Designation: C 968 – 99

Standard Test Methods for Analysis of Sintered Gadolinium Oxide-Uranium Dioxide Pellets[1]

This standard is issued under the fixed designation C 968; 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 analysis of sintered gadolinium oxide-uranium dioxide pellets to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

	Sections
Carbon (Total) by Direct Combustion—Thermal Conductivity Method	[2]
C 1408 Test Method for Carbon (Total) in Uranium Oxide Powders and Pellets By Direct Combustion-Infrared Detection Method	[3]
Chlorine and Fluorine by Pyrohydrolysis Ion-Selective Electrode Method	16 to 22
Gadolinia Content by Energy-Dispersive X-Ray Spectrometry	23 to 32
Hydrogen by Inert Gas Fusion	33 to 40
Isotopic Uranium Composition by Multiple-Filament Surface-Ionization Mass Spectrometric Method	[2]
C 1413 Test Method for Isotopic Analysis Of Hydrolysed Uranium Hexafluoride And Uranyl Nitrate Solutions By Thermal Ionization Mass Spectrometry	[3]
Nitrogen by Distillation—Nessler Reagent (Photometric) Method	50 to 60
Oxygen-to-Metal Ratio of Sintered Gadolinium Oxide-Uranium Dioxide Pellets	61 to 70
Spectrochemical Determination of Trace Impurity Elements	71 to 77
Total Gas by Hot Vacuum Extraction	[2]
Ceramographic Determination of Free Gd_2O_3 and Free UO_2 to Estimate the Homogeneity of $(U,Gd)O_2$ Pellets	86 to 93

1.3 The values stated in SI units are to be regarded as the standard.

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

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 889 Test Methods for Chemical and Mass Spectrographic Analysis of Nuclear-Grade Gadolinium Oxide (Gd_2O_3) Powder[3]

C 922 Specification for Sintered Gadolinium Oxide-Uranium Dioxide Pellets[3]

C 1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis[3]

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

C 1413 Test Method for Isotopic Analysis Of Hydrolysed Uranium Hexafluoride And Uranyl Nitrate Solutions By Thermal Ionization 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]

E 146 Methods for Chemical Analysis of Zirconium and Zirconium Alloys[5]

3. Significance and Use

3.1 The test methods in this method are designed to show whether a given material is in accordance with Specification C 922.

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 Reagent 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

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

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[2] Discontinued 1999. See C 968–94

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

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 conforming to Type IV of Specification D 1193.

5. Safety Precautions

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

CARBON (TOTAL) BY DIRECT COMBUSTION—THERMAL CONDUCTIVITY METHOD

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

CHLORINE AND FLUORINE BY PYROHYDROLYSIS ION-SELECTIVE ELECTRODE METHOD

6. Scope

6.1 This test method describes the determination of chlorine and fluorine in gadolinium oxide-uranium dioxide pellets (Gd_2O_3/UO_2). With a 1 to 10-g sample, concentrations from 5 to 200 μg of chlorine and 1 to 200 μg of fluorine are determined without interference.

7. Summary of Test Method

7.1 The halogens are separated from the gadolinium oxide-uranium dioxide pellets by pyrohydrolysis in a quartz tube with a stream of wet oxygen sparge gas 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, and measured with ion-selective electrodes (**4, 5, 6**). Chloride can also be determined by amperometric titration.

8. Apparatus

8.1 *Pyrohydrolysis Equipment*—A suitable assembly of apparatus is shown in Fig. 1.

8.1.1 *Gas Flow Regulator and Flowmeter*.

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

8.1.3 *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.

8.1.4 *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.

8.1.5 *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.

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

8.2 *Ion-Selective Electrodes*—A chloride-ion-selective activity electrode[8] and a fluoride-ion-selective activity electrode.[9]

8.3 *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.

8.4 *Magnetic Stirrer*.

8.5 *Beakers*, 50-mL, polyethylene.

9. Reagents and Materials

9.1 *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 advantageous. (See Test 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 it to a coarse powder. Store the flux in an airtight bottle. Mix about 8 g of flux with each sample to be pyrohydrolyzed.

9.2 *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.

9.3 *Chloride, Reference Solution* (1 mL = 100 μg Cl)—Dissolve 165 mg of dry sodium chloride (NaCl) in water and dilute to 1 L.

