Designation: C 697 – 98

Standard Test Methods for
Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets[1]

This standard is issued under the fixed designation C 697; 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:

	Sections
Plutonium Sample Handling	8 to 10
Plutonium by Controlled-Potential Coulometry	2
Plutonium by Ceric Sulfate Titration	11 to 18
Plutonium by Amperometric Titration with Iron(II)	2
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Nitrogen by Distillation Spectrophotometry Using Nessler Reagent	19 to 26
Carbon (Total) by Direct Combustion–Thermal Conductivity	27 to 38
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Plutonium-238 Isotopic Abundance by Alpha Spectrometry	95 to 102
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Rare Earths By Copper Spark-Spectroscopy	103 to 112
Plutonium Isotopic Analysis by Mass Spectrometry	113 to 121
Oxygen-To-Metal Atom Ratio by Gravimetry	122 to 130

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see Sections 6, 23, 32, 127, and 60.9 and 117.5.1 .

2. Referenced Documents

2.1 *ASTM Standards:*

C 757 Specification for Nuclear-Grade Plutonium Dioxide Powder, Sinterable[5]

C 852 Guide for Design Criteria for Plutonium Gloveboxes[5]

C 1009 Guide for Establishing a Quality Assurance Program for Analytical Chemistry Laboratories Within the Nuclear Industry[5]

C 1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry[5]

C 1108 Test Method for Plutonium by Controlled-Potential Coulometry[5]

C 1128 Guide for Preparation of Working Reference Materials for Use in the Analysis of Nuclear Fuel Cycle Materials[5]

C 1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials[5]

C 1165 Test Method for Determining Plutonium by Controlled-Potential Coulometry in H_2SO_4 at a Platinum Working Electrode[4]

C 1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis[5]

C 1206 Test Method for Plutonium by Iron (II)/Chromium (VI) Amperometric Titration[4]

C 1210 Guide for Establishing a Measurement System Quality Control Program for Analytical Chemistry Laboratories Within the Nuclear Industry[5]

C 1268 Test Method for Quantitative Determination of Americium 241 in Plutonium by Gamma-Ray Spectrometry[5]

C 1297 Guide for Qualification of Laboratory Analysts for the Analysis of Nuclear Fuel Cycle Materials[5]

C 1307 Test Method for Plutonium Assay by Plutonium(III) Diode Array Spectrophotometry[5]

D 1193 Specification for Reagent Water[6]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[7]

E 115 Practices for Photographic Processing in Optical

Emission Spectrographic Analysis[7]

E 116 Practice for Photographic Photometry in Spectrochemical Analysis[7]

E 909 Master Matrix for Development of Standards to Assist in Safeguarding of Nuclear Materials[3]

3. Significance and Use

3.1 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 C 757.

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

3.1.2 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.

3.1.3 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).

4. Committee C-26 Safeguards Statement[8]

4.1 The materials (plutonium dioxide powders and pellets) to which these test methods apply are subject to nuclear safeguards regulations governing their possession and use. The following analytical procedures in these test methods have been designated as technically acceptable for generating safeguards accountability measurement data: Plutonium by Controlled-Potential Coulometry; Plutonium by Ceric Sulfate Titration; Plutonium by Amperometric Titration with Iron (II); Plutonium by Diode Array Spectrometry Plutonium-238 Isotopic Abundance by Alpha Spectrometry; and Plutonium Isotopic Analysis by Mass Spectrometry.

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

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.[9] 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 D 1193.

6. Safety Precautions

6.1 Since plutonium bearing materials are radioactive and toxic, adequate laboratory facilities, gloved boxes, fume hoods, etc., along with safe techniques, must be used in handling samples containing these materials. A detailed discussion of all the precautions necessary is beyond the scope of these test methods; however, personnel who handle these materials should be familiar with such safe handling practices as are given in Guide 852 and in Refs **(1)** through **(3).**[10]

7. Sampling and Dissolution

7.1 Criteria for sampling this material are given in Specification C 757.

7.2 Samples can be dissolved using the appropriate dissolution technique described in Practice C 1168.

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 $-23°C$ 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 in an atmosphere with a dew point no greater than $-23°C$.

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°C for at least 1 h and kept in a desiccator until used.

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

[9] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

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

NOTE 1—It has been shown that plutonium dioxide will sorb water from apparently dry aluminum foil. The foil should be dried at 110°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 C 1165.)

PLUTONIUM BY CONTROLLED-POTENTIAL COULOMETRY

(With appropriate sample preparation, controlled-potential coulometric measurement as described in Test Method C 1108 may be used for plutonium determination.)
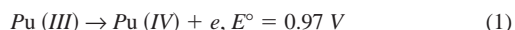
PLUTONIUM BY CERIC SULFATE TITRATION

11. Scope

11.1 This test method **(4)** covers the determination of the plutonium content of nuclear-grade plutonium dioxide powders.

12. Summary of Test Method

12.1 Weighed samples of low-fired (less than 950°C) plutonium dioxide are dissolved in a mixture of hydrochloric acid-hydrofluoric acid or nitric acid-hydrofluoric acid. The sample solution is fumed with sulfuric acid to remove nitrates, nitrites, and fluoride. Plutonium in a sample aliquot is reduced to Pu (III) by the addition of an excess of titanous trichloride. The excess reductant is oxidized by a standard ceric sulfate solution and the Pu (III) titrated to Pu (IV). The end points are determined potentiometrically.

13. Interferences

13.1 Iron, copper, tungsten, uranium, nitrates, nitrites, and those ions which have oxidation potential above

$$Pu\ (III) \rightarrow Pu\ (IV) + e, E° = 0.97\ V \qquad (1)$$

or below

$$Ti\ (III) + H_2O \rightarrow TiO\ (II) + 2H^- + e, E° = 0.0\ V \qquad (2)$$

14. Apparatus

14.1 *Dry Box*—A box with humidity controlled to a dew point of less than −23° C.

14.2 *Microburet*, 1 to 7-mL capacity.

14.3 *Potentiometer*, having a range from 0 to 1400 mV.

15. Reagents

15.1 *Ceric Sulfate Solution* (0.1 *N*)—Dissolve 65 g of ceric ammonium sulfate [$(NH_4)_4\ Ce(SO_4)_4 \cdot 2\ H_2O$] in 600 mL of 1 *M* H_2SO_4 and dilute to 1 L with water. Standardize **(15)** as follows: Weigh out between 0.15 to 0.2 g (± 0.1 mg) of pure, dry, arsenous oxide (As_2O_3) and dissolve with 15 mL of 2 *N* NaOH solution. Cool and add 25 mL of a mixture of 1 part

H_2SO_4 (sp gr 1.84) and 5 parts of water. Dilute to 100 mL and add 3 drops of 0.01 *M* osmium tetroxide solution (0.25 g of osmium tetroxide in 100 mL of 0.1 *N* H_2SO_4) and 1 drop of ferroin indicator. Titrate with 0.1 *N* ceric sulfate solution until orange-red color changes to pale blue. The equivalent weight of arsenous oxide = 49.455.

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

15.3 *Hydrochloric Acid* (6 *N*)—Prepare by diluting 500 mL of HCl (sp gr 1.19) to 1 L with water.

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

15.5 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

15.6 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

15.7 *Titanous Trichloride Solution*—A 20 % solution is available commercially. Store $TiCl_3$ under a nitrogen atmosphere.

16. Procedure

16.1 In a humidity-controlled glove box, accurately weigh approximately 1 g of PuO_2 powder.

16.2 Dissolve the sample in a platinum crucible with HCl or HNO_3 and 150 µL HF.

16.3 Fume the samples with H_2SO_4 to remove nitrates, nitrites, and fluoride. Samples dissolved with only HCl do not require fuming. Add sufficient aluminum chloride to complex fluorides.

16.4 Transfer the solution to a 50-mL flask and dilute to volume with 6 *N* HCl.

16.5 Transfer 2.00 mL of the sample solution to a 50-mL beaker. Add 10 mL of water and stir the solution. Aliquots may be taken by weight.

16.6 Add sufficient $TiCl_3$ reagent to give a meter reading of approximately 1100 mV. The solution should be a blue-purple color.

16.7 Titrate the sample and excess $TiCl_3$ with standard ceric sulfate solution. Record the volume of titrant and the millivolt reading after each addition. The end point is the point at which $\Delta mV/\Delta mL$ reaches a maximum. Record the volume of titrant corresponding to this point. At this point the excess Ti (III) is oxidized to Ti (IV) and the oxidation of Pu (III) begins.

16.8 Continue the titration until a second end point occurs near 500 mV, which is the point at which the oxidation of Pu (III) to Pu (IV) is complete. Record the volume of titrant at this point. The difference in volume between these two end points is the amount of ceric sulfate solution required to titrate the plutonium.

17. Calculation

17.1 Calculate the plutonium content (Pu), mass %, as follows:

$$Pu = [(V_1)(V_2)(N)(W_P)/(A)(W)] \times 100 \qquad (3)$$

where:
V_1 = volume of sample solution, mL,

V_2 = volume of ceric sulfate consumed to oxidize Pu (III) to Pu (IV) mL,

N = normality of ceric sulfate solution,

W_P = milliequivalent weight of plutonium adjusted for isotopic composition,

A = aliquot of sample solution titrated, mL, and

W = mass of PuO_2 dissolved, g.

17.2 *Impurity Correction*:

17.2.1 Correct the percent of plutonium, in 17.1, for the equivalent amount of iron, tungsten, or uranium known to be in the sample. The correction is the ratio of the plutonium equivalent weight to the impurity equivalent weight.

18. Precision

18.1 A relative standard deviation of 0.27 % has been found in oxides with a plutonium concentration of 88 % by weight.

PLUTONIUM BY AMPEROMETRIC TITRATION WITH IRON (II)

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

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

(With appropriate sample preparation, the measurement described in Test Method C 1307 may be used for plutonium determination.)

NITROGEN BY DISTILLATION SPECTROPHOTOMETRY USING NESSLER REAGENT

19. Scope

19.1 This test method covers the determination of 5 to 100 µg/g of nitride nitrogen in 1-g samples of nuclear-grade plutonium dioxide.

20. Summary of Test Method

20.1 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 **(26,71).**

21. Apparatus

21.1 *Distillation Apparatus*, see Fig. 1.

21.2 *Spectrophotometer*, visible range.

22. Reagents

22.1 *Ammonium Chloride* (NH_4Cl)—Dry salt for 2 h at 110 to 120°C.

22.2 *Boric Acid Solution* (40 g/L)—Dissolve 40 g of boric acid (H_3BO_3) in 800 mL of hot water. Cool to approximately 20°C and dilute to 1 L.

