



Designation: C 696 – 99

Standard Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets¹

This standard is issued under the fixed designation C 696; 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 uranium dioxide powders and pellets to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

	Sections
Uranium by Ferrous Sulfate Reduction in Phosphoric Acid and Dichromate Titration Method	2
C 1267 Test Method for Uranium By Iron (II) Reduction In Phosphoric Acid Followed By Chromium (VI) Titration In The Presence of Vanadium	3
Uranium and Oxygen Uranium Atomic Ratio by the Ignition (Gravimetric) Impurity Correction Method	7-13
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
Total Chlorine and Fluorine by Pyrohydrolysis Ion-Selective Electrode Method	14-20
Moisture by the Coulometric, Electrolytic Moisture Analyzer Method	21-28
Nitrogen by the Kjeldahl Method	29-36
Isotopic Uranium Composition by Multiple-Filament Surface Ionization Mass Spectrometric Method	4
Spectrochemical Determination of Trace Elements in High-Purity Uranium Dioxide	37-44
Silver, Spectrochemical Determination of, by Gallium OxideCarrier D-C Arc Technique	45 to 46
Rare Earths by Copper Spark-Spectrochemical Method	2
Impurity Elements by a Spark-Source Mass Spectrographic Method	2
C 761 Test Method 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
Surface Area by Nitrogen Absorption Method	47-53
Total Gas in Reactor-Grade Uranium Dioxide Pellets	2
Thorium and Rare Earth Elements by Spectroscopy	2
Hydrogen by Inert Gas Fusion	54-63
Uranium Isotopic Analysis by Mass Spectrometry	2

Sections

C 1413 Test Method for Isotopic Analysis of Hydrolysed Uranium Hexafluoride and Uranyl Nitrate Solutions By Thermal Ionization Mass Spectrometry

3

2. Referenced Documents

2.1 ASTM Standards:

- C 753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder³
- C 761 Test Method for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride³
- C 776 Specification for Sintered Uranium Dioxide Pellets³
- C 1267 Test Method for Uranium By Iron (II) Reduction In Phosphoric Acid Followed By Chromium (VI) Titration In The Presence of Vanadium³
- C 1287 Test Method for Determination of Impurities In Uranium Dioxide By Inductively Coupled Plasma Mass Spectrometry³
- C 1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis³
- C 1408 Test Method for Carbon (Total) in Uranium Oxide Powders and Pellets By Direct Combustion-Infrared Detection Method³
- C 1413 Test Method for Isotopic Analysis of Hydrolysed Uranium Hexafluoride and Uranyl Nitrate Solutions By Thermal Ionization Mass Spectrometry³
- D 1193 Specification for Reagent Water⁵
- E 115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis⁶
- E 116 Practice for Photographic Photometry by Spectrochemical Analysis⁶
- E 130 Practice for Designation of Shapes and Sizes of Graphite Electrodes⁶
- E 217 Test Method for Uranium by Controlled-Potential Coulometry³

¹ These test methods are under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle.

Current edition approved Jan. 10, 1999. Published March 1999. Originally published as C 696 – 72. Last previous edition C 696 – 93^{ε1}.

² Discontinued January 1999. See C 696–80.

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

⁴ Discontinued as of May 30, 1980.

⁵ *Annual Book of ASTM Standards*, Vol 11.01.

⁶ *Annual Book of ASTM Standards*, Vol 03.05.

E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves⁶

E 402 Test Method for Spectrographic Analysis of Uranium Oxide (U₃O₈) by Gallium Oxide-Carrier Technique⁷

3. Significance and Use

3.1 Uranium dioxide is used as a nuclear-reactor fuel. In order to be suitable for this purpose, the material must meet certain criteria for uranium content, stoichiometry, 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 Specifications C 753 and C 776.

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

3.1.2 The stoichiometry of the oxide is useful for predicting its sintering behavior in the pellet production process.

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

3.1.4 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. 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.⁸ 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 Specification D 1193.

5. Safety Precautions

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

6. Sampling

6.1 Criteria for sampling this material are given in Specification C 753 and Specification C 776.

6.2 Samples can be dissolved using the appropriate dissolution techniques described in Practice C 1347, but final determination of applicability must be made by the user.

⁷ *Annual Book of ASTM Standards*, Vol 03.06.

⁸ *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.