9.4 *Distilled Water*—Use ASTM Type IV water as specified in Specification D 1193.

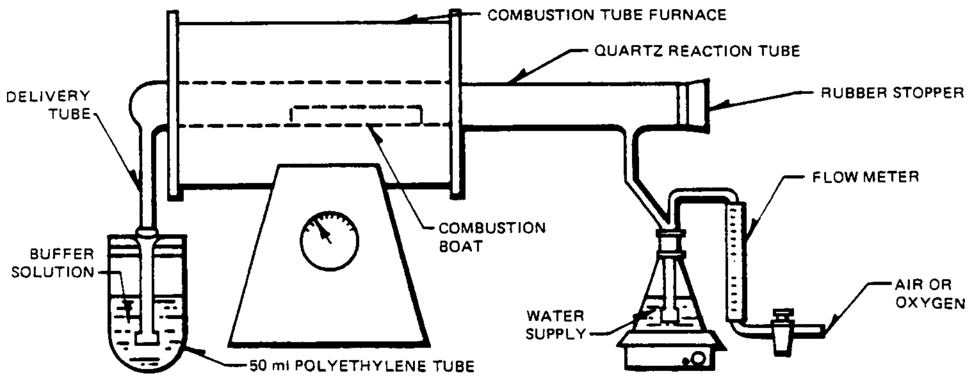

FIG. 1 Pyrohydrolysis of Gadolinium Oxide

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

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

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

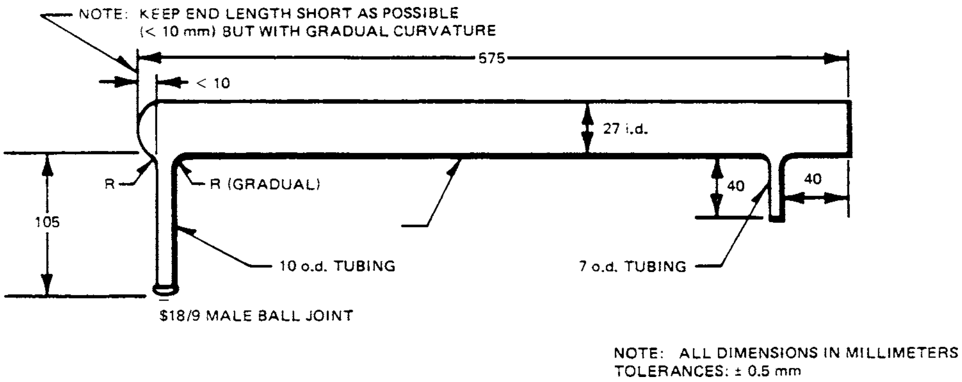

FIG. 2 Quartz Reaction Tube

9.5 *Fluoride, Reference 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.

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

10. Procedure

10.1 Adjust the pyrohydrolysis system to operating condition as follows:

10.1.1 Heat the furnace to 950 ± 50°C.

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

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

10.2 Flush the reaction tube and boat with moist oxygen in accordance with pyrohydrolysis procedures in 10.4.

10.3 Run a pyrohydrolysis blank using a halide-free uranium oxide or tungstate flux in accordance with the procedure in 10.4. A blank run should be made each day and after any sample that contains abnormally high levels of chloride or fluoride.

10.4 *Sample Pyrohydrolysis*:

10.4.1 Weigh 1 to 5 g of the crushed gadolinium oxide-uranium dioxide pellet 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/UO_2 before spreading in the boat.

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

10.4.3 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.

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

10.4.5 Continue the reaction for 1 h. (Thirty minutes may be sufficient with the tungstate flux.)

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

10.4.7 When the pyrohydrolysis is completed, transfer the buffer solution 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.

10.5 *Determination of Chlorine and Fluorine with Ion-Selective Electrodes*:

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

10.5.2 Use successive dilutions of the chloride and fluoride reference solutions 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 10-mL aliquots of three or more references 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.

11. Calculation

11.1 Calculate the chlorine and fluorine content as follows:

$$\text{Chlorine or fluorine, µg/g of } Gd_2O_3/UO_2 = (H_S - H_B)/W \qquad (1)$$

where:

H_S = halide in buffer solution + blank, µg,
H_B = halide in pyrohydrolysis blank, µg, and
W = sample mass, grams of Gd_2O_3/UO_2.

