

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 C696; 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 nucleargrade 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
C1267 Test Method for Uranium By Iron (II) Reduc- tion In Phosphoric Acid Followed By Chromium (VI) Titration In The Presence of Vanadium	3
Uranium and Oxygen Uranium Atomic Ratio by the	4
C1453 Standard Test Method for the Determination of Uranium by Ignition and Oxygen to Uranium Ratio (O/U) Atomic Ratio of Nuclear Grade Uranium Diox- ide Powders and Pellets	3
Carbon (Total) by Direct Combustion-Thermal Con- ductivity Method	2
C1408 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	4
C1502 Standard Test Method for the Determina- tion of Total Chlorine and Fluorine in Uranium Diox- ide and Gadolinium Oxide	3
Moisture by the Coulometric, Electrolytic Moisture Analyzer Method	7 – 14
Nitrogen by the Kjeldahl Method Isotopic Uranium Composition by Multiple-Filament	15 – 22 5
Surface Ionization Mass Spectrometric Method Spectrochemical Determination of Trace Elements in High-Purity Uranium Dioxide	23 – 30

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

- Current edition approved Sept. 1, 2011. Published October 2011. Originally approved in 1972. Last previous edition approved in 2005 as C696 99(2005). DOI: 10.1520/C0696-11.
 - ² Discontinued January 1999. See C696-80.
- 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 September 2011.
 - ⁵ Discontinued as of May 30, 1980.

Silver, Spectrochemical Determination of, by Gallium	31 and 32
OxideCarrier D-C Arc Technique	
Rare Earths by Copper Spark-Spectrochemical	2
Method	
Impurity Elements by a Spark-Source Mass Spectro-	2
graphic Method	
C761 Test Method for Chemical, Mass	3
Spectrometric, Spectrochemical, Nuclear, and Ra-	
diochemical Analysis of Uranium Hexafluoride	
C1287 Test Method for Determination of Impurities	3
In Uranium Dioxide By Inductively Coupled Plasma	
Mass Spectrometry	
Surface Area by Nitrogen Absorption Method	33 – 39
Total Gas in Reactor-Grade Uranium Dioxide Pellets	2
Thorium and Rare Earth Elements by Spectroscopy	2
Hydrogen by Inert Gas Fusion	4
C1457 Standard Test Method for Determination of	3
Total Hydrogen Content of Uranium Oxide Powders	
and Pellets by Carrier Gas Extraction	
Uranium Isotopic Analysis by Mass Spectrometry	2
C1413 Test Method for Isotopic Analysis of Hydro-	3
lysed Uranium Hexafluoride and Uranyl Nitrate Solu-	
tions By Thermal Ionization Mass Spectrometry	

2. Referenced Documents

2.1 ASTM Standards:³

- C753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder
- C761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride
- C776 Specification for Sintered Uranium Dioxide Pellets
- C1267 Test Method for Uranium by Iron (II) Reduction in Phosphoric Acid Followed by Chromium (VI) Titration in the Presence of Vanadium
- C1287 Test Method for Determination of Impurities in Nuclear Grade Uranium Compounds by Inductively Coupled Plasma Mass Spectrometry
- 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
- C1453 Test Method for the Determination of Uranium by

Ignition and the Oxygen to Uranium (O/U) Atomic Ratio of Nuclear Grade Uranium Dioxide Powders and Pellets

- 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
- D1193 Specification for Reagent Water
- E115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis (Withdrawn 2002)⁶
- E130 Practice for Designation of Shapes and Sizes of Graphite Electrodes (Withdrawn 2013)⁶
- E402 Test Method for Spectrographic Analysis of Uranium Oxide (U_3O_8) by Gallium Oxide-Carrier Technique (Withdrawn 2007)⁶

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 C753 and C776.

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.⁷ 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 D1193.

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 C753 and Specification C776.

6.2 Samples can be dissolved using the appropriate dissolution techniques described in Practice C1347, but final determination of applicability must be made by the user.

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

This test method was withdrawn in January 1999 and replaced by Test method C1267.

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

This test method was withdrawn in September 2011 and replaced by Test Method C1453.

CARBON (TOTAL) BY DIRECT COMBUSTION-THERMAL CONDUCTIVITY METHOD

This test method was withdrawn in January 1999 and replaced by Test Method C1408.

TOTAL CHLORINE AND FLUORINE BY PYROHYDROLYSIS ION-SELECTIVE ELECTRODE METHOD

This test method was withdrawn in September 2011 and replaced by Test Method C1502.

MOISTURE BY THE COULOMETRIC ELECTROLYTICMOISTURE ANALYZER METHOD

7. Scope

7.1 This test method covers the determination of moisture in uranium dioxide samples. Detection limits are as low as $10 \mu g$.