22.3 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).
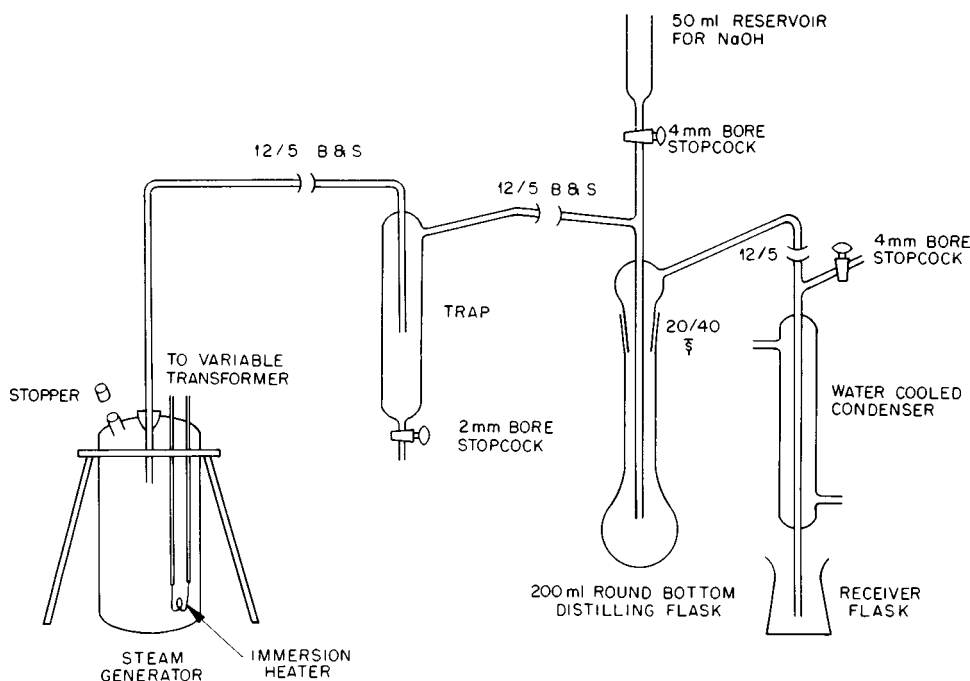
FIG. 1 Distillation Apparatus

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

22.5 *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 ($HgCl_2$, 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.

22.6 *Nitrogen Standard Solution* (1 mL = 0.01 mg N)— Dissolve 3.819 g of NH_4Cl 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.

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

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

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

23. Precautions

23.1 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.

24. Procedure

24.1 *Dissolution of Sample*:

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

Note 2—Crush the pellet samples to a particle size of 1 mm or less in a diamond mortar.

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

Note 3—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.

24.2 *Distillation*:

24.2.1 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).

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

24.2.3 Add 5 mL of 4 % H_3BO_3 solution to a 50-mL graduated flask and position this trap so that the condenser tip is below the surface of the H_3BO_3 solution.

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

24.2.5 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.

Note 4—The NaOH solution must be added slowly to avoid a violent reaction which may lead to a loss of sample.

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

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

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

24.2.9 Prepare a reagent blank solution by following 24.1 through 24.2.8.

24.3 *Measurement of Nitrogen*:

24.3.1 Add 1.0 mL of Nessler reagent to each of the distillates collected in 24.2.8 and 24.2.9 and dilute to volume with ammonia-free water, mix, and let stand 10 min.

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

24.4 *Calibration Curve*:

24.4.1 Add 0, 5, 10, 25, 50, 100, and 150 µg 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.

24.4.2 Process each solution by the procedure in 24.2 through 24.3 (omit 24.2.9).

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

25. Calculation

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

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

$$N = (A - B)/W \qquad (4)$$

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

26. Precision

26.1 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

27. Scope

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

28. Summary of Test Method

28.1 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.

29. Interferences

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

30. Apparatus

30.1 *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.

30.1.1 *Combustion Apparatus*[11]—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.

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

30.1.3 *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.

30.1.4 *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.

30.1.5 *Catalytic Furnace and Tube*—This unit, which is used to ensure complete oxidation of CO to CO_2, consists of a tube containing copper oxide and maintained at a temperature of 300°C by a small furnace.

30.1.6 *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_2 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_2 given off by materials containing sulfur is removed by MnO_2 and any water vapor is absorbed in a tube containing $Mg(ClO_4)_2$. 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.

30.2 *Vibratory Sample Pulverizer Apparatus*,[12] capable of reducing ceramic materials 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.

31. Reagents and Materials

31.1 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4) to be used in the oxygen purification train.

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

31.3 *Standard Materials*—Institute for Standards and Technology (NIST) SRM 131b Low-Carbon Steel (0.0018 % carbon) and SRM 336 Steel (0.567 % carbon) or their replacements.

32. Safety Precautions

32.1 *Samples Containing Plutonium*—Due to the extreme toxicity of plutonium and the certainty that some plutonium will become airborne during the analytical operations, it is mandatory to perform all operations within an approved glove box fitted with off-gas filters capable of sustained operation with dust-laden atmospheres.

33. Sampling

33.1 *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.

33.2 *Sample Preparation*—Pellet or particulate samples shall be reduced 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.

34. Preparation of Apparatus

34.1 *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.

35. Calibration

35.1 *Preparation of Standards for Combustion*—Mix a weighed portion of an accelerator and a weighed portion of approximately 1 g of NIST 131b in each of three sample crucibles. Repeat with NIST 336, using approximately 30 to 40 mg.

[11] A Leco Low Carbon Analyzer, manufactured and sold by Laboratory Equipment Co., St. Joseph, MI, or equivalent, has been found satisfactory for this purpose.

[12] Wig-L-Bug, manufactured and sold by Spex Industries, Inc., Scotch Plains, NJ, has been found satisfactory for this purpose.

35.1.1 The NIST 336 steel is assigned a carbon content 0.567 % (5670 µg/g). Therefore, amounts ranging up to approximately 40 mg are used for standardization. Weigh the steel into a tared container (a small nickel-sample boat if convenient), 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.

35.2 *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 intergrated value of the carbon dioxide response signal is helpful in detecting and correcting for analyzer drift and noise.

36. Procedure

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

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

36.3 Transfer the sample powder, not to exceed 1 g or of such size as to give not more than 200 µg of carbon, to the crucible. Weigh the crucible and contents to the nearest 0.01 g and find the specimen mass by difference.

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

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

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

37. Calculation

37.1 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:

$$C, \mu g/g = (C_s - C_b)/W \qquad (5)$$

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.

38. Precision

38.1 The relative standard deviation of this test method is approximately 10 % for a concentration of 30 µg of carbon/g of sample.

TOTAL CHLORINE AND FLUORINE BY PYROHYDROLYSIS

39. Scope

39.1 This test method covers the determination of 5 to 100 µg/g of chlorine and 1 to 100 µg/g of fluorine in 1-g samples of nuclear-grade plutonium dioxide.

40. Summary of Test Method

40.1 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 (8–9).

41. Interferences

41.1 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.

42. Apparatus (see Fig. 2 and Fig. 3)

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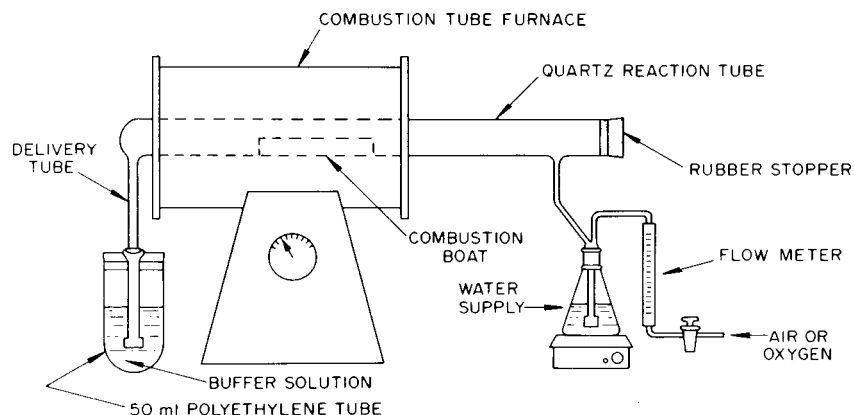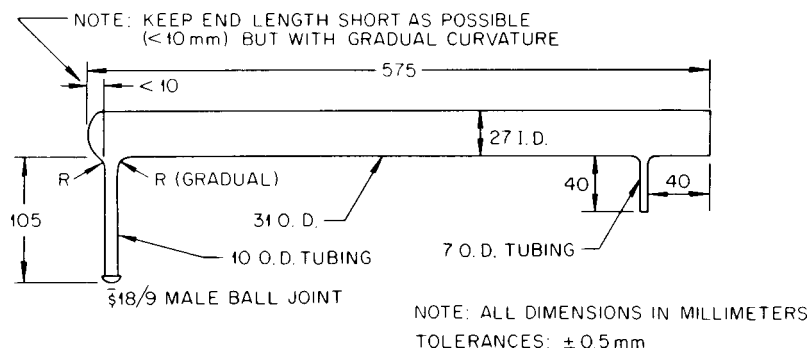

FIG. 2 Pyrohydrolysis Apparatus

ASTM C 697

FIG. 3 Quartz Reaction Tube

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

42.3 *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.

42.4 *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).

42.5 *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.

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

42.7 *Automatic Chloride Titrator.* [13]

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

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

42.10 *Spectrophotometer*, ultraviolet to visible range and absorption cells. For a discussion on spectrophotometers and their use see Practice E 60.

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

43. Reagents

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

43.2 *Air or Oxygen*, compressed.

43.3 *Buffer Solution* (0.001 *N*)—Prepare by adding 50 μL 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.

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

43.5 *Chloride, Standard Solution* (1 mL = 5 μg Cl)—Prepare by diluting 5 mL of chloride solution (1 mL = 1 mg Cl) to 1 L with water.

43.6 *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.

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

43.8 *Fluoride, Standard Solution* (1 mL = 10 μg F)—Dilute 10 mL of fluoride solution (1 mL = 1 mg F) to 1 L with water.

43.9 *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.

43.10 *Lanthanum-Alizarin Complexone*[14]—Dissolve 0.048 g of alizarin complexone (3-aminomethylalizarin-*N*, *N*-diacetic acid) in 100 μL of concentrated ammonium hydroxide (NH_4OH), 1 mL of an ammonium acetate solution ($NH_4C_2H_3O_2$, 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 ($NaC_2H_3O_2$) and 6 mL of concentrated glacial acetic acid (CH_3CO_2H, sp gr 1.05) to the filtrate. Add 100 mL of acetone while swirling the filtrate. Add 0.040 g of lanthanum oxide (La_2O_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 5—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.

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

43.12 *Nitric Acid-Acetic Acid Solution* (1 *N* Nitric Acid and 4 *N* Acetic Acid)—Prepare by adding 64 mL of nitric acid (HNO_3, sp gr 1.42) to a 1-L volumetric flask which contains

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[13] A Cotlove Titrator, sold by American Instrument Co., Silver Spring, MD, or by Buchler Instruments, Inc., Fort Lee, NJ, or equivalent, has been found satisfactory for this purpose.

[14] The reagent is available commercially under the name Amadac-F.

500 mL of water. Swirl the solution in the flask and add 230 mL of acetic acid (CH_3CO_2H, sp gr 1.05). Dilute the solution with water to 1 L.

44. Pyrohydrolysis Procedure

44.1 Prepare the pyrohydrolysis apparatus for use as follows:

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

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

44.1.3 Adjust the temperature of the furnace to 950 ± 50°C.

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

44.2 Weigh accurately, 1 to 2 g of the powdered plutonium dioxide and transfer to a combustion boat. If an accelerator, U_3O_8, is used mix 4 g with the sample before loading into the boat.

44.3 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.

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

44.5 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 45.

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

44.7 Run a pyrohydrolysis blank with halogen-free U_3O_8 by following the procedures, given in 44.3-44.6.

45. Measurement of Chloride and Fluoride

45.1 *Determination of Chloride by Spectrophotometry*:

45.1.1 Prepare a calibration curve by adding 0, 1, 2, 5, and 10 mL of the chloride solution (1 mL = 5 µg 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.

45.1.2 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 6—A calibration curve can be prepared by drying measured aliquots of a chloride solution on some halogen-free U_3O_8 and proceeding through pyrohydrolysis steps.

45.1.3 Calculate the chloride, Cl, µg/g, as follows:

$$Cl, µg/g = (A - B)V_{1/WV_2} \tag{6}$$

where:
A = micrograms of chlorine in aliquot measured,
B = micrograms of chlorine in blank,
W = grams of $PuO2$ pyrohydrolyzed,
V_1 = millilitres of scrub solution, and
V_2 = aliquot of scrub solution analyzed, mL.