12. Precision and Bias

12.1 The relative standard deviation for the measurement of chlorine is 5 % in the range from 5 to 50 µg/g Gd_2O_3/UO_2 and increases to 10 % below the 5-µg/g level.

12.2 The relative standard deviation for the measurement of fluorine is 7 % in the range from 5 to 50 µg/g of Gd_2O_3/UO_2 and increases to 10 % for the range from 1 to 5 µg/g.

12.3 Recoveries from prepared reference spiked powder samples do not indicate the presence of a bias.

GADOLINIA CONTENT BY ENERGY-DISPERSIVE X-RAY SPECTROMETRY

13. Scope

13.1 This test method describes the determination of gadolinia in gadolinium oxide-uranium dioxide pellets (Gd_2O_3/UO_2) by energy-dispersive X-ray spectrometry. Concentrations from 0.4 to 10.0 % Gd_2O_3 may be determined with a 10-g sample pellet.

14. Summary of Test Method

14.1 X-ray fluorescence is a standard analytical technique in which an intense source of high-energy X rays excites atoms in the sample causing them to fluoresce or emit their characteristic X rays. The intensity of the emitted X rays is measured with a liquid-nitrogen-cooled, solid-state detector. The method is calibrated by comparing the measured intensity with that produced by reference materials of known gadolinia concentration at an averaged *K*α peak of 42.76 keV **(7, 8)**.

14.2 This determination is carried out on an energy-dispersive X-ray spectrometer, where the radiation from an americium-241 or other source is used to activate the secondary radiation due to gadolinium and uranium. These secondary radiations can be detected with Si(Li), Ge(Li), or an intrinsic germanium solid state detector maintained at liquid nitrogen temperatures. By means of a single-channel analyzer the radiation is selected so as to record only those radiations due to the *K*α radiation of gadolinium.

14.3 This analysis may also be performed by wavelength dispersive X-ray analysis. The user must demonstrate the equivalency to the energy dispersive method.

15. Interferences

15.1 Rare earths interfere when concentrations are in excess of 1 % of Gd_2O_3/UO_2.

16. Apparatus

16.1 *Solid-State X-Ray Detector*, ≥30 mm^2 in area, ≥5 mm in thickness, with a resolution of 0.2 keV at 45 keV.

16.2 *Energy-Dispersive X-Ray Spectrometer System*—See Fig. 3.[10]

16.3 *Cryogenic Subsystem*, 17 L.[10]

16.4 *Annular X-Ray Source*—Americium-241 ≥ 0.10 Ci.

16.5 *Collimator*—5-mm, machinable tungsten with 5 % copper.[11]

16.6 *Diamond Blade Cut-Off Machine*, blade thickness 1.02 mm (0.040 in.).

16.7 *Grinding Wheel*, horizontally mounted.

16.8 *Ultrasonic Cleaner Apparatus*.

16.9 *Aluminum Sample Holder*—Inside diameter of the holder shall be of sufficient size to contain a plastic mounting ring 25.4 mm (1 in.) in diameter. This fit should be snug to align the sample geometrically and mount in the same position with each repetitive analysis.

17. Calibration Reference Materials

17.1 Pellet reference materials covering the weight percent range of interest must be carefully prepared. X-ray fluorescence excites only the surface atoms; hence differences in gadolinium content within each pellet must be no greater than 1 %. Gadolinia is hygroscopic and must be heated to assure ≤1 % water retention by weight when reference materials are initially prepared by blending weighed amounts of Gd_2O_3 and UO_2.

17.2 The gadolinia content of the sintered pellet reference materials should be independently verified by another analytical method such as by oxalate precipitation **(9).**

18. Reagents and Materials

18.1 *Liquid Nitrogen*.

18.2 *Plastic Rings*, 25.4 mm (1-in.) diameter.

18.3 *Cap Plugs*, 25.4 mm (1-in.) diameter.

18.4 *Isopropyl Alcohol*.

18.5 *Epoxy Resin and Hardener*.

18.6 *Grinding Disks*, 320, 400, 600-grit.