URANIUM BY FERROUS SULFATE REDUCTION IN PHOSPHORIC ACID AND DICHROMATE TITRATION METHOD

This Test method was discontinued in January 1999 and replaced by Test method C 1267.

URANIUM AND OXYGEN TO URANIUM ATOMIC RATIO BY THE IGNITION (GRAVIMETRIC) IMPURITY CORRECTION METHOD

7. Scope

7.1 This test method covers the determination of uranium and the oxygen to uranium atomic ratio in nuclear-grade uranium dioxide powder and pellets.

8. Summary of Test Method

8.1 A weighed portion of UO₂ is dried under reduced pressure in a nitrogen atmosphere, desiccated, and weighed. The dried oxide is then converted to U₃O₈ by ignition at 900°C (8, 9).

9. Interferences

9.1 The weight of U₃O₈ is corrected for the nonvolatile impurities present as determined by spectrographic analysis. An extended ignition time may be required if significant amounts of anions that are difficult to decompose are present.

10. Apparatus

10.1 *Vacuum Oven*, capable of maintaining and controlling temperatures to 180°C and equipped with double stopcocks and a vacuum gage (range from 0 to 102 kPa (0 to 30 in. Hg)).

10.2 *Drying Tower*— Prepare a U-tube filled with a carbon dioxide absorbent⁹ and a suitable moisture absorbent, that is, anhydrous magnesium perchlorate Mg(ClO₄)₂.

10.3 *Muffle Furnace*, capable of maintaining and controlling temperatures to 1000°C.

11. Procedure

11.1 Transfer approximately 5 to 10 g of UO₂ powder or up to 50 g of pellets to a tared platinum crucible and weigh to within 0.1 mg.

11.2 Place the crucible in a vacuum oven set at room temperature, seal the oven, and reduce the pressure to approximately 95 to 102 kPa (28 to 30 in. Hg).

11.3 Close the vacuum valve and slowly flush the oven with dry nitrogen.

11.4 Close the nitrogen inlet and reduce the pressure to 95 to 102 kPa (28 to 30 in. Hg). Repeat the nitrogen flush as in step 11.3 to give a total of three flushes.

11.5 Close the nitrogen inlet valve, reduce the pressure to 95 to 102 kPa (28 to 30 in. Hg), set the temperature at 45°C for powder samples or 160°C for pellets, and maintain these conditions for 4 h. After 4 h of heating turn off the heat and allow the oven to cool to room temperature while under reduced pressure.

⁹ Ascarite has been found satisfactory for this purpose.

11.6 Turn off the vacuum valve and slowly introduce dry nitrogen until the oven door can be opened.

11.7 Transfer the crucible to a desiccator and cool. Remove the crucible and weigh immediately (8).

11.8 Place the crucible containing the dried oxide in a muffle furnace set at 900°C. Ignite powder samples for 3 h. Pellets should be preheated at 500°C for 3 h, then ignited 3 h at 900°C.

11.9 Remove the crucible from the furnace, allow to cool in the air 2 to 3 min then place the crucible in a desiccator and cool to room temperature. Weigh the crucible and repeat steps 11.8 and 11.9 until a constant weight is obtained.

11.10 Submit the ignited sample for spectrographic analysis.

12. Calculation

12.1 *Loss on Vacuum Drying*—Calculate as follows based on original sample:

$$\text{Loss, wt \%} = [(S - W_1)/S] \times 100 \quad (1)$$

where:

S = initial sample mass, and

W_1 = sample mass after vacuum drying, g.

12.2 *Uranium Content*— Calculate as follows:

$$U, \text{ wt \%} = [(0.8480 (W_2 - W_2I)/S) \times 100] - 0.01 \% \text{ (Note 1)} \quad (2)$$

where:

0.8480 = U_3O_8 to uranium conversion factor for natural uranium. Corrections must be made in this factor as the uranium isotopic abundance deviates from natural uranium,

W_2 = grams of U_3O_8 after ignition,

S = initial sample mass, and

I = total grams of all impurity-element oxides per gram of ignited U_3O_8 (Note 2).

NOTE 1—All nonvolatile impurity values reported as less than the threshold of detection are considered to contribute a total correction of 0.01 % to the uranium percent.

NOTE 2—See Table 1 to obtain conversion factors for many common impurity elements encountered.

