circ\text{C}$ .

35.1.4 Add 15 mL of buffer solution to the collection vessel and place around the delivery tube.

35.2 Weigh accurately, 1 to 2 g of the powdered plutonium dioxide and transfer to a combustion boat. If an accelerator,  $\text{U}_3\text{O}_8$ , is used mix 4 g with the sample before loading into the boat.

35.3 Place the boat containing the sample into the reactor tube and quickly close the tube. The boat should be in the middle of the furnace.

35.4 Allow the pyrohydrolysis to proceed for at least 30 min.

35.5 Remove the collection vessel and wash down the delivery tube with some buffer solution. Dilute the solution to 25 mL with the acetate buffer. Determine the chloride and fluoride by one or more of the measurement procedures covered in Section 36.

35.6 Remove the boat from the reactor tube and dispose of the sample residue.

35.7 Run a pyrohydrolysis blank with halogen-free  $\text{U}_3\text{O}_8$  by following the procedures, given in 35.3 – 35.6.

## 36. Measurement of Chloride and Fluoride

36.1 *Determination of Chloride by Spectrophotometry:*

36.1.1 Prepare a calibration curve by adding 0, 1, 2, 5, and 10 mL of the chloride solution (1 mL = 5  $\mu\text{g}$  Cl) to separate 25-mL flasks. Dilute each to 20 mL with buffer solution, and add 2 mL of the ferric ammonium sulfate solution and 2 mL of the mercuric thiocyanate solution. Mix the solution and dilute to 25 mL with water. Mix the solutions again and allow them to stand 10 min. Transfer some of the solution from the flask to a 1-cm absorption cell and read the absorbance at 460 nm using water as the reference liquid. Plot the micrograms of Cl per 25 mL *versus* the absorbance reading.

36.1.2 To determine Cl in the pyrohydrolysis condensate transfer 15 mL of the buffer solution to a 25-mL volumetric flask. Add 2 mL of the ferric ammonium sulfate solution and 2 mL of the mercuric thiocyanate solution. Mix the solutions, dilute to volume with water, and mix again. Allow the solution to stand 10 min. Transfer some of the solution from the flask to a 1-cm absorption cell and read the absorbance at 460 nm *versus* water as the reference. Read the micrograms of Cl present from the calibration curve.

NOTE 5—A calibration curve can be prepared by drying measured aliquots of a chloride solution on some halogen-free  $\text{U}_3\text{O}_8$  and proceeding through pyrohydrolysis steps.

36.1.3 Calculate the chlorine, Cl,  $\mu\text{g/g}$ , as follows:

$$\text{Cl, } \mu\text{g/g} = (A - B)V_{1/WV_2} \quad (3)$$

where:

*A* = micrograms of chlorine in aliquot measured,

*B* = micrograms of chlorine in blank,

*W* = grams of  $\text{PuO}_2$  pyrohydrolyzed,

$V_1$  = millilitres of scrub solution, and

$V_2$  = aliquot of scrub solution analyzed, mL.

36.2 *Determination of Chloride by Amperometric Microtitrimetry:*

36.2.1 Calibrate the titrimeter by adding 5 mL of the buffer solution, 1 mL of the nitric acid-acetic acid solution, and 2 drops of the gelatin solution to a titration cell. Pipet 50  $\mu\text{L}$  of the chloride solution (1 mL = 1 mL Cl) into the titration cell. Place the cell on the chloride titrator and follow the manufacturer's suggested sequence of operations for chloride (Note 6). Record the time required to titrate 50  $\mu\text{g}$ . Run a reagent blank titration.

NOTE 6—The Cl-analyzer generates silver ions which react to precipitate the chloride ion. The instrument uses an amperometric end point to obtain an automatic shut-off of the generating current at a pre-set increment of indicator current. Since the rate of generating silver ion is constant, the amount of chloride precipitated is proportional to the time required for the titration.

36.2.2 Determine Cl in the pyrohydrolysis-scrub solution by adding 5 mL to a titration cell which contains 1 mL of the nitric acid-acetic acid solution and 2 drops of the gelatin solution.

36.2.3 Place the cell in position on the titrator. Start the titrator and record the time required to titrate the Cl present.

36.2.4 Calculate the chlorine as follows:

$$\text{Cl}, \mu\text{g/g} = V_1 F (T_s - T_B) / V_2 W \quad (4)$$

where:

$V_1$  = volume of scrub solutions = 25,  
 $V_2$  = aliquot of scrub solution analyzed, mL,  
 $F$  =

$$\frac{\mu\text{Cl standard titrated}}{\text{titration time of standard} - \text{titration time of blank}}$$

or

$$F = 50 / (T_{\text{Cl}} - T_B), \quad (5)$$

$T_s$  = titration time to titrate sample and blank,  
 $T_{\text{Cl}}$  = titration time to titrate 50  $\mu\text{g}$  of Cl and blank,  
 $T_B$  = titration time to titrate reagent blank, and  
 $W$  = grams of  $\text{PuO}_2$  pyrohydrolyzed.

### 36.3 Determination of Chloride and Fluoride with Ion-Selective Electrodes:

36.3.1 Preparation of the calibration curves requires the assembly of the meter and the ion-selective electrode with a suitable reference electrode. From these standards take the millivolt readings for each ion-selective electrode and determine the halogen content per 25 mL *versus* millivolts, using computer software or a plot on semi-log paper. Prepare a series of standards in acetate buffer solution by pipeting aliquots of the halogen standards into separate 25-mL flasks ranging in concentrations as follows:

Cl from 10 to 100  $\mu\text{g}/25 \text{ mL}$

F from 5 to 100  $\mu\text{g}/25 \text{ mL}$

36.3.2 Determine the Cl and F in the scrub solution from the pyrohydrolysis by using the appropriate ion-selective electrode. Record the micrograms of Cl or F from the calibration curve and calculate the halide as follows:

$$\text{Cl or F}, \mu\text{g/g} = (H_s - H_b) / W \quad (6)$$

where:

$H_s$  = halide in aliquot of scrub solution + blank,  $\mu\text{g}$ ,  
 $H_b$  = halide in pyrohydrolysis blank,  $\mu\text{g}$ , and  
 $W$  = sample mass, g.

### 36.4 Determination of Fluoride by Spectrophotometry:

36.4.1 Prepare a calibration curve by adding to separate 10-mL flasks 0, 50, 100, 200, 500, and 1000  $\mu\text{L}$  of the fluoride solution (1 mL = 10  $\mu\text{g}$  F). Add 2.0 mL of the lanthanum-alizarin complexone solution and dilute to volume with water. Mix and let stand 1 h. Read the absorbance at 622 nm *versus* the reagent blank. Plot the micrograms of F per 10 mL *versus* absorbance reading.

36.4.2 Measure F in the pyrohydrolysis scrub solution by pipeting 5 mL into a 10-mL volumetric flask. Add 2.0 mL of the lanthanum-alizarin complexone and dilute to volume. Mix and let stand 1 h. Read the absorbance at 622 nm *versus* a reagent blank and obtain the fluoride content from the calibration curve.

36.4.3 Calculate the fluorine concentration,  $F$ , in the  $\text{PuO}_2$  sample as follows:

$$F, \mu\text{g/g} = [(F_s - F_b) / W] \times V_1 / V_2 \quad (7)$$

where:

$F_s$  = fluorine in aliquot of scrub solution + the blank,  $\mu\text{g}$ ,  
 $F_b$  = micrograms of fluorine in pyrohydrolysis blank,  
 $V_1$  = total volume of the scrub solution, mL,  
 $V_2$  = aliquot of scrub solution analyzed, mL, and  
 $W$  = grams of  $\text{PuO}_2$  sample.

36.5 *Determination of Chloride and Fluoride by Ion Chromatography*—Determine the Cl and F in the scrub solution from the pyrohydrolysis in accordance with Test Method D4327. Record the micrograms of Cl or F from the calibration curve and calculate the halide using Eq 6.

## 37. Precision

37.1 The relative standard deviations for the measurements of fluorine are approximately 7 % for the range from 5 to 50  $\mu\text{g/g}$  and 10 % for the range from 1 to 5  $\mu\text{g/g}$ . The relative standard deviations for the measurements of chlorine vary from 5 % at the 5 to 50- $\mu\text{g/g}$  level up to 10 % below the 5- $\mu\text{g/g}$  range.

## SULFUR BY DISTILLATION SPECTROPHOTOMETRY

## 38. Scope

38.1 This test method covers the determination of sulfur in the concentration range from 10 to 600  $\mu\text{g/g}$  for samples of nuclear-grade plutonium dioxide powders or pellets.

## 39. Summary of Test Method

39.1 Sulfur is measured spectrophotometrically as Lauth's Violet following its separation by distillation as hydrogen sulfide (8). Higher oxidation states of sulfur are reduced to sulfide by a hypophosphorous-hydriodic acid mixture, the hydrogen sulfide is distilled into zinc acetate, and *p*-phenylenediamine and ferric chloride are added to form Lauth's Violet. The quantity of sulfur is calculated from the measured absorbance at 595 nm and the absorbance per microgram of sulfur obtained for calibration materials having known sulfur contents. The relative standard deviation ranges from 12 to 3 % for the concentration range from 10 to 600  $\mu\text{g}$  of sulfur per gram of sample.

## 40. Interference

40.1 None of the impurity elements interfere when present in amounts up to twice their specification limits for plutonium dioxide.

## 41. Apparatus

41.1 *Boiling Flask*, adapted with a gas inlet line and fitted with a water-cooled condenser and delivery tube.

41.2 *Spectrophotometer*, with matched 1-cm cells.

41.3 *Sulfur*, distillation apparatus (see Fig. 4 for example).

## 42. Reagents

42.1 *Argon Gas*, cylinder.

42.2 *Ferric Chloride Solution*, 2 %  $\text{FeCl}_3$  in 6 M HCl.

42.3 *Formic Acid* ( $\text{HCOOH}$ ), redistilled.

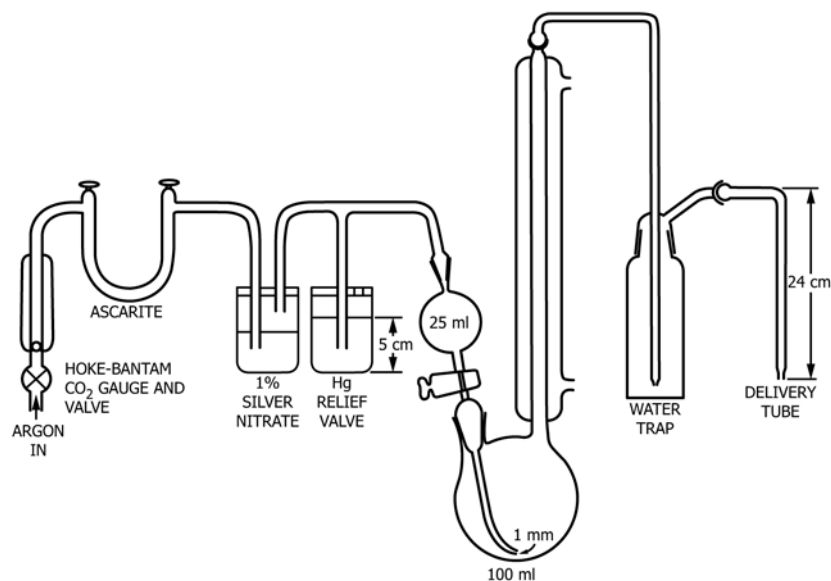


FIG. 4 Sulfur Distillation Apparatus

42.4 *Hydriodic-Hypophosphorous Acid Reducing Mixture*—Mix 400 mL of 7.6 *M* hydriodic acid (HI) with 200 mL of hypophosphorous acid ( $\text{H}_3\text{PO}_2$ , 31 %) and boil under reflux for 30 min with a continuous argon sparge. Test for sulfur content by analyzing a 15-mL aliquot as described in procedure. Reboil if necessary to reduce the sulfur content to below 1  $\mu\text{g/mL}$ .

42.5 *Hydrochloric Acid (0.6 M)*—Dilute 10 mL of 12 *M* hydrochloric acid (HCl) to 200 mL with water.