8. Summary of Test Method

8.1 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

⁶ The last approved version of this historical standard is referenced on www.astm.org.

⁷ 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.

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 (P₂O₅) (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.

8.2 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.

9. Apparatus

9.1 *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 cm³/min air, and a dryer assembly.⁸

9.2 *Balance*,⁹ for weighing samples in the range from 1 to 100 mg.

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

10. Reagents

10.1 Barium Chloride Dihydrate (BaCl₂·2 H₂O).

11. Operation

11.1 Turn the main power switch ON.

11.2 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.

11.3 Weigh the sample into a small, dry, aluminum boat (Note 1) and insert it into the instrument oven as follows:

Note 1—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. 11.3.1 Open the top of the analyzer and remove the TFE-fluorocarbon plug. Do not touch with gloves.

11.3.2 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.

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

11.4 Reset the counter to $0 \mu g$.

11.5 Set the timer at 1 h.

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

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

12. Standardization

12.1 Determine the blank by processing dry, empty, aluminum boats according to steps 11.3 - 11.7 until constant values are obtained.

12.2 Weigh and analyze replicate 5-mg samples of BaCl₂·2 H₂O until consistent results are obtained. Sodium tungstate dihydrate (Na₂WO₄ ·2 H₂O) may also be used for calibration.

13. Calculation

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

$$Z = (A - B)147.2Y$$
 (1)

where:

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

13.2 Calculate the percent moisture in the sample as follows:

Moisture,
$$\% = [(S - B)/1000 WZ] \times 100 = (S - B)/10 WZ$$
 (2)

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.

14. Precision

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

NITROGEN BY THE KJELDAHL METHOD

15. Scope

15.1 This test method covers the determination of nitride nitrogen in uranium dioxide in the range from 10 to 250 μ g.

⁸ A CEC Solids Moisture Analyzer, of Type 26-321A-MA is available from DuPont Instruments Inc., S. Shamrock Ave., Monrovia, CA 91016. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

⁹ A Cahn Electrobalance, or equivalent, available from Cahn Division, Ventrum Instrument Corp., Paramount, CA has been found satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

16. Summary of Test Method

16.1 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 2—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 (1) ¹⁰ 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.

17. Interferences

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

18. Apparatus

18.1 Nitrogen Distillation Apparatus, micro.¹¹

18.2 Heater, 750-W electric, full-control.

18.3 Burner, bunsen-type.

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

19. Reagents

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

19.2 *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.

19.3 *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.

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

Note 3—Some lots of H₃PO₄ give high blanks and cannot be used.

19.5 Potassium Dichromate Solution (65 g/litre)—Dissolve 65 g of potassium dichromate ($K_2Cr_2O_7$) 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 (1).

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

19.7 Sulfuric Acid, Standard— $(H_2SO_4, 0.01 N)$ — Standardize against a standard sodium hydroxide solution that has been standardized against potassium hydrogen phthalate. Note 4—Hydrochloric acid (HCl, 0.01 N) may be used instead of H_2SO_4 .

20. Procedure

20.1 Blank Determinations:

20.1.1 Fill the boiler of the distillation apparatus with ammonia-free water and distill for at least 30 min with a digestion flask in place in order to purge the apparatus of any traces of ammonia present.

20.1.2 Place 10 mL of H_3PO_4 and 15 mL of potassium dichromate solution (65 g/litre) in a digestion flask and attach to the apparatus. Add 50 mL of NaOH solution and start passing the steam from the boiler through the digestion flask.

20.1.3 Place a 125-mL Erlenmeyer flask containing 5 mL of the boric acid-indicator solution over the tip of the condenser and collect 25 mL of distillate. Lower the flask so that the tip of the condenser is above the level of the distillate and continue the distillation for an additional 30 s to rinse down the inside of the tube.

20.1.4 Titrate the distillate with the 0.01 N H₂SO₄ from a microburet until the solution turns to a pink color.

20.1.5 Repeat the blank determination, steps 20.1.2 - 20.1.4, until the blanks are constant. If the blank exceeds 0.03 to 0.04 mL, look for a source of contamination.

20.2 Analysis of the Sample:

20.2.1 Transfer up to 2 g of a weighed, powdered sample (Note 5) to the digestion flask.

Note 5—Samples in pellet form must be crushed in a diamond mortar to -100 mesh powder and sampled by riffling or quartering to obtain a representative sample.

20.2.2 Add 10 mL of H_3PO_4 and heat the flask gently with a small burner until a clear green solution is obtained. Inspect the solution carefully to ensure that no undissolved uranium nitrides remain.