12.3 *Oxygen-to-Uranium Ratio*—Calculate as follows from the original sample, U wt %:

$$O/U = [(100 - U \text{ wt \%} - Z - n)(A)]/[15.999(U \text{ wt \%})] \quad (3)$$

where:

A = atomic mass of uranium based on isotopic abundance,

O = atom % of oxygen,

U = atom % of uranium,

n = moisture content, %, and

Z = total impurities correction, %.

13. Precision and Accuracy

13.1 For atomic ratios of O/U in the range from 2.00 to 2.10 the standard deviation was found to be 0.007 absolute at 95 % confidence level.

TABLE 1 Conversion Factors for Impurity Correction

Impurity	Assumed Oxide Form	Gravimetric Factor
Al	Al_2O_3	1.89
Ba	BaO	1.12
Be	BeO	2.78
Bi	Bi_2O_3	1.11
Ca	CaO	1.40
Cd	CdO	1.14
Co	Co_2O_3	1.41
Cr	Cr_2O_3	1.46
Cu	CuO	1.25
Fe	Fe_2O_3	1.43
Li	Li_2O	2.15
Mg	MgO	1.66
Mn	MnO_2	1.58
Mo	MoO_3	1.50
Na	Na_2O	1.35
Ni	NiO	1.27
P	P_2O_5	2.29
Pb	PbO_2	1.15
Sb	Sb_2O_4	1.26
Si	SiO_2	2.14
Sn	SnO_2	1.27
Ti	TiO_2	1.67
V	V_2O_5	1.79
Zn	ZnO	1.24
Zr	ZrO_2	1.35
Ta	Ta_2O_5	1.22
W	WO_3	1.26

CARBON (TOTAL) BY DIRECT COMBUSTION-THERMAL CONDUCTIVITY METHOD

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

TOTAL CHLORINE AND FLUORINE BY PYROHYDROLYSIS ION-SELECTIVE ELECTRODE METHOD

14. Scope

14.1 This test method covers the determination of chlorine and fluorine in nuclear-grade uranium dioxide. With a 1 to 10-g sample, concentrations of 5 to 200 $\mu\text{g/g}$ of chlorine and 1 to 200 $\mu\text{g/g}$ of fluorine are determined without interference.

15. Summary of Test Method

15.1 The halogens are separated from powdered uranium dioxide by pyrohydrolysis in a quartz tube with a stream of wet oxygen at a temperature of 900 to 1000°C (10, 11, 12, 13). Chloride and fluoride are volatilized as acids, absorbed in a buffer solution, and measured with ion-selective electrodes (13, 14, 15).

16. Apparatus

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

16.1.1 *Gas Flow Regulator and Flowmeter.*

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

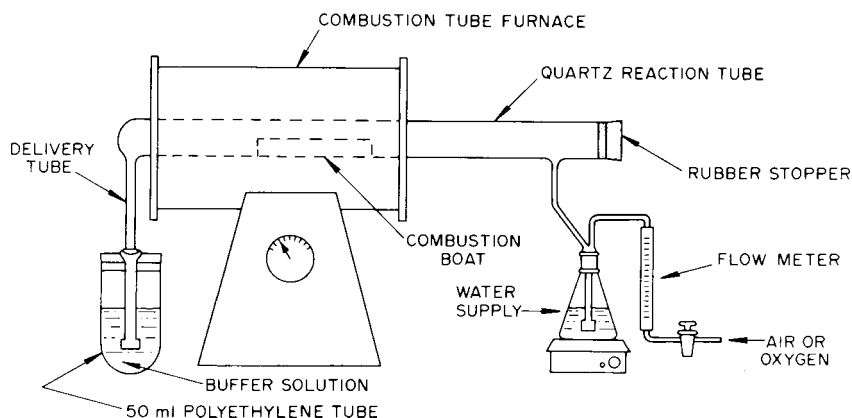


FIG. 1 Pyrohydrolysis Apparatus

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

16.1.4 *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.

16.1.5 *Combustion Boat*—A 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).

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

16.2 *Ion-Specific Electrodes*—A fluoride-specific activity electrode¹⁰; chloride-specific electrode.¹¹

16.3 *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.

16.4 *Magnetic Stirrer*.

16.5 *Beakers*, 50-mL polyethylene.

17. Reagents

17.1 *Accelerator*, U₃O₈ halogen-free, can be used but a flux of sodium tungstate (Na₂WO₄) with tungsten trioxide (WO₃) may be used to advantage (10, 11). Special preparation of the mixture is necessary.

