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

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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:

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^{1a} Discontinued as of May 30, 1980.

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.

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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](#)²–[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](#)

² Annual Book of ASTM Standards, Vol 12.01.

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 Vol 11.01 volume information, refer to the standard's Document Summary page on the ASTM website.

⁴ Annual Book of ASTM Standards, Vol 03.05.

⁴ Discontinued September 2011.

⁵ Annual Book of ASTM Standards, Vol 03.06.

⁵ Discontinued as of May 30, 1980.

- ~~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~~
~~E116 Practice for Photographic Photometry by Spectrochemical Analysis~~⁴~~Practice for Photographic Processing in Optical Emission Spectrographic Analysis~~
~~E130 Practice for Designation of Shapes and Sizes of Graphite Electrodes~~⁴
~~E217 Test Method for Uranium by Controlled-Potential Coulometry~~²
~~E305 Practice for Establishing and Controlling Spectrochemical Analytical Curves~~⁴~~Practice for Designation of Shapes and Sizes of Graphite Electrodes~~
~~E402 Test Method for Spectrographic Analysis of Uranium Oxide (U₃O₈) by Gallium Oxide-Carrier Technique~~

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~~^{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.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 Specification ~~D-1193~~^{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 ~~C-753~~^{C753} and Specification ~~C-776~~^{C776}.

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

7. Scope

7.1 This general test method covers the determination of uranium in nuclear-grade uranium dioxide. Test portions of sample will be adjusted to contain approximately 100 mg of uranium.

7.2 A variation in the procedure that will give increased precision permits a sample size of 3 g.

8. Summary of Test Method

8.1 An excess of ferrous sulfate is employed to reduce U(VI) to U(IV) in a concentrated phosphoric acid solution containing sulfamic acid. The excess ferrous ion is subsequently oxidized by nitric acid in the presence of Mo(VI) as a catalyst. After the addition of water and vanadyl sulfate dihydrate, the determination is completed by titrating the U(IV) with standard potassium dichromate solution to a potentiometric end point (1, 2, 3).

8.2 Increased precision may be attained by using a large sample, 3 g, dissolving the sample in phosphoric acid to obtain chiefly U(IV), and by oxidizing most of the total U(IV) by the addition of a weighed portion of solid potassium dichromate prior to the final titration with potassium dichromate solution.

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.

9. Significance

9.1 The selection of a test method for determining uranium will depend upon such factors as the amount of sample, the purity of the material, the precision required, and the equipment available.

9.2 The volumetric method is tolerant of most impurities encountered in reactor-grade uranium dioxide, capable of high precision (relative standard deviation of 0.02% on sample weights in the range from 100 to 200 mg), and requires no extraordinary equipment. Increased precision (relative standard deviation of 0.008%) can be obtained by the use of larger sample sizes, 3 to 5 g, and by adding most of the oxidant as an accurately weighed solid.

9.3 The gravimetric procedure is probably the simplest method, but larger samples (10 to 50 g) are required for highest precision, and a correction for impurities based on spectrochemical analysis, must be applied in order to obtain accurate results.

9.4 Where a controlled-potential coulometer is available (4), the coulometric method (see Test Method E 217E 217) will analyze sample aliquots containing less than 10 mg of uranium with a precision of 0.2 to 0.3%, and under very carefully controlled conditions a precision of 0.1% has been obtained. Small amounts of many impurities can be tolerated without causing interference.

10. Interferences

10.1 Interfering elements are generally not present in UO_2 product material. However, elements that cause an error when present in milligram quantities are silver, mercury, vanadium, platinum, palladium, ruthenium, osmium, iridium, and iodine. Interference from tin, arsenic, antimony, manganese, molybdenum, chlorine, and bromine are eliminated when the procedure is followed as given (2, 3, 5, 6, 7). When large amounts of plutonium are present, a variation of the procedure is employed.

11. Apparatus

11.1 *Burets*, 10, 50, or 100-mL, with a bulb reservoir.

11.2 *Magnetic Stirrer and TFE-Fluorocarbon-Coated Stirring Bar*

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.