45.2 *Determination of Chloride by Amperometric Microtitrimetry*:

45.2.1 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 µL 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 7). Record the time required to titrate 50 µg. Run a reagent blank titration.

NOTE 7—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.

45.2.2 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.

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

45.2.4 Calculate the chlorine as follows:

$$Cl, µg/g = V_1 F(T_s - T_B)/V_2 W \tag{7}$$

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

$$\frac{µC1 \text{ standard titrated}}{\text{titration time of standard} - \text{titration time of blank}}$$

or

$$F = 50/(T_{C1} - T_B), \tag{8}$$

T_s = titration time to titrate sample and blank,
T_{C1} = titration time to titrate 50 µg of Cl and blank,
T_B = titration time to titrate reagent blank, and
W = grams of PuO_2 pyrohydrolyzed.

45.3 *Determination of Chloride and Fluoride with Ion-Selective Electrodes*:

45.3.1 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 plot on semi-log paper the halogen content per 25 mL *versus* millivolts. 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 µg/25 mL
F from 5 to 100 µg/25 mL

45.3.2 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:

$$Cl \text{ or } F, \text{µg/g} = (H_s - H_b)/W \qquad (9)$$

where:
H_s = halide in aliquot of scrub solution + blank, µg,
H_b = halide in pyrohydrolysis blank, µg, and
W = sample mass, g.

45.4 *Determination of Fluoride by Spectrophotometry*:

45.4.1 Prepare a calibration curve by adding to separate 10-mL flasks 0, 50, 100, 200, 500, and 1000 µL of the fluoride solution (1 mL = 10 µg 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.

45.4.2 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.

45.4.3 Calculate the fluorine concentration, F, in the PuO_2 sample as follows:

$$F, \text{µg/g} = [(F_s - F_b)/W] \times V_1/V_2 \qquad (10)$$

where:
F_s = fluorine in aliquot of scrub solution + the blank, µg,
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 PuO_2 sample.

46. Precision

46.1 The relative standard deviations for the measurements of fluorine are approximately 7 % for the range from 5 to 50

µg/g and 10 % for the range from 1 to 5 µg/g. The relative standard deviations for the measurements of chlorine vary from 5 % at the 5 to 50-µg/g level up to 10 % below the 5-µg/g range.

SULFUR BY DISTILLATION SPECTROPHOTOMETRY

47. Scope

47.1 This test method coves the determination of sulfur in the concentration range from 10 to 600 µg/g for samples of nuclear-grade plutonium dioxide powders or pellets.

48. Summary of Test Method

48.1 Sulfur is measured spectrophotometrically as Lauth's Violet following its separation by distillation as hydrogen sulfide **(10).** 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 µg of sulfur per gram of sample.
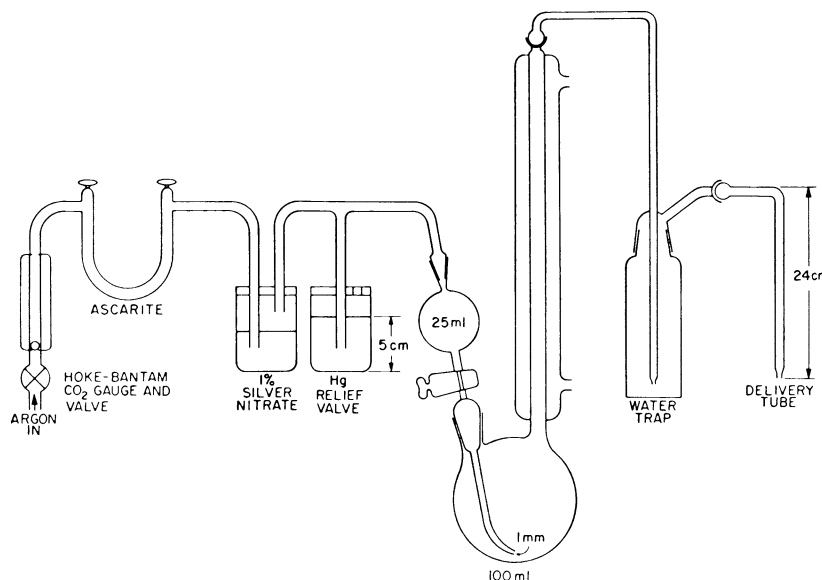
49. Interference

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

50. Apparatus

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

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

50.3 *Sulfur*, distillation apparatus (see Fig. 4).

FIG. 4 Sulfur Distillation Apparatus

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51. Reagents

51.1 *Argon Gas*, cylinder.

51.2 *Ferric Chloride Solution*, 2 % $FeCl_3$ in 6 M HCl.

51.3 *Formic Acid* (HCOOH), redistilled.

51.4 *Hydriodic-Hypophosphorous Acid Reducing Mixture*—Mix 400 mL of 7.6 M hydriodic acid (HI) with 200 mL of hypophosphorous acid (H_3PO_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 μg/mL.

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

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

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

51.8 *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 μg/10 mL and prepare the diluted acids with this reagent.

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

51.10 *Hydroxylamine Hydrochloride* ($NH_2OH \cdot HCl$), 20 % aqueous solution.

51.11 *Nitric Acid* (15.6 M), 70 % HNO_3.

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

51.13 *Silver Nitrate* ($AgNO_3$), 1 % aqueous solution.

51.14 *Sulfur Calibration Solution* (1 mL = 5 μg S)— Dissolve 2.717 g of dry potassium sulfate (K_2SO_4) in water and dilute to 1 L. Dilute 2.00 mL to 200 mL with water.

51.15 *Zinc Acetate Solution* (4 %)—Dissolve 20 g of zinc acetate ($Zn(C_2H_3O_2)_2$) in 500 mL of water and filter.

52. Calibration

52.1 Use aliquots of standard sulfur solution (1 mL = 5 μg S) to test the method and check the apparatus. Ideally, blends of oxides and sulfur (20 to 600 μg S/g) should be analyzed to simulate actual sample conditions.

52.2 Prepare a calibration curve of absorbance *versus* sulfur (using aliquots of the sulfur standard solution) covering a concentration range from 5 to 50 μg/50 mL.

53. Procedure

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

53.2 Transfer a sample, weighed to ±0.2 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 μg/g or less.

53.3 Add 5 mL of 15.6 M 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.

53.4 Add additional amounts of HNO_3 and HF acids until the sample dissolves.

NOTE 8—The sealed-tube technique (7) is an alternate method that may be used to advantage for the dissolution of some samples.

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

53.6 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 9—The reduction of HNO_3 by formic acid is vigorous. Keep the dish or beaker covered with a watch glass between additions of formic acid.

53.7 Rinse the cover glass with water. Add 0.5 mL of formic acid and slowly evaporate the rinse and sample solution to dryness.

NOTE 10—Nitrate must be completely removed because it reacts explosively with the reducing acid.

53.8 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).

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

53.10 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.

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

53.12 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.

53.13 Adjust the flow rate of argon to 100 cm^3 min; then turn on the heating mantle and boil the solution for 35 min.

53.14 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.

53.15 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 11—Rapid mixing after each reagent addition prevents formation of a brown reduction product that interferes with the spectrophotometric measurement.

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

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

54. Calculations

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

$$S = (S - B)/W \tag{11}$$

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

55. Precision

55.1 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 113 to 121.)

RARE EARTH ELEMENTS BY SPECTROSCOPY

56. Scope

56.1 This test method covers the determination of dysprosium, europium, gadolinium, and samarium in plutonium dioxide (PuO_2) in concentrations of 0.1 to 10 µg/g of PuO_2.

57. Summary of Test Method

57.1 PuO_2 is dissolved in a nitric-hydrofluoric acid (HNO_3-HF) mixture and evaporated to dryness. The residue is redissolved in dilute HNO_3, 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.

58. Interferences

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

58.2 Calcium and other alkaline earths interfere in concentrations in excess of 100 µg/g PuO_2. 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_2.

59. Apparatus

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

59.2 *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 aperature of the spectrograph field lens. Gas is allowed to escape where the electrodes enter the 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.[15]
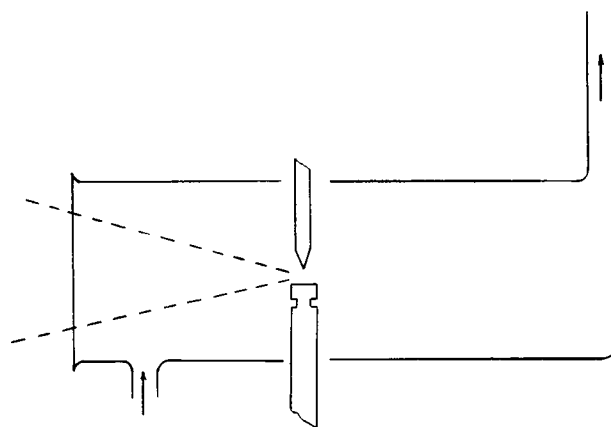
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[15] Commercially available alternative systems are Stallwood Jet, available from Spex Industries Inc., Scotch Plains, NJ, and Atmo-Jet from Zeebac Inc., Berea, OH.

FIG. 5 Schematic Diagram of Atmosphere Chamber

59.3 *Spectrograph*—A grating spectrograph having a minimum effective resolution of 50 000 and a reciprocal linear dispersion of at least 4 Å/mm at the focal plane and grating angle employed.

59.4 *Photographic Processing Equipment*—Developing, fixing, washing and drying equipment should be used that conforms to the requirements of Practices E 115.

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

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

59.7 *Filters*, 0.45-µm with filter pads, 25-mm diameter.

59.8 *Small Vacuum Pump or Aspirator*.

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

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

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

59.12 *Separatory Funnels*, 125-mL capacity.

59.13 *Hotplate*.

59.14 *Heat Lamp*.

59.15 *Electrodes*, ASTM Type C-1 and S-14.

59.16 *Photographic Plates*, Eastman Kodak, SA-1 or equivalent.

60. Reagents

60.1 *Controlled Atmosphere*—80 % argon (Ar)-20 % oxygen (O_2), premixed gas. In practice, the oxygen content may vary by ±5 % without adverse effects.

60.2 *Graphite Powder*, spectroscopically pure, capable of passing through a 100-mesh sieve.

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

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

60.5 *Hydrogen Peroxide* (H_2O_2), 30 % solution, analytical reagent grade.

60.6 *Nitric Acid* (HNO_3), *hydrofluoric acid* mixture, (10 *N* HNO_3-0.05 *N* HF).

60.7 *Nitric Acid, diluted* (4 *N* HNO_3).

60.8 *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_2O_3 or better) in minimum quantities of HNO_3. Dilute each solution with water to a concentration of 1.0 µg of rare-earth element per millilitre of solution.

60.9 *Tributyl Phosphate (TBP) in n-Hexane*[16]—30 % TBP in *n*-hexane. **Caution**—This solution is flammable. Assure adequate ventilation.

60.10 *Uranium Standard Solution*—Dissolve 300 g of pre-ignited uranium oxide (U_3O_8) (NIST SRM 950b or its replacement) in 500 mL of 4 N HNO_3. Additional 4 N HNO_3 should be used, if required, to complete dissolution. Transfer to a 1-L container and add sufficient 4 N HNO_3 to adjust the volume to approximately 1 L. Uranium is used as a stand-in for plutonium.

60.11 *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.

60.12 *Yttrium Carrier Solution*—Dissolve an accurately weighed quantity of preignited yttrium oxide (Y_2O_3) (99.99 % or better) in a minimum amount of concentrated HNO_3 and dilute with water to a concentration of 0.8 mg of yttrium per millilitre of solution.