42.6 *Hydrochloric Acid (3 M)*—Dilute 50 mL of 12 *M* HCl to 200 mL with water.

42.7 *Hydrochloric Acid (6 M)*—Dilute 100 mL of 12 *M* HCl to 200 mL with water.

42.8 *Hydrochloric Acid (12 M)*—Analyze an aliquot of HCl (sp gr 1.19) for sulfur content. Use only a reagent in which the sulfur content is less than 1  $\mu\text{g}/10\text{ mL}$  and prepare the diluted acids with this reagent.

42.9 *Hydrofluoric Acid (HF)*, 48 %.

42.10 *Hydroxylamine Hydrochloride* ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ), 20 % aqueous solution.

42.11 *Nitric Acid (15.6 M)*, 70 %  $\text{HNO}_3$ .

42.12 *p-phenylenediamine (1 %)*—Dissolve 1 g of *p*-phenylenediamine in 100 mL of 0.6 *M* HCl.

42.13 *Silver Nitrate* ( $\text{AgNO}_3$ ), 1 % aqueous solution.

42.14 *Sulfur Calibration Solution* (1 mL = 5  $\mu\text{g S}$ )—Dissolve 2.717 g of dry potassium sulfate ( $\text{K}_2\text{SO}_4$ ) in water and dilute to 1 L. Dilute 2.00 mL to 200 mL with water.

42.15 *Zinc Acetate Solution (4 %)*—Dissolve 20 g of zinc acetate ( $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ ) in 500 mL of water and filter.

### 43. Calibration

43.1 Use aliquots of standard sulfur solution (1 mL = 5  $\mu\text{g S}$ ) to test the method and check the apparatus. Ideally, blends

of oxides and sulfur (20 to 600  $\mu\text{g S/g}$ ) should be analyzed to simulate actual sample conditions.

43.2 Prepare a calibration curve of absorbance *versus* sulfur (using aliquots of the sulfur standard solution) covering a concentration range from 5 to 50  $\mu\text{g}/50\text{ mL}$ .

### 44. Procedure

44.1 Pulverize plutonium dioxide pellets in a mixer-mill with a tungsten carbide container and a tungsten carbide ball.

44.2 Transfer a sample, weighed to  $\pm 0.2\text{ mg}$ , to a 20-mL beaker or a 30-mL platinum dish. Use a 0.5-g sample when the expected level of sulfur is 100  $\mu\text{g/g}$  or less.

44.3 Add 5 mL of 15.6 *M*  $\text{HNO}_3$  and 3 to 4 drops of 28 *M* HF and heat the solution below its boiling point. Watch glasses or platinum lids are recommended to avoid spattering.

44.4 Add additional amounts of  $\text{HNO}_3$  and HF acids until the sample dissolves.

NOTE 7—The sealed-tube technique (4) is an alternate method that may be used to advantage for the dissolution of some samples.

44.5 Evaporate the solution just to dryness, but do not fume intensely to dryness.

44.6 Add dropwise 0.5 mL of formic acid, and heat the solution at a moderate heat until the vigorous reaction subsides and gases are no longer evolved.

NOTE 8—The reduction of  $\text{HNO}_3$  by formic acid is vigorous. Keep the dish or beaker covered with a watch glass between additions of formic acid.

44.7 Rinse the cover glass with water. Add 0.5 mL of formic acid and slowly evaporate the rinse and sample solution to dryness. (**Warning**—Nitrate must be completely removed because it reacts explosively with the reducing acid.)

44.8 Dissolve the residue in a minimum volume of 3 *M* HCl and dilute to approximately 5 mL with water. Heat to just

below the boiling point and add 20 drops of hydroxylamine solution (Pu (III) blue is formed).

44.9 Add 30 mL of water to the trap of the distillation apparatus (Fig. 4) and insert the trap tube.

44.10 Pipet 10.0 mL of zinc acetate solution into a 50-mL glass-stoppered graduated cylinder, dilute to 35 mL with water, and position the cylinder so the end of the delivery tube is immersed in the solution.

44.11 Transfer the sample solution (71.8), with a minimum of water rinses, to the distillation flask and insert the reducing-acid delivery tube.

44.12 Add 15 mL of the reducing acid mixture and 10 mL of 12 M HCl to the delivery bulb, insert the argon sweep gas tube, and start the flow of the reducing acid mixture to the distillation flask.

44.13 Adjust the flow rate of argon to 100 cm<sup>3</sup> min; then turn on the heating mantle and boil the solution for 35 min.

44.14 Disconnect the distillate delivery tube, and rinse it with 2.00 mL of 3 M HCl followed by approximately 2 mL of water, collecting these rinses in the zinc acetate solution. Zinc sulfide formed inside the tube is rinsed into the zinc acetate solution.

44.15 Pipet 1.00 mL of 1 % *p*-phenylenediamine into the solution and mix rapidly by swirling. Pipet 1.00 mL of ferric chloride solution, and again mix rapidly.

NOTE 9—Rapid mixing after each reagent addition prevents formation of a brown reduction product that interferes with the spectrophotometric measurement.

44.16 Dilute to 50 mL with water, stopper the cylinder, mix the solution, and let stand 1 h.

44.17 Measure the absorbance within 10 min at a wavelength of 595 nm *versus* a reagent reference.

## 45. Calculations

45.1 Calculate the sulfur, S, µg/g, as follows:

$$S = (S - B)/W \quad (8)$$

where:

*S* = micrograms of S in sample,  
*B* = micrograms of S in blank, and  
*W* = grams of sample.

## 46. Precision

46.1 The relative standard deviations in analyzing 0.1-g samples are 6 to 3 % for the range from 50 to 600 µg/g and in analyzing 0.5-g samples are 12 to 5 % for the range from 10 to 20 µg/g.

## PLUTONIUM ISOTOPIC ANALYSIS BY MASS SPECTROMETRY

(This test method was discontinued in 1980 and replaced by Sections 88 to 96.)

## RARE EARTH ELEMENTS BY SPECTROSCOPY

(Test Methods C1432 or C1637 may be used instead of the method in Sections 47 to 54 with appropriate sample preparation, such as Practice C1168, and instrumentation.)

## 47. Scope

47.1 This test method covers the determination of dysprosium, europium, gadolinium, and samarium in plutonium dioxide (PuO<sub>2</sub>) in concentrations of 0.1 to 10 µg/g of PuO<sub>2</sub>.

## 48. Summary of Test Method

48.1 PuO<sub>2</sub> is dissolved in a nitric-hydrofluoric acid (HNO<sub>3</sub>-HF) mixture and evaporated to dryness. The residue is redissolved in dilute HNO<sub>3</sub>, and the plutonium is extracted into 30 % tributyl phosphate in *n*-hexane. The aqueous phase is treated with yttrium carrier and HF and the resulting rare earth precipitate separated by filtration. The fluoride precipitate is ignited, mixed with graphite, and excited with a d-c arc. An argon atmosphere containing approximately 20 % oxygen envelopes the electrode system. The spectra of samples and standards are recorded on photographic plates, and concentrations are determined by visual comparison.

## 49. Interferences

49.1 Plutonium plus americium in excess of 3 mg in the separated sample will contribute a high background and suppress rare-earth element intensities.

49.2 Calcium and other alkaline earths interfere in concentrations in excess of 100 µg/g PuO<sub>2</sub>. Compensation for this interference may be made by the addition of appropriate amounts of interfering elements up to 1000 µg/g to the standards before separation. This changes the detection limit for rare-earth elements to 0.15 µg/g PuO<sub>2</sub>.

## 50. Apparatus

50.1 *Excitation Source*—A stable d-c arc source unit capable of providing 15 A.

50.2 *Atmosphere Chamber*—A chamber or device that is capable of providing a controlled atmosphere about the sample electrodes during excitation. A typical chamber is shown in Fig. 5. Provision should be made for the gas to flow from the quartz window, past the electrodes, to the chamber exit. The inner diameter of the chamber should be large enough not to restrict the aperture of the spectrograph field lens. Gas is allowed to escape where the electrodes enter the chamber.

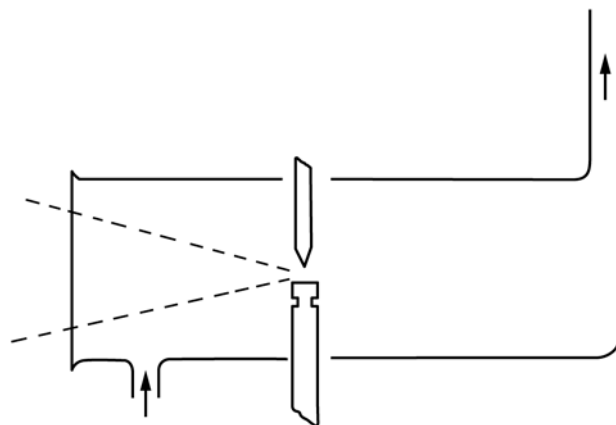


FIG. 5 Schematic Diagram of Atmosphere Chamber

Clearance between the electrodes and the chamber walls is not critical. The total length should be a minimum of 102 mm (4 in.) and a maximum to allow convenient use of the arc stand.

50.3 *Spectrograph*—A grating spectrograph having a minimum effective resolution of 50 000 and a reciprocal linear dispersion of at least 0.4 nm/mm at the focal plane and grating angle employed.

50.4 *Photographic Processing Equipment*—Developing, fixing, washing and drying equipment should be used that conforms to the requirements of Practices E115.

50.5 *Projection Comparator*, capable of displaying standard and sample spectra for visual comparison.

50.6 *Filter Assembly*—A polyethylene or fluorocarbon filter assembly for 25-mm diameter filter membranes.

50.7 *Filters*, 0.45- $\mu$ m with filter pads, 25-mm diameter.

50.8 *Small Vacuum Pump or Aspirator*.

50.9 *Muffle Furnace*, capable of heating to 900°C.

50.10 *Crucibles*, platinum, 15 to 30-mL capacity.

50.11 *Beakers*, TFE-fluorocarbon, 150-mL capacity.

50.12 *Separatory Funnels*, 125-mL capacity.

50.13 *Hotplate*.

50.14 *Heat Lamp*.

50.15 *Electrodes*, ASTM Type C-1 and S-14, as described in Practice E130 (withdrawn).

50.16 *Photographic Plates*.

## 51. Reagents

51.1 *Controlled Atmosphere*—80 % argon (Ar)-20 % oxygen (O<sub>2</sub>), premixed gas. In practice, the oxygen content may vary by  $\pm 5$  % without adverse effects.

51.2 *Graphite Powder*, spectroscopically pure, capable of passing through a 149  $\mu$ m (100-mesh) sieve.

51.3 *Hydrofluoric Acid* (HF), 48 % solution, analytical reagent grade.

51.4 *Hydrofluoric Acid Wash Solution*, 2.5 M HF.

51.5 *Hydrogen Peroxide* (H<sub>2</sub>O<sub>2</sub>), 30 % solution, analytical reagent grade.

51.6 *Nitric Acid* (HNO<sub>3</sub>), *hydrofluoric acid* mixture, (10 N HNO<sub>3</sub>-0.05 N HF).

51.7 *Nitric Acid*, *diluted* (4 N HNO<sub>3</sub>).

51.8 *Rare-Earth Element Solutions*—Prepare separate standard solutions of Dy, Eu, Gd, and Sm by dissolving accurately weighed quantities of preignited rare-earth oxides (99.9 % RE<sub>2</sub>O<sub>3</sub> or better) in minimum quantities of HNO<sub>3</sub>. Dilute each solution with water to a concentration of 1.0  $\mu$ g of rare-earth element per millilitre of solution.

51.9 *Tributyl Phosphate (TBP) in n-Hexane*<sup>10</sup>—30 % TBP in *n*-hexane. (**Warning**—This solution is flammable. Assure adequate ventilation.)

<sup>10</sup> A more stable diluent may be substituted for *n*-hexane provided it is shown that the results obtained are comparable.

