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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Methods for Chemical and Mass Spectrographic Analysis of Nuclear-Grade Gadolinium Oxide (Gd_2O_3) Powder[1]

This standard is issued under the fixed designation C 889; 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 and mass spectrographic analysis of nuclear-grade gadolinium oxide powders to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

	Sections
Carbon by Direct Combustion—Thermal Conductivity	[2]
C 1408 Test Method for Carbon (Total) in Uranium Oxide Powders and Pellets By Direct Combustion-Infrared Detection Method	[3]
Total Chlorine and Fluorine by Pyrohydrolysis Ion—Selective Electrode	7-13
Loss of Weight on Ignition	14-20
Sulfur by Combustion—Iodometric Titration	[2]
Impurity Elements by a Spark-Source Mass Spectrographic	[2]
C 761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical,Nuclear, and Radiochemical Analysis of Uranium Hexafluoride	[3]
C 1287 Test Method for Determination of Impurities In Uranium Dioxide By Inductively Coupled Plasma Mass Spectrometry	[3]
Gadolinium Content in Gadolinium Oxide by Impurity Correction	21-24

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 hazard statements, see Section 5.

2. Referenced Documents

2.1 *ASTM Standards:*

C 696 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets[3]

C 761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical,Nuclear, and Radiochemical Analysis of Uranium Hexafluoride[3]

C 888 Specification for Nuclear-Grade Gadolinium Oxide (Gd_2O_3) Powder[3]

C 1287 Test Method for Determination of Impurities In Uranium Dioxide By Inductively Coupled Plasma Mass Spectrometry[3]

D 1193 Specification for Reagent Water[4]

E 115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis[5]

E 116 Practice for Photographic Photometry in Spectrochemical Analysis[5]

E 130 Practice for Designation of Shapes and Sizes of Graphite Electrodes[5]

C 1408 Test Method for Carbon (Total) in Uranium Oxide Powders and Pel lets By Direct Combustion-Infrared Detection Method[3]

3. Significance and Use

3.1 Gadolinium oxide powder is used, with subsequent processing, in nuclear fuel applications, such as an addition to uranium dioxide. These test methods are designed to determine whether the material meets the requirements described in Specification C 888.

3.1.1 The material is analyzed to determine whether it contains the minimum gadolinium oxide content specified.

3.1.2 The loss on ignition and impurity content are determined to ensure that the weight loss and the maximum concentration limit of specified impurity elements are not exceeded.

4. Reagents

4.1 *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.[6] 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.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined

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[1] These test methods are under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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[2] Discontined January 1999. See C 889–90.

[3] *Annual Book of ASTM Standards*, Vol 12.01.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] *Annual Book of ASTM Standards*, Vol 03.05.

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

in Specification D 1193.

5. Hazards

5.1 Proper precautions should be taken to prevent inhalation or ingestion of gadolinium oxide powders or dust during grinding or handling operations.

5.2 Workers should observe precautions as specified in vendor supplied Material Safety Data Sheets (MSDS).

6. Sampling

6.1 Criteria for sampling this material are given in Specification C 888.

CARBON BY DIRECT COMBUSTION—THERMAL CONDUCTIVITY

This Test Method was discontinued in January 1999 and replaced by C 1408

TOTAL CHLORINE AND FLUORINE BY PYROHYDROLYSIS ION—SELECTIVE ELECTRODE

7. Scope

7.1 This test method covers the determination of chlorine and fluorine in nuclear-grade gadolinium oxide (Gd_2O_3) powder. With a 1 to 10-g sample of Gd_2O_3, concentrations of 5 to 200 µg of chlorine and 1 to 200 µg of fluorine per gram of Gd_2O_3 are determined without interference.

8. Summary of Test Method

8.1 The halogens are separated from powdered gadolinium oxide by pyrohydrolysis in a quartz tube with a stream of wet oxygen at a temperature of 900 to 1000°C **(1, 2, 3, 4).**[7] Chlorine and fluorine are volatilized simultaneously as acids, absorbed in a buffer solution as chloride and fluoride, and measured with ion-selective electrodes **(4, 5, 6).**

9. Apparatus

9.1 *Pyrohydrolysis Equipment*—A suitable assembly of apparatus as shown in Fig. 1.