61. Procedure

61.1 *Preparation of Sample*:

61.1.1 Dissolve duplicate 3.0 $\pm$ 0.1-g portions of each sample in 30 mL of 10 N HNO_3– 0.05 N HF in a 150-mL beaker.

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

61.1.2.1 Evaporate to dryness, at approximately 80°C, and redissolve the residue in 20 mL of 4 N HNO_3.

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

61.1.2.3 Add 5 drops of hydrogen peroxide (H_2O_2) and stir.

61.1.2.4 Transfer to a 125-mL separatory funnel with the aid of about 5 mL of 4 N HNO_3, add 40 mL of 30 % TBP in *n*–hexane, and shake vigorously for 2 min.

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

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

61.1.2.7 Transfer the aqueous phase to a 150-mL plastic or TFE-fluorocarbon beaker, rinse the separatory funnel with 10 mL of 4 N HNO_3, and transfer the aqueous rinse to the beaker.

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

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

61.1.2.10 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.

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

61.1.2.12 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.

61.2 *Spectrographic Procedure*:

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

61.2.2 Place a sample electrode in the lower electrode holder.

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

61.2.4 Produce and record the spectrum under the following conditions.

61.2.4.1 Primary voltage, 230 V,

61.2.4.2 Current, 15-A dc (shorted),

61.2.4.3 Spectral region, 3100 to 4500 Å,

61.2.4.4 Slit width, 10 μm,

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

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

61.2.4.7 Preburn, 0 s, and

61.2.4.8 Exposure, 35 s.

NOTE 12—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.
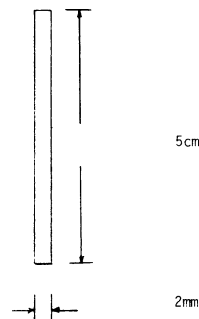
61.3 *Photographic Processing*:

61.3.1 Process the photographic plates in accordance with Practices E 115.

62. Calculation

62.1 *Interpretation of Spectra*:

62.1.1 The following spectral lines are used for analysis (see Note 13).

FIG. 6 Packing Tool (Stainless Steel)

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[16] A more stable diluent may be substituted for *n*-hexane provided it is shown that the results obtained are comparable.

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Element	Wavelength, Å	Concentration Range, µg/g
Dysprosium	4045.98	0.1 to 10
Europium	3971.96, 3907.10	0.1 to 10
Gadolinium	3422.47	0.1 to 10
Samarium	3885.29, 4256.40	0.15 to 10

NOTE 13—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.

62.1.2 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_2.

63. Precision

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

TRACE ELEMENTS BY CARRIER-DISTILLATION SPECTROSCOPY

64. Scope

64.1 This test method covers the determination of 36 impurity elements in nuclear-grade plutonium dioxide (PuO_2). The concentration ranges covered by the method and the analytical lines used for each element are listed in Table 1.

65. Summary of Test Method

65.1 Powdered PuO_2 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 $NaF\cdot Co_2O_3$ carrier while molybdenum, vanadium, and tungsten are determined with a $AgCl\cdot PdCl_2$ carrier (11).

66. Apparatus

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

66.2 *Spectrograph*—An instrument having a reciprocal linear dispersion of 5.12 Å/mm in first order from 4400 to 7800 Å, and 2.5Å/ mm in second order, from 2100 to 4100 Å. 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.

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

66.4 *Photographic Development Equipment*, necessary to permit developing, fixing, washing, and drying operations to conform to Practices E 115.

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

66.6 *Calculating Board*, useful for converting microphoto-metric readings to log intensity ratios.

TABLE 1 Impurity Elements, Lines, and Concentration Limits

Element	Wavelength, Å	Concentration Range, ppm
Al	2567.99[A]	10–500
Al	3082.68[A]	
Ag	3280.68	1–250
As	2349.84	10–250
Au	2427.95	2.5–50
B	2497.73	1–50
Ba	4554.03 (first order)	2.5–100
Be	2348.61	0.5–25
Bi	3067.72	2.5–100
Ca	3933.67	10–1000
Cd	2288.02	1–100
Co	2407.25	10–1000
Co	3044.00	
Cu	3247.54	1–250
Cr	2835.63[A]	5–500
Fe	2983.57[A]	10–1000
Ga	2450.07[A]	1–500
Ga	2943.64	
In	3039.36	2.5–100
K	7664.91 (first order)	3–1000
Mg	2802.70	1–1000
Mn	2798.27	5–250
Mo[B]	3132.59	5–250
Ni	3002.49[A]	10–1000
P	2553.28	100–1000
Pb	2614.18	5–100
Pd	3242.70	2.5–100
Sb	2598.05	2.5–100
Si	2514.32[A]	10–300
Sn	2863.33	2.5–100
Sr	4607.33 (first order)	5–100
Ti	3223.52	5–100
V[B]	3183.98[A]	5–100
W[B]	2724.35[A]	20–200
Zn	3345.02	10–250
Zr	3438.23	5–100

[A]These elements are determined with the aid of a microphotometer.
[B]These elements are analyzed by using a AgCl carrier and $PdCl_2$ as an internal standard. Mix 20 mg of $PdCl_2$ with 10.0 g of AgCl. Add 80 mg of this mixture to 120 mg of PuO_2 sample-blend before loading 50-mg charges in a graphite electrode ASTM-Type-S-4 (follow 96.2.2).

66.7 *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.

66.8 *Pulverizer Mixer*.

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

67. Reagents and Materials

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

67.2 *Cobalt (III) Oxide-Sodium Fluoride Carrier* ($Co_2O_3\cdot NaF$)—Weigh 5.000 g of NaF and add 0.0967 g of Co_2O_3, crush, and blend the material in a pulverizer mixer.

67.3 *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).

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

67.5 *Plutonium Dioxide* (PuO_2)—Powdered material of known impurity content suitable as a diluent for impurity element standards.

67.6 *Palladium Choride* ($PdCl_2$), 99.99 % purity.

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

67.8 *Silver Chloride-Palladium Chloride Carrier* ($AgCl \cdot PdCl_2$)—Weigh 10.0 g of AgCl and add 20 mg of $PdCl_2$. Blend this mixture in a mixer.

68. Calibration

68.1 Follow Practice E 116 for emulsion calibration and prepare an emulsion calibration curve.

68.2 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.

69. Procedure

69.1 *Preparation of Standards*:

69.1.1 Prepare a series of standards covering a range from 2 to 1000 μg/g of the impurity elements in PuO_2 by blending the oxides of the elements with PuO_2. An alternative method for preparing the standard consists of adding measured volumes of the solutions of the impurity elements to a solution of NIST SRM 949e plutonium 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, NIST SRM 945, a Pu metal standard matrix certified for impurities, may be used to compare calibration standards.

69.1.2 Mix 13 mg of $Co_2O_3 \cdot NaF$ carrier with 247 mg of PuO_2 (prepared in 69.1.1) in the mixer.

69.1.3 Weigh three or four 50-mg portions of the PuO_2 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.

69.2 *Sample Preparation*:

69.2.1 Weigh 247 mg of the PuO_2 sample. Add 13 mg of $Co_2O_3 \cdot NaF$ carrier if internal cobalt standard method is used, or 13 mg NaF carrier if only visual comparisons are to be made.

69.2.2 Grind the mixture for 1 min in the amalgamator and prepare the pellets as described in 69.1.3.

69.3 *Excitation and Exposure*:

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

69.3.2 Use a spectral region from 4400 to 7800 Å first order, from 2100 to 4100 Å second order, slit width 10 μm, slit length 2 mm, and a 45-s exposure. Use the following photographic plates from 2100 to 3400 Å second order, SA-1, from 3400 to 4100 Å second order, 1N, from 4400 to 6800 Å first order, SA-1, and from 6800 to 7800Å first order, 1N.

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

69.3.4 Process the emulsion in accordance with Practices E 115.

69.3.5 Measure the transmittance of the analytical lines for aluminum, chromium, iron, gallium, nickel, and silicon with a microphotometer. Use the 3044.00-Å line of cobalt as the standard for iron, chromium, and nickel and the 2407-Å 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.

70. Calculation

70.1 Determine the log-intensity ratio for each analytical pair from the emulsion calibration curve. Obtain concentrations from the appropriate analytical curve. Use the cobalt 3044.00-Å line with a 10 % filter transmission as the internal standard.

71. Precision and Bias

71.1 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

72. Scope

72.1 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.

73. Summary of Test Methods

73.1 Spark-source mass spectrography (**12–18**) is the most 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^2 (0.005 to 0.01 $in.^2$) 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.

73.2 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.

74. Apparatus

74.1 *Analog Computer*, [17] H&D.

74.2 *Balance*, analytical.

_____

[17] Jarrell-Ash Model 23-515 or equivalent has been found satisfactory.

NOTICE: This standard has either been superceded and replaced by a new version or discontinued.
Contact ASTM International (www.astm.org) for the latest information.

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74.3 *Beakers*, TFE-fluorocarbon.

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

74.5 *Forceps*, tantalum.

74.6 *Isostatic Pressure Vessel*.

74.7 *Laboratory*, with clean-room environment.

74.8 *Microphotometer*, [18] recording.

74.9 *Oven*, vacuum.

74.10 *Photographic Plates*. [19]

74.11 *Plate Viewer*. [20]

74.12 *Shaker*. [21]

74.13 *Spark-Source Mass Spectrograph*. [21]

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

75. Reagents

75.1 *Acetone*.

75.2 *Darkroom Supplies*, consisting of developer,[22] short stop, dilute acetic acid, and fixer.[23]

75.3 *Naphthalene*, flakes (resublimed, Baker and Adamson)

75.4 *Silver Powder* (99.999 % Ag).

76. Procedure

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

76.2 *Sample Preparation*:

76.2.1 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.

76.2.2 Mix the contents on a shaker for 5 min.

76.2.3 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.

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

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

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

76.3 *Sparking the Samples*:

76.3.1 Detailed instructions for operating the spectrograph should be followed.

76.3.2 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 (1×10^{-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 (2×10^{-9} mm Hg).

76.3.3 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	1×10^{-7} or less
Analyzer pressure, mm Hg	1×10^{-8} or less
Spark repetition rate, pulses/s	10 to 300
Spark duration, µs	25 to 100

76.3.4 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.

76.3.5 Exposures needed for a specific detection limit are:

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

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

76.4 *Developing the Plates*:

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

76.4.2 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.

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

77. Calculation

77.1 *Visual Estimation of Line Density*[24]:

77.1.1 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:

$$PS = (E_{min}/E_{max}) \times (A_s/100) \times (I_s/100) \times 10^6 \qquad (12)$$

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:

$$C_i = PS \times (E_{max}/E_{det}) \times (100/I_i) \qquad (13)$$

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

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[18] Jarrell-Ash Model 24-310 or equivalent has been found satisfactory.

[19] Ilford QII have been found satisfactory.

[20] Surveyor Microfilm Readers or equivalent has been found satisfactory.

[21] A Spectrometer Type MS-7 or MS-702, made by Associated Electrical Industries, Ltd., has been found satisfactory.

[22] Eastman Kodak D-19 developer has been found satisfactory.

[23] Eastman Kodak rapid fixer has been found satisfactory.

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[24] The SSMS2 Program for CEIR Computer Service has been satisfactory for this estimation.

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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:

$$W_i = C_i \times (I_d/M_a) \tag{14}$$

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.)

77.2 *Measurement of Line Density*[25]:

77.2.1 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.

77.2.2 When a standard having the same ratio of PuO_2 to silver metal and containing the same impurity elements as the sample is available, then under the same conditions of exposure:

$$C_i = (I_u/I_s) \times C_s \tag{15}$$

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.

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

$$C_i = (D_i/D_s) \times (A_s/100) \times (I_s/I_i) \times (E_s/E_i) \times (S_s/S_i) \times (M_i/M_s) \tag{16}$$

where:
C_i = concentration of the impurity in the sample, atom %,
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 %,
I_s = isotopic abundance of the standard isotope, %,
I_i = isotopic abundance of the impurity isotope, %,
E_s = exposure at which the standard line is measured, nC,
E_i = exposure at which the impurity line is measured, nC,
S_s = relative sensitivity factor for the standard element,
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).