20.2.3 Cool the flask, then add 15 mL of $K_2Cr_2O_7$ solution (65 g/litre) slowly with mixing. Warm at low heat for 3 to 4 min.

20.2.4 Attach the digestion flask to the distillation apparatus and add 50 mL of NaOH solution.

20.2.5 Place the receiving flask containing 5 mL of the boric acid-indicator solution over the condenser tip and distill and titrate following the procedure used to determine the blank.

21. Calculation

21.1 Calculate the nitrogen content as follows:

N,
$$\mu g/g$$
 on UO₂ basis = $(A - B)$ 14.01 N × 10³/W (3)

where:

A = millilitres of standard acid to titrate sample,

B = millilitres of standard acid to titrate blank,

N = normality of standard acid solution, and

 $W = \text{grams of UO}_2 \text{ sample.}$

22. Precision

22.1 This test method will determine nitrogen to within 7 μ g of the amount present.

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

¹¹ Kemmerer-Hallett Type, Fisher Scientific Co., has been found satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

ISOTOPIC URANIUM COMPOSITION BY MULTIPLE-FILAMENT SURFACE-IONIZATION MASS SPECTROMETRIC METHOD (This test method was withdrawn in 1980 and replaced by Test Method C1413.)

SPECTROCHEMICAL DETERMINATION OF TRACE ELEMENTS IN HIGH-PURITY URANIUM DIOXIDE

23. Scope

23.1 This test method covers the spectrographic analysis of nuclear-grade UO_2 for the 26 elements in the ranges indicated in Table 1.

23.2 For simultaneous determination of trace elements by plasma emission spectroscopy refer to Test Method C761.

24. Summary of Test Method

24.1 The sample of UO₂ is converted to U_3O_8 and mixed with a spectrochemically pure carrier consisting of 16.4 mol % strontium fluoride in silver chloride. A given quantity of this mixture is placed in a special cupped electrode and excited in a d-c arc. The spectrum is recorded on photographic plates and the selected lines are either visually compared with standard plates or photometrically measured and compared with synthetically prepared standards exposed on the same plate.

25. Significance

25.1 Carrier distillation methods for the analysis of uranium over the past years have used a variety of carriers. Test Method

TABLE 1 Recommended Analytical Spectral Lines and Concentration Range of Trace Elements

Element	Analytical Line, °A ^A	Concentration range, µg/g of U
Ag ^B	3280.68	0.1 to 50
AĬ	2367.06	10 to 200
As	2349.84	5 to 50
В	2497.73	0.10 to 5
Ba	4554.04	10 to 300
Be	2348.61	0.1 to 3
Bi	3067.72	5 to 50
Ca	4226.73	1 to 50
Cd	2288.02	0.15 to 5
Co	3453.51	5 to 50
Cr	2843.25	10 to 100
Cu	3247.54	1 to 10
Fe	2462.64	10 to 300
In	3256.09	5 to 50
Mg	2779.83	10 to 100
Mn	2605.69	5 to 50
Mo	3132.59	0.5 to 10
Na	3302.32	80 to 400
Ni	3050.82	5 to 100
Р	2553.28	50 to 500
Pb	2833.07	5 to 50
Sb	2598.05	1 to 50
Si	2435.16	10 to 200
Sn	3175.02	5 to 50
Ti	3361.26	1 to 100
V	3183.41	1 to 100
Zn	3345.02	20 to 300
7r	3438 23	25 to 300

^A All of the above lines are photographed in the second order, except barium and calcium which are first order lines.

^B A gallium oxide carrier must be used for silver. See Test Method E402.

E402, approved by ASTM Committee E-2 on Emission Spectroscopy, called for gallium oxide as the carrier. This method involves the use of a mixture of silver chloride and strontium fluoride (2, 3). The fluoride gives an increased sensitivity for aluminum, zirconium, titanium, and niobium.

25.2 For the analysis of refractory elements in uranium, a separation is required for maximum sensitivity. However, recent work (4, 5) has improved the sensitivity of some elements using a mixed carrier technique.

26. Apparatus

26.1 *Spectrograph*—A spectrograph with sufficient resolving power and linear dispersion to separate the analytical lines from other lines in the spectrum of the sample in the spectral region 4200 to 7000 Å is required. Instruments with a reciprocal linear dispersion of approximately 5 Å/mm, first order or less, are satisfactory. A direct-reading spectrograph of comparable quality may be substituted for the equipment listed, in which case the directions given by the manufacturer should be followed rather than those given in the succeeding steps of this procedure.

26.2 *Excitation Source*—Use a high-voltage spark source capable of providing a 14-A d-c arc (short circuit).

26.3 *Excitation Stand*—Conventional type with adjustable water-cooled electrode holders.