9.1.1 *Gas Flow Regulator and Flowmeter*.

9.1.2 *Hot Plate*, used to warm the water saturating the sparge gas to 50 to 80°C.

9.1.3 *Combustion Tube Furnace*, having a bore of about 32 mm (1¼in.), a length of about 305 mm (12 in.), and the capability of maintaining a temperature of 1000°C.

9.1.4 *Quartz Reaction Tube* (Fig. 2)—The exit end should not extend over 51 mm (2 in.) beyond the furnace with a ground joint connecting to the delivery tube. The delivery tube extends into a polyethylene absorption vessel with a tip capable of giving a stream of fine bubbles.

9.1.5 *Combustion Boat*—A ceramic, platinum, or quartz boat with a 10-mL capacity, 89 to 102 mm (3½ to 4 in.) long, 12.7 mm (½ in.) wide, and 9.53 mm (⅜ in.) high.

9.1.6 *Absorption Vessel*—A 50-mL polyethylene graduate or tube is satisfactory.

9.2 *Ion-Selective Electrodes*—A chloride-ion-selective activity electrode;[8] fluoride-ion-selective activity electrode.[9]

9.3 *pH Meter and Double-Junction Reference Electrode*, such as a mercuric sulfate, sleeve junction type. The meter should have an expandable scale with a sensitivity of 1 mV.

9.4 *Magnetic Stirrer*.

9.5 *Beakers*, 50-mL, polyethylene.

10. Reagents

10.1 *Accelerator, U_3O_8 (Halogen-free)*, can be used, but a flux of sodium tungstate (Na_2WO_4) with tungsten trioxide (WO_3) may be used to advantage **(1).** (See Method C 696.) Special preparation of the mixture is necessary, that is, dehydrate 165 g of Na_2WO_4 in a large platinum dish. Transfer the dried material to a mortar, add 116 g of WO_3, and grind the mixture to ensure good mixing. Transfer the mixture into a platinum dish and heat with a burner for 2 h. Cool the melt, transfer the flux to a mortar, and grind to a coarse powder. Store the flux in an airtight bottle. Mix about 8 g of flux with each portion of sample to be pyrohydrolyzed.

10.2 *Buffer Solution* (*0.001 N*)—Dissolve 0.1 g of potassium acetate ($KC_2H_3O_2$) in water, add 0.050 mL of acetic acid (CH_3CO_2H, sp gr 1.05), and dilute to 1 L.

