Designation: C968 – 12

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

This standard is issued under the fixed designation C968; 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:

	Section
Carbon (Total) by Direct Combustion—Thermal Conductivity Method	[2]
C1408 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	[4]
C1502 Test Method for Determination of Total Chlorine and Fluorine in Uranium Dioxide and Gadolinium Oxide	[3]
Gadolinia Content by Energy-Dispersive X-Ray Spectrometry	[4]
C1456 Test Method for Determination of Uranium or Gadolinium, or Both, in Gadolinium Oxide-Uranium Oxide Pellets or by X-Ray Fluorescence (XRF)	[3]
Hydrogen by Inert Gas Fusion	[4]
C1457 Test Method for Determination of Total Hydrogen Content of Uranium Oxide Powders and Pellets by Carrier Gas Extraction	[3]
Isotopic Uranium Composition by Multiple-Filament Surface-Ionization Mass Spectrometric Method	[2]
C1413 Test Method for Isotopic Analysis of Hydrolysed Uranium Hexafluoride And Uranyl Nitrate Solutions By Thermal Ionization Mass Spectrometry	[3]
C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis	[3]
Nitrogen by Distillation—Nessler Reagent (Photometric) Method	6 to 16
Oxygen-to-Metal Ratio of Sintered Gadolinium Oxide-Uranium Dioxide Pellets	[4]
C1430 Test Method for Determination of Uranium, Oxygen to Uranium, and Oxygen to Metal (O/M) in Sintered Uranium Dioxide and Gadolinia-Uranium Dioxide Pellets by Atmospheric Equilibration	[3]
Spectrochemical Determination of Trace Impurity Elements	[4]
C1517 Test Method for Determination of Metallic Impurities in Uranium Metal or Compounds by DC-Arc Emission Spectroscopy	[3]
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	17 to 24
Ceramographic Determination of Average Grain Size by Linear Intercept after Chemical Etching	25 to 32

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:*[3]

C922 Specification for Sintered Gadolinium Oxide-Uranium Dioxide Pellets

C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis

C1408 Test Method for Carbon (Total) in Uranium Oxide Powders and Pellets By Direct Combustion-Infrared Detection Method

C1413 Test Method for Isotopic Analysis of Hydrolyzed Uranium Hexafluoride and Uranyl Nitrate Solutions by Thermal Ionization Mass Spectrometry

C1430 Test Method for Determination of Uranium, Oxygen to Uranium (O/U), and Oxygen to Metal (O/M) in Sintered Uranium Dioxide and Gadolinia-Uranium Dioxide Pellets by Atmospheric Equilibration

C1456 Test Method for Determination of Uranium or Gadolinium (or both) in Gadolinium Oxide-Uranium Oxide Pellets or by X-Ray Fluorescence (XRF)

C1457 Test Method for Determination of Total Hydrogen Content of Uranium Oxide Powders and Pellets by Carrier Gas Extraction

C1502 Test Method for Determination of Total Chlorine and Fluorine in Uranium Dioxide and Gadolinium Oxide

C1517 Test Method for Determination of Metallic Impurities in Uranium Metal or Compounds by DC-Arc Emission Spectroscopy

D1193 Specification for Reagent Water

E112 Test Methods for Determining Average Grain Size

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

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[2] Discontinued 1999. See C968 – 94.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] Discontinued 2005. See C968 – 99.

E146 Methods of Chemical Analysis of Zirconium and Zirconium Alloys (Silicon, Hydrogen, and Copper) (Withdrawn 1989)[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 C922.

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 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 D1193.

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 C1408

CHLORINE AND FLUORINE BY PYROHYDROLYSIS ION-SELECTIVE ELECTRODE METHOD

This Test Method was discontinued in March 2005 and replaced by Test Method C1502

GADOLINIA CONTENT BY ENERGY-DISPERSIVE X-RAY SPECTROMETRY

This Test Method was discontinued in March 2005 and replaced by Test Method C1456

HYDROGEN BY INERT GAS FUSION

This Test Method was discontinued in March 2005 and replaced by Test Method C1457

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

This Test Method was discontinued in January 1999 and replaced with C1413

Samples can be dissolved using the appropriate dissolution techniques described in Practice C1347

NITROGEN BY DISTILLATION—NESSLER REAGENT (PHOTOMETRIC) METHOD

6. Scope

6.1 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.