26.4 *Developing Equipment*—Use developing, fixing, washing, and drying equipment conforming to the requirements of Practice E115 (6).

26.5 *Microphotometer*, having a precision of at least $\pm 1 \%$ for transmittances.

26.6 *Mixer*, for dry materials.¹²

26.7 Platinum Crucible, 10-mL capacity.

26.8 Venting Tool-See Fig. 1 for diagram.

26.9 *Calculating Boards*, or other special equipment are optional, their use depending to a large extent on how frequently analyses are made and how much speed is required.

26.10 Muffle Furnace, capable of heating up to 900°C.

26.11 *Electrode Forceps*, with each V-tip bent to form a semicircular grasp around the electrodes.

26.12 *Balances*, torsion-type, one with a capacity up to 1 g and capable of weighing to ± 0.1 mg, and one with a capacity of 500 g.

27. Reagents and Materials

27.1 Agate Mortars.

¹² The Fisher-Kendall mixer was found to be satisfactory for large quantities and the Wig-L-Bug (Spex Industries) for small quantities. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.



27.2 *Electrodes*—The anode, pedestal, and counter electrodes should be respectively of the S-1, S-2, and C-1 types as given in Practice E130.¹³

27.3 Glassine Paper.

27.4 Tissue-A suitable wiping tissue is necessary.

27.5 *Mixing Vial*, plastic, having a 12.7-mm ($\frac{1}{2}$ -in.) diameter and a 25.4-mm (1-in.) length with cap, and a 9.6-mm ($\frac{3}{8}$ -in.) diameter plastic ball.

¹³ Upper electrode, Ultra Carbon 1992, lower electrode, Ultra Carbon 1998, electrode pedestal, Ultra Carbon 1993.

27.6 Nitric Acid (HNO₃, sp gr 1.42).

27.7 *Photographic Processing Solutions*—Prepare solutions as noted in Practice E115.

27.8 Silver Chloride-Strontium Fluoride Carrier (16.4 mol % SrF_2 in AgCl¹⁴)—Since AgCl decomposes when exposed to light, all grinding, sieving, and transferring operations involving this material must be done in a darkroom under the safelight¹⁵ and all blending must be done in opaque polyethylene bottles.

27.9 Standard U_3O_8 Diluent—Use NBS SRM 950b U_3O_8 or its replacement of known impurity content as a diluent.

27.10 *Photographic Film*—Use photo emulsion EK SA No. 1 or equivalent.

28. Standards

28.1 Standards can be synthetized by adding the impurity elements to purified U_3O_8 (NBS SRM 950b) and homogenizing. Impurities in a solid or powder form, preferably as oxides, may be blended in U_3O_8 , impurities in solution may be added to U_3O_8 and the mixture dried, blended, and reignited, or the impurities and uranium may be combined in solution and reconverted to U_3O_8 . The individual elements should grade in such a ratio as to facilitate visual comparisons, covering the desired analytical range for each. No single standard should have a total concentration of impurities exceeding 2000 µg/g. The bulk densities of the standards and the sample U_3O_8 should be as nearly identical as possible.

28.2 The elements or compounds used to make U_3O_8 impurity standards should be of the highest purity.

29. Procedures

29.1 Preliminary Sample Preparation:

29.1.1 Clean a 10-mL platinum crucible in HNO_3 (sp gr 1.42). Rinse with distilled water and dry. Transfer approximately 3 to 5 g of the UO₂ sample to a clean platinum crucible and heat in a muffle furnace at 800°C for 30 min. Remove from furnace and cool.

29.1.2 Grind the U_3O_8 residue in an agate mortar and transfer to a clean labeled sample vial.

29.2 Preparation of Electrode Charge:

29.2.1 Weigh 450 \pm 2 mg of the sample as U₃O₈ and transfer to a plastic mixing vial containing a plastic ball.

29.2.2 Perform operations at this point rapidly to minimize exposure to light. Cover the sample with a dark cover if possible. Weigh 50 \pm 0.5 mg of the silver chloride-strontium fluoride carrier and transfer to the same mixing vial.

29.2.3 Mix by rolling the vial between the fingers, and then process in the mixer for 30 s.

29.2.4 Weigh 100 ± 1.0 mg of this mixture and transfer it into an S-2 graphite electrode. (Grade U-7 or equivalent).

29.2.5 Load duplicate electrodes for each sample and the plate standards. Use an electrode board to hold the electrodes, and identify the sample in each electrode by marking the board with the corresponding sample numbers.

29.2.6 To hold the electrodes use only clean forceps reserved for this purpose. Discard any electrodes accidentally touched or dropped.