10.3 *Chloride, Standard Solution (1 mL = 100 µg Cl)*—

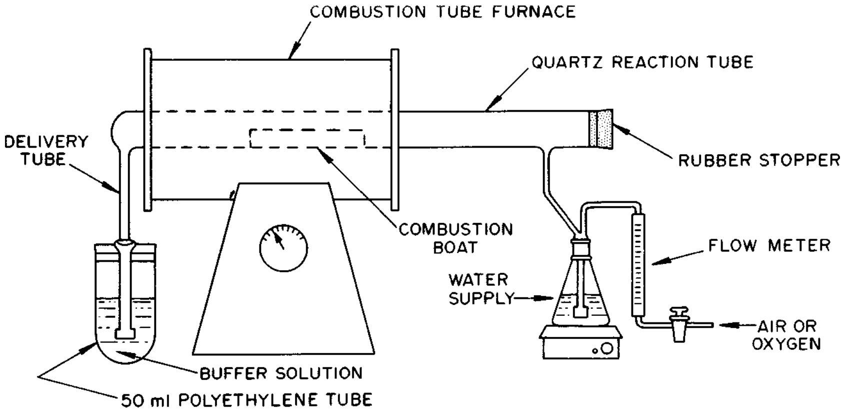

FIG. 1 Pyrohydrolysis of Gadolinium Oxide

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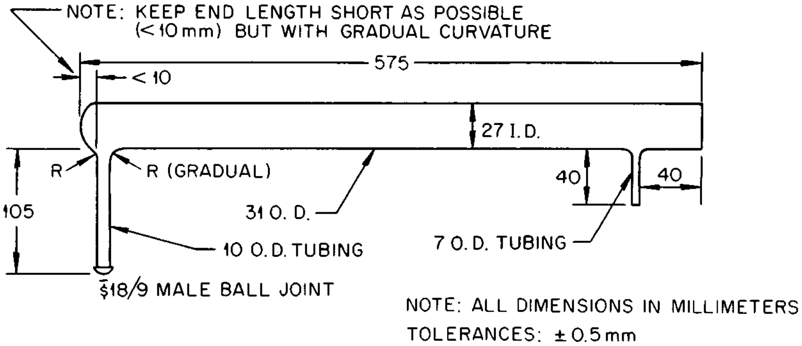
[7] The boldface numbers in parentheses refer to the list of references appended to this standard.

[8] The Orion Model No. 96–17 has been found satisfactory.

[9] The Orion Model No. 9409 has been found satisfactory.



NOTE: KEEP END LENGTH SHORT AS POSSIBLE (<10 mm) BUT WITH GRADUAL CURVATURE

NOTE: ALL DIMENSIONS IN MILLIMETERS
TOLERANCES: ±0.5 mm

FIG. 2 Quartz Reaction Tube

Dissolve 165 mg of dry sodium chloride (NaCl) in water and dilute to 1 L.

10.4 *Compressed Oxygen, Nitrogen, Helium, or Air.*

10.5 *Distilled Water*—The water must be free of all chlorides and fluorides.

10.6 *Fluoride, Standard Solution (1 mL = 50 µg F)*—Dissolve 111 mg of sodium fluoride (NaF) in water and dilute to 1 L. Store the solution in a polyethylene bottle.

11. Procedure

11.1 Adjust the pyrohydrolysis system to operating condition as follows:

11.1.1 Heat the furnace to 950 ± 50°C.

11.1.2 Fill the water reservoir and heat to 50 to 80°C.

11.1.3 Adjust the oxygen flow to about 1.5 to 2 L/min.

11.2 Flush the reaction tube and boat with moist oxygen in accordance with pyrohydrolysis procedures in 11.4.

11.3 Run a pyrohydrolysis blank using a halide-free uranium oxide in accordance with the procedure in 11.4. A blank run should be made each day and after any sample that contains abnormally high levels of chloride or fluoride.

11.4 *Sample Pyrohydrolysis*:

11.4.1 Weigh 1 to 5 g of powdered Gd_2O_3 and spread in the combustion boat. If an accelerator is desired, mix 4 g of U_3O_8 or 8 g of the tungstate flux with the Gd_2O_3 before spreading in the boat.

11.4.2 Place 15 mL of acetate buffer solution in the collection flask and submerge the delivery tip in the solution.

11.4.3 Remove the stopper from the entrance of the reaction tube and insert the boat into the hot area of the furnace. Restopper the furnace tube.

11.4.4 Check the oxygen flow and adjust to 1.5 to 2 L/min.

11.4.5 Continue the reaction for 1 h. Thirty min may be sufficient with the tungstate flux.

11.4.6 To establish the time required for complete pyrohydrolysis, replace the buffer solution and continue the reaction for an additional 30 min.

11.4.7 When the pyrohydrolysis is completed, the buffer solution is transferred to a 25-mL flask. Rinse the delivery tube and collection tube with a minimum of buffer solution. Make up to volume. Use 10-mL aliquots of the diluted condensate for each determination.

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

11.5.1 Assemble the meter and electrode in accordance with the instructions provided with the ion-selective electrode and the expanded scale meter being used.

11.5.2 Use successive dilutions of the chloride and fluoride standards in the buffer solution on a 25-mL volume basis to prepare calibration curves for each electrode. Plot the millivolt readings of a series of three or more standards versus the concentration in micrograms per 25 mL on semi-log paper. The concentration of chloride should cover 10 µg/25 mL to 100 µg/25 mL and the fluoride from 5 µg/25 mL to 100 µg/25 mL.