18.7 *Gadolinium Oxide-Uranium Dioxide Reference Pellets*—Accurately prepare a series of working reference (Gd_2O_3/UO_2) sintered pellets covering the range of gadolinia concentrations anticipated in the pellets to be tested, using the purest gadolinia and urania available.

19. Sample Preparation

19.1 It must be assured that samples and reference materials receive the same preparation. Sample holders and positioning devices will minimize geometrical effects when used properly.

19.2 Place sample or reference material of Gd_2O_3/UO_2 pellet longitudinally in the holding device of the diamond blade cut-off machine. Secure firmly but not so tight that mechanical damage will occur.

19.3 Cut the pellet in half using care not to force the cutting rate, as excessive pullout of the matrix will occur.

19.4 After sectioning, grind the pellet flat by hand using water as a coolant on 320-grit silicon carbide paper.

19.5 Clean ultrasonically in isopropyl alcohol; air dry.

19.6 Place polyethylene cap plug on the plastic ring forms.

19.7 Center the sectioned Gd_2O_3/UO_2 pellet in the plastic ring form.

19.8 Fill with proper mixture of epoxy and hardener and let stand till the mount sets.

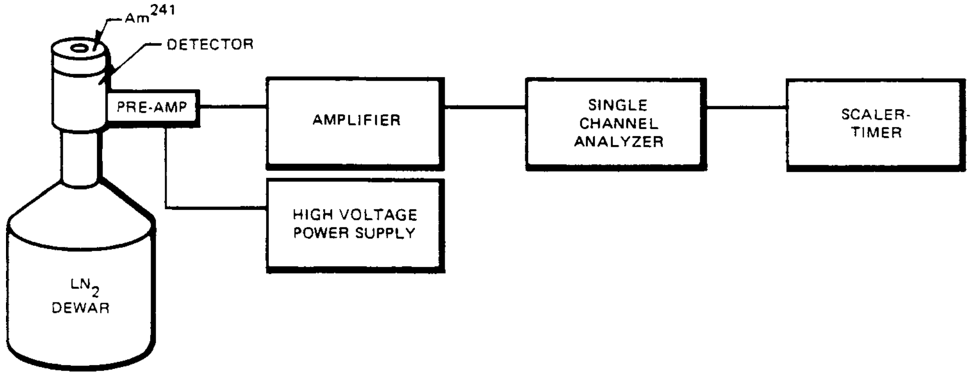

FIG. 3 Dispersive X-Ray Spectrometer System

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[10] A commercially available unit, fully automatic, is manufactured and sold by KEVEX Corp., Burlingame, CA. Other systems may use component parts of other manufacturers.

[11] Material provided by Kulite Corp., Indianapolis, IN, has been found acceptable.

19.9 After mounting operation, process the specimen using 320-grit grinding paper through the 500-grit series using water as a lubricant.

19.10 Use medium pressure throughout the grinding operation with about 2 min spent on each grit size.

19.11 After final grinding, clean the sample ultrasonically in deionized water followed by isopropyl alcohol.

19.12 Dry with warm air.

20. Calibration

20.1 Place the mounted pellet standard specimen prepared in Section 28 into the aluminum sample holder. Place this on top of the americium-241 source of the energy-dispersive X-ray spectrometer.

20.2 Follow instructions manual for operation of instrument.

20.3 Set the instrument for a count of 10 000.

20.4 Record the reference material value and time in seconds for the 10 000 counts.

20.5 Calculate a least-squares straight line fit to the reference material data, converted to counts per second, versus concentration of gadolinia.

20.5.1 Calculate the "intercept" and "slope" constants of the pellet reference material as follows:

Intercept:

$$A = \frac{\Sigma C_i^2 \, \Sigma G_i - \Sigma C_i \Sigma C_i G_i}{N \Sigma C_i^2 - (\Sigma C_i)^2} \tag{2}$$

Slope:

$$B = \frac{N \Sigma C_i G_i - \Sigma C_i \Sigma G_i}{N \Sigma C_i^2 - (\Sigma C_i)^2} \tag{3}$$

where:

C_i = count rate of reference material i,
= $10\,000/T_i$, counts per second,
T_i = time for 10 000 counts, s,
G_i = weight percent of Gd_2O_3 in reference material i, and
N = number of reference materials.

21. Procedure for Unknown Samples

21.1 Follow 19.1 through 19.4 as required for Gd_2O_3/UO_2 reference material pellets. Always count a reference material with weight percent near nominal value of unknown.