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[25] The use of SSMS Program for CEIR Computer Service has been satisfactory for this computation.

78. Precision and Bias

78.1 The microphotometric method for spectral density interpretation should be employed for PuO_2 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_2. Since standards are used, this test method is unbiased.

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

MOISTURE BY THE COULOMETRIC ELECTROLYTIC MOISTURE ANALYZER

79. Scope

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

80. Summary of Test Method

80.1 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.

80.2 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

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

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

81. Apparatus

81.1 *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 cm³/min of air, and a dryer assembly.[26]

81.2 *Balance*,[27] for weighing samples in the range from 1 to 100 mg.

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

82. Reagents

82.1 *Barium Chloride Dihydrate* ($BaCl_2 \cdot 2H_2O$).

83. Operation

83.1 Turn the main power switch ON.

83.2 Adjust the nitrogen gas pressure to 41.4 kPa (6 psi) and the flow rate to 50 cm³/mn, measured at the exit of the apparatus.

83.3 Weigh the sample into a small, dry aluminum boat (Note 14) and insert it into the instrument oven as follows:

NOTE 14—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.

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

83.3.2 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.

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

83.4 Reset the counter to 0 µg.

83.5 Set the timer at 1 h.

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

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

84. Standardization

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

84.2 Weigh and analyze replicate 5-mg samples of $BaCl_2 \cdot 2H_2O$ until consistent results are obtained. Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$) may also be used for calibration.

85. Calculation

85.1 Calculate the moisture recovery, Z, for the standard as follows:

$$Z = (A - B)/147.2Y \qquad (17)$$

where:
A = micrograms of moisture on counter when standard is tested,
B = micrograms of moisture on counter from blank, and
Y = milligrams of $BaCl_2 \cdot 2 H_2O$. Each milligram of $BaCl_2 \cdot 2 H_2O$ contains 147.2 µg of water.

85.2 Calculate the percent moisture in the sample as follows:

$$Moisture, \% = [(S - B)/1000 \, WZ] \times 100 = (S - B)/10 \, WZ \qquad (18)$$

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.

86. Precision

86.1 The relative standard deviation for moisture in a concentration range of 100 µg/g is approximately 2 % but increases to 10 % at the 20 µg/g level.

TOTAL GAS IN REACTOR-GRADE PLUTONIUM DIOXIDE PELLETS

87. Scope

87.1 This test method covers the measurement of volatiles other than water in reactor-grade plutonium dioxide pellets (**19**). The lower limit of the test method using the described equipment and a sample of approximately 1 g is 0.01 cm³ per gram of sample at STP conditions.

88. Summary of Test Method

88.1 A weighed sample is transferred into the outgassing section of the apparatus in a position for subsequent dropping into a tungsten crucible. The system is evacuated and the tungsten crucible without the sample is outgassed at 1600°C until the gas released from the empty crucible during a 35-min collection period decreases to less than 0.01 cm³ at STP conditions. After the crucible cools, the sample is dropped into it and heated at 1600°C for 35 min. The released gas passes through a magnesium perchlorate trap to remove water vapor and thence into a calibrated volume where the temperature and pressure are measured. The gas content of the sample is calculated at STP conditions assuming that the released gas is ideal. Since this is an empirical test method, it is important that the steps of the procedure be followed carefully in order to ensure results that have a reliability approximating that given in Section 94.

89. Interferences

89.1 No interferences are expected with the exception of water in the sample which partially reacts with the tungsten crucible to produce hydrogen. The magnitude of this interference, although unknown, probably is insignificant because of rapid removal of water vapor from the vicinity of the crucible.

[26] A CEC Solids Moisture Analyzer, of Type 26-321A-MA, available from Du Pont Instruments, Inc., S. Shamrock Ave., Monrovia, CA 91016.
[27] A Cahn Electrobalance or equivalent available from Cahn Division, Ventron Instruments Corp., Paramount, CA, has been found to be satisfactory.

90. Apparatus

90.1 *Vacuum Outgassing and Gas Measuring Apparatus*, (see Figs. 7-9).

90.1.1 *Outgassing Section* (Figs. 7 and 8), consisting of a water-cooled, fused-silica furnace tube heated with induction coils, and a pellet loading arm with an externally operated magnet feed. A glass wool plug is placed in the line just after the furnace tube adapter to prevent transfer of small particles of plutonium dioxide to the gas-measuring section.

90.1.2 *Gas Measuring Section* (Fig. 9), consisting of a mercury diffusion pump capable of transferring the gas against a forepressure equivalent to 666 Pa (5 torr), a magnesium perchlorate trap to remove water, another mercury diffusion pump, a Toepler pump fitted with a removable calibrated-volume sample tube and a McLeod gage, a mercury diffusion pump, and a mechanical forepump. The Toepler pump cycle is controlled by electrically timed solenoid valves in the vacuum and pressure lines. This method of control eliminates the possibility of reactions caused by electrical sparks in a system controlled by mercury contacts. The mechanical pump should be used to maintain vacuum in the system during periods when the equipment is not in use.

91. Reagents

91.1 *Grease*, high-vacuum (silicone).

91.2 *Magnesium Perchlorate*, anhydrous ($Mg(ClO_4)_2$).

92. Procedure

92.1 Determine a crucible blank for the entire system before each sample is analyzed. The procedure for the crucible blank is included in 92.3.

92.2 The apparatus can be calibrated by either of the two following methods:

FIG. 7 Induction Furnace
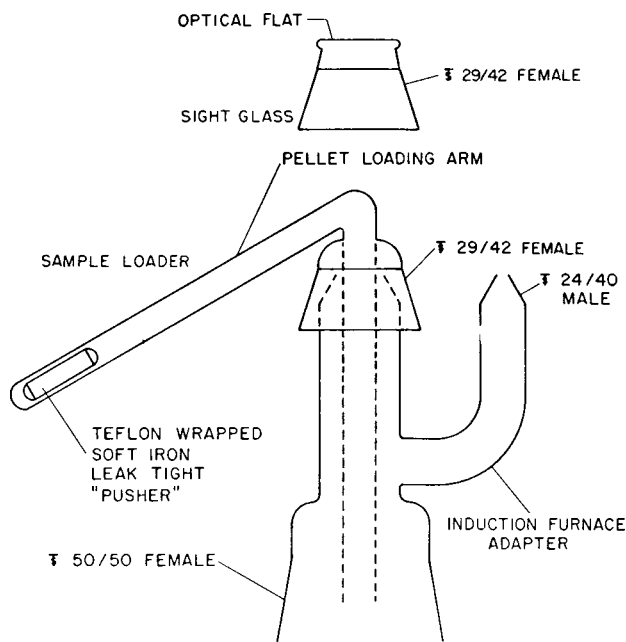
FIG. 8 Furnace Tube Adapter and Sample Loader

92.2.1 Measure the volume of the removable sample tube on the Toepler pump or,

92.2.2 A more accurate method is to introduce known volumes of gas into the system through V in Fig. 9 and measure these in the gas-measuring section in the same manner as the samples are measured. The calibration gas for this method can be hydrogen, usually a major component of the gas released from samples. A series of known volumes covering the range from 0.01 to approximately 0.2 STP cm^3 is recommended for this method. This technique corrects for slight losses in the vacuum pumps.

92.3 *Analysis of Samples*:

NOTE 15—Only results that fall within the linear range of the calibration curve should be accepted. If results on samples are beyond this range the test should be repeated with a smaller sample.

92.3.1 Start the three diffusion pumps. Refer to Fig. 9 for all steps.

92.3.2 Close valves V_2 and V_3.

92.3.3 Open the valve V_1 and flush the furnace tube with argon while placing the sample in the sample loader.

92.3.4 Transfer a weighed sample into the arm of the sample loader.

92.3.5 Replace the sample loader on the furnace tube adapter, using silicone grease to make a seal.
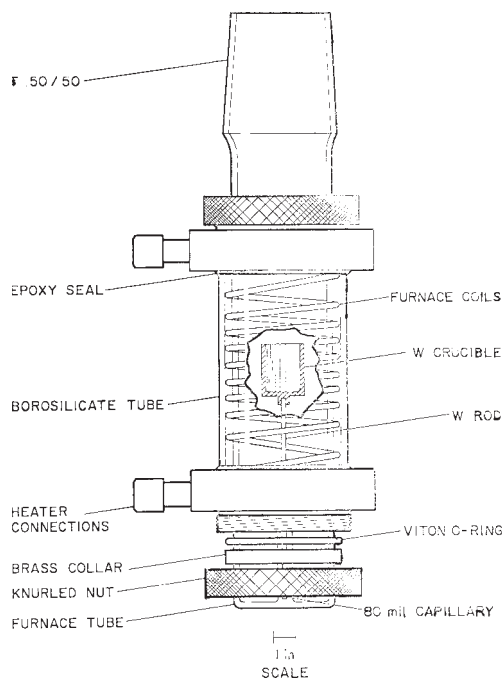
92.3.6 Close valves V_1, V_4, V_5, V_7, V_8, V_{10}, V_{12}, and V_{16}.

92.3.7 Slowly open valve V_3 to evacuate the system with the mechanical pump, Q.
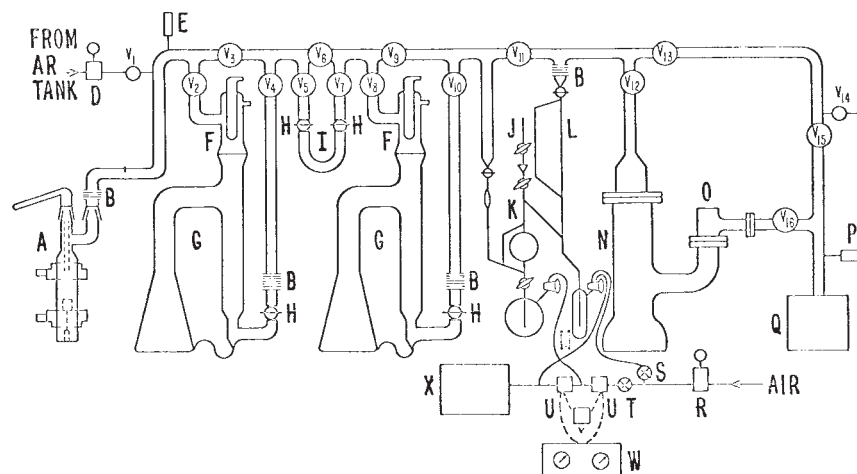
NOTE 16—Rapid opening of valve V_3 will cause violent agitation of the mercury in the Toepler pump and possible breakage of the pump.

92.3.8 When the pressure indicated on thermocouple gage, P, decreases to 67 Pa (0.5 torr), open valves V_2, V_4, V_5, V_7, V_8, V_{10}, V_{12}, and V_{16}, and close valves V_3, V_6, V_9, V_{13}, and V_{15}.

92.3.9 When the pressure decreases to less than 1.33 Pa (0.01 torr), start the induction generator and slowly heat the crucible up to 1600°C over a period of approximately 4 h.

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A—Induction furnace.
B—Monel bellows.
D—Low pressure regulator.
E—Thermocouple gage.
F—Water-cooled condenser.
G—Mercury diffusion pumps.
H—Semi ball joint.
I—Magnesium perchlorate trap.
J—Calibrated sample volume.
K—Toepler pump.
L—McLeod gage.

M—Mercury reservoir.
N—Mercury diffusion pump.
O—Water-cooled condenser.
P—Thermocouple gage.
Q—Mechanical forepump.
R—Low pressure regulator.
S—Needle valve.
U—Solenoid valves.
V—Electric counter.
W—Electric timer.
X—Mechanical vacuum pumps.