29.2.7 Firmly grip the electrode with the modified forceps and pack the charge by gently tapping on a glassine-covered solid surface.

29.2.8 Further, compress and vent the charge with the venting tool shortly before arcing the sample. Wipe the venting tool point with a wiping tissue between different samples.

Note 6—Caution: Use extreme care to prevent jarring the electrodes after venting.

29.2.9 On a plate envelope, list the samples in the order in which they will be exposed and the spectrographic conditions.

29.3 Exposure:

29.3.1 Wipe the upper and lower electrode clamps with a wiping tissue before use. Place a pedestal and upper electrode in the appropriat clamps. Place the lower electrode firmly on the pedestal without jarring.

29.3.2 Expose the plate standards in order to obtain a line for the emulsion calibration curve.

29.3.3 Close the arc-enclosure door and critically adjust the electrodes to the 4-mm gap setting as indicated on the viewing screen.

29.3.3.1 Exposure Conditions:

Spectral range, A	2250-5000
Slit width	optimum for the spectograph used
Preburn, s	0
Exposure, s	40
Current, A (short-circuit)	14
Voltage, V (open circuit)	250

29.3.4 Initiate the arc.

29.3.5 During the exposure continuously maintain the critical alignment of the arc image to the proper index lines on the viewing screen until the arc is automatically terminated.

29.3.6 Rack the plate holder for the next exposure. Drop spent electrodes into the container in the arc enclosure. Use a new upper electrode for each sample electrode arced. Replace the pedestal after 10 electrodes have been arced.

29.3.7 Repeat the exposure cycle until all the electrodes have been arced.

29.3.8 Rack the plate holder up to the end of travel and remove for processing.

29.4 Photographic Processing:

29.4.1 Process the photographic plate in accordance with Practice E115.

29.5 Photometry and Calculation of Results:

29.5.1 With the microphotometer, measure the transmittance of the analytical lines and the adjacent background. Measure an appropriate step yielding between 15 and 75 % transmittance.

29.5.2 Measure the transmittance at seven steps of a suitable unfiltered line for the purpose of preparing an emulsion calibration curve. Repeat.

¹⁴ Mallinckrodt A. R. AgCl and Spex Industries N. 1153 SrF₂.

¹⁵ The Eastman Safelight Filter, Wratten Series 1, has been found satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

29.5.3 Plot the mean transmittance values on the *y*-axis versus the corresponding step numbers of the *x*-axis. Carefully draw a smooth curve through the points. Use linear graph paper.

29.5.4 Clip the emulsion calibration curve to the calculating board and determine the relative intensity, corrected for background, on the measured analytical lines for each standard and sample.

29.5.5 Obtain the results in $\mu g/g$, UO₂ basis, for each element in each sample from the appropriate analytical curve with reference to the plate standard.

30. Precision and Accuracy

30.1 Precision-The relative standard deviation is 25 %.

30.2 *Accuracy*—The accuracy of the test method can approach the precision provided the appropriate standards are used.

SILVER, SPECTROCHEMICAL DETERMINATION OF, BY GALLIUM OXIDE CARRIER D-C ARC TECHNIQUE

31. Scope

31.1 This test method covers the spectrochemical determination of silver in nuclear-grade uranium dioxide. The relative standard deviation is 15 % for the concentration range of 0.1 to 50 μ g/g.

32. Summary of Test Method

32.1 The uranium dioxide is ignited to U_3O_8 , weighed, and mixed with gallium sesquioxide (Ga₂O₃) in the ratio of 98 parts of U_3O_8 to 2 parts of Ga₂O₃, and an appropriate internal standard is added to the mixture. The mixture is placed in a special cupped electrode and excited in a d-c arc. The Ga₂O₃ carries silver (Ag), as a vapor or particulate, into the arc stream for excitation. The spectrum is recorded on a photographic plate and the selected silver lines are compared with standard plates of silver prepared according to standard spectrochemical procedures. Consult Test Method E402 for procedural details.

RARE EARTHS BY COPPER SPARK-SPECTROCHEMICAL METHOD

With appropriate sample preparation ICP-AES as described in C761 or Inductively Coupled Plasma Mass Spectrometry (ICP-MS) as described in C1287 may be used to determine rare earths and impurity elements.

IMPURITY ELEMENTS BY A SPARK-SOURCE MASS SPECTROGRAPHIC METHOD

With appropriate sample preparation ICP-AES as described in C761 or Inductively Coupled Plasma Mass Spectrometry (ICP-MS) as described in C1287 may be used to determine rare earths and impurity elements.

SURFACE AREA BY NITROGEN ABSORPTION METHOD

33. Scope

33.1 This procedure is designed for a rapid determination of surface area of nuclear-grade uranium dioxide (UO_2) powders.