12. Calculation

12.1 *Chloride and Fluoride*—Calculate as follows:

$$\text{Cl or F, µg/g of } Gd_2O_3 = (H_S - H_B) / W \tag{1}$$

where:

H_S = halide in aliquot of scrub solution = blank, µg,
H_B = halide in pyrohydrolysis blank, µg, and
W = sample mass, g of Gd_2O_3.

13. Precision and Bias

13.1 The relative standard deviation for the measurement of chlorine is 5 % in the range from 5 to 50 µg/g of Gd_2O_3 and increases to 10 % below the 5-µg/g level.

13.2 The relative standard deviation for the measurement of fluorine is 7 % in the range from 5 to 50 µg/g of Gd_2O_3 and increases to 10 % for the range from 1 to 5 µg/g.

13.3 Since there is no accepted reference material for determining bias in this test method, no statement on bias is being made.

LOSS OF WEIGHT ON IGNITION

14. Scope

14.1 This test method covers the loss-on-ignition of volatile constituents from nuclear-grade gadolinium oxide (Gd_2O_3) powder.

15. Summary of Test Method

15.1 A weighed sample of gadolinium oxide is heated to a minimum of 900°C for 2 h in air. Upon cooling, the sample is reweighed. The loss in weight is the difference between the initial and final weight.

16. Apparatus

16.1 *Combustion Equipment*—A suitable muffle furnace capable of heating to 1000°C.

16.2 *Crucible*, ceramic, nickel, or platinum with a 10-g capacity.

16.3 *Desiccator*.

16.4 *Balance*.

17. Reagent

17.1 *Drying Desiccant*.

18. Procedure

18.1 Heat the furnace to 925 ± 25°C.

18.2 Weigh 5 g of Gd_2O_3 to the nearest 1 mg.

18.3 Insert the crucible into the furnace.

18.4 Heat for 2 h.

18.5 Cool the Gd_2O_3 sample in a desiccator to room temperature.

18.6 Remove the crucible from the desiccator and reweigh.

19. Calculation

19.1 Calculate the percent weight loss as follows:

$$\text{Percent weight loss} = (A - B)(100) / W \tag{2}$$

where:

A = weight of crucible plus Gd_2O_3 before heating, g,

B = weight of crucible plus Gd_2O_3 after heating, g, and

W = sample mass, g of Gd_2O_3.

20. Precision and Bias

20.1 The relative standard deviation for measuring loss of volatile constituents on ignition is 1%.

20.2 Since there is no accepted reference material suitable for determining bias for the procedure in this test method, no statement on bias is being made.

SULFUR BY COMBUSTION—IODOMETRIC TITRATION

This Test Method was discontinued in January 1999.

IMPURITY ELEMENTS BY A SPARK-SOURCE MASS SPECTROGRAPHIC METHOD

ICP-AES as described in C761 or Inductively Coupled Plasma Mass Spectrometry (ICP-MS) described in C1287 may be used to determine boron, cadmium, thorium, dysprosium, europium, samarium, terbium, and ytterbium as impurity elements and other impurities. Powder must be analyzed as-received (not ignited), and reported in μg oxide per g gadolinium oxide to perform impurity calculations in sections 21-24

GADOLINIUM CONTENT IN GADOLINIUM OXIDE BY IMPURITY CORRECTION METHOD

21. Scope

21.1 The percent gadolinium oxide content of powders, exclusive of volatiles, is determined by calculation after the material has been analyzed to determine the total impurities.

22. Summary of Test Method

22.1 The total gadolinium content of gadolinium oxide powders is determined by calculation after the sample has been analyzed by the following procedures:

22.1.1 Loss of Weight on Ignition, Sections 14-20.

22.1.2 Impurity Elements by ICP-MS or ICP-AES, elements as specified in C 888

23. Calculation

23.1 If the concentration of an impurity element is a“ less-than” (<), (that is, a concentration expressed as being less than the lower detection limit of the analytical method), this less-than value shall be used as the concentration of that element in the following calculations.