51.10 *Uranium Standard Solution*—Dissolve 300 g of preignited uranium oxide (U<sub>3</sub>O<sub>8</sub>) (NBL CRM 129-A or its replacement, or equivalent reference material from another national standards body) in 500 mL of 4 N HNO<sub>3</sub>. Additional 4 N HNO<sub>3</sub> should be used, if required, to complete dissolution. Transfer to a 1-L container and add sufficient 4 N HNO<sub>3</sub> to adjust the volume to approximately 1 L. Uranium is used as a stand-in for plutonium.

51.11 *Working Standards*—Prepare a reagent blank and a minimum of four reference standard solutions, over the concentration range of interest, by adding 10 mL of standard uranium solution to 150-mL Erlenmeyer flasks. To the flasks for the reference standards add the appropriate amounts of each rare earth and thorium standard solution. Dilute with water or evaporate as necessary to adjust the volume to approximately 50 mL.

51.12 *Yttrium Carrier Solution*—Dissolve an accurately weighed quantity of preignited yttrium oxide (Y<sub>2</sub>O<sub>3</sub>) (99.99 % or better) in a minimum amount of concentrated HNO<sub>3</sub> and dilute with water to a concentration of 0.8 mg of yttrium per millilitre of solution.

## 52. Procedure

### 52.1 Preparation of Sample:

52.1.1 Dissolve duplicate 3.0  $\pm$  0.1-g portions of each sample in 30 mL of 10 N HNO<sub>3</sub>- 0.05 N HF in a 150-mL beaker.

52.1.2 Treat the sample solutions and reference standard solutions as follows:

52.1.2.1 Evaporate to dryness, at approximately 80°C, and redissolve the residue in 20 mL of 4 N HNO<sub>3</sub>.

52.1.2.2 Add 5 mL of yttrium carrier solution to each solution.

52.1.2.3 Add 5 drops of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and stir.

52.1.2.4 Transfer to a 125-mL separatory funnel with the aid of about 5 mL of 4 N HNO<sub>3</sub>, add 40 mL of 30 % TBP in *n*-hexane, and shake vigorously for 2 min.

52.1.2.5 Allow the phases to separate and discard the organic in a suitable waste container for later recovery of the plutonium.

52.1.2.6 Repeat the extraction with 40 mL of 30 % TBP in *n*-hexane two additional times, discarding the organic each time.

52.1.2.7 Transfer the aqueous phase to a 150-mL plastic or TFE-fluorocarbon beaker, rinse the separatory funnel with 10 mL of 4 N HNO<sub>3</sub>, and transfer the aqueous rinse to the beaker.

52.1.2.8 Add 10 mL of 48 % HF to each solution.

52.1.2.9 Digest the solutions for 40 to 60 min at 80  $\pm$  5°C, and immediately filter them through separate 25-mm 0.45- $\mu$ m plastic membrane filters mounted in a plastic filter assembly. A slight vacuum should be applied to facilitate filtration. Discard the solution to waste.

52.1.2.10 Carefully char on a hotplate or over a burner and ignite each precipitate in a platinum crucible, in a muffle furnace at 700  $\pm$  25°C for 20 min.

52.1.2.11 Add 15 mg of graphite powder to each ignited precipitate, and mix the material thoroughly.

52.1.2.12 Load each mixture into separate ASTM Type S-14 electrodes, and tamp the charges as they are loaded with a packing tool (Fig. 6) or the blunt end of an ASTM Type C-1 electrode cleaned with a tissue between samples.

#### 52.2 Spectrographic Procedure:

52.2.1 Place an ASTM Type C-1 electrode in the upper electrode holder.

52.2.2 Place a sample electrode in the lower electrode holder.

52.2.3 Adjust the electrode gap to 4.0 mm centered on the optical axis of the spectrograph; maintain this gap distance during the exposure.

52.2.4 Produce and record the spectrum under the following conditions.

52.2.4.1 Primary voltage, 230 V,

52.2.4.2 Current, 15-A dc (shorted),

52.2.4.3 Spectral region, 310 to 450 nm,

52.2.4.4 Slit width, 10  $\mu$ m,

52.2.4.5 Filter, 100 % transmission with 100/25 % T split field lens or rotating sector,

52.2.4.6 Atmosphere, 20 % oxygen - 80 % argon at a 3 L/min flow rate through the chamber,

52.2.4.7 Preburn, 0 s, and

52.2.4.8 Exposure, 35 s.

NOTE 10—The instructions given in this section apply to most spectrographs; however, some settings and adjustments may need to be varied, and depending on the particular equipment, additional preparation of the equipment may be required. It is not within the scope of an ASTM test method to prescribe the minute details of the apparatus preparation which differ not only for each manufacturer, but also often for different equipment from the same manufacturer. For a description of and further details of operation of a particular spectrograph, refer to the manufacturer's handbook.

#### 52.3 Photographic Processing:

52.3.1 Process the photographic plates in accordance with Practices E115.

### 53. Calculation

#### 53.1 Interpretation of Spectra:

53.1.1 The following spectral lines are used for analysis (see Note 11).

| Element    | Wavelength, nm   | Concentration Range, $\mu$ g/g |
|------------|------------------|--------------------------------|
| Dysprosium | 404.598          | 0.1 to 10                      |
| Europium   | 397.196, 390.710 | 0.1 to 10                      |
| Gadolinium | 342.247          | 0.1 to 10                      |
| Samarium   | 388.529, 425.640 | 0.15 to 10                     |

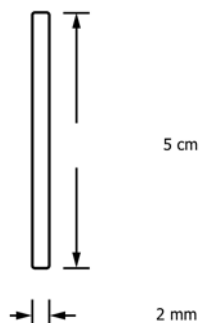


FIG. 6 Packing Tool (Stainless Steel)

NOTE 11—The lines listed have been proven satisfactory for the elements and concentration ranges described in the scope. Other analytical lines may be used provided it is shown that the results obtained are comparable.

53.1.2 Utilizing a comparator, visually compare the density of the analytical lines in the sample spectrum with the corresponding lines in the standard spectrum to obtain the concentration of each impurity in PuO<sub>2</sub>.

### 54. Precision

54.1 For the precision of the measurement by visual comparison, factor-of-two (that is,  $-1/2$  to  $+2$ ), reproducibility is reported at 0.1  $\mu$ g/g.

### TRACE ELEMENTS BY CARRIER-DISTILLATION SPECTROSCOPY

(Test Methods C1432 or C1637 (Impurities by ICP-AES) may be used instead of the method in Sections 55–62 with appropriate sample preparation and instrumentation.)

### 55. Scope

55.1 This test method covers the determination of 36 impurity elements in nuclear-grade plutonium dioxide (PuO<sub>2</sub>). The concentration ranges covered by the method and the analytical lines used for each element are listed in Table 1.

### 56. Summary of Test Method

56.1 Powdered PuO<sub>2</sub> is blended with sodium fluoride-cobalt oxide or silver chloride-palladium chloride and the mixture is pressed into a pellet. The pellet is placed in an electrode and d-c arced. The concentration of cobalt and palladium, and many other elements listed in Table 1, are estimated by visual comparison with suitable standards. The internal standard technique is used to determine aluminum, chromium, gallium, iron, and nickel with a NaF·Co<sub>2</sub>O<sub>3</sub> carrier while molybdenum, vanadium, and tungsten are determined with a AgCl·PdCl<sub>2</sub> carrier (8).

### 57. Apparatus

57.1 *Excitation Source*—A d-c arc source, 15 A (short-circuited).

57.2 *Spectrograph*—An instrument having a reciprocal linear dispersion of 0.512 nm/mm in first order from 440 to 780 nm, and 0.25 nm/mm in second order, from 210 to 410 nm. A direct-reading spectrograph of comparable quality may be substituted for the equipment listed, in which case the directions given by the manufacturer should be followed rather than those given in the succeeding steps of this procedure.

57.3 *Spark Stand*, located in a glove box.

57.4 *Photographic Development Equipment*, necessary to permit developing, fixing, washing, and drying operations to conform to Practices E115.

57.5 *Microphotometer*—An instrument with a precision of 1.0 % for transmittances between 5 and 90 % is required.

57.6 *Calculating Board*, useful for converting microphotometric readings to log intensity ratios.

**TABLE 1 Impurity Elements, Lines, and Concentration Limits**

| Element         | Wavelength, nm       | Concentration Range, ppm |
|-----------------|----------------------|--------------------------|
| Al              | 256.799 <sup>A</sup> | 10–500                   |
| Al              | 308.268 <sup>A</sup> |                          |
| Ag              | 328.068              | 1–250                    |
| As              | 234.984              | 10–250                   |
| Au              | 242.795              | 2.5–50                   |
| B               | 249.773              | 1–50                     |
| Ba              | 455.403              | 2.5–100                  |
|                 | (first order)        |                          |
| Be              | 234.861              | 0.5–25                   |
| Bi              | 306.772              | 2.5–100                  |
| Ca              | 393.367              | 10–1000                  |
| Cd              | 228.802              | 1–100                    |
| Co              | 240.725              | 10–1000                  |
| Co              | 304.400              |                          |
| Cu              | 324.754              | 1–250                    |
| Cr              | 283.563 <sup>A</sup> | 5–500                    |
| Fe              | 298.357 <sup>A</sup> | 10–1000                  |
| Ga              | 245.007 <sup>A</sup> | 1–500                    |
| Ga              | 294.364              |                          |
| In              | 303.936              | 2.5–100                  |
| K               | 766.491              | 3–1000                   |
|                 | (first order)        |                          |
| Mg              | 280.270              | 1–1000                   |
| Mn              | 279.827              | 5–250                    |
| Mo <sup>B</sup> | 313.259              | 5–250                    |
| Ni              | 300.249 <sup>A</sup> | 10–1000                  |
| P               | 255.328              | 100–1000                 |
| Pb              | 261.418              | 5–100                    |
| Pd              | 324.270              | 2.5–100                  |
| Sb              | 259.805              | 2.5–100                  |
| Si              | 251.432 <sup>A</sup> | 10–300                   |
| Sn              | 286.333              | 2.5–100                  |
| Sr              | 460.733              | 5–100                    |
|                 | (first order)        |                          |
| Ti              | 322.352              | 5–100                    |
| V <sup>B</sup>  | 318.398 <sup>A</sup> | 5–100                    |
| W <sup>B</sup>  | 272.435 <sup>A</sup> | 20–200                   |
| Zn              | 334.502              | 10–250                   |
| Zr              | 343.823              | 5–100                    |

<sup>A</sup> These elements are determined with the aid of a microphotometer.

<sup>B</sup> These elements are analyzed by using a AgCl carrier and PdCl<sub>2</sub> as an internal standard. Mix 20 mg of PdCl<sub>2</sub> with 10.0 g of AgCl. Add 80 mg of this mixture to 120 mg of PuO<sub>2</sub> sample-blend before loading 50-mg charges in a graphite electrode ASTM-Type-S-4.

**57.7 Pellet Press and Die**—The die should be capable of making a pellet 12.7 mm (½ in.) in diameter and 0.762 mm (0.030 in.) thick. The press should be capable of 27.6 MPa (4000 psi) pressure.

**57.8 Pulverizer Mixer.**

**57.9 Drying Oven,** with a temperature control required for a 370°C operation.

## 58. Reagents and Materials

**58.1 Cobalt (III) Oxide**—Particle size of powder should be less than 10 µm.

**58.2 Cobalt (III) Oxide-Sodium Fluoride Carrier (Co<sub>2</sub>O<sub>3</sub>·NaF)**—Weigh 5.000 g of NaF and add 0.0967 g of Co<sub>2</sub>O<sub>3</sub>, crush, and blend the material in a pulverizer mixer.

**58.3 Electrodes**—Upper ASTM Type C-1 and lower ASTM S-12 (6.4 mm (0.250 in.) in diameter and 38.1 mm (1.5 in.) long with a crater 4.22 mm (0.166 in.) in diameter and 4.22 mm deep), as described in Practice E130 (withdrawn).

**58.4 Sodium Fluoride Carrier (NaF)**—Particle size should be less than 10 µm.

**58.5 Plutonium Dioxide (PuO<sub>2</sub>)**—Powdered material of known impurity content suitable as a diluent for impurity element standards.