NOTE 3—Dehydrate 165 g of Na₂WO₄ in a large platinum dish. Transfer the dried material to a mortar, add 116 g of WO₃, 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.

17.2 *Buffer Solution*— Dissolve 0.1 g potassium acetate (KC₂H₃O₂) in water, add 0.050 mL of acetic acid (CH₃CO₂H, sp gr 1.05), and dilute to 1 litre.

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

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

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

17.6 *Compressed Oxygen or Air*.

18. Procedure

18.1 Adjust the pyrohydrolysis system to operating condition as follows:

- 18.1.1 Heat the furnace to 950 ± 50°C.
- 18.1.2 Fill the water reservoir, and heat to 50 to 80°C.
- 18.1.3 Adjust the gas flow to about 1.5 to 2 litres/min.

18.2 Flush the reaction tube and boat with moist oxygen or according to the pyrohydrolysis procedure in 18.4.

18.3 Run a pyrohydrolysis blank using a halide-free uranium oxide according to the procedure in 18.4. A blank run should be made each day.

¹⁰ The Orion Model 9409 has been found satisfactory.

¹¹ The Orion Model No. 96-17-00 has been found satisfactory.

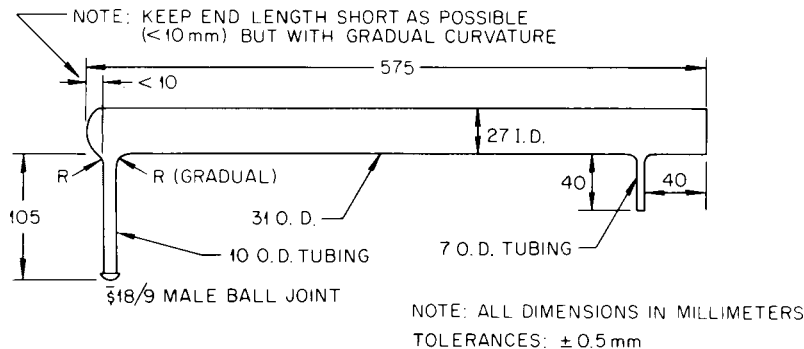


FIG. 2 Quartz Reaction Tube

18.4 Sample Pyrohydrolysis:

18.4.1 Weigh 1 to 5 g of powdered UO_2 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 UO_2 before spreading in the boat.

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

18.4.3 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.

18.4.4 Check the gas flow and adjust to 1.5 to 2 litres/min.

18.4.5 Continue the reaction for 1 h. Thirty minutes may be sufficient with the tungstate flux.

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

18.4.7 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.

18.5 Chloride and Fluoride Measurement:

18.5.1 Assemble the meter and electrode in accordance with the instructions with the ion-specific electrode and the expanded scale meter being used.

18.5.2 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 standards versus the concentration in micrograms per 25 mL on semi-log paper. The concentration of chloride should cover 10 $\mu\text{g}/25\text{ mL}$ to 100 $\mu\text{g}/25\text{ mL}$ and the fluoride from 5 $\mu\text{g}/25\text{ mL}$ to 100 $\mu\text{g}/25\text{ mL}$.

19. Calculation

19.1 Chlorine—Calculate as follows:

$$\text{Cl, } \mu\text{g/g} = (C - B)/W \quad (4)$$

where:

C = micrograms of total chlorine in absorber solution,

B = micrograms of total chlorine in the pyrohydrolysis blank, and

W = grams of UO_2 specimen pyrohydrolyzed

19.2 Fluorine—Calculate as follows:

$$\text{F, } \mu\text{g/g} = (F - B)/W \quad (5)$$

where:

F = micrograms of total fluorine in absorber solution,

B = micrograms of total fluorine in the pyrohydrolysis blank, and

W = grams of UO_2 specimen pyrohydrolyzed.

20. Precision

20.1 Recovery test runs with spiked oxide samples indicate that a precision of at least 10 % can be expected.

MOISTURE BY THE COULOMETRIC ELECTROLYTIC MOISTURE ANALYZER METHOD

21. Scope

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

22. Summary of Test Method

22.1 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 phosphorus pentoxide (P_2O_5) (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.

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

23. Apparatus

23.1 *Moisture Analyzer*, for solids, with quartz glass oven capable of being heated from ambient temperatures to 1000°C. The assembly includes electrolytic cell, flow meter, range 30 to 140 cm^3/min air, and a dryer assembly.¹²

23.2 *Balance*,¹³ for weighing samples in the range from 1 to 100 mg.