7. Summary of Test Method

7.1 Pellet samples of gadolinium oxide-uranium dioxide are crushed, then dissolved in phosphoric acid. Hydrochloric acid

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[5] The last approved version of this historical standard is referenced on www.astm.org.

[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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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 E146). 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 (**1**, **2**).[7]

NOTE 1—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.

8. Interferences

8.1 There are no known interfering elements.

9. Apparatus

9.1 *Nitrogen Distillation Apparatus,* with 100-mL flask, Fig. 1; micro-Kjeldahl apparatus.

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

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

10. Reagents and Materials

10.1 *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.

10.2 *Ammonium Chloride* (NH_4 Cl)—Dry the ammonium chloride at 110 to 120°C for 2 h.

10.3 *Nitrogen Reference Solution* (1 mL = 10 µg 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.

10.4 *Hydrochloric Acid* (6 N)—Dilute 6 volumes of concentrated hydrochloric acid (HCl) to 12 volumes.

10.5 *Hydrogen Peroxide* (30 %).

11. Precautions

11.1 The use of ammonia or other volatile nitrogenous compounds in the vicinity of the experiment can lead to serious

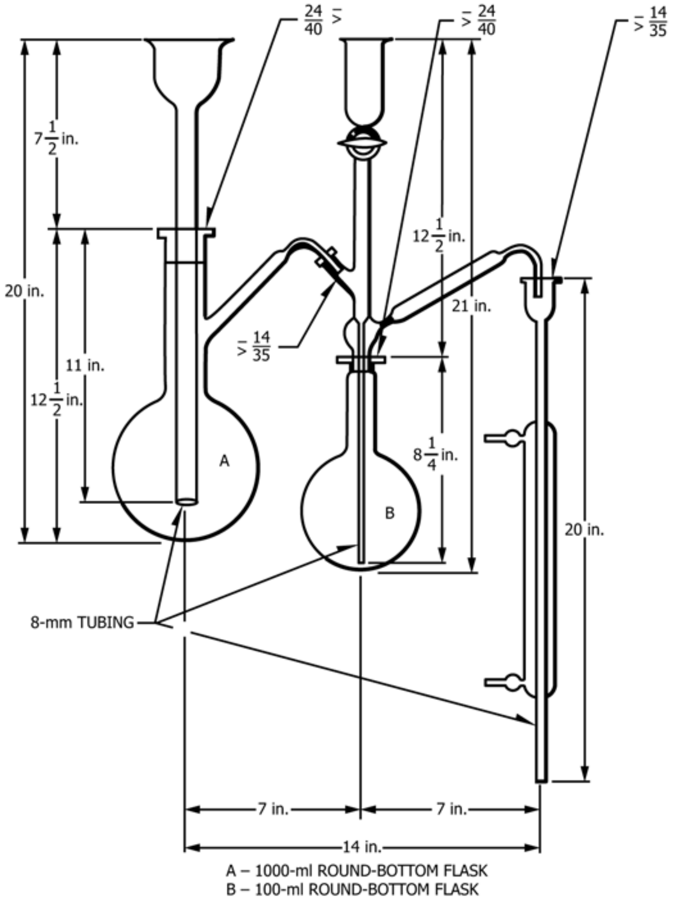

FIG. 1 Micro-Kjeldahl Apparatus

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

errors. To ensure freedom from contamination, take the following precautionary measures:

11.1.1 Steam clean all glassware immediately prior to use.

11.1.2 Use ammonia-free water in all cases.

12. Purity of Water

12.1 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.