**58.6 Palladium Chloride (PdCl<sub>2</sub>)**, 99.99 % purity.

**58.7 Silver Chloride (AgCl)**, 99.99 % purity.

**58.8 Silver Chloride-Palladium Chloride Carrier (AgCl·PdCl<sub>2</sub>)**—Weigh 10.0 g of AgCl and add 20 mg of PdCl<sub>2</sub>. Blend this mixture in a mixer.

## 59. Calibration

**59.1** Follow Practice E116 for emulsion calibration and prepare an emulsion calibration curve.

**59.2** Prepare analytical curves by converting the transmittance readings of the analytical and internal standard lines to log-intensity ratios using the emulsion calibration curve. Prepare analytical curves by plotting log-intensity ratio *versus* log concentration.

## 60. Procedure

**60.1 Preparation of Standards:**

**60.1.1** Prepare a series of standards covering a range from 2 to 1000 µg/g of the impurity elements in PuO<sub>2</sub> by blending the oxides of the elements with PuO<sub>2</sub>. An alternative method for preparing the standard consists of adding measured volumes of the solutions of the impurity elements to a solution of NBL CRM 126-A plutonium metal standard and converting to the oxides by drying at 125°C and then slowly raising the temperature to 800°C. Unless proper precautions are taken during the ignition step, possible losses of the more volatile elements such as B, Zn, Cd, Mo, W, and Pd may occur. Alternately, a Pu metal standard reference material from another national standards body, certified for impurities, may be used to compare calibration standards.

**60.1.2** Mix 13 mg of Co<sub>2</sub>O<sub>3</sub>·NaF carrier with 247 mg of PuO<sub>2</sub> (prepared in 60.1.1) in the mixer.

**60.1.3** Weigh three or four 50-mg portions of the PuO<sub>2</sub> and carrier mixture and prepare pellets by pressing from 13.8 to 27.6 MPa (2000 to 4000 psi). Place one pellet per lower electrode and heat to 370°C for 10 min before exciting in the arc.

**60.2 Sample Preparation:**

**60.2.1** Weigh 247 mg of the PuO<sub>2</sub> sample. Add 13 mg of Co<sub>2</sub>O<sub>3</sub>·NaF carrier if internal cobalt standard method is used, or 13 mg NaF carrier if only visual comparisons are to be made.

**60.2.2** Grind the mixture for 1 min in the amalgamator and prepare the pellets as described in 60.1.3.

**60.3 Excitation and Exposure:**

**60.3.1** Arc, d-c, 15 A (short-circuit).

**60.3.2** Use a spectral region from 440 to 780 nm first order, from 210 to 410 nm second order, slit width 10 µm, slit length 2 mm, and a 45-s exposure. Use the following photographic plates from 210 to 340 nm second order, SA-1, from 340 to 410

nm second order, 1N, from 440 to 680 nm first order, SA-1, and from 680 to 780 nm first order, 1N.

60.3.3 Make triplicate exposures of each sample and duplicate exposures of two or more standards representing high and low concentrations.

60.3.4 Process the emulsion in accordance with Practices E115.

60.3.5 Measure the transmittance of the analytical lines for aluminum, chromium, iron, gallium, nickel, and silicon with a microphotometer. Use the 304.400-nm line of cobalt as the standard for iron, chromium, and nickel and the 240.7-nm line of cobalt for aluminum, silicon, and gallium. The remainder of the elements listed in Table 1 are estimated by visual comparison with standard plates.

## 61. Calculation

61.1 Determine the log-intensity ratio for each analytical pair from the emulsion calibration curve. Obtain concentrations from the appropriate analytical curve. Use the cobalt 304.400-nm line with a 10 % filter transmission as the internal standard.

## 62. Precision and Bias

62.1 The precision of the test method was estimated from duplicate measurements of aluminum, iron, and nickel in a single sample over a period of 5 days. An overall relative standard deviation of 25 % was obtained.

## IMPURITY ELEMENTS BY SPARK-SOURCE MASS SPECTROGRAPHY

## 63. Scope

63.1 This test method covers the spark source spectrographic analysis of plutonium dioxide for impurity elements. Because of its extreme sensitivity, it may be the most practical test method for the determination of certain impurities whose concentration is below the detectable limits of other spectrographic methods.

## 64. Summary of Test Methods

64.1 Spark-source mass spectrography (9-15) is a convenient method for determining impurity elements in plutonium dioxide which occur in low concentration. Detection limits for most elements are in the atom-parts-per-billion range in plutonium dioxide. The procedure consists of forming the sample into rods with a cross-sectional area from 3.22 to 6.45 mm<sup>2</sup> (0.005 to 0.01 in.<sup>2</sup>) and a length of 12.7 mm (0.5 in.). A radio frequency spark is generated between two such rods mounted in a high-vacuum chamber. The ions formed in the spark are focused according to their energy and according to their mass-to-charge ratio, on a photographic plate. The densities of the resulting lines are compared with standards or with minor isotope lines of the matrix materials. Bias and precision vary with the method of data interpretation and the concentration of the impurities.

64.2 Some impurities, such as iron, occur as inclusions. If metallographic examination indicates the presence of inclusions, a representative portion must be homogenized by grinding before preparation of the electrodes.

## 65. Apparatus

65.1 *Analog Computer*, H&D.

65.2 *Balance*, analytical.

65.3 *Beakers*, TFE-fluorocarbon.

65.4 *Darkroom*, equipped with photographic developing tanks and plate drying ovens.

65.5 *Forceps*, tantalum.

65.6 *Isostatic Pressure Vessel*.

65.7 *Laboratory*, with clean-room environment.

65.8 *Microphotometer*, recording.

65.9 *Oven*, vacuum.

65.10 *Photographic Plates*.

65.11 *Plate Viewer*.

65.12 *Shaker*.

65.13 *Spark-Source Mass Spectrograph*.

65.14 *Vials*, with caps, plastic 51 by 19.1 mm (2 by ¾ in.).

## 66. Reagents

66.1 *Acetone*.

66.2 *Darkroom Supplies*, consisting of developer, short stop, dilute acetic acid, and fixer.

66.3 *Naphthalene*, flakes (resublimed)

66.4 *Silver Powder* (99.999 % Ag).

## 67. Procedure

67.1 Samples must be prepared and loaded in a clean room environment. Grind pellets to a fine powder in a mixer-mill.

67.2 *Sample Preparation*:

67.2.1 Weigh, to the nearest 0.1 mg, about 1 g of a plutonium dioxide sample and 1 g of powdered silver metal (99.999 % Ag) and transfer them to a 51 by 19.1-mm (2 by ¾-in.) plastic vial.

67.2.2 Mix the contents on a shaker for 5 min.

67.2.3 Load the sample-silver mixture into a cylindrical naphthalene mold and press the mixture isostatically into a sample rod by applying a pressure of about 1034.2 MPa (150 000 psi) for 1 min.

67.2.4 Remove the naphthalene mold from the sample rod either by sublimation or by solution in acetone.

67.2.5 Place the sample rod in a vacuum oven and allow it to dry for at least 30 min.

67.2.6 The sample is now ready to be loaded in the instrument for evacuation.

67.3 *Sparking the Samples*:

67.3.1 Follow manufacturer instructions for operating the spectrograph.

67.3.2 Load two sample rods, each approximately 12.7 mm (0.5 in.) long, counter to each other in the ion source of the mass spectrograph. (If only one sample rod is available, load it counter to a high-purity silver or gold probe electrode.) Evacuate the ion source to a pressure of approximately 13 µPa ( $1 \times 10^{-7}$  mm Hg). If it is necessary to measure carbon,

oxygen, and nitrogen in the sample, bake the source at 150°C for 12 h. The ultimate pressure reached is about 266 nPa ( $2 \times 10^{-9}$  mm Hg).

67.3.3 When the pressure is low enough, spark the samples so that an ion beam is generated. The instrument parameters are:

|                                 |                                 |
|---------------------------------|---------------------------------|
| Accelerating voltage, kV        | 20                              |
| R-f voltage, kV                 | 30 (60 for insulators)          |
| Magnet current, mA              | 305 (105 for lithium and boron) |
| Source pressure, mm Hg          | $1 \times 10^{-7}$ or less      |
| Analyzer pressure, mm Hg        | $1 \times 10^{-8}$ or less      |
| Spark repetition rate, pulses/s | 10 to 300                       |
| Spark duration, $\mu$ s         | 25 to 100                       |

67.3.4 The ion beam produced is measured electronically by intercepting 50 % of the beam before separating according to the mass-to-charge ratio. By use of the electronic monitor, a series of graded exposures are made on the photographic plate.

67.3.5 Exposures needed for a specific detection limit are:

| Detection Limit | Exposure, in Coulombs (C) |
|-----------------|---------------------------|
| 1 to 3 ppb atom | $1 \times 10^{-6}$        |
| 10 ppb atom     | $1 \times 10^{-7}$        |
| 100 ppb atom    | $1 \times 10^{-8}$        |
| 1000 ppb atom   | $1 \times 10^{-9}$        |
| 1 ppm atom      | $1 \times 10^{-9}$        |
| 10 ppm atom     | $1 \times 10^{-10}$       |

The average detection limit has been about two parts per billion atom for a  $1 \times 10^{-6}$ C exposure.

#### 67.4 Developing the Plates:

67.4.1 Remove the photographic plate from the instrument and transfer it to the darkroom.

67.4.2 Process the photographic plate as follows: develop for 3 min, short stop in dilute acetic acid, fix for 45 s in a rapid fixer, and rinse thoroughly with distilled water.

67.4.3 Place the developed plate in an oven and dry it for at least 10 min.

## 68. Calculation

### 68.1 Visual Estimation of Line Density:

68.1.1 Visual estimation of line density is used for all low-level impurities (<1.0 ppm atomic) and for many high-level impurities. This type of interpretation usually gives data that are accurate within a factor of two. This calculation is:

$$PS = (E_{min}/E_{max}) \times (A_s/100) \times (I_s/100) \times 10^6 \quad (9)$$

where:

|           |                                                                                      |
|-----------|--------------------------------------------------------------------------------------|
| $PS$      | = plate sensitivity,                                                                 |
| $E_{min}$ | = shortest exposure on the photographic plate, nC,                                   |
| $E_{max}$ | = longest exposure on the photographic plate, nC,                                    |
| $A_s$     | = concentration of the chosen internal standard, atom %, and                         |
| $I_s$     | = isotopic abundance of the chosen isotope of the internal standard element, atom %. |

Then:

$$C_i = PS \times (E_{max}/E_{det}) \times (100/I_i) \quad (10)$$

where:

|           |                                                   |
|-----------|---------------------------------------------------|
| $C_i$     | = concentration of the impurity, ppm atomic,      |
| $PS$      | = plate sensitivity,                              |
| $E_{max}$ | = longest exposure on the photographic plate, nC, |

|           |                                                                            |
|-----------|----------------------------------------------------------------------------|
| $E_{det}$ | = shortest exposure on which the impurity isotope can be detected, nC, and |
| $I_i$     | = isotopic abundance of the chosen impurity isotope, atom %.               |

Now:

$$W_i = C_i \times (I_a/M_a) \quad (11)$$

where:

|       |                                              |
|-------|----------------------------------------------|
| $W_i$ | = concentration of the impurity, ppm mass,   |
| $C_i$ | = concentration of the impurity, ppm atomic, |
| $I_a$ | = atomic mass of the impurity, and           |
| $M_a$ | = average atomic mass of the matrix.         |

(When mixed pressed samples are used, it is necessary to correct for the impurities present in the silver support material.)

### 68.2 Measurement of Line Density:

68.2.1 When more accurate and precise values are required, it is necessary to measure the line densities on the photographic plate with a microphotometer. The line transmission is measured and the percent transmission is converted to the line density with the analog computer and a previously determined emulsion calibration curve. From the measured line densities, composition may be derived in two ways.