FIG. 9 Outgassing and Gas Measuring Apparatus

NOTE 17—A slow outgassing rate is required to prevent excessive coating of the furnace tube walls with tungsten oxides formed by the reaction between tungsten and water vapor. An excessive deposit causes overheating of the O-ring seals and leakage of cooling water.

92.3.10 Heat the crucible at 1600°C for 0.5 h; then close valve V_{11}, and adjust the pressure in the mercury reservoir, M, using needle valve, S, until mercury half fills the side arm leading to the Toepler pump.

92.3.11 Turn on the Toepler pump timer, W, and collect the gas evolved from the crucible in the sample tube, J, for 70 cycles of the Toepler pump as registered on the counter, V.

NOTE 18—The time required for collection is dependent on the construction of the Toepler pump. The use of large-bore stopcocks and tubing will permit a cycle rate of 1 cycle per 25 to 30 s.

92.3.12 At the completion of the collection period close the stopcock between the Toepler pump mercury reservoir and the expansion volume with the mercury at the top of its cycle.

92.3.13 Open valve V_{11} and raise the mercury in the side arm by opening needle valve S_1 until the level reaches a predetermined calibration mark on the sample tube.

92.3.14 Measure the difference in heights of the columns of mercury in the sample tube and the adjacent McLeod gage, L. This difference is the total pressure of the collected gas.

92.3.15 Record the temperature of the sample tube and the pressure of the gas, and calculate the volume of the gas at STP conditions.

92.3.16 Evacuate the sample tube by turning the two-way stopcock on the mercury reservoir M to vacuum and lowering the level of mercury in the side arm.

92.3.17 When a stable crucible blank of less than 0.01 cm^3 is attained, turn off the induction generator and allow the crucible to cool.

92.3.18 Transfer the sample to the crucible by pushing it along the arm of the sample loader with an iron piece guided from outside with a magnet.

92.3.19 Close valve V_{11} and start the induction generator to heat the crucible and sample to 1600°C.

92.3.20 Collect the evolved gases in the same manner as in the blank determination.

92.3.21 Turn off the induction generator and record the pressure and the temperature of the sample tube.

92.3.22 If a gas sample is desired for a gas composition analysis, remove the sample tube and transfer it to the desired analytical apparatus.

93. Calculation

93.1 Where the sample tube has been calibrated with a series of known volumes of gas calculate as follows: Use least-squares formulas to calculate the best linear equation relating the known volumes of gas in STP cm^3 to the measured pressure in the sample tube in torr corrected to 273 K:

$$P_M = a + b\,(STP\ \mathrm{cm}^3{}_I) \qquad (19)$$

where:

P_M = measured pressure, in torr, corrected to 273 K,

    = $273\,P_0/(T_0 + 273)$,

a = intercept of least-squares equation, and

b = slope of least-squares equation.

20

STP cm^3_I = known volume introduced corrected to 760 torr and 273 K,
$$= (P_0/760)\cdot [273\ V_0/(273 + T_0)]$$

where:
P_0 = observed pressure, torr,
V_0 = observed volume, cm^3, and
T_0 = observed temperature, °C.

Gas in sample per gram of sample:

$$STP\ cm^3_s/g = (P_S - P_B)/bW \qquad (20)$$

where:
STP cm^3_s/g = cm^3 of total gas per gram of sample at 760 torr and 273 K,
P_S = measured pressure for sample, in torr, corrected to 273 K,
P_B = pressure for blank, in torr, corrected to 273 K,
b = slope of least-squares equation, and
W = sample mass, g.

93.2 Where the volume of the sample tube has been measured calculate the total gas content per gram of sample as follows:

$$Total\ gas,\ STP\ cm^3_s/g = [(273\ P_S V/760\ T_S) - (273\ P_B V/760\ T_B)]/W \qquad (21)$$

where:
STP cm^3_s/g = cm^3 of total per gram of sample, at 760 torr and 273 K,
P_S = recorded pressure, torr, for sample,
V = measured volume, cm^3, of sample tube,
T_S = recorded temperature of sample tube, for sample gas, K (°C + 273),
P_B = pressure, torr, for blank,
T_B = recorded temperature of sample tube for blank, K, and
W = mass of sample, g.

94. Precision and Bias

94.1 Since pellets with known volatile gas contents are not available, the bias of the test method is not known. Estimates of the precision, including the between-pellet variability, indicate a relative standard deviation of about 25 % at a level of approximately 0.050 cm^3/g of sample at STP conditions.

PLUTONIUM-238 ISOTOPIC ABUNDANCE BY ALPHA SPECTROMETRY

95. Scope

95.1 This test method covers the determination of the^{238}Pu isotopic distribution in plutonium dioxide (PuO$_2$) samples. It is particularly useful for samples in which the ^{238}Pu content is in the range from 0.01 to 1 %.

96. Summary of Test Method

96.1 The isotopic analysis of plutonium for the ^{238}Pu isotope involves the prior separation of interferences. After dissolution of the sample the plutonium is separated from interferences by an anion exchange technique (20–22). Nitric acid HNO$_3$(4 M) is used to adsorb the plutonium fraction on the resin and to elute interfering ions principally uranium and americium. The plutonium is then eluted with HNO$_3$ (0.5 M). Since an alpha-activity ratio is measured in the determination, quantitative recovery of the plutonium is not required. The alpha spectrum in the 5 to 6-MeV region is then obtained. The total counts in the ^{238}Pu and the ^{239}Pu + ^{240}Pu peaks are obtained and corrected for background. The ^{238}Pu abundance is calculated from the ratio of the alpha activity due to ^{238}Pu and that due to ^{239}Pu + ^{240}Pu. The abundance of ^{239}Pu and ^{240}Pu is determined by mass spectrometry on a separate portion of the purified sample.

97. Interferences

97.1 ^{241}Am is always present as a result of ^{241}Pu decay and is a direct interference which must be removed prior to the determination of ^{238}Pu. Other nuclides which would interfere such as ^{232}U, ^{243}Am, ^{245}Cm, and ^{249}Bk are not likely to be present following the separation. Uranium, while not a direct interference to the alpha-pulse height determination, can contribute a high-salt content to the sample mount which can decrease resolution of the alpha spectra and consequently decrease the sensitivity of the test method. The uranium is an interference for the mass spectrometer analysis part of this procedure.

97.2 Alpha spectrometry is done within a day or two of the purification, especially if the abundance of ^{241}Pu is high, since ^{241}Am will grow in again from the beta decay of ^{241}Pu. However, if prompt analysis is not possible, suitable corrections for the bias due to ^{241}Am interference may be made up to a period of several weeks following the purification.

98. Apparatus

98.1 *Ion-Exchange Column*, disposable polyethylene (see Fig. 10). Enough glass wool is added to the column to hold the resin. Approximately 32 mm of converted resin (see Section 99) is added. The resin is then washed with 10 mL of 10 M HNO$_3$.

98.2 *Counting Disks*, polished platinum, tantalum, or stainless steel, sized to fit the detection chamber. A disk 25 mm in diameter and 0.5 mm thick is commonly used.

98.3 *Alpha Spectrometer*—This should consist of the following components:

98.3.1 *Silicon Surface Barrier Detector*, with an active area of at least 100 mm^2, 100 μm or greater depletion depth, and a resolution of 20 keV or less full width at half maximum (FWHM) (for ^{241}Am 5.486 MeV alphas) is suitable. A detector with a rear microdot connector should be specified.

98.3.2 *Evacuable, Light-Tight Chamber*, [28] in which the detector and the counting plate on its support can be mounted.

98.3.3 *Preamplifier*, charge-sensitive field effect transistor, with noise less than 4.6 keV when used with above detector (100 pF capacitance).

98.3.4 *Detector Bias Supply*, 0 to 1000 V, continuously variable, well-regulated and stable, with noise and ripple less than 0.0002 %.

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[28] A simple but adequate chamber is commercially available from ORTEC or Tennelec, Oak Ridge, TN.
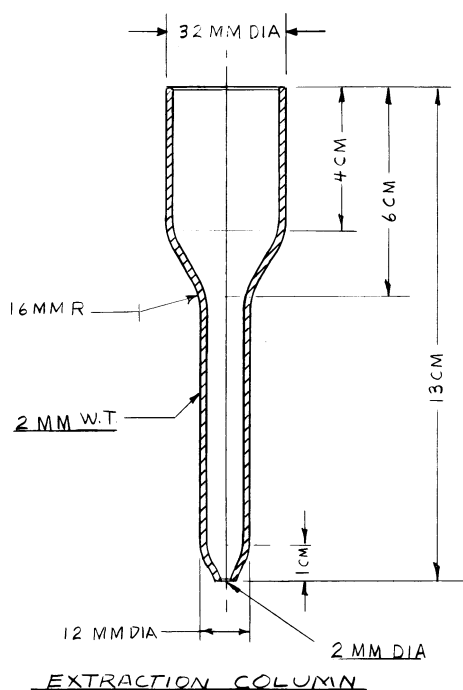
FIG. 10 Extraction Column

98.3.5 *Main Spectroscopy Amplifier*, low noise, with variable shaping constants and baseline restoration.

98.3.6 *Biased Amplifier and Pulse Stretcher*, with continuously adjustable post-gain and automatic pile-up rejection.

98.3.7 *Multichannel Pulse-Height Analyzer*—A multichannel analyzer is most versatile and convenient, since it can be used for the acquisition of data from one to four detectors simultaneously. Even if only one detector is used, such an analyzer has the advantage that background may be stored in another subgroup and subtracted electronically from the spectrum of interest, and that several spectra can be stored and compared. An analyzer that permits setting windows around the peaks of interest and electronic integration is especially convenient. The analyzer should accept pulses 0 to 10 V and 3 to 6 μs in width, and should have a capacity of at least $10^7 - 1$ counts full scale per channel.

98.3.8 *Teletype, Typewriter, or Other Peripheral Device*, may be used for output of the data from the multichannel analyzer.

98.4 *Micropipets*, 50 μL.

98.5 *Infrared Heat Lamp*.

99. Reagents and Materials

99.1 *Anion Exchange Resin*[29] (50 to 100 mesh) containing pyridinium exchange groups (basic resin-chloride ionic form) is prepared by washing thoroughly with 1 *M* sodium hydroxide (NaOH) solution until the resin turns dark brown in color then with 1 *M* nitric acid (HNO_3) wash until the resin returns to its original yellow color. Repeat once and store in deionized water.

99.2 *Deionized Water*.

99.3 *Hydrochloric Acid* (HCl), 6 *M*.

99.4 *Hydrofluoric Acid* (HF), concentrated.

99.5 *Nitric Acid* (HNO_3) (0.5 *M*, 1 *M*, 4 *M*, 10 *M*).

99.6 *Nitric Acid* (HNO_3), concentrated.

99.7 *Sodium Hydroxide Solution* (NaOH) (1 *M*).

100. Calibration of the Alpha Spectrometer

100.1 *Initial Alignment*—Set the biased amplifier so that channel zero is at about 5 MeV. Use a standard alpha source such as the 5.30 MeV particle of ^{210}Po, or the 5.49 MeV particle of ^{241}Am, for calibration. Establish the system gain at some convenient value, such as 5 keV per channel.

100.2 *Resolution*—Count the standard source and determine the energy span at half the peak height. A FWHM of 30 keV or less is desirable, but 50 keV can be tolerated.

100.3 *Background*—Obtain a background spectrum with a clean counting disk in the chamber.

100.4 *Frequency of Calibration*—The system gain and resolution should be checked periodically, in order to maintain the same operating conditions and to check whether any deterioration of the spectrometer has taken place. Daily background counting is advisable, to ensure that there has been no contamination of the chamber or detector.