13. Preparation of Calibration Curve

13.1 *Calibration Solutions*—Pipet 5, 10, 25, 50, 100, and 150 µg of the reference nitrogen solution (1 mL = 10 µg N) into 50-mL volumetric flasks containing 25 mL of water. Pipet 1.0 mL of Nessler reagent into each flask and dilute to the mark with water. Stopper the flask and mix well.

13.2 *Reference Solution*—Pipet 1.0 mL of Nessler reagent into a small volume of water in a 50-mL volumetric flask. Dilute to volume with water. Stopper and mix well.

13.3 *Photometry*—Transfer a suitable portion of water to a 2-cm absorption cell and adjust the photometer to the initial setting, using a light band centered at approximately 430 nm. While maintaining this photometer adjustment, take the photometric readings of the reference solution and the calibration solutions.

13.4 *Calibration Curve*—Correct for the blank (reference solution) reading and plot the photometric readings of the calibration solutions against micrograms of nitrogen per 50 mL of solution.

14. Procedure

14.1 *Test Solution:*

14.1.1 Weigh and transfer to a 500-mL Erlenmeyer flask 2 to 3 g of the crushed gadolinium oxide-uranium dioxide pellet sample. (The pellets should be crushed to a fine powder with a stainless steel mortar and pestle.)

14.1.2 Add to the distillation flask 60 mL of 6 N hydrochloric acid and 20 mL of 30 % hydrogen peroxide.

14.1.3 Boil for 10 min. While the solution is boiling, carefully add additional 30 % hydrogen peroxide dropwise until the solids are dissolved and a clear yellow solution is obtained; cool the solution.

14.1.4 While the samples are dissolving, fill the steam-generating flask of the distillation unit with water. Apply heat and pass steam through the distillation flask and into the condenser. Collect 50-mL portions of the distillate and add 1.0 mL of Nessler reagent to each. When the absorbance of these solutions shows the apparatus to be free of ammonia, the distillation unit is ready for use with the samples.

14.1.5 Transfer quantitatively the dissolved gadolinia-urania solution into the 100-mL distillation flask.

14.1.6 Connect the distillation flask containing the sample solution to the distillation unit. Add 25 mL of NaOH solution (37.5 %) to the sample solution through the thistle tube so as to form two layers in the flask. Close the thistle tube stopcock and distill until 40 mL of distillate is collected. (The NaOH solution must be added slowly to avoid a violent reaction which may lead to a loss of sample.)

14.1.7 Pipet 1.0 mL of Nessler reagent to the distillate, dilute to the mark with water, stopper, and mix well.

14.2 *Reference Solution*—Carry a reagent blank through the entire procedure, using the same amount of all reagents.

14.3 *Photometry*—Take the photometric reading of the samples as described in 13.3.

15. Calculation

15.1 Correct for the blank and convert the photometric reading of the sample to micrograms of nitrogen by means of the calibration curve.

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

$$N = A/W \tag{1}$$

where:

A = micrograms of nitrogen found, and
W = sample mass, grams of Gd_2O_3/UO_2.

16. Precision and Bias

16.1 The relative standard deviation for the measurement of nitrogen at the 100 µg/g level is 3 %.

OXYGEN-TO-METAL RATIO OF SINTERED GADOLINIUM OXIDE-URANIUM DIOXIDE PELLETS

This Test Method was discontinued in March 2005 and replaced by Test Method C1430

SPECTROCHEMICAL DETERMINATION OF TRACE, IMPURITY ELEMENTS

This Test Method was discontinued in March 2005 and replaced by Test Method C1517

TOTAL GAS BY HOT VACUUM EXTRACTION

This procedure was discontinued in January 1999

CERAMOGRAPHIC DETERMINATION OF FREE Gd_2O_3 AND FREE UO_2 TO ESTIMATE THE HOMOGENEITY OF $(U,Gd)O_2$ PELLETS

17. Scope

17.1 The homogeneity of Gd_2O_3 in UO_2 has been cited in Specification C922 as an important requirement for this fuel form. The uniform distribution of gadolinia in urania will result in up to three components in the pellet: free Gd_2O_3, free UO_2, and a Gd_2O_3-UO_2 solid solution. There are a number of ways for assessing uniformity of which the ceramographic method described here may not be the most definitive. This technique has been used over the gadolinia concentration range from 1 to 10 weight %.