68.2.2 When a standard having the same ratio of  $\text{PuO}_2$  to silver metal and containing the same impurity elements as the sample is available, then under the same conditions of exposure:

$$C_i = (I_u/I_s) \times C_s \quad (12)$$

where:

|       |                                                     |
|-------|-----------------------------------------------------|
| $C_i$ | = concentration of the impurity in the sample,      |
| $I_u$ | = density of the impurity line in the sample,       |
| $I_s$ | = density of the impurity line in the standard, and |
| $C_s$ | = concentration of the impurity in the standard.    |

68.2.3 If the calculations are based on standard impurity elements other than those desired, the calculation becomes:

$$C_i = (D_i/D_s) \times (A_s/100) \times (I_s/I_i) \times (E_s/E_i) \times (S_s/S_i) \times (M_i/M_s) \quad (13)$$

where:

|           |                                                                                    |
|-----------|------------------------------------------------------------------------------------|
| $C_i$     | = concentration of the impurity in the sample, atom %, and                         |
| $D_i$     | = density or intensity of the impurity line,                                       |
| $D_s$     | = density or intensity of the standard line,                                       |
| $A_s$     | = concentration of the standard, atom %, and                                       |
| $I_s$     | = isotopic abundance of the standard isotope, %, and                               |
| $I_i$     | = isotopic abundance of the impurity isotope, %, and                               |
| $E_s$     | = exposure at which the standard line is measured, nC, and                         |
| $E_i$     | = exposure at which the impurity line is measured, nC, and                         |
| $S_s$     | = relative sensitivity factor for the standard element, and                        |
| $S_i$     | = relative sensitivity factor for the impurity element, and                        |
| $M_i/M_s$ | = single-to-multiple-charge ratio for the two elements in question (preferably 1). |

## 69. Precision and Bias

69.1 The microphotometric method for spectral density interpretation should be employed for PuO<sub>2</sub> samples. The relative standard deviation for the technique of impurity evaluation is no greater than 15 %. This precision is applicable to all specification limits set forth for each impurity in the PuO<sub>2</sub>. Since standards are used, this test method is unbiased.

69.2 Examples of some of the lower practical limits of detection are listed in Table 2.

### MOISTURE BY THE COULOMETRIC ELECTROLYTIC MOISTURE ANALYZER

## 70. Scope

70.1 This test method covers the determination of moisture in plutonium dioxide samples. Detection limits are as low as 10 µg.

## 71. Summary of Test Method

71.1 The sample is heated in an oven (up to 400°C) to drive off any water. The moisture is carried from the oven into the electrolytic cell by a flowing stream of *dry* nitrogen. Two parallel platinum wires wound in a helix are attached to the inner surface of the tube, the wall of which is evenly coated with phosphorous pentoxide (a strong desiccant that becomes electrically conductive when wet). A potential applied to the wires produces a measurable electrolysis current when moisture wets the desiccant. Electrolysis of the water continuously regenerates the cell enabling it to accept additional water.

71.2 Precautions must be taken to prevent interference from the following sources. Hydrogen fluoride will cause permanent damage to the cell and sample system and should not be run under any conditions. Corrosive acidic gases such as chlorine and hydrogen chloride will corrode the instrument. Entrained liquids and solids can cause cell failure and should be prevented from entering the gas stream. Ammonia and other basic materials react with the acidic cell coating and renders the cell unresponsive. Hydrogen, and to a lesser extent, oxygen or air, may cause a high reading due to recombination in the cell, or in the case of hydrogen due to reaction with oxide coating of the sample boat to produce water. Alcohols and

glycols, particularly the more volatile ones, respond like water and therefore must not be present.

## 72. Apparatus

72.1 *Moisture Analyzer*, for solids, with a quartz glass oven, capable of being heated from ambient temperatures to 1000°C; the assembly to include electrolytic cell, flow meter, range 30 to 140 cm<sup>3</sup>/min of air, and a dryer assembly.

72.2 *Balance*, for weighing samples in the range from 1 to 100 mg.

72.3 *Nitrogen Gas Cylinder*, with a pressure regulator, a flow meter, and a drying tower.

## 73. Reagents

73.1 *Barium Chloride Dihydrate* (BaCl<sub>2</sub>·2H<sub>2</sub>O).

## 74. Operation

74.1 Turn the main power switch ON.

74.2 Adjust the nitrogen gas pressure to 41.4 kPa (6 psi) and the flow rate to 50 cm<sup>3</sup>/mn, measured at the exit of the apparatus.

74.3 Weigh the sample into a small, dry aluminum boat (Note 12) and insert it into the instrument oven as follows:

NOTE 12—For samples that have been reduced in a hydrogen atmosphere and thus contain excess hydrogen, the use of a platinum boat in place of the aluminum tube and nickel boat will minimize any interference due to the hydrogen.

74.3.1 Open top of analyzer and remove the TFE-fluorocarbon plug. Do not touch with gloves.

74.3.2 With forceps pull the nickel boat one third of the way out of the tube and place the aluminum boat and sample inside the nickel boat. Then reposition the nickel boat near the center of the heating coils.

74.3.3 Replace the TFE-fluorocarbon plug and close the lid of the analyzer.

74.4 Reset the counter to 0 µg.

74.5 Set the timer at 1 h.

74.6 Set the temperature at 400°C; this will activate the analyzer and start the heating cycle.

74.7 When the preset temperature has been reached and the counter ceases counting, record the reading, *S*.

## 75. Standardization

75.1 Determine the blank by processing dry, empty, aluminum boats in accordance with 111.3 through 111.7 until constant values are obtained.

75.2 Weigh and analyze replicate 5-mg samples of BaCl<sub>2</sub>·2H<sub>2</sub>O until consistent results are obtained. Sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O) may also be used for calibration.

## 76. Calculation

76.1 Calculate the moisture recovery, *Z*, for the standard as follows:

$$Z = (A - B)/147.2Y \quad (14)$$

TABLE 2 Impurity Elements and Detection Limits

| Impurity | Lower Limit of Detection, ppm |
|----------|-------------------------------|
| Al       | 1 ± 1                         |
| B        | 0.1 ± 0.1                     |
| Cd       | 1 ± 1                         |
| Co       | 0.3 ± 0.3                     |
| Ca       | 0.5 ± 0.5                     |
| Cr       | 0.5 ± 0.5                     |
| Fe       | 0.5 ± 0.5                     |
| Mg       | 0.3 ± 0.3                     |
| Mn       | 0.3 ± 0.3                     |
| Mo       | 0.5 ± 0.5                     |
| K        | 0.3 ± 0.3                     |
| Ni       | 0.5 ± 0.5                     |
| Si       | 1 ± 1                         |
| Ti       | 0.3 ± 0.3                     |
| Hg       | 1 ± 1                         |
| Th       | 1 ± 1                         |

where:

A = micrograms of moisture on counter when standard is tested,

B = micrograms of moisture on counter from blank, and

Y = milligrams of  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$ . Each milligram of  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$  contains 147.2  $\mu\text{g}$  of water.

76.2 Calculate the percent moisture in the sample as follows:

$$\text{Moisture, \%} = [(S - B)/1000 WZ] \times 100 = (S - B)/10 WZ \quad (15)$$

where:

S = micrograms of moisture on counter when sample is tested,

B = micrograms of moisture on counter from blank,

W = milligrams of sample, and

Z = recovery of moisture from standard.

## 77. Precision

77.1 The relative standard deviation for moisture in a concentration range of 100  $\mu\text{g/g}$  is approximately 2 % but increases to 10 % at the 20  $\mu\text{g/g}$  level.

### TOTAL GAS IN REACTOR-GRADE PLUTONIUM DIOXIDE PELLETS

(This method was discontinued as of June 2016.)

### PLUTONIUM-238 ISOTOPIC ABUNDANCE BY ALPHA SPECTROMETRY

(This test method was discontinued in 2003 and replaced by Test Method C1415.)

### AMERICIUM-241 IN PLUTONIUM BY GAMMA-RAY SPECTROMETRY

(Test Method C1268 may be used for the determination of Americium-241 in plutonium.)

### RARE EARTHS BY COPPER SPARK- SPECTROSCOPY

## 78. Scope

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

## 79. Summary of Test Method

79.1 The general principles of emission spectrographic analysis are given in Methods for Emission Spectrochemical Analysis (16). Determination of rare earth content requires their separation from oxides of plutonium by solvent extraction followed by copper-spark spectrographic measurement (17, 18).

## 80. Apparatus

80.1 *Spectrograph*—Commercially available equipment with reciprocal dispersion of approximately 0.25 nm/mm (2nd order). A direct reading spectrograph of comparable quality may be substituted for the equipment listed, in which case the directions given by the manufacturer should be followed rather than those given in the succeeding steps of this procedure. The

excitation stand must be mounted in a glove box. Power controls must be able to supply the conditions called for in 82.4.

80.2 *Microdensitometer*, having a precision of  $\pm 1.0$  % for transmittances between 5 and 90 %.

80.3 *Electrodes*—Electrolytic copper, 6.4 mm (0.25 in.) in diameter and 38.1 mm (1.5 in.) long

80.4 *Magnetic Stirrer*.

80.5 *Photographic Plates*.

## 81. Reagents and Materials

81.1 *Boric Acid Crystals* ( $\text{H}_3\text{BO}_3$ ).

81.2 *Dissolution Mixture*—Add 10 drops of hydrofluoric acid (HF, 1 + 20) to 10 mL of nitric acid ( $\text{HNO}_3$ , sp gr 1.42).

81.3 *Hydrochloric Acid* (6.7 M)—Dilute 56 mL of hydrochloric acid (HCl, sp gr 1.19) to 100 mL with water.

81.4 *Hydrochloric Acid* (1 M)—Dilute 16.7 mL of hydrochloric acid (HCl, sp gr 1.19) to 200 mL with water.

81.5 *Internal Standard Solution, Yttrium* (1 mL = 2.5  $\mu\text{g}$  Y)—Dissolve 100 mg of yttrium metal in HCl (1 + 1) and dilute to 100 mL with HCl (1 + 1). Dilute 250  $\mu\text{L}$  of this solution to 100 mL with HCl (1 + 1).

81.6 *Nitric Acid* (4 M)—Dilute 2.6 mL of nitric acid ( $\text{HNO}_3$ , sp gr 1.42) to 10 mL with water.

81.7 *Rare Earth Standard Solutions*—Prepare separate solutions of samarium, europium, gadolinium, and dysprosium in HCl (1 + 1). Weigh and dissolve sufficient metal or oxide to obtain 10  $\mu\text{g}$  of element per millilitre of solution.

81.8 *Tri-n-Octylamine* (TOA), 20 volume % in xylene.

## 82. Procedure

82.1 *Dissolution of Sample*:

82.1.1 Weigh a pellet (approximately 1.5 g) or powder (approximately 1 g) to  $\pm 0.001$  g and place in a 50-mL volumetric flask.

82.1.2 Add 5 mL of the dissolution mixture and heat slowly until dissolution is complete. Allow the solution to cool, then dilute to volume with 6.7 M HCl and mix thoroughly.

82.2 *Separation from Actinides*:

82.2.1 Transfer a 10-mL aliquot of the solution from Section 82.1 to a 35-mL vial containing 10 mL of TOA, 4 mL of the internal standard solution, 5 mg of  $\text{H}_3\text{BO}_3$  crystals, and a magnetic stirring bar.

82.2.2 Stir vigorously for 3 min. Let the solution stand for 15 min to permit phase separation.

82.2.3 Discard the organic phase (upperlayer).

82.2.4 Add 10 mL of TOA and repeat 82.2.2 and 82.2.3.

82.2.5 Add 2 mL of xylene and stir for 1 min. Allow the phases to separate and discard the organic phase.

82.2.6 Evaporate the aqueous phase to dryness under a heat lamp.

82.2.7 Add 1 mL of 1 M HCl. Warm and swirl to dissolve the residue.

82.3 *Preparation of Electrode*:

82.3.1 Transfer 50  $\mu\text{L}$  of the solution from 82.2.7 to a pair of cleaned copper electrodes and evaporate to dryness under a heat lamp. Evaporate slowly to avoid spattering of the sample. Adjust the analytical gap to 2.0 mm.