21.2 Calculate the gadolinia weight percent using the calibration intercept and slope measured in 29.5.1.

21.3 Therefore:

$$\%\ Gd_2O_3 = A + BC_i \tag{4}$$

22. Precision and Bias

22.1 The accuracy of the method is a function of the accuracy of the reference material and the care with which it is assured that no bias is produced between reference materials and samples. If the reference materials are accurate to <1 % and the bias between reference materials and samples is <1 %, then accuracy of about 1 % can be achieved.

22.2 The precision is a combination of the variances due to electronic drift, σ_e^2; counting variations, σ_c^2; geometry variations, σ_g^2; and calibration precision, σ_p^2.

22.3 Therefore:

$$\text{Total } \sigma^2 = \sigma_e^2 + \sigma_c^2 + \sigma_g^2 + \sigma_p^2 \tag{5}$$

With care, standard deviations of 1 % are achievable for each term; therefore, a total standard deviation of 2 % is possible.

HYDROGEN BY INERT GAS FUSION

23. Scope

23.1 This test method describes the determination of hydrogen in gadolinium oxide-uranium dioxide pellets (Gd_2O_3/UO_2) from all sources contained in the pellet. This measurement covers a range from 0.05 to 100 µg.

24. Summary of Test Method

24.1 A gadolinium oxide-uranium dioxide pellet is heated in a graphite crucible in an inert-gas atmosphere to temperatures greater than 1800°C. At that temperature, hydrogen, nitrogen, and oxygen (as carbon dioxide gas) are released. After the interfering carbon dioxide and nitrogen are removed, the hydrogen is measured by integrating the output peak from a thermal-conductivity cell detector.

24.2 The instrument may be calibrated using either high-purity hydrogen or NIST SRM 352C or equivalent material standards.

25. Apparatus

25.1 *Automatic Hydrogen Determination*, [12] consisting of an electrode furnace suitable for operation up to 2500°C; carbon dioxide, oxygen, and nitrogen collection traps; a thermal conductivity cell for measuring hydrogen, and an auxiliary purification system.

25.2 *Crucibles, Expendable Graphite*, 13 mm in outside diameter by 37 mm long.

25.3 *Argon Regulator*.

25.4 *Hydrogen Regulator*.

26. Reagents and Materials

26.1 *Argon* (Ar), industrial grade, 99.999 %.

26.2 *Glass Wool*.

26.3 *High-Vacuum Silicone Lubricant*.

26.4 *Hydrogen* (H_2), industrial grade, 99.999 %.

26.5 *Schutze Reagent*—Iodine pentoxide on silica gel.

26.6 *Magnesium Perchlorate* —[$Mg(ClO_4)_2$].

26.7 *Rare Earth Copper Oxide*.

26.8 *Sodium Hydroxide Over Asbestos*.

26.9 *Tin Flux*.

26.10 *Unalloyed Titanium Reference Material*—National Institute of Standards Technology SRM 352C, or equivalent material standards.

27. Operation of Instrument

27.1 Follow the operating instructions provided by the manufacturer of the specific equipment used. (See Test Methods C 696.) After having properly set the operating controls of

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[12] A commercially available unit, fully automatic and supplied with reagents, accessory parts, and standards, is manufactured and sold by Laboratory Equipment Corp., St. Joseph, MI.

the instrument system, condition the apparatus by combusting several blanks using sample crucibles. Successive blank values should approach a constant value, allowing for normal statistical fluctuations.

NOTE 1—Determine a hydrogen blank on the tin flux by using 1 g of tin during blanking and calibration operations.

28. Calibration with Metal Reference Materials

28.1 Weigh an appropriate amount of NIST SRM 352C unalloyed titanium. Wash in acetone and dry before weighing. Other certified standards such as hydrogen in steel may be used.

28.2 Load and analyze the reference materials and record the results. Adjust the calibration controls in such a way as to produce the correct readout value on the direct readout meter. Analyze additional reference materials as needed to maintain the correct direct readout.

29. Procedure

29.1 Weigh a whole Gd_2O_3/UO_2 pellet to the nearest 1 mg.

29.2 Place the pellet into the loading chamber.

29.3 Outgas the crucible and analyze the pellet by dropping the pellet into the furnace crucible as recommended by the instruction manual. Record the hydrogen value indicated by the direct readout meter.