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

24. Reagents

24.1 *Barium Chloride Dihydrate* ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$).

25. Operation

25.1 Turn the main power switch ON.

¹² A CEC Solids Moisture Analyzer, of Type 26-321A-MA is available from DuPont Instruments Inc., S. Shamrock Ave., Monrovia, CA 91016.

¹³ A Cahn Electrobalance, or equivalent, available from Cahn Division, Ventrum Instrument Corp., Paramount, CA has been found satisfactory.

25.2 Adjust nitrogen gas pressure to 41.4 kPa (6 psi) and the flow rate to 50 mL/min measured at the exit of the apparatus.

25.3 Weigh the sample into a small, dry, aluminum boat (Note 4) and insert it into the instrument oven as follows:

NOTE 4—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.

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

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

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

25.4 Reset the counter to 0 μg .

25.5 Set the timer at 1 h.

25.6 Set the temperature at 400°C. This will activate the analyzer and start the heating cycle.

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

26. Standardization

26.1 Determine the blank by processing dry, empty, aluminum boats according to steps 25.3-25.7 until constant values are obtained.

26.2 Weigh and analyze replicate 5-mg samples of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ until consistent results are obtained. Sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) may also be used for calibration.

27. Calculation

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

$$Z = (A - B)147.2Y \quad (6)$$

where:

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

B = micrograms of moisture on counter from blank, and

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

27.2 Calculate the percent moisture in the sample as follows:

$$\text{Moisture, \%} = [(S - B)/1000 WZ] \times 100 = (S - B)/10 WZ \quad (7)$$

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.

28. Precision

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

NITROGEN BY THE KJELDAHL METHOD

29. Scope

29.1 This test method covers the determination of nitride nitrogen in uranium dioxide in the range from 10 to 250 μg .

30. Summary of Test Method

30.1 The sample is decomposed with acid, the resulting solution is made strongly alkaline with sodium hydroxide solution, and the nitrogen is separated as ammonia by steam distillation. The distillate is collected in boric acid solution and the ammonia present is titrated with 0.01 *N* standard acid using a mixed indicator.

NOTE 5—Although a simple acid digestion is usually adequate for dissolution of uranium samples, some uranium nitrides do not yield to such treatment. The use of potassium dichromate in phosphoric acid (16) has proved to be successful with nitrides that are difficult to decompose. Therefore, this medium has been recommended although, in most cases, a mixture of phosphoric and sulfuric acids would be adequate.

31. Interferences

31.1 There should be no interferences in nuclear-grade uranium dioxide.

32. Apparatus

32.1 *Nitrogen Distillation Apparatus*, micro.¹⁴

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

32.3 *Burner*, bunsen-type.

32.4 *Buret*, micro, class A, 5 or 10-mL capacity, graduated in 0.02-mL divisions.

33. Reagents

33.1 *Ammonia-Free Water*—Prepare by distillation or from an ion-exchange column.

33.2 *Boric Acid-Indicator Solution*—Dissolve 20 g of boric acid (H_3BO_3) in 800 mL of hot ammonia-free water, cool the solution, add 4 mL of mixed indicator solution (52.3), and dilute to 1 litre.

33.3 *Mixed Indicator Solution*—Mix 100 mL of a 1 % alcoholic solution of bromocresol green and 20 mL of a 1 % alcoholic solution of methyl red.

33.4 *Phosphoric Acid* (H_3PO_4 , 85 %)—Heat acid to 190°C to remove excess water.

NOTE 6—Some lots of H_3PO_4 give high blanks and cannot be used.

33.5 *Potassium Dichromate Solution (65 g/litre)*—Dissolve 65 g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in ammonia-free water and dilute to 1 litre. If necessary to reduce the blanks prepare the dichromate by recrystallization of K_2CrO_4 from alkaline solution (16).

33.6 *Sodium Hydroxide Solution*—Dissolve 500 g of sodium hydroxide (NaOH) in 1 litre of ammonia-free water.

33.7 *Sulfuric Acid, Standard*—(H_2SO_4 , 0.01 *N*)—Standardize against a standard sodium hydroxide solution that has been standardized against potassium hydrogen phthalate.

¹⁴ Kemmerer-Hallett Type, Fisher Scientific Co., has been found satisfactory.