82.4 *Excitation and Exposure*—Produce and record the spectra according to the following conditions:

|                               |           |
|-------------------------------|-----------|
| <i>Electrical Parameters:</i> |           |
| Discharge,                    | H V spark |
| Voltage, V (Primary)          | 90        |
| Capacitance, $\mu\text{H}$    | 0.0025    |
| Current, A, r-f               | 10        |
| <i>Exposure Conditions:</i>   |           |
| Analytical gap, mm            | 2.0       |
| Prespark                      | 0         |
| Exposure, s                   | 30        |
| Slit width, $\mu\text{m}$     | 10        |
| Slit height, mm               | 2         |
| Filter, percent transmittance | 100/50    |

### 83. Photo Processing

83.1 Process the emulsion in accordance with Practices E115.

### 84. Photometry

84.1 Measure the percentage of transmittance of the analytical lines with the microphotometer. .

### 85. Calibration

85.1 *Emulsion Calibration*—Calibrate the emulsion in accordance with Practice E116.

85.2 *Preparation of Analytical Curve*—Read and record transmittance measurements of the spectra for each of five standard samples that cover the test range. Convert the transmittance measurements of the analytical line and the internal standard line to log-intensity ratios, using the emulsion calibration curve.

### 86. Calculation

86.1 Convert the transmittances of the analytical and the internal standard lines of the sample into log-intensity ratios. Determine percentage concentration from the analytical curves. Report the average of triplicate determinations for each sample.

TABLE 3 Principal Alpha Peaks of Interest<sup>A</sup>

| Nuclide           | <i>t</i> 1/2, years | Alpha-Particle Energy, MeV | Alpha-Particle Abundance, % |
|-------------------|---------------------|----------------------------|-----------------------------|
| <sup>238</sup> Pu | 87.75               | 5.50                       | 72                          |
|                   |                     | 5.46                       | 28                          |
| <sup>239</sup> Pu | 24 400              | 5.16                       | 73.3                        |
|                   |                     | 5.14                       | 15.1                        |
| <sup>240</sup> Pu | 6 540               | 5.11                       | 11.5                        |
|                   |                     | 5.17                       | 76                          |
| <sup>241</sup> Am | 433                 | 5.12                       | 24                          |
|                   |                     | 5.49                       | 86                          |
|                   |                     | 5.44                       | 12.7                        |
|                   |                     | 5.40                       | 1.3                         |

<sup>A</sup> Data taken from Ref 20. Half-lives have been updated to values accepted as of July 1974. Peaks of low abundance (less than 0.1 %) have been omitted.

TABLE 4 Suggested Analytical Lines

| Element             | Wavelength, nm |
|---------------------|----------------|
| Sm                  | 356.827        |
| Eu                  | 381.967        |
| Gd                  | 336.223        |
| Dy                  | 353.170        |
| Y                   | 371.030        |
| (internal standard) |                |

### 87. Precision and Bias

87.1 *Precision*—The precision of the test method is based on a duplicate measurement of the rare earths over a period of several days. An overall average relative standard deviation of 10 % was obtained.

87.2 *Bias*—The bias of the test method is dependent on the reliability of the solution standards. Using carefully prepared standards, the test method is unbiased.

## PLUTONIUM ISOTOPIC ANALYSIS BY MASS SPECTROMETRY

(Test Methods C1625 or C1672 may be used instead of the method in Sections 88 – 96 with appropriate sample preparation and instrumentation.)

### 88. Scope

88.1 This test method covers the determination of the isotopic composition of plutonium in nuclear-grade plutonium dioxide powders and pellets.

### 89. Summary of Test Method

89.1 The plutonium sample is purified from other elements that would interfere by selective extraction or anion exchange purification. The plutonium fraction is mounted and dried on rhenium filaments. Tungsten or tantalum filaments may be substituted with minor modifications in the procedure. The prescribed ion beam and intensity are obtained, the spectrum is scanned, the peaks are recorded, and the relative abundances of the isotopes are calculated.

NOTE 13—For the highest precision and bias, all steps of the mass spectrometric analytical procedure must be strictly adhered to in order to maintain the same experimental conditions for all analyses. Failure to be consistent will have a direct effect on the observed data and will be detrimental to the precision and bias of the ratio measurement. Steps included are sample preparation, sample mounting, sample degassing, and the heating pattern for obtaining ion emission for the ratio measurements.

### 90. Interferences

90.1 Uranium-238, if present, interferes with the measurement of <sup>238</sup>Pu, and <sup>241</sup>Am interferes with the measurement of <sup>241</sup>Pu, thereby requiring chemical separation. Separation of other components provides uniform ionization of plutonium, hence improved precision, and reduces the interference from molecular species of the same mass number as the plutonium isotopes.

### 91. Apparatus

91.1 *Mass Spectrometer*—A typical mass spectrometer laboratory would have 305-mm (12-in.) radius of curvature, 60 or

90° sector, single or double focusing, and single- or multiple-filament thermal ionization instruments designed for isotopic abundance measurements on high-atomic mass elements. Resolution and abundance sensitivity specifications are dictated by the end performance desired of the instrument. In general, a typical (19, 20) well-designed single-stage mass spectrometer should resolve adjacent masses in the 230 to 245 mass range with less than  $1 \times 10^{-4}$  interaction between tails. Abundance sensitivities of less than 1 in 20 000 should be obtained.

91.2 The mass spectrometer should also be equipped with the following: a collector that adequately suppresses electrons; an expanded scale strip-chart recorder; or a suitable scaler-timer and voltage-to-frequency converter combination for digital measurements. Without this type of measuring circuit, the limit of error for a ratio measurement is  $\pm 0.5$  relative %.

91.3 An *Optical Pyrometer* should be available to determine the filament temperature.

## 92. Reagents

### 92.1 Anion Exchange Resin

92.2 *Ferrous Sulfamate Solution* (3.2 M)—Dissolve 794 g of ferrous sulfamate ( $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ ) in water and dilute to 1 L.

92.3 *Hydrochloric Acid* (2 M)—Dilute 17 mL of hydrochloric acid (HCl, sp gr 1.19) to 100 mL with water.

92.4 *Hydrochloric Acid* (12 M)—The hydrochloric acid must be at least 12 M and can be prepared by bubbling hydrogen chloride gas through hydrochloric acid of lower concentrations. Determine the molarity by titration with a standard base.

92.5 *Hydrochloric-Hydriodic Acid Mixture* (12 M HCl-0.1 M HI)—This mixture must be made just before use. Add a calculated amount of hydriodic acid to 12 M HCl (77.13). The hydriodic acid must be free of hypophosphorus acid that is used in stabilized hydriodic acid. This can be done by distilling the hydriodic acid.

92.5.1 **Warning**—To avoid danger of explosions, hydriodic acid should be distilled only in an inert atmosphere. Determine the molarity of the hydriodic acid by titration with a standard base.

92.6 *Hydrofluoric Acid* (1 M)—Dilute 1 mL of hydrofluoric acid (HF, sp gr 1.18) to 29 mL with water.

92.7 *Hydroxylamine Hydrochloride Solution* (5 M)—Dissolve 348 g of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH} \cdot \text{HCl}$ ) in water and dilute to 1 L.

92.8 *Nitric Acid* (0.75 M)—Dilute 4.8 mL of nitric acid ( $\text{HNO}_3$ , sp gr 1.42) to 100 mL with water.

92.9 *Nitric Acid* (1 M)—Dilute 6.3 mL of nitric acid ( $\text{HNO}_3$ , sp gr 1.42) to 100 mL with water.

92.10 *Nitric Acid* (8 M)—Dilute 50 mL of nitric acid ( $\text{HNO}_3$ , sp gr 1.42) to 100 mL with water.

92.11 *Nitric-Hydrofluoric Acid Mixture* (15 M  $\text{HNO}_3$ -0.05 M HF)—Add 0.9 mL of hydrofluoric acid (HF, sp gr 1.15) to 485 mL of nitric acid ( $\text{HNO}_3$ , sp gr 1.42) and dilute to 500 mL with water.

92.12 *Perchloric Acid* (1 M)—Dilute 17 mL of perchloric acid ( $\text{HClO}_4$ , sp gr 1.67) to 200 mL with water. See safety precaution in 6.4.

92.13 *Perchloric Acid* (6 M)—Dilute 5 mL of perchloric acid ( $\text{HClO}_4$ , sp gr 1.67) to 10 mL with water. See safety precaution in 6.4.

92.14 *Sodium Nitrite Solution* (2 M)—Dissolve 138 g of sodium nitrite ( $\text{NaNO}_2$ ) in water and dilute to 1 L.

92.15 *Thenoyltrifluoroacetone* (0.5 M)—Dissolve 110 g of thenoyltrifluoroacetone (TTA) in xylene and dilute to 1 L with xylene.

## 93. Calibration of the Mass Spectrometer

93.1 *Mass Discrimination*—The measurement and correction for mass discrimination is a critical factor in obtaining precise and accurate results. Equally critical to the accuracy of the measurement is the linearity of the total measuring circuit including the collector. Calibration of the mass spectrometer is based upon the assumption that these are the only two sources of significant ( $>1$  in  $10^4$ ) systematic error in the measurement. Thus, accurate calibration is made by analyzing standards of known isotopic composition under conditions in which cross-contamination between samples does not occur.

93.2 The recommended calibration standard, for determination of mass discrimination to be used to correct plutonium ratios, is NBL CRM U500 (Note 14). The deviation from the certified value is a measure of the mass discrimination of the spectrometer for a three mass unit difference. Using the  $^{235}\text{U}/^{238}\text{U}$  mass discrimination factor, the mass discrimination is then calculated for each ratio and mass range to be calibrated. The  $^{235}\text{U}/^{238}\text{U}$  mass discrimination factor,  $B$ , is calculated as follows:

$$B = (1/\Delta M) \left[ (\bar{R}/R_s) - 1 \right] \quad (16)$$

where:

$B$  = mass discrimination factor,  
 $\Delta M$  = mass unit difference = (238-235),  
 $R_s$  = certified value of CRM, and  
 $\bar{R}$  = average measured value of  $^{235}\text{U}/^{238}\text{U}$  for  $n$  different analyses.

At the 95 % confidence level, the mass discrimination correction for  $^{235}\text{U}/^{238}\text{U}$  can, under ideal conditions, be determined with a precision that is equal to or less than 2 in 10 000.

NOTE 14—Corrections for mass discrimination of plutonium are made by assuming that under equivalent analytical conditions the mass-dependent isotopic fractionation effects for uranium and plutonium are identical. This method of calibrating for plutonium mass discrimination is highly dependent upon establishing equivalency of analytical conditions and can be subject to significant systematic errors. Although the plutonium isotopic CRMs available from NBL, certified relative to uranium, present some unfavorable factors, magnitude of the  $^{239}\text{Pu}/^{240}\text{Pu}$  ratios and the small (one) mass difference, for the most precise and accurate mass discrimination determination; it is an attractive alternative that establishes a common measurement base using plutonium.

93.3 *Linearity*—The linearity of the mass spectrometer may be determined over the ratio range from 0.1 to 10, 0.05 to 20, or 0.005 to 200 by measuring the  $^{235}\text{U}/^{238}\text{U}$ , under identical analytical conditions, of NBL CRMs U100-U500-U900,

CRMs U050 through CRM U930, or CRMs U005 through U970, respectively. Equivalent reference materials from other national standards bodies may also be used. The ratio of the certified  $^{235}\text{U}/^{238}\text{U}$  ratio to the experimental  $^{235}\text{U}/^{238}\text{U}$  ratio is a dimensionless number and is independent of isotopic ratio, if the system is linear. Under ideal conditions, any deviation from a constant value greater than 4 in 10 000 is likely to be nonlinearity. Uranium CRMs are used because the range of isotopic ratios of existing plutonium CRMs is not adequately large.

## 94. Procedure

94.1 *Sample Preparation*—Dissolve a few milligrams of  $\text{PuO}_2$  in 15 M  $\text{HNO}_3$ -0.05 M HF mixture by heating. Dilute the sample solution in enough 1 M  $\text{HClO}_4$  to give a solution containing 100  $\mu\text{g}$  Pu/mL.

94.2 *Separation of Plutonium by Solvent Extraction:*

94.2.1 Take an aliquot of the sample solution containing 10  $\mu\text{g}$  of Pu and evaporate to dryness.

94.2.2 Dissolve the residue in 2 M HCl; heat slightly if necessary.

94.2.3 Add 10  $\mu\text{L}$  of ferrous sulfamate solution and 50  $\mu\text{L}$  of 5 M hydroxylamine hydrochloride. Digest for 5 min at 80°C.