23.2 Calculate the percent gadolinium oxide as follows:

$$G = 100 - (I_S)\,(10^{-4}) + (I_{LI})(100) \tag{3}$$

where:

G = percent gadolinium oxide

I_S = total μg spectrographic impurities as oxides, per gram gadolinium oxide powder sample,

I_{LI} = gram loss-on-ignition impurity per gram gadolinium oxide powder sample,

24. Precision and Bias

24.1 Since this is a calculation, precision and bias will depend upon relative standard deviation of the individual impurities analyzed. Therefore, no statement on precision and bias is being made.

REFERENCES

(**1**) American Standards Association, Inc.," Referee Methods for the Chemical Analysis of Nuclear Fuels," ASA N5.7, 1965, p. 37.

(**2**) Powell, R. H., and Menis, O., "Separation of Fluoride from Inorganic Compounds by Pyrolysis," *Analytical Chemistry,* ANCHA, Vol 30, 1958, p. 1546.

(**3**) Warf, J. C., Cline, W. E., and Tevebaugh, R. D., "Pyrohydrolysis in the Determination of Fluoride and Other Halides," *Analytical Chemistry,* ANCHA, Vol 26, 1954, p. 342.

(**4**) Plucinski, C. E., "Determination of Microgram Quantities of Fluoride in Metal Oxides," USAEC Document BNWL-601, AEROB, 1968.

(**5**) Frant, M. S., and Ross, J. W., Jr., "Electrode for Sensing Fluoride Ion Activity in Solution," *Science,* KAGTA, Vol 154, 1966, p. 1553.

(**6**) Rechnitz, G. A., "Ion-Selective Electrodes," *Chemical and Engineering News,* CENEA, Vol 25, 1967, p. 1946.

(**7**) Carter, J. A., "Analysis of Solution and Radioactive Samples by Spark-Source Mass Spectrometry," U.S. Atomic Energy Commission, ORNL-P-3051, 1967, Oak Ridge, Tenn.

(**8**) Carter, J. A., "Quantitative Spark-Source Mass Spectrometric Techniques for the Simultaneous Determination of the Lanthanide and Actinide Elements in Microgram and Sub-Microgram Transuranium Samples," Ph.D. Dissertation, 1970, University of Tennessee, Knoxville, Tenn.

(**9**) Carter, J. R. and Suites, J. R., "Analytical Chemistry Division Annual Progress Report," Raaen, H. P., ed., U.S. Atomic Energy Commission Report, AERDB, ORNL-4466, Oak Ridge, Tenn., 1970, pp. 93–94.

(**10**) Ahern, A. J., ed., "Mass Spectrometric Analysis of Solids," Elsevier Publishing Co., New York, N. Y., 1966.

(**11**) Franklin, J. C., Griffin, E. B., and Catlett, C. E., "Spark-Source Mass Spectrographic Analysis of Uranium Metal," U.S. Atomic Energy Commission Report, AERDB, YKG-44, Oak Ridge, Tenn., 1967.

(**12**) Johnson, A. J., Kozy, A., Morris, R. N., "Sodium Fluoride as a Spectrographic Carrier for Plutonium Metal Analysis," U.S. Atomic Energy Commission Report, AERDB, RFP-143, Golden, Colo., 1969.

(**13**) Nichalls, G. D., and Graham, A. L., "Precision and Accuracy in Trace Element Analysis of Geological Materials Using Solid Source Spark Mass Spectrography," *Analytical Chemistry,* ANCHA, Vol 39, 1967, p. 584.

(**14**) Rein, J. E., Matlack, G. M., Waterbury, G. R., Phelps, R. T., and Metz, C. F., eds., "Methods of Chemical Analysis for FBR Uranium-Plutonium Oxide Fuel and Source Materials," USAEC Document LA-4622, 1971, pp. 127–131.

(**15**) Wieczorek, F. J., ed., "Chemical, Metallurgical, and Spectrochemical Methods," General Electric Co. Document NEDE-11373, 1979.