The determination of surface area by this procedure is automatic, simple, and fast enough to be used in quality control work. The range of analysis is from 1 to $1500 \text{ m}^2/\text{g}$.

34. Summary of Test Method

34.1 The surface area of UO_2 powder is measured by low temperature gas adsorption using a surface area analyzer. The instrument is designed to give equilibrium adsorption at a predetermined relative pressure. Corrections are automatically made for sample bulb "dead space" and for the intercept on the ordinate of the multipoint Brunauer, Emmett, Teller (B.E.T.) plot. Nitrogen gas is used as the adsorbate. Automatic programming of the instrument produces a direct digital presentation of total surface area after equilibrium adsorption has occurred at a pre-set pressure and at liquid nitrogen temperature.

35. Apparatus and Equipment

35.1 Surface Area Analyzer.¹⁶

35.2 *Nitrogen Gas Tank*, with a regulator, and pressure supplied to the instrument between 34 and 69 kPa gage (5 and 10 psig).

- 35.3 Sample Bulb, 15-cm³ capacity.¹⁷
- 35.4 Sample Tube Filler Funnel.¹⁸
- 35.5 *Heating Mantle*, with thermocouple.¹⁹
- 35.6 Dewar Flasks, two, 500-mL (1-pt) volume.²⁰
- 35.7 Liquid Nitrogen.
- 35.8 Crushed Ice.
- 35.9 Drying Oven.
- 35.10 Vacuum Manifold.²¹
- 35.11 Mechanical-Vacuum Pump.²²

¹⁶ A Micromeritics Surface Area Analyzer, Model 2200, has been found satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

¹⁷ Micromeritics No. 04-61002 has been found satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

¹⁸ Micromeritics No. 04-25846 has been found satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

¹⁹ Micromeritics No. 03-26019 has been found satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

²⁰ Micromeritics No. 04-61001 has been found satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

²¹ The Numec AFA-409 model Vacuum Manifold has been found satisfactory for this purpose. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

²² Precision Scientific Co., Model 15, has been found satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

35.12 Thermocouple Vacuum Gage.²³

36. Reagents and Chemicals

36.1 Titanium Oxide (TiO₂) (10.3 m²/g).²⁴

36.2 Zinc Oxide (ZnO), (3.9 m²/g).

37. Procedure

37.1 Initial Setup:

37.1.1 Turn master switch ON, CONTROL switch OFF, and SELECT switch to PREPARE.

37.1.2 Attach nitrogen to system.

NOTE 7—The nitrogen gas cylinder equipped with a pressure regulator capable of supplying 34 to 69 kPa gage (5 to 10 psig) pressure should be attached by means of heavy-walled or vacuum hose to the connector in the side of the instrument cabinet.

37.1.3 Set all three SAMPLE VALVES in PREPARE position for 5 min; then clockwise to OFF.

Note 8—All intermediate positions between labeled positions on sample valves are OFF positions.

(Master switch should have been on at least 10 min or more for instrument to operate properly in following steps):

37.1.4 Put the CONTROL switch in TEST.

37.1.5 Turn any one SAMPLE VALVE clockwise from OFF position to TEST. This will activate the counting mechanism. 37.1.6 Engage the RAPID-ADVANCE switch.

37.1.7 When the counting stops turn the SAMPLE VALVE clockwise to OFF between TEST and FILL.

37.1.8 Place the CONTROL switch in OFF position.

37.1.9 Place a Dewar flask of liquid nitrogen on sorption pump probe.

Note 9—Sorption pump probe is the short metal cylinder with the hemispherical end located immediately behind the sample-tube position.

37.1.10 Place the SELECT switch in TEST.

37.1.11 Leave for 5 to 8 min.

37.1.12 Place the SELECT switch in PREPARE.

37.1.13 Place the CONTROL switch to RESET position. This will activate the motor which drives the piston upward.

37.1.14 Turn the SAMPLE VALVE clockwise to FILL and remove liquid nitrogen bath.

37.1.15 When piston stops upward travel or the red light on the instrument panel *just* goes out or both, turn the SAMPLE VALVE *immediately* clockwise to OFF. (If the red light goes out before the piston completes upward travel, turn the SAMPLE VALVE to OFF until piston stops, then turn the SAMPLE VALVE to FILL until red light *just* goes out again, then immediately to OFF.)

Note 10-Turning off immediately prevents gas from continuing to flow into the variable volume portion of the system and attaining a

pressure too great for later operations.

37.1.16 Place the CONTROL switch to OFF position.

Note 11—The initial setup procedure is to fill the instrument with nitrogen gas. It needs to be repeated only when the master switch has been turned off or a fresh nitrogen cylinder attached to the instrument.