11.3 *pH Meter*, with platinum and calomel electrodes. The electrodes are best stored in separate containers of water when not in use. The fast response of a platinum electrode made sluggish by certain impurities such as halides and mercury can generally be restored by a nitric acid treatment followed by a flaming in a burner flame.

12. Reagents

12.1 *Ferrous Sulfate Solution (1.0 M)*—Add 100 mL of sulfuric acid (H_2SO_4 , sp gr 1.84) to 750 mL of water as the solution is stirred. Add 280 g of ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and dilute the solution to 1 litre with water.

12.2 *Nitric Acid (8 M)-Sulfamic Acid (0.15 M)-Ammonium Molybdate (0.4%) Solution*—Dissolve 4 g of ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) in 400 mL of water, and add 500 mL of nitric acid (HNO_3 , sp gr 1.42). Mix, then add 100 mL of 1.5 M sulfamic acid solution (12.7) and mix.

12.3 *Orthophosphoric Acid (H_3PO_4), 85%*.

12.4 *Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) Solid*, NBS SRM 136c or its replacement.

12.5 *Potassium Dichromate Solution (2%)*—Dissolve 2 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 100 mL of water.

12.6 *Potassium Dichromate Solution (0.025 N)*—Weigh precisely about 1.23 g $\text{K}_2\text{Cr}_2\text{O}_7$, NBS SRM 136c or its replacement, into a 1-litre volumetric flask, dissolve in water, and dilute to the mark. After the solution is thoroughly mixed, record its temperature (13.1.11). Correct weight of dichromate for buoyancy and then for oxidizing power. Use the corrected weight for calculating normality.

12.7 *Sulfamic Acid Solution (1.5 M)*—Dissolve 146 g of sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$) in water, filter the solution, and dilute to 1 litre.

12.8 *Sulfuric Acid (1+1)*—To 500 mL of water which is stirred vigorously, slowly add 500 mL of sulfuric acid (H_2SO_4 , sp gr 1.84). Cool the solution during mixing.

12.9 *Vanadyl Sulfate ($\text{VO}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$)*, crystals.

13. Procedure

13.1 *Basic Procedure:*

13.1.1 Accurately weigh about 1 g of UO_2 sample and transfer it to a 400-mL beaker.

13.1.2 Add 20 mL of $\text{HNO}_3(1+1)$ to the beaker, cover, and heat until the sample has dissolved.

13.1.3 Rinse down the cover and sides of the beaker, cool, and carefully transfer the solution to a tared 100-mL volumetric flask or glass bottle. Cool to room temperature, dilute to 100 mL, and reweigh the flask to get the sample solution weight.

13.1.4 Transfer a weighed portion of sample solution containing 100 to 150 mg of uranium to a 400-mL beaker.

13.1.5 Add 3 mL of HClO₄ (72%) or H₂SO₄ (sp gr 1.84) and heat to strong fumes; then cool.

13.1.6 Rinse down the sides of the beaker with about 10 ml of water and place a magnetic stirring bar in the solution.

Note 1—The volume of the solution must not exceed 15 mL.

13.1.7 Add the following reagents in order given, mixing after each addition: 5 mL of 1.5 M NH₂SO₃H solution, 40 mL of H₃PO₄ to which 2 drops of 2% K₂Cr₂O₇ solution has been added, and 5 mL of 1.0 M FeSO₄ solution.

Note 2—Do not allow the ferrous sulfate solution to contact the walls of the beaker.

13.1.8 Wait a minimum of 30 s, then add 10 mL of the oxidizing solution (12.2) and swirl.

13.1.9 Allow the solution to stand for an additional 3-min period after the dark brown color which is produced in the solution has disappeared. Swirl occasionally during this period.

Note 3—Because this reaction is temperature dependent, the length of time specified assumes reagent temperatures from 23 to 39°C.

13.1.10 Add 100 mL of water and approximately 100 mg of VOSO₄·2H₂O estimated visually.

13.1.11 Stir rapidly without splashing and insert electrodes. Add 0.025 N K₂Cr₂O₇ solution rapidly from a 50-mL buret until a potential of about 525 mV is reached. Then titrate dropwise (finally washing fractions of drops of titrant from tip of buret with a small amount of water) to 590 mV. At some point in the titration between 525 to 590 mV, wash walls of beaker and electrodes with a small amount of water from a wash bottle and continue titration. Allow no more than 7 min to elapse between the dilution step and the completion of the titration. Correct volume of titrant for effect of temperature as required.