94.2.4 Add 2 mL of 0.5 M TTA, stir for 2 min, and centrifuge the sample. Transfer the aqueous phase to a clean vial.

94.2.5 Add 500  $\mu\text{L}$  of 2 M  $\text{NaNO}_2$  and digest for 5 min at 80°C.

94.2.6 Add 2 mL of 0.5 M TTA, stir for 2 min, and centrifuge the sample. Transfer the TTA phase (Pu fraction) to a clean vial.

94.2.7 To the TTA phase, add 2 mL of 1 M  $\text{HNO}_3$ , stir for 2 min, centrifuge, and transfer the TTA phase to a clean vial.

94.2.8 Repeat 94.2.7.

94.2.9 Add 1 mL of 8 M  $\text{HNO}_3$ , stir for 2 min, centrifuge, and transfer the aqueous phase to a clean vial.

94.2.10 Evaporate the solution to dryness by heating the vial on an aluminum block at 120°C.

94.2.11 Dissolve the plutonium residue in 0.5 mL of 0.75 M  $\text{HNO}_3$ .

94.3 *Column Preparation:*

94.3.1 Place a glass or plastic wool plug in the bottom of a 6 by 60-mm column.

94.3.2 Slurry the resin in water and pour the resin into the column, avoiding formation of air bubbles, until the resin is 50 mm in height.

94.3.3 Condition the column just before use by passing 5 mL of 12 M HCl through the column.

94.4 *Separation of Plutonium by Ion Exchange (21):*

94.4.1 Add 10 drops of 6 M  $\text{HClO}_4$  and 10 drops of 1 M HF to an aliquot of the sample solution (145.1) containing approximately 30  $\mu\text{g}$  of plutonium and evaporate to dryness.

94.4.2 Dissolve the residue in 0.5 mL of 12 M HCl and transfer with the aid of a 0.5-mL rinse of 12 M HCl to the prepared column.

94.4.3 Elute the americium with 4 mL of 12 M HCl and discard.

94.4.4 Elute the plutonium with 4 mL of 12 M HCl-0.1 M HI and evaporate to dryness.

94.4.5 Add 0.5 mL of 15.4 M  $\text{HNO}_3$  and fume to dryness to expel chloride and destroy any organic matter.

94.4.6 Repeat 94.4.5.

94.4.7 Dissolve the plutonium residue in 1.5 mL of 0.75 M  $\text{HNO}_3$ .

94.5 *Mass Spectrometer Measurement:*

94.5.1 Mount the sample by placing 10  $\mu\text{L}$  of solution, containing 0.2  $\mu\text{g}$  of plutonium on each suitably prepared 0.031 by 0.762-mm (0.0012 by 0.030-in.) rhenium sample filament (Note 15) and evaporate to dryness with a heat lamp and electrical current adjusted in the following manner: 1 A for 10 min, 1.3 A for 3 min, and slowly increase the filament current to a maximum, usually 1.8 to 2.2 A in air, that is safely below red-heat (approximately 600°C). The temperature of the filament during the final stages of sample mounting is a critical factor and must be carefully controlled to prevent significant variations in the fractionation between runs.

NOTE 15—The rhenium filaments may be cleaned by heating in 5 M HCl for several hours to remove surface contaminants, then rinsed in high-purity water, and dried in a clean air environment. The final cleaning, which is the minimum recommended, is degassing in a vacuum station and under a potential field for 0.5 h at approximately 2000°C.

94.5.2 Insert the filament assembly into the mass spectrometer and obtain a source pressure of less than 400  $\mu\text{Pa}$  ( $3 \times 10^{-6}$  torr).

94.5.3 Degas by adjusting the ionizing filament temperature to 2140°C and set the sample filament currents at 1.5 A. After 3 min of heating, readjust the ionizing filament temperature to 2140°C and set the sample filament currents at 1.7 A. After 15 min of heating, turn off all filaments and allow to cool for 30 min for high-accuracy measurement and for 15 min for production analyses.

NOTE 16—Sample degassing may be considered optional for plutonium isotope analysis but is strongly recommended for high reliability. Degassing is considered essential for measurements with high-sensitivity electron detectors where low-level interference from organic and inorganic molecules is a major problem. Degassing is also essential with conventional faraday cup detectors when there are small amounts of organic or inorganic impurities in the sample.

94.5.4 *Heating Pattern and Isotopic Ratio Measurement:*

94.5.4.1 During the first minute, adjust the ionizing filament temperature to 2140°C set the sample filament currents at 1.5 A, locate the  $^{187}\text{Re}$  peak, and focus for maximum intensity.

NOTE 17—The  $^{187}\text{Re}$  signal is normally  $1.5$  to  $1.8 \times 10^{-11}$  A and decaying. If the rhenium signal is unstable or erratic, the analysis should be terminated. The most probable causes of an unstable signal are a defective filament, large alkali background, and electronic instability.

94.5.4.2 At 5 min, readjust the ionizing filament temperature to 2140°C. Increase the sample filament currents to yield a  $\text{Pu}^+$  signal of  $2 \times 10^{-12}$  A. Focus for maximum signal intensity.

94.5.4.3 At 10 min, adjust sample filament currents to yield a  $\text{Pu}^+$  signal of  $5 \times 10^{-12}$  A. Focus for maximum signal intensity.

94.5.4.4 At 15 min, check the ionizing filament temperature and adjust to 2120°C if necessary.

94.5.4.5 At 20 min, adjust the sample filament currents to yield a  $\text{Pu}^+$  signal of  $1 \times 10^{-11}$  A.

94.5.4.6 At 25 min, readjust, if necessary, the sample filament currents to yield a  $\text{Pu}^+$  signal of  $1 \times 10^{-11}$  A. Focus for maximum intensity. Determine baselines for  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  (see Note 20).

94.5.4.7 At 30 min, start the ratio measurement (Note 18). The  $\text{Pu}^+$  signal intensity should be approximately  $1.0\text{--}1.2 \times 10^{-11}$  A and slowly changing. For complete isotopic characterization, measure the ratios (Note 19) on a strict time schedule that is the same for each analysis and in the following sequence:  $^{239}\text{Pu}/^{240}\text{Pu}$ ;  $^{241}\text{Pu}/^{240}\text{Pu}$ ;  $^{242}\text{Pu}/^{240}\text{Pu}$ ;  $^{238}\text{Pu}/^{240}\text{Pu}$ ;  $^{242}\text{Pu}/^{240}\text{Pu}$ ;  $^{241}\text{Pu}/^{240}\text{Pu}$ ;  $^{239}\text{Pu}/^{240}\text{Pu}$ . Exception to the recommended ratio sequence is suggested when the measurement uncertainty of the isotopic ratio is very large with respect to the mass discrimination factor. For many samples, the ratio sequence may be changed to:  $^{239}\text{Pu}/^{240}\text{Pu}$ ;  $^{241}\text{Pu}/^{240}\text{Pu}$ ;  $^{242}\text{Pu}/^{240}\text{Pu}$ ;  $^{241}\text{Pu}/^{240}\text{Pu}$ ;  $^{239}\text{Pu}/^{240}\text{Pu}$ ; and then measure  $^{238}\text{Pu}/^{240}\text{Pu}$ . The number of ratio sets per ratio determination can be varied but will usually fall within the range from 7 to 10. The number of ratio sets is determined by the point at which the internal standard deviation is smaller than the external or between-filament standard deviation.

NOTE 18—The “peak-hopping” technique of ratio measurements is normally preferred to the “mass-scanning” technique. Baselines are therefore determined immediately before or after each ratio determination within the analysis, or both. If there is significant baseline drift or resolution problems, then mass scanning must be used.

NOTE 19—The peak top observation time is governed by many factors including: response of the measuring circuit; emission stability; rate of signal decay; settling time of magnet switching circuit; and desired precision and bias of the measurement. For most systems equipped with vibrating reed electrometers, there is a minimum delay of 5 s for circuits to stabilize after peak switching occurs in the ratio range from 0.05 to 20. Outside of this range, longer delay times may be required to minimize the effects of system response and should be determined for each measuring circuit/mass spectrometer.

## 95. Calculation

95.1 *Averaging Peak Intensities*—Obtain the peak intensity for a single ratio by subtracting the average baseline reading from the average peak heights of a set of three peaks. Take the averages for the peak heights at the center of time for the set and consists of two peaks for one isotope and one peak for the other. Calculate the ratios of the determination using a “dependent” set in which all peaks are used twice in the calculation, exclusive of the first and last. The “independent” set in which all peaks are used only once in the calculation is not preferred because a significant amount of data is rejected; the ratio is biased when the ion emission is nonlinear or the rate of change is great.

NOTE 20—For automated and semiautomated systems, the baseline and peak height determinations are performed by a computer. However, the basic principles are the same whether the ratios are determined manually from a strip-chart recorder or by computer. The  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  baselines are the average of the initial and final low-mass and high-mass reading. Usually, the initial and final  $^{239}\text{Pu}/^{240}\text{Pu}$  baseline values will not differ significantly. It can be observed that the low-mass baseline value is always slightly greater than the high-mass value. For most ratios, this difference is not a significant source of bias. In most instances where averaging this difference is significant, the baseline must be determined at a point in the spectrum or on the high-mass side of each peak. Because of possible

scatter tails, the proper background zero for the  $^{238}\text{Pu}$  and other low-abundance isotopes is estimated as follows:

$$\text{LMZ} + (1/5) [\text{HMZ} - \text{LMZ}]$$

where:

LMZ = low-mass baseline, and

HMZ = high-mass baseline.

95.2 The average raw isotopic ratios are obtained from the ratios calculated by interpolation by use of appropriate scale factors and are designated as follows:

$$^{239}\text{Pu}/^{240}\text{Pu} = \bar{R}_{90} \quad (17)$$

$$^{241}\text{Pu}/^{240}\text{Pu} = \bar{R}_{10} \quad (18)$$

$$^{242}\text{Pu}/^{240}\text{Pu} = \bar{R}_{20} \quad (19)$$

$$^{238}\text{Pu}/^{240}\text{Pu} = \bar{R}_{80} \quad (20)$$

95.3 The final isotopic ratios are corrected for mass discrimination as follows:

$$\bar{R}' = [\bar{R}/(1 + CB)], \quad (21)$$

$$\text{since } B = 1/\Delta M \left[ (\bar{R}/R_s) - 1 \right]$$

$$\text{then } 1 + \Delta MB = \bar{R}/R_s$$

where:

$\bar{R}'$  = final isotopic ratios corrected for mass discrimination,

$\bar{R}$  = average raw ratio,  $\Delta$

$M$  = mass unit difference,

$B$  = mass discrimination factor as determined in 93.2, and

$R$  = average measured value of  $^{235}\text{U}/^{238}\text{U}$  for  $n$  different analyses.

95.4 Calculate the atom and mass percent for all isotopes as follows:

$$\text{Atom } \%, A = 100 \bar{R}' / (1 + \bar{R}'_{90} + \bar{R}'_{10} + \bar{R}'_{20} + \bar{R}'_{80}) \quad (22)$$

$$\text{Mass } \%, W_m = 100 M \bar{R}' / (240.05 + 239.05 \bar{R}'_{90} \quad (23)$$

$$+ 241.06 \bar{R}'_{10} + 242.06 \bar{R}'_{20} + 238.05 \bar{R}'_{80})$$

where:

$A$  = atom percent of a given isotope,

$\bar{R}'$  = average corrected ion current ratio of the given isotope to the  $^{240}\text{Pu}$  isotope (Note that  $\bar{R}'$  for  $^{240}\text{Pu}$  is equal to 1.),

$W_m$  = mass percent for isotopes,  $m$ ,

$W$  = mass percent of a given isotope, and

$M$  = nuclidic mass of the given isotope.