37.2 Sample Preparation:

37.2.1 Weigh an empty, clean, dry sample bulb.

37.2.2 Fill the sample bulb with approximately 6 g of sample and weigh.

Note 12—Sample masses must be such as to obtain 10 to 140 m² of surface. Best results are accomplished between 50 and 140 m² of surface. However, 30 m² of surface were measured for UO₂ without any loss of accuracy. This means that sample mass of UO₂ can vary between 5 and 10 g if the measured surface area is about 5 m²/g. For standard TiO₂, use about 3 g. For standard ZnO, use about 6 g.

37.2.3 Outgas the sample under vacuum, at 200°C for 2 h using a separate vacuum manifold.²¹

Note 13—Degassing of UO_2 samples should be done on a separate manifold.

37.2.4 Remove the sample bulb from the manifold and attach the bulb to the instrument.

Note 14—Insert the sample tubes into the connectors in the recessed part of the instrument panel, being sure to push them all the way to the stop. Tighten the thumb nuts firmly by hand.

37.2.5 Turn the SAMPLE VALVE to PREPARE.

37.2.6 Place a heating mantle around the sample bulb and set the temperature to 150° C for 10 min.

Note 15—The sample has already been outgassed on a separate manifold but needs to be heated to release all gases adsorbed during the transfer of the sample. Heating is accomplished by purging nitrogen in order to drive off the released gases. Produce the gas flow by turning the SAMPLE VALVE to the PREPARE position. The outgassing temperature is indicated by the pyrometer at the upper left of instrument when the thermocouple probe of heating mantle is inserted into the jack labeled THERMOCOUPLE. Adjust the heating temperature by means of the variable transformer knob directly above the socket into which the mantle is plugged. (Setting of 35 to 40 will result in a temperature of about 150°C.)

37.2.7 Turn the SAMPLE VALVE clockwise to OFF between PREPARE and TEST.

37.2.8 Remove the heating mantle.

37.3 Sample Analysis:

37.3.1 Have the CONTROL switch in OFF,

37.3.2 Place the SELECT switch in PREPARE, and

37.3.3 Put the SAMPLE VALVE on OFF.

37.3.4 Place a Dewar flask of ice water around the sample bulb.

Note 16—The ice should be finely crushed and should be of sufficient quantity to encompass completely the sample bulb. Replenish the supply of ice, in the Dewar flask, two or three times a day during normal analysis conditions. The ice water level should be such that it just comes to the bottom of the frosted spot on the sample bulb. Stir the ice water before placing it on each sample and stir at least once during the time it is around the sample.

37.3.5 Turn the CONTROL switch to TEST.

37.3.6 Turn the SAMPLE VALVE to TEST position. The center red light should come on and the counter should indicate several counts. If this does not occur proceed to step 37.5.

 $^{^{23}}$ Bendix GTC-100 (range 0–1000 µm) has been found satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

²⁴ Material available from Particle Information Service, Los Altos, CA, has been found satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

37.3.7 Wait until the counter stops and the green light comes on.

37.3.8 Turn the SAMPLE VALVE counterclockwise to OFF position between PREPARE and TEST.

Note 17—The ice water bath procedure is used to establish a known quantity of gas in the sample bulb. That is why the preparation of ice-water slurry in the bath, the temperature, and the level of ice water are all very important.

37.3.9 Place the CONTROL switch to RESET until the motor stops, then to OFF.

37.3.10 Remove the ice water bath and dry the sample bulb.

37.3.11 Place the Dewar flask of liquid nitrogen around the sample tube making sure that the level of the liquid comes to the bottom of the frosted spot.

37.3.12 *Immediately* place SELECT switch and CONTROL switch in TEST positions.

37.3.13 In approximately 1 to 2 min, the red light will come on and the counter will run several counts.

37.3.14 After the counter stops, place the CONTROL switch in OFF position.

37.3.15 Zero the counter.

37.3.16 Place the CONTROL switch in TEST position.

37.3.17 Turn the SAMPLE VALVE to TEST position.

37.3.18 Engage RAPID ADVANCE switch.

Note 18—If there is a significant drop in the liquid nitrogen level while counting proceeds, add liquid nitrogen to maintain the level just at the bottom of the frosted spot. The Dewar flask should be covered with a styrofoam cup.

37.3.19 When equilibrium is reached, the green light will come on.

37.3.20 Record the reading on the counter as the total surface area of the sample in square metres.

37.4 Reset Conditions:

 $37.4.1\,$ Turn the SAMPLE VALVE clockwise to OFF between TEST and FILL.