13.2 High-Precision Procedure:

13.2.1 Transfer a 3-g sample to a 400-mL beaker. Correct sample weight for buoyancy.

13.2.2 Add 50 mL of H₃PO₄ (85%) to which 2 drops of 2% K₂Cr₂O₇ solution have been added, and 3 to 5 drops of HF (48%) have been added.

13.2.3 Heat on a steam bath (or to a temperature of about 85°C) until dissolution of the sample is complete. Carefully inspect for complete dissolution.

13.2.4 Cool the solution to room temperature and add 10 ml of H₂SO₄(1+1).

13.2.5 Add in the order given, mixing thoroughly after each addition by swirling, 5 mL of 1.5 M NH₂SO₃H, 2 mL of 1 M FeSO₄ solution, and, after a minimum of 30 s, 10 mL of oxidizing solution (12.2).

13.2.6 When the dark brown color that develops in the solution disappears, allow the solution to stand for a minimum of 3 min.

13.2.7 Stir rapidly, without splashing; add 100 mL of water and about 100 mg of vanadyl sulfate dihydrate (VOSO₄·2H₂O). Wash down the walls of the beaker with water. Increase stirring speed as appropriate.

13.2.8 Estimate as accurately as possible, the amount of U(IV) to be titrated, using the buoyancy corrected sample weight. Weigh into an aluminum weighing dish an amount of K₂Cr₂O₇, NBS SRM 136c, equivalent to 5 mg less than the quantity of uranium estimated. Take into account corrections for buoyancy and oxidizing power of the dichromate. Add the K₂Cr₂O₇ to the solution to be titrated. Rinse the dish with water into the beaker.

13.2.9 Insert the electrodes into the solution. Wash down the walls of the beaker and titrate slowly with 0.01 N K₂Cr₂O₇ solution (12.4). Near the end point of 590 mV add the titrant in 0.10-mL increments. After each addition wash the tip of the buret with water. Allow the potential to stabilize after each increment and record its value. Proceed in this manner for at least one increment beyond the endpoint.

13.3 Determine the volume of dichromate required to reach the end point by second derivative techniques. For example:

Volume, mL	Potential, V	dmV	d ² mV
6.00	0.470	24	+143
6.10	0.491	164	-132
6.20	0.655	32	
6.30	0.687		

volume of titrant = $V = 6.10 + 0.10(143/143 + 132) = 6.152$.

14. Calculation

14.1 Calculate the uranium content as follows:

14.1.1 Basic Procedure:

$$U, \text{g/g} = \frac{TVG}{W} \text{C0696-93E01}_1 \quad (1)$$

14.1.2 High-Precision Procedure:

$$U, \% = \frac{TV + [D \times 2.4273]}{W} 100G \text{C0696-93E01}_2 \quad (2)$$

where:

F = grams of normal uranium equivalent to 1 mL of titrant;

V = millilitres of standard potassium dichromate solution used, corrected for temperature variation;

W = grams of sample in portion titrated;

- D = weight of solid potassium dichromate corrected for buoyancy and purity,
 G = uranium enrichment factor = atomic weight of uranium in sample/238.03, and
 2.4273 = grams U per gram of potassium dichromate.

15. Precision and Accuracy

- 15.1 The limit of error at the 95% confidence level for a single determination is $\pm 0.1\%$ relative for a 100-mg sample.
 15.2 With the high-precision method results with a relative standard deviation of 0.005% and better have been obtained.

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

16. Scope

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

17. Summary of Test Method

17.1 A weighed portion of UO_2 is dried under reduced pressure in a nitrogen atmosphere, desiccated, and weighed. The dried oxide is then converted to U_3O_8 by ignition at 900°C (8, 9).

18. Interferences

18.1 The weight of U_3O_8 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.

19. Apparatus

19.1 *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)).