18. Summary of Test Method

18.1 This ceramographic test, similar to those reported by Rooney (**3**) and by Hammerschmidt and Saiger (**4**), consists of making micrographs of polished pellet surfaces that have been chemically etched with a hydrogen peroxide-sulfuric acid solution. Oxidation makes it possible to differentiate between components.

19. Apparatus

19.1 *Diamond Saw,* low-speed.

19.2 *Ultrasonic Cleaner.*

19.3 *Polisher/Grinder Table.*

19.4 *Metallurgical Microscope,* with camera attachment.

20. Reagents and Materials

20.1 *Hydrogen Peroxide* (30 %).

20.2 *Hydrogen Peroxide–Sulfuric Acid Etch Solution*—10 parts 30 % hydrogen peroxide mixed with 1 part concentrated sulfuric acid.

20.3 *Silicon Carbide Grinding Disks,* 240, 320, 400, and 600-grit.

20.4 *Diamond Paste,* 7, 3, and 1-µm grains.

20.5 *Color Film.*

21. Sample Preparation

21.1 Cut the fuel pellet in the longitudinal axis, somewhat off center, using a low-speed diamond saw.

21.2 Cast the larger pellet part in cold-setting resin.

21.3 Grind the cast specimen on a polisher/grinder table using successively, silicon carbide in four stages from 240 to 600 grit; then polish with diamond pastes in stages with 7, 3, and 1-µm grains.

21.4 Clean the specimen in an ultrasonic cleaner after each stage of grinding and polishing.

22. Sample Analysis

22.1 Generate a weak grain surface by applying a 1-min wiping etch to the polished surface with hydrogen peroxide-sulfuric acid solution.

22.2 Flush the sample with water, then alcohol, and dry with warm air.

22.3 Dip the specimen into a 30 % hydrogen peroxide solution. (Eventually heat the specimen to 45°C and dip it into the etch solution maintained at 45°C).

NOTE 2—Over-etched specimens must be reground and polished.

22.4 Allow the etch to develop for 3 min: 45 s. Touch the top of the peroxide solution every 30 to 40 s to dispel bubbles formed on the specimen surface.

22.5 Flush the sample with water, clean ultrasonically in alcohol, and dry with warm air.

22.6 Examine and photograph the samples under a metallurgical microscope at a magnification of 100× in white light (bright-field illumination with no filters).

23. Evaluation

23.1 Measure the weight percent of free gadolinia by scanning the entire micrograph surface for gadolinia inclusions (white-colored) and using the following calculation:

$$\text{Free Gd}_2\text{O}_3\text{wt\%} = \frac{A(0.72)10\,000}{\%\text{Gd}_2\text{O}_3(A_c)} \tag{2}$$

where:

A = total observed surface of all Gd_2O_3 inclusions, cm^2,
A_c = total pellet surface examined without Gd_2O_3, cm^3 nominal weight percent of Gd_2O_3, and
0.72 = factor from the density ratio $Gd_2O_3/(U,Gd)O_2$.

23.2 Measure the weight percent of free uranium dioxide by means of a blue spot analysis on a representative color photo using a calibrated grid, counting the number of uranium particles covered by crosses and converting this count to weight percent of free UO_2. (Estimate the average particle size and assume sphericity to assign a particle weight.)

23.3 Calculate the weight percent of solid $(U,Gd)O_2$ solution by difference:

$$\begin{aligned} \text{w/o}(\text{U,Gd})\text{O}_2 &= 100 - \text{wt\% free UO}_2 \\ &\quad - \text{wt\% free Gd}_2\text{O}_3\left(\frac{\text{wt\% Gd}_2\text{O}_3}{100}\right) \end{aligned} \tag{3}$$

24. Precision and Bias

24.1 This test method is subjective, and inadequate data are available for a statistical evaluation.

CERAMOGRAPHIC DETERMINATION OF AVERAGE GRAIN SIZE BY LINEAR INTERCEPT AFTER CHEMICAL ETCHING

25. Scope

25.1 This test method covers the average grain size determination of (U,Gd)O2 pellets after ceramographic preparation and chemical etching. The evaluation of the average grain size is done by a linear intercept method.