101. Procedure

101.1 *Preparation of Sample*:

101.1.1 Weigh sufficient sample to provide 50 ± 5 mg of plutonium. Transfer to a vial. Add 10 to 15 mL of 10 *M* HNO_3 and one drop of concentrated HF. Bring to slow boiling on a hot plate, at medium setting. The sample should be dissolved in approximately 1 h.

101.1.2 Transfer 250 μL of the plutonium sample solution (~1 mg Pu) to a freshly prepared ion exchange column (98.1 and 99.1).

101.1.3 Wash the ion exchange column with approximately 4 column volumes of 4 *M* HNO_3.

101.1.4 Elute the plutonium from the resin by washing with 10 mL of 0.5 *M* HNO_3.

101.1.5 Mount 10 μL from the elution on a counting disk and dry under a heat lamp.

101.1.6 Fire the disk by slowly heating the disk to dull redness in a flame.

101.1.7 Place the counting disk in the chamber of the alpha spectrometer and evacuate the chamber. Count the sample until there are at least 2500 and preferably 10 000 counts or more in the 5.50-MeV peak of ^{238}Pu.

101.1.8 Obtain the total count for an equal number of channels over the ^{238}Pu (5.50 + 5.46 MeV) peaks and the ^{239}Pu + ^{240}Pu (5.11 to 5.17 MeV). Subtract the background counts in the same channels, adjusted for the same counting time, from the total counts in the peaks, to obtain the net counts.

101.1.9 Using an aliquot from the purified sample obtained in 126.1.4, perform analysis for ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu by mass spectrometry in accordance with Sections 113 to 121.

101.1.10 Calculate the weight percent ^{238}Pu as follows:

$$W_8 = \frac{C_8(W_9 A_9 + W_0 A_0)}{A_g C_9} \tag{22}$$

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[29] Bio Rad Laboratories "Bio-Rex 9" has been used successfully.

where:
W_8 = weight % of ^{238}Pu,
W_9 = weight % of ^{239}Pu from mass spectrometry (normalized),[30]
W_0 = weight % of ^{240}Pu from mass spectrometry (normalized),[30]
A_8 = alpha specific activity of ^{238}Pu,
A_9 = alpha specific activity of ^{239}Pu,
A_0 = alpha specific activity of ^{240}Pu,
C_8 = observed counts in ^{238}Pu peaks, and
C_9 = observed counts in ^{239}Pu peaks + ^{240}Pu peak

The specific activity of a nuclide is calculated from its halflife by the formula:

$$\text{Specific activity, d/min·µg} = \frac{7.942 \times 10^{11}}{At_{1/2}} \qquad (23)$$

where:
d = disintegrations,
A = atomic weight of the nuclide, and
$t_{1/2}$ = half-life, years (see Table 3).

Units of the specific activity are disintegrations per minute per microgram.

102. Precision and Bias

102.1 The relative standard deviation of the test method for a single determination is 2 % or better, depending on the total integrated counts in each peak. The 2 % figure is based on accumulating at least 2500 counts in the ^{238}Pu alpha peak for samples containing 0.01 % of that isotope. For most samples, a much larger count will be accumulated in this peak, with correspondingly better precision. The inaccuracy with which the half-lives of the plutonium isotopes are known constitutes a bias of the test method.

AMERICIUM-241 IN PLUTONIUM BY GAMMA-RAY SPECTROMETRY

(Test Method 1268 may be used for the determination of Americium-241 in plutonium.)

RARE EARTHS BY COPPER SPARK-SPECTROSCOPY

103. Scope

103.1 This test method covers the determination of rare earths in plutonium dioxide over the range from 10 to 200 µg/g.

104. Summary of Test Method

104.1 The general principles of emission spectrographic analysis are given in Methods for Emission Spectrochemical Analysis (23). Determination of rare earth content requires their separation from oxides of plutonium by solvent extraction followed by copper-spark spectrographic measurement (24, 25).

105. Apparatus

105.1 *Spectrograph*—Commercially available equipment with reciprocal dispersion of approximately 2.5 Å/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 107.4.

105.2 *Microdensitometer*, having a precision of ±1.0 % for transmittances between 5 and 90 %.

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

105.4 *Magnetic Stirrer*.

105.5 *Photographic Plates*. [31]

106. Reagents and Materials

106.1 *Boric Acid Crystals* (H_3BO_3).

106.2 *Dissolution Mixture*—Add 10 drops of hydrofluoric acid (HF, 1 + 20) to 10 mL of nitric acid(HNO_3, sp gr 1.42).

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

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

106.5 *Internal Standard Solution, Yttrium* (1 mL = 2.5 µg Y)—Dissolve 100 mg of yttrium metal in HCl (1 + 1) and dilute to 100 mL with HCl (1 + 1). Dilute 250 µL of this solution to 100 mL with HCl (1 + 1).

106.6 *Nitric Acid* (4 M)—Dilute 2.6 mL of nitric acid (HNO_3, sp gr 1.42) to 10 mL with water.

106.7 *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 µg of element per millilitre of solution.

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

107. Procedure

107.1 *Dissolution of Sample*:

107.1.1 Weigh a pellet (approximately 1.5 g) or powder (approximately 1 g) to ±0.001 g and place in a 50-mL volumetric flask.

107.1.2 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.

107.2 *Separation from Actinides*:

107.2.1 Transfer a 10-mL aliquot of the solution from Section 107 to a 35-mL vial containing 10 mL of TOA, 4 mL of the internal standard solution, 5 mg of H_3BO_3 crystals, and a magnetic stirring bar.

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

107.2.3 Discard the organic phase (upperlayer).

107.2.4 Add 10 mL of TOA and repeat 107.2.2 and 107.2.3.

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

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

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[30] The mass spectrometry values for ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu should be normalized to 100 %.

[31] Eastman Kodak SA-1 or equivalent are to be used.

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

107.3 *Preparation of Electrode*:

107.3.1 Transfer 50 µL of the solution from 107.2.7 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.

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

Electrical Parameters:	
Discharge,	H V spark
Voltage, V (Primary)	90
Capacitance, µH	0.0025
Current, A, r-f	10
Exposure Conditions:	
Analytical gap, mm	2.0
Prespark	0
Exposure, s	30
Slit width, µm	10
Slit height, mm	2
Filter, percent transmittance	100/50

108. Photo Processing

108.1 Process the emulsion in accordance with Practices E 115.

109. Photometry

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

110. Calibration

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

110.2 *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.

111. Calculation

111.1 Convert the transmittances of the analytical and 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[A]

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

[A]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,Å
Sm	3568.27
Eu	3819.67
Gd	3362.23
Dy	3531.70
Y	3710.30
	(internal standard)

112. Precision and Bias

112.1 *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.

112.2 *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

113. Scope

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

114. Summary of Test Method

114.1 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 19—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.

115. Interferences

115.1 Uranium-238, if present, interferes with the measurement of ^{238}Pu, and ^{241}Am interferes with the measurement of^{241}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.

116. Apparatus

116.1 *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 **(26), (27)** well-designed single-stage mass spectrometer should resolve adjacent masses in the 230 to 245 mass range with less than 1×10^{-4} interaction between tails. Abundance sensitivities of less than 1 in 20 000 should be obtained.

116.2 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 ±0.5 relative %.

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

117. Reagents

117.1 *Anion Exchange Resin* [32]

117.2 *Ferrous Sulfamate Solution* (3.2 *M*)—Dissolve 794 g of ferrous sulfamate ($Fe(NH_2SO_3)_2$) in water and dilute to 1 L.

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

117.4 *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.

117.5 *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 as a preservative in reagent grade hydriodic acid. This can be done by distilling the hydriodic acid.

117.5.1 **Caution**—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.

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

117.7 *Hydroxylamine Hydrochloride Solution* (5 *M*)—Dissolve 348 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in water and dilute to 1 L.

117.8 *Nitric Acid* (0.75 *M*)—Dilute 4.8 mL of nitric acid (HNO_3, sp gr 1.42) to 100 mL with water.

117.9 *Nitric Acid* (1 *M*)—Dilute 6.3 mL of nitric acid (HNO_3, sp gr 1.42) to 100 mL with water.

117.10 *Nitric Acid* (8 *M*)—Dilute 50 mL of nitric acid (HNO_3, sp gr 1.42) to 100 mL with water.

117.11 *Nitric-Hydrofluoric Acid Mixture* (15 *M* HNO_3-0.05 *M* HF)—Add 0.9 mL of hydrofluoric acid (HF, sp gr 1.15) to 485 mL of nitric acid (HNO_3, sp gr 1.42) and dilute to 500 mL with water.

117.12 *Perchloric Acid* (1 *M*)—Dilute 17 mL of perchloric acid ($HClO_4$, sp gr 1.67) to 200 mL with water.

117.13 *Perchloric Acid* (6 *M*)—Dilute 5 mL of perchloric acid ($HClO_4$, sp gr 1.67) to 10 mL with water.

117.14 *Sodium Nitrite Solution* (2 *M*)—Dissolve 138 g of sodium nitrite ($NaNO_2$) in water and dilute to 1 L.

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

118. Calibration of the Mass Spectrometer

118.1 *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.

118.2 The recommended calibration standard, for determination of mass discrimination to be used to correct plutonium ratios, is NIST SRM U500 (Note 20). The deviation from the certified value is a measure of the mass discrimination of the spectrometer for a three mass unit difference. Using the $^{235}U/^{238}U$ mass discrimination factor, the mass discrimination is then calculated for each ratio and mass range to be calibrated. The $^{235}U/^{238}U$ mass discrimination factor, *B*, is calculated as follows:

$$B = (1/\Delta M)\left[\bar{R}/R_s\right] - 1] \qquad (24)$$

where:
B = mass discrimination factor,
ΔM = mass unit difference = (238-235),
R_s = certified value of SRM, and
$\bar{R}$ = verage measured value of $^{235}U/^{238}U$ for *n* different analyses.

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

NOTE 20—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 SRMs available from NIST, certified relative to uranium, present some unfavorable factors, magnitude of the $^{239}Pu/^{240}Pu$ ratios and the small (one) mass difference, for the most precise and accurate mass discriminatiuon determination; it is an attractive alternative that establishes a common measurement base using plutonium.

118.3 *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 $^{235}U/^{238}U$, under identical analytical conditions, of NIST SRMs U100-U500-U900, SRMs U050 through SRM U930, or SRMs U005 through U970, respectively. The ratio of the certified $^{235}U/^{238}U$ ratio to the experimental $^{235}U/^{238}U$ 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 SRMs are used because the range of isotopic ratios of existing plutonium SRMs is not adequately large.

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[32] Bio-Rad AGMP-1, 50–100 mesh, has been found satisfactory.

119. Procedure

119.1 *Sample Preparation*—Dissolve a few milligrams of PuO_2 in 15 M HNO_3-0.05 M HF mixture by heating. Dilute the sample solution in enough 1 M $HClO_4$ to give a solution containing 100 µg Pu/mL.

119.2 *Separation of Plutonium by Solvent Extraction*:

119.2.1 Take an aliquot of the sample solution containing 10 µg of Pu and evaporate to dryness.

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

119.2.3 Add 10 µL of ferrous sulfamate solution and 50 µL of 5 M hydroxylamine hydrochloride. Digest for 5 min at 80°C.

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

119.2.5 Add 500 µL of 2 M $NaNO_2$ and digest for 5 min at 80°C.

119.2.6 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.