37.4.2 Set the CONTROL switch to OFF.

37.4.3 Turn the SELECT switch to PREPARE.

37.4.4 Set the CONTROL switch to RESET.

37.4.5 Turn the SAMPLE VALVE to FILL.

37.4.6 When the motor stops or the red light just goes out, or both, turn SAMPLE VALVE clockwise to OFF.

37.4.7 Remove liquid nitrogen.

37.4.8 Turn the SAMPLE VALVE clockwise to PREPARE.

37.4.9 Turn the CONTROL switch to OFF.

37.4.10 Allow the sample bulb to warm. When at room temperature turn the SAMPLE VALVE clockwise to OFF. Remove the sample bulb.

37.4.11 Weigh the sample bulb and sample. Subtract the mass of the sample bulb to obtain the mass of sample.

Note 19—The three SAMPLE VALVES have the same function. Thus, while one sample is being analyzed prepare two others for analysis, one of them being outgassed with heating mantle and the other having ice water bath around bulb.

37.5 *Correction for Overfill*—If in step 37.3.6, the red light did not come on and the counter did not indicate positive counts, the chamber has been overfilled with gas. To correct this condition proceed as follows:

37.5.1 Turn the SAMPLE VALVE clockwise to OFF position.

37.5.2 Set the CONTROL switch to OFF.

37.5.3 Place the liquid nitrogen bath on the sorption pump probe of a previously run sample.

37.5.4 Turn the SELECT switch to TEST position for 10 to 20 s.

37.5.5 Set the SELECT switch to PREPARE. The red light should come on. If it does not, repeat step 37.5.4.

37.5.6 Zero the counter.

37.5.7 Set the CONTROL switch to TEST.

37.5.8 Engage the RAPID ADVANCE switch.

37.5.9 Let counter run for 100 counts (10.0 m^2).

37.5.10 Then turn the CONTROL switch to OFF.

37.5.11 If the red light is not off, turn the sample valve to FILL position until the red light goes off.

37.5.12 Turn the SAMPLE VALVE counterclockwise to TEST position.

37.5.13 Set the CONTROL switch to RESET until the red light comes on.

37.5.14 Turn the CONTROL switch back to TEST position.

37.5.15 Remove the liquid nitrogen.

37.5.16 Return to step 37.3.6 and proceed with the analysis.

38. Calculation

38.1 Divide the square metres obtained from step 37.3.20 of the procedure by the mass of the sample.

Example:

Number of square metres: 16.2

Mass of sample in g: 3.39

Surface area in m^2/g : = 16.2/3.39 = 10.4

39. Precision and Accuracy

39.1 *Precision* is better than $\pm 0.3 \text{ m}^2/\text{g}$.

39.2 Accuracy is within 2 %.

TOTAL GAS IN REACTOR-GRADE URANIUM DIOXIDE PELLETS

This method was discontinued in January 1999.

THORIUM AND RARE EARTH ELEMENTS BY SPECTROSCOPY

With appropriate sample preparation ICP-AES as described in C761 or Inductively Coupled Plasma Mass Spectrometry (ICP-MS) as described in C1287 may be used to determine rare earths and impurity elements.

HYDROGEN BY INERT GAS FUSION

This test method was withdrawn in September 2011 and replaced by Test Method C1457.

URANIUM ISOTOPIC ANALYSIS BY MASS SPECTROMETRY

This Test Method was discontinued in January 1999 and replaced by Test Method C1413.

40. Keywords

40.1 impurity content; isotopic composition; stoichiometry; uranium content; uranium dioxide



REFERENCES

- (1) Kallmann, S., Hobert, E. W., Oberthin, H. K., and Brienzo, W. C., Jr., "Determination of Traces of Nitrogen in Refractory Metals and Alloys by Hydrofluoric Acid-Phosphoric Acid-Potassium Dichromate Decomposition and Indophenol Photometry," *Analytical Chemistry*, ANCHA, Vol 40, 1969, p. 332.
- (2) Vogel, R. S., *MCW-1475, Quarterly Progress Report*, QMLEA, August 1962.
- (3) Harrison, G. R., and Kent, R., "Spectrographic Determination of

Trace Materials in Uranium Salts and in Magnesium, Dolomite, and Lime," USAEC Report MDDC-1581, AERDB, 1948.

- (4) Morris, W. F., UCID-15644-7-2, Quarterly Progress Report, QMLEA, July 27, 1970.
- (5) Yuster, H. G., and Nintzel, I. V., USAEC Report NBL-258, Annual Progress Report, AERDB, April 1971.
- (6) ASTM Methods for Emission Spectrochemical Analysis, American Society for Testing and Materials, ASTSA, 1967.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/