## 96. Precision and Bias

96.1 *Precision*—The ultimate precision and accuracy of isotopic ratio measurements by thermal ionization mass spectrometry requires consideration of factors that are not necessarily readily apparent in the description of the test method. It is assumed that these factors are under rigid control during high-precision and high-accuracy measuring conditions. Since control of these factors may be relaxed during routine or production analyses, the precision of the test method is given for two sets of laboratory conditions. These precision statements are also based in part upon an experience factor in

analyzing isotopic ratios using an average plutonium ion current intensity of  $1$  to  $2 \times 10^{-11}$  A.

| Ratio | 95 % Confidence Limit for High-Precision Conditions, % | 95 % Confidence Limit for Production Conditions, % |
|-------|--------------------------------------------------------|----------------------------------------------------|
| 1     | 0.02                                                   | 0.05 to 0.2                                        |
| 100   | 0.1 to 0.2                                             | 0.2 to 0.5                                         |
| 200   | 0.3 to 0.5                                             | 0.5 to 1.0                                         |
| 500   | 0.5 to 1                                               | 1 to 3                                             |
| 1000  | 2 to 4                                                 | 5 to 10                                            |

**96.2 Bias**—The bias of an isotope ratio measurement, under ideal conditions where synthetic calibration mixes are prepared from high-purity separated isotopes, is obtained by the summation of three uncertainty components: mass spectrometric analytical error (precision of the ratio measurement); possible systematic error in the composition of separated isotopes; and possible systematic error in chemical analysis. Under these conditions and with the most favorable isotopic ratio of unity, the accuracy will normally fall between 0.03 and 0.07 relative %. Until the uncertainty components for plutonium are properly evaluated, the accuracy is estimated to be within 0.15 % for the ratio range from 1 to 20. Outside of this range, the increased imprecision of the ratio measurement and the analytical conditions, high accuracy versus routine, will normally require larger limits for the accuracy.

NOTE 21—The assumption that uranium and plutonium have the same mass discrimination factor under identical or equivalent analytical conditions, or both, is tenuous because of the difficulty in defining these conditions and obtaining the proper relationship. Unless these conditions are accurately produced, there can be systematic errors of 0.2 % per mass unit in the mass discrimination factor. This systematic error is due to variable isotopic fractionation for different analytical conditions and can be demonstrated to range from less than zero to nearly 0.2 % per mass unit for uranium. Approximately the same magnitude can be obtained for plutonium by changing the analytical conditions of the mass spectrometry. Based upon these experimental data, the uncertainty in the accuracy for the most precise plutonium ratio measurement must be larger until proper calibration using synthetic calibrating standards is performed.

## OXYGEN-TO-METAL ATOM RATIO BY GRAVIMETRY

### 97. Scope

97.1 This test method is applicable to the determination of the oxygen-to-metal atom ratio (O/M) in plutonium dioxide pellets and powders.

### 98. Summary of Test Method

98.1 The sample is weighed before and after heating under conditions that are reported by McNeilly and Chikalla to produce a stoichiometric oxide (ratio = 2.000) (22). These conditions are heating at 800°C for a minimum of 6 h in an atmosphere of hydrogen-helium saturated with water vapor at 0°C. The O/M is calculated from the weight change.

### 99. Interferences

99.1 Depending upon the contents and natures of impurities in the sample, the weight change during analysis may be affected by loss of volatile impurities or by oxidation or reduction of impurities. High concentrations of inert impurities would also reduce the weight change. The O/M values obtained should be evaluated considering possible biases caused by impurities.

99.2 The test method is not applicable to determining O/M in plutonium dioxide powders produced by low-temperature calcination of plutonium salts, particularly plutonium oxalate which is a common source of  $\text{PuO}_2$ . These low-temperature calcined oxides often contain a variety of impurities which will interfere significantly with this O/M measurement.

### 100. Apparatus

100.1 *Analytical Balance*, capable of weighing within  $\pm 0.1$  mg or better.

100.2 *Moisture Analyzer*, capable of measuring water contents of argon or helium to less than 200 ppm.

100.3 *O/M Apparatus*—See Fig. 7 for an example.

### 101. Reagents

101.1 *Argon*, prepurified grade (23) or equivalent, <20 ppm water. Test water content with a moisture analyzer to assure that the level is less than 20 ppm.

101.2 *Helium*, high-purity grade (23) or equivalent, <20 ppm water. Test water content with a moisture analyzer to assure that the level is less than 200 ppm.

101.3 *Hydrogen-Helium Mixture*, 6 % hydrogen, prepared from prepurified grade (23) or equivalent gases.

101.4 *Ice*.

101.5 *Magnesium Perchlorate*, anhydrous, for the drying tube in the O/M apparatus.

### 102. Procedure

NOTE 22—This test method is based on a one-step heating cycle. Other thermogravimetric methods using a two-step heating cycle also are satisfactory for this analysis (24,25).

#### 102.1 Pellets:

102.1.1 Adjust the flow rate of the hydrogen-helium (B) (see Fig. 7) to 300 to 500 mL/min, adjust valves so that the gas passes through the water bubbler (F), add ice to the Dewar flask (G), turn on the furnace (J), and adjust its temperature to 800°C.

102.1.2 Heat the boats (L) under the above conditions for 1 h, remove the furnace tube from the furnace to allow rapid cooling, and allow the boats to cool to room temperature in the hydrogen-helium atmosphere.

102.1.3 Remove the boats from the furnace tube, weigh each within  $\pm 0.1$  mg, and repeat 102.1.2 and 102.1.3 until a constant tare weight (W) is obtained for each empty boat.

102.1.4 Place a whole pellet or pieces of a pellet having a total weight of 1 g or more in each boat and weigh within  $\pm 0.1$  mg ( $W_1$ ) at room temperature.

102.1.5 Place the boats containing the samples into the furnace tube, replace the furnace tube in the furnace, and heat the samples for a minimum of 6 h under the conditions given in 102.1.1 (300 to 500 mL/min of water-saturated hydrogen-helium with the furnace at 800°C).

102.1.6 Remove the furnace tube from the furnace and allow the samples to cool to room temperature in the hydrogen-helium atmosphere.

102.1.7 Remove the boats from the furnace tube and weigh each within  $\pm 0.1$  mg ( $W_2$ ).

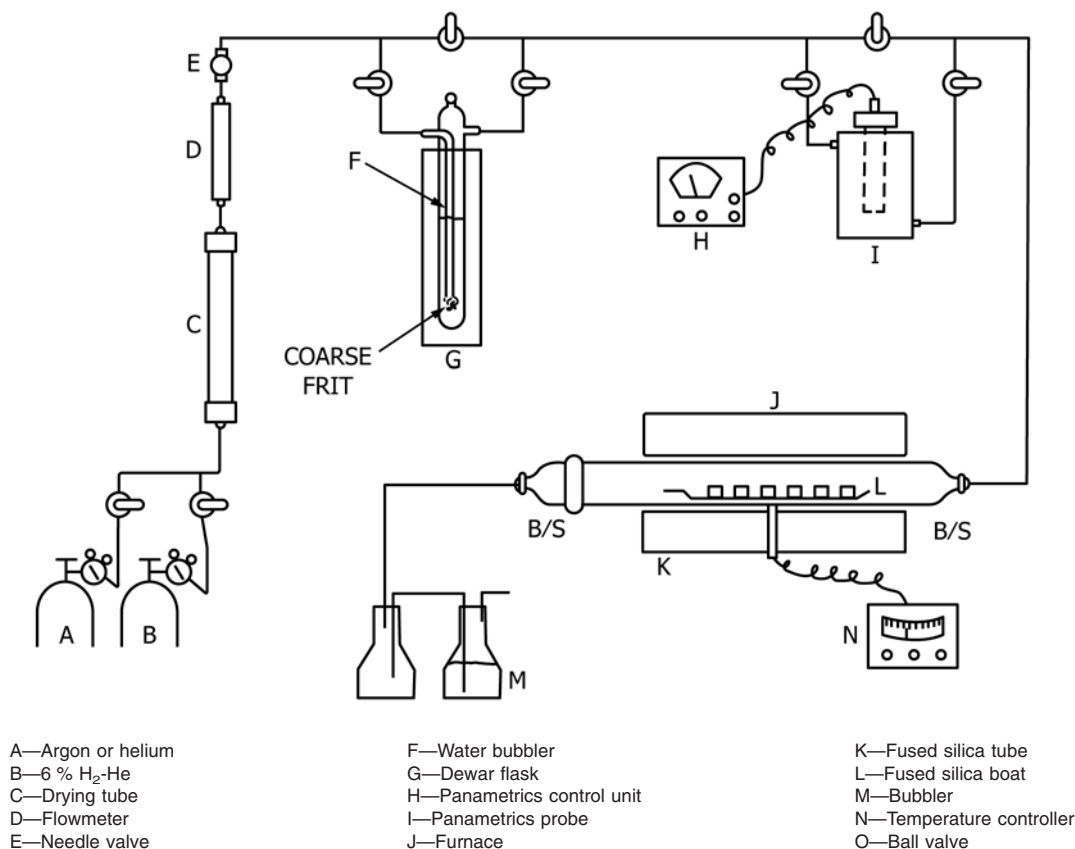


FIG. 7 O/M Apparatus

102.1.8 Repeat 102.1.5 through 102.1.7 until each boat weight remains constant within  $\pm 0.2$  mg. (Heating for 6 h in 102.1.5 should be sufficient to attain constant weight.)

#### 102.2 Powders:

102.2.1 Adjust the flow rate of dry helium or argon (A) (see Fig. 7) to 300 mL/min, adjust valves so that the gas does not pass through the bubbler, turn on the furnace (J), and adjust its temperature to 800°C.

102.2.2 Heat the boats (L) under the above conditions for 1 h, remove the furnace tube from the furnace, and allow boats to cool in the dry gas atmosphere to room temperature.

102.2.3 Remove the boats from the furnace tube, weigh each within  $\pm 0.1$  mg, and repeat 102.2.2 and 102.2.3 until a constant tare weight ( $W_T$ ) is obtained from each empty boat.

102.2.4 Add approximately 1.5 g of powder sample to each boat, adjust the furnace temperature to 150°C, replace the furnace tube in the furnace, place the boats with samples in the furnace tube, and dry the samples at 150°C for 1 h in the dry argon or helium flowing at 300 mL/min.

102.2.5 Transfer each boat and dried sample to a desiccator; allow the sample to cool to room temperature; quickly weigh the boat and sample ( $W_1$ ) within  $\pm 0.1$  mg.

102.2.6 Prepare the O/M apparatus as described in 102.1.1, place the boats and samples into the furnace tube, and heat a minimum of 6 h under the conditions given in 102.1.1 (300 to 500 mL/min water-saturated, hydrogen-helium gas flow; 800°C).

102.2.7 Adjust the furnace temperature to 150°C, and adjust the valves so that the hydrogen-helium gas bypasses the ice-bath bubbler.

102.2.8 Keep the samples at 150°C, increase the hydrogen-helium gas flow rate to about 1200 mL/min, and measure the moisture content of the exit gas with the moisture analyzer.

102.2.9 When the moisture content of the gas is reduced below 20 ppm, transfer the boats and samples to a desiccator, allow them to cool to room temperature, and quickly weigh each boat and sample ( $W_2$ ) within  $\pm 0.1$  mg.

102.2.10 Repeat 102.2.7 through 102.2.9, if necessary, to obtain constant weights ( $W_2$ ).

### 103. Calculation

103.1 Calculate the O/M ratio as follows:

$$O/M = 2.000 - \frac{(W_2 - W_1) F}{(W_2 - W_T)} \quad (24)$$

where:

$W_2$  = final weight of sample and boat,  
 $W_1$  = initial weight of sample and boat,  
 $F$  = (formula weight of metal oxide)/15.999, and  
 $W_T$  = tare weight of boat.

### 104. Precision and Bias

104.1 The standard deviations obtained with pellets are 0.001 to 0.002 in the O/M.

104.2 The bias of the test method cannot be tested reliably because of the lack of suitable reference or calibration materials. The absence of bias depends upon quantitative conversion of the sample to the stoichiometric dioxide. The conditions of analysis were selected on the basis of thermodynamic data to ensure complete conversion to the stoichiometric dioxide, and therefore, no measurable bias should exist.

## 105. Keywords

105.1 impurity content; isotopic composition; plutonium content; plutonium dioxide pellets; plutonium dioxide powders

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