119.2.7 To the TTA phase, add 2 mL of 1 M HNO_3, stir for 2 min, centrifuge, and transfer the TTA phase to a clean vial.

119.2.8 Repeat 119.2.7.

119.2.9 Add 1 mL of 8 M HNO_3, stir for 2 min, centrifuge, and transfer the aqueous phase to a clean vial.

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

119.2.11 Dissolve the plutonium residue in 0.5 mL of 0.75 M HNO_3.

119.3 *Separation of Plutonium by Ion Exchange* (**28**):

119.3.1 Add 10 drops of 6 M $HClO_4$ and 10 drops of 1 M HF to an aliquot of the sample solution (145.1) containing approximately 30 µg of plutonium and evaporate to dryness.

119.3.2 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.

Note 21—Prepare a column as follows: place a glass or plastic wool plug in the bottom of a 6 by 60-mm column. 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. Condition the column just before use by passing 5 mL of 12 M HCl through the column.

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

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

119.3.5 Add 0.5 mL of 15.4 M HNO_3 and fume to dryness to expel chloride and destroy any organic matter.

119.3.6 Repeat 119.3.5.

119.3.7 Dissolve the plutonium residue in 1.5 mL of 0.75 M HNO_3.

119.4 *Mass Spectrometer Measurement*:

119.4.1 Mount the sample by placing 10 µL of solution, containing 0.2 µg of plutonium on each suitably prepared 0.031 by 0.762-mm (0.0012 by 0.030-in.) rhenium sample filament (Note 22) 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 22—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 ½ h at approximately 2000°C.

119.4.2 Insert the filament assembly into the mass spectrometer and obtain a source pressure of less than 400 µPA (3×10^{-6} torr).

119.4.3 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 23—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.

119.4.4 *Heating Pattern and Isotopic Ratio Measurement*:

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

Note 24—The ^{187}Re signal is normally 1.5 to 1.8×10^{-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.

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

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

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

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

119.4.4.6 At 25 min, readjust, if necessary, the sample filament currents to yield a Pu$^+$ signal of 1×10^{-11}A. Focus for maximum intensity. Determine baselines for ^{239}Pu and ^{240}Pu (see Note 27).

119.4.4.7 At 30 min, start the ratio measurement (Note 25). The Pu$^+$ signal intensity should be approximately $1.0–1.2 \times 10^{-11}$A and slowly changing. For complete isotopic characterization, measure the ratios (Note 26) on a strict time schedule that is the same for each analysis and in the following sequence: ^{239}Pu/^{240}Pu; ^{241}Pu/^{240}Pu; ^{242}Pu/^{240}Pu; ^{238}Pu/^{240}Pu; ^{242}Pu/^{240}Pu; ^{241}Pu/^{240}Pu; ^{239}Pu/^{240}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: $^{239}Pu/^{240}Pu$; $^{241}Pu/^{240}Pu$; $^{242}Pu/^{240}Pu$; $^{241}Pu/^{240}Pu$; $^{239}Pu/^{240}Pu$; and then measure $^{238}Pu/^{240}Pu$. 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 25—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 26—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.

120. Calculation

120.1 *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 27—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}Pu and ^{240}Pu baselines are the average of the initial and final low-mass and high-mass reading. Usually, the initial and final $^{239}Pu/^{240}Pu$ 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}Pu and other low-abundance isotopes is estimated as follows:

$$LMZ + (1/5) [HMZ - LMZ]$$

where:
LMZ = low-mass baseline, and
HMZ = high-mass baseline.

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

$$^{239}Pu/^{240}Pu = \bar{R}_{90} \qquad (25)$$

$$^{241}Pu/^{240}Pu = \bar{R}_{10} \qquad (26)$$

$$^{242}Pu/^{240}Pu = \bar{R}_{20} \qquad (27)$$

$$^{238}Pu/^{240}Pu = \bar{R}_{80} \qquad (28)$$

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

$$\bar{R}' = [\bar{R}/(1 + CB)], \text{ since } B$$

$$= 1/\Delta M[\bar{R}/R_s) - 1] \text{ then } 1 + \Delta MB$$
$$= \bar{R}/R_s \qquad (29)$$

where:
$\bar{R}'$ = final isotopic ratios corrected for mass discrimination,
$\bar{R}$ = average raw ratio, Δ
M = mass unit difference,
B = mass discrimination factor as determined in 118.2, and
R = average measured value of $^{235}U/^{238}U$ for n different analyses.

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

$$Atom \%, A = 100 \bar{R}'/(1 + \bar{R}'_{90} + \bar{R}'_{10} + \bar{R}'_{20} + \bar{R}'_{80}) \qquad (30)$$

$$Mass \%, W_m = 100 M\bar{R}'/(240.05 + 239.05 \bar{R}'_{90} \\ + 241.06 \ \bar{R}'_{10} + 242.06 \bar{R}'_{20} + 238.05 \bar{R}'_{80}) \qquad (31)$$

where:
A = atom percent of a given isotope,
$\bar{R}'$ = average corrected ion current ratio of the given isotope to the ^{240}Pu isotope (Note that $\bar{R}'$ for ^{240}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.

121. Precision and Bias

121.1 *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 2×10^{-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

121.2 *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 28—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

122. Scope

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

123. Summary of Test Method

123.1 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) **(29)**. These conditions are heating at 800°C for a minimum of 6 h in an atmosphere of hydrogen-helium saturated with water vapor at O°C. The O/M is calculated from the weight change.

124. Interferences

124.1 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.

124.2 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 PuO_2. These low-temperature calcined oxides often contain a variety of impurities which will interfere significantly with this O/M measurement.

125. Apparatus

125.1 *Analytical Balance*, capable of weighing within ±0.1 mg or better.

125.2 *Moisture Analyzer*, capable of measuring water contents of argon or helium to less than 200 ppm. [A Panametrics probe has been found satisfactory for this purpose.]

125.3 *O/M Apparatus*—See Fig. 11.

126. Reagents

126.1 *Argon*, prepurified grade **(30)** or equivalent, <20 ppm water. Test water content with a moisture analyzer to assure that the level is less than 20 ppm.

126.2 *Helium*, high-purity grade **(30)** or equivalent, <20 ppm water. Test water content with a moisture analyzer to assure that the level is less than 200 ppm.

126.3 *Hydrogen-Helium Mixture*, 6 % hydrogen, prepared from prepurified grade **(30)** or equivalent gases.

126.4 *Ice*.

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

127. Safety Precautions

127.1 Because of the toxicity of plutonium, all operations should be performed within an approved glove box fitted with appropriate filters to contain any small particles of plutonium. A detailed discussion of the necessary precautions is beyond the scope of these test methods; personnel involved in these analyses should be familiar with safe handling practices as given in Refs **(1-3)** through.

128. Procedure

NOTE 29—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 **(31, 32)**.

128.1 *Pellets*:

128.1.1 Adjust the flow rate of the hydrogen-helium (*B*) (see Fig. 11) 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.

128.1.2 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.

128.1.3 Remove the boats from the furnace tube, weigh each within ±0.1 mg, and repeat 128.1.2 and 128.1.3 until a constant tare weight (*W*) is obtained for each empty boat.

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

128.1.5 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 128.1.1 (300 to 500 mL/min of water-saturated hydrogen-helium with the furnace at 800°C).

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

128.1.7 Remove the boats from the furnace tube and weigh each within ±0.1 mg (W_2).

128.1.8 Repeat 128.1.5 through 128.1.7 until each boat weight remains constant within ±0.2 mg. (Heating for 6 h in 128.1.5 should be sufficient to attain constant weight.)

128.2 *Powders*:

128.2.1 Adjust the flow rate of dry helium or argon (*A*) (see Fig. 11) to 300 mL/min, adjust valves so that the gas does not
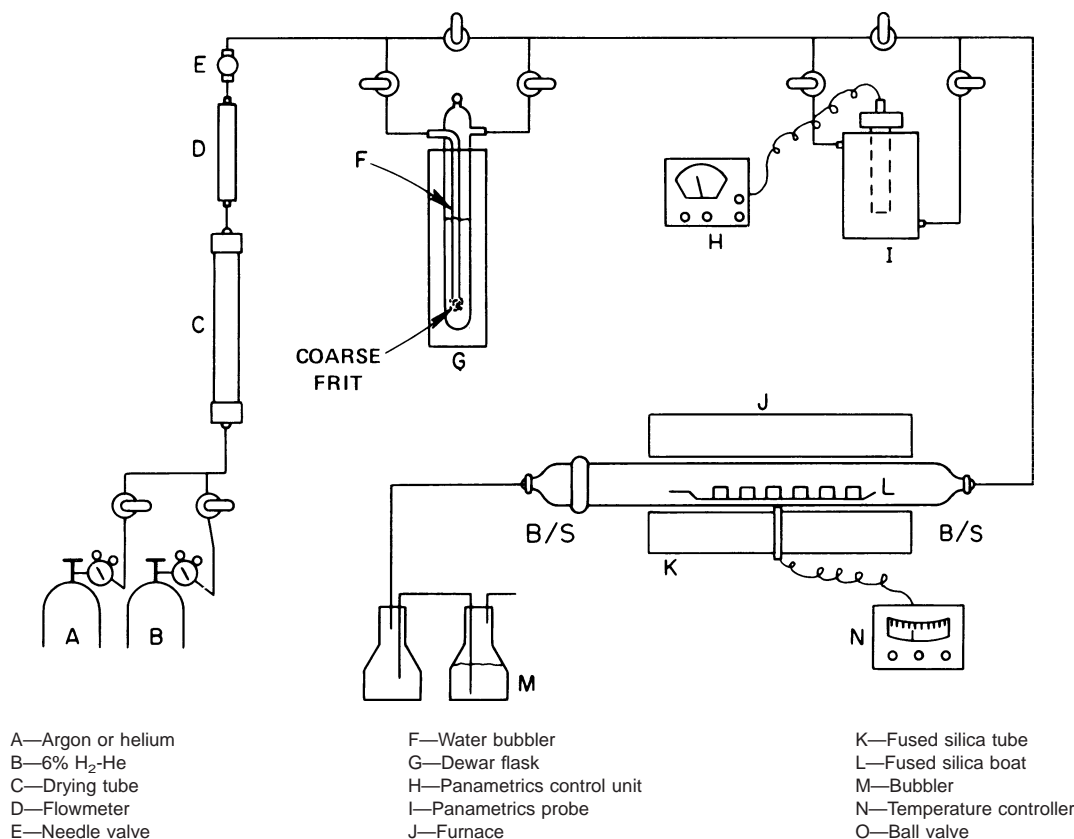
A—Argon or helium
B—6% H_2-He
C—Drying tube
D—Flowmeter
E—Needle valve

F—Water bubbler
G—Dewar flask
H—Panametrics control unit
I—Panametrics probe
J—Furnace

K—Fused silica tube
L—Fused silica boat
M—Bubbler
N—Temperature controller
O—Ball valve

FIG. 11 O/M Apparatus

pass through the bubbler, turn on the furnace (J), and adjust its temperature to 800°C.

128.2.2 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.

128.2.3 Remove the boats from the furnace tube, weigh each within ±0.1 mg, and repeat 128.2.2 and 128.2.3 until a constant tare weight (W_T) is obtained from each empty boat.

128.2.4 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.

128.2.5 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 ±0.1 mg.

128.2.6 Prepare the O/M apparatus as described in 128.1.1, place the boats and samples into the furnace tube, and heat a minimum of 6 h under the conditions given in 128.1.1 (300 to 500 mL/min water-saturated, hydrogen-helium gas flow; 800°C).

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

128.2.8 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.

128.2.9 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 ±0.1 mg.

128.2.10 Repeat 128.2.7 through 128.2.9, if necessary, to obtain constant weights (W_2).

129. Calculation

129.1 Calculate the O/M ratio as follows:

$$O/M = 2.000 - \frac{(W_2 - W_1) F}{(W_2 - W_T)} \tag{32}$$

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.

130. Precision and Bias

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

130.2 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.

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131. Keywords

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

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