26. Summary of Test Method

26.1 A (U,Gd)O2 pellet is cut, ground and polished to obtain a smooth pellet surface. After these ceramographic preparation steps, the revelation of the grain borders is obtained by chemical etching using a hydrogen peroxide-sulfuric acid solution. Finally, the average grain size is determined using a linear intercept method.

27. Apparatus

27.1 *Diamond Saw,* low-speed, with water cooling system.

27.2 *Ultrasonic Cleaner.*

27.3 *Polisher/Grinder Table.*

27.4 *Metallurgical Microscope,* with camera attachment, eventually equipped with image analysis system.

28. Reagents and Materials

28.1 *Hydrogen Peroxide* (30 %).

28.2 *Hydrogen Peroxide–Sulfuric Acid Etch Solution*—One part 30 % hydrogen peroxide mixed with nine parts concentrated sulfuric acid.

28.3 *Silicon Carbide Grinding Disks,* 120, 320, and 600-grit or Resin bounded diamond discs with similar abrasive effect.

28.4 *Polishing Cloth,* for fine polishing.

28.5 *Diamond Paste,* 3-µm grains or similar.

28.6 *Cold setting resin,* two or three components, polyester, epoxy, or acrylic based.

28.7 *Alcohol,* industrial grade.

29. Sample Preparation

29.1 Cut the fuel pellet along the longitudinal axis, somewhat off center, using a low-speed diamond saw.

29.2 Cast the larger pellet part in cold-setting resin.

29.3 Grind the cast specimen on a polisher/grinder table in three or more stages from 120 to 600 grit. After every stage, the scratches from the previous stage must be disappeared.

29.4 Polish in one or more stages with diamond paste having 7 to 1 µm grains on a short fibre polishing cloth until a smooth pellet surface is obtained.

29.5 Clean the specimen, eventually in an ultrasonic cleaner, after each stage of grinding and polishing.

29.6 After preparation, check the polished surface under the microscope. If scratches are present, disturbing the measurement, the grinding/polishing steps can be repeated.

30. Sample Analysis

30.1 Immerge the pellets in an etching bath containing the hydrogen peroxide-sulfuric acid solution for about 5 min.Other etching solutions and etching times may also be effective to reveal the grain borders.

30.2 Flush the sample with water, then alcohol, and dry with warm or pressurized air.

30.3 Examine the samples under a metallurgical microscope at a magnification of 100 to 1000× in white light (bright-field illumination with no filters) depending on the grain size. Take photographs if requested for the project or for the measurement.

31. Evaluation

31.1 Draw an arbitrary, straight line on the analysed area of the pellet surface and count the number of intersections N where the straight line cuts the grain boundaries. Adopt the magnification of the microscope or length L of the linear line in order to obtain at least 50 intersections.

31.2 Calculate the average grain size at this area by dividing the length of the straight line for exactly N intersections (in µm) by the number of intersections N.

31.3 Perform this calculation in at least three different areas (at the border, at 1/4th distance, and in the middle) of the pellet surface to take into account a possible heterogeneity in grain size at different areas in the pellet.

31.4 Calculate the average grain size of the pellet by averaging all results of average grain size at the different measured areas in the pellet.

31.5 Besides the linear intercept method as explained in this method, also any other evaluation method described in Test Methods E112 may be used.

32. Precision and Bias

32.1 In order to get an estimation of the precision of the method, repetitive grain size measurements were performed at the same area of a pellet surface with homogeneous grain size distribution. The relative standard deviation of a single determination can be estimated at 15 % relative at 95 % confidence level for grain sizes from 5 to 35 µm.

REFERENCES

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