30. Precision and Bias

30.1 The within-laboratory relative standard deviation of a single determination is 15 % for Gd_2O_3/UO_2 pellets having a hydrogen level from 0.1 to 0.25 µg/ g. A bias cannot be determined since no hydrogen-certified Gd_2O_3/UO_2 reference materials exist. The above information is provided for guidance as to the possible precision and accuracy of the analytical method, but it is not a guarantee of performance. The laboratory precision and bias can only be determined by using surrogate hydrogen in metal standards in a measurement control program.

ISOTOPIC URANIUM COMPOSITION BY MULTIPLE-FILAMENT SURFACE-IONIZATION MASS SPECTROMETRIC METHOD

This Test Method was discontinued in January 1999 and replaced with C 1413

Samples can be dissolved using the appropriate dissolution techniques described in Practice C 1347

NITROGEN BY DISTILLATION—NESSLER REAGENT (PHOTOMETRIC) METHOD

31. Scope

31.1 This test method describes the determination of nitrogen in gadolinium oxide-uranium dioxide pellets (Gd_2O_3/UO_2). With a 2 to 5-g sample, concentrations from 5 to 100 µg of nitrogen are determined without interference.

32. Summary of Test Method

32.1 Pellet samples of gadolinium oxide-uranium dioxide are crushed, then dissolved in phosphoric acid. Hydrochloric acid with hydrogen peroxide can also be used. The resulting solution is made alkaline with sodium hydroxide, and the nitrogen is separated as ammonia by steam distillation (see Method E 146). 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, using a cell depth of 2 cm (**14, 15**).

NOTE 2—This procedure has been written for a cell having a 2-cm light path. The range of the method can be extended by suitably varying sample mass, aliquot size, amounts of reagents, and cell depth.

33. Interferences

33.1 There are no known interfering elements.

34. Apparatus

34.1 *Nitrogen Distillation Apparatus*, with 100-mL flask, Fig. 4; micro-Kjeldahl apparatus.

34.2 *Photometer*—A filter photometer with a narrow-band filter; or a *spectrophotometer* equipped with 2-cm cells.

34.3 *Heater*, 750-W, electric, full-control.

35. Reagents and Materials

35.1 *Nessler Reagent*—Dissolve 50 g of potassium iodide (KI) in a minimum of cold water (approximately 35 mL). Add a saturated solution of mercuric chloride ($HgCl_2$) slowly until the first slight precipitate of red mercuric iodide persists. Add 400 mL of potassium or sodium hydroxide solution (505 g of KOH or 360 g of NaOH/L). Dilute the solution to 1 L with ammonia-free water, mix, and allow the solution to stand overnight. Decant the supernatant liquid and store it in a brown bottle. This reagent is stable indefinitely.

35.2 *Ammonium Chloride* (NH_4Cl)—Dry the ammonium chloride at 110 to 120°C for 2 h.

35.3 *Nitrogen Reference Solution* (1 mL = 10 mg N)—Dissolve 3.819 g of dried NH_4Cl in water and dilute the solution to 1 L. Transfer 10 mL of this solution to a 1-L volumetric flask and dilute it to volume with water.

35.4 *Hydrochloric Acid* (6 *N)*—Dilute 6 volumes of concentrated hydrochloric acid (HCl) to 11 volumes.

35.5 *Hydrogen Peroxide* (30 %).

36. Precautions

36.1 The use of ammonia or other volatile nitrogenous compounds in the vicinity of the experiment can lead to serious errors. To ensure freedom from contamination, take the following precautionary measures:

36.1.1 Steam clean all glassware immediately prior to use.

36.1.2 Use ammonia-free water in all cases.

37. Purity of Water

37.1 Unless otherwise indicated, all references to water in this method shall be understood to mean ammonia-free water, prepared as follows: Pass distilled water or other water of equivalent purity through a mixed-bed resin demineralizer. Prepare all solutions in an ammonia-free atmosphere and store them in tightly stoppered chemical-resistant glass bottles. Boil all rubber stoppers used for 30 min in sodium hydroxide solution (100 g NaOH/L) and rinse them with ammonia-free water.