19.2 *Drying Tower*—Prepare a U-tube filled with a carbon dioxide absorbent and a suitable moisture absorbent, that is, anhydrous magnesium perchlorate $Mg(ClO_4)_2$.

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.

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

20. Procedure

20.1 Transfer approximately 5 to 10 g of UO_2 powder or up to 50 g of pellets to a tared platinum crucible and weigh to within 0.1 mg.

20.2 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).

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

20.4 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 20.3 to give a total of three flushes.

20.5 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.

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

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

20.8 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.

20.9 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 20.8 and 20.9 until a constant weight is obtained.

20.10 Submit the ignited sample for spectrographic analysis.

21. Calculation

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

$$\text{Loss, wt\%} = [(S - W_1)/S] \times 100 \quad \text{C0696-93E01_3} \quad (3)$$

where:

S = initial sample mass, and

W_1 = sample mass after vacuum drying, g.
21.2 Uranium Content—Calculate as follows:

$$U, wt\% = [(0.8480(W_2 - W_2f)/S) \times 100] - 0.01\% \text{ (Note 3)} \quad \text{C0696-93E01_4} \quad (4)$$

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

f = total grams of all impurity element oxides per gram of ignited U_3O_8 (Note 5).

Note 4—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 5—See Table 1 to obtain conversion factors for many common impurity elements encountered.

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

$$O/U = [(100 - Uwt\% - Z - n)(A)] / [15.999(U)wt\%] \quad \text{C0696-93E01_5} \quad (5)$$

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, %.

22. Precision and Accuracy

22.1 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.

CARBON (TOTAL) BY DIRECT COMBUSTION-THERMAL CONDUCTIVITY METHOD

23. Scope

23.1 This test method covers the determination of 10 to 200 μg of residual carbon in nuclear-grade uranium dioxide.

24. Summary of Test Method

24.1 Powdered test specimens of uranium dioxide are mixed with an appropriate accelerator in a crucible, placed within an induction-heated furnace and burned in a stream of oxygen. The products of combustion, scavenged free of sulfur compounds, halogens, and water vapor, are swept through a heated copper oxide bed and the purified carbon dioxide trapped on a molecular sieve. Carbon dioxide is eluted from the molecular sieve by heat into a stream of helium and passed through a thermal conductivity cell. The amount of carbon is read directly from a digital voltmeter or a strip-chart recorder as a function of the integrated change in the detector cell current.

25. Interferences

25.1 The purification system, associated with the recommended combustion and detection equipment, eliminates all known interferences.

26. Apparatus

26.1 *Low-Carbon Analyzer*, consisting of an induction-heated furnace suitable for operation at 1600°C, a carbon dioxide collection trap, a thermal conductivity cell for measuring carbon dioxide, and auxiliary purification systems.

26.1.1 *Carbon Dioxide Purifier*—Finely divided metal oxides are removed from the combustion gases during passage through quartz wool. Sulfur dioxide is removed by manganese dioxide (MnO_2), water vapor by magnesium perchlorate ($Mg(ClO_4)_2$), and halogens trapped on silver, if needed. A copper oxide catalyst, heated to 300°C, ensures conversion of carbon monoxide (CO) to carbon dioxide (CO_2). The materials used in the purification train must be checked frequently to ensure that their absorbing capacity has not been exhausted.

26.1.2 *Oxygen Purifier*—The system includes a H_2SO_4 bubbler, a carbon dioxide absorbent (NaOH on asbestos), a moisture absorbent, $Mg(ClO_4)_2$, and a flowmeter.

26.2 *Combustion Tube, Quartz*, made with an integral baffle shall be used.

26.3 *Crucibles*—Expendable alumina or similar refractory crucibles. Both the crucible and cover, if used, must be ignited at a temperature of 1000°C or higher for a time sufficient to produce constant blank values.

26.4 *Sample Disintegrator, Vibratory*—The pulverizer must be capable of reducing pellets of UO_2 to 100-mesh powder. A stainless-steel capsule and mixing ball must be used to reduce contamination of the sample with carbon.

27. Reagents and Materials

27.1 *Accelerators*—Granular tin, iron chip, copper oxide, or copper ring accelerators shall be used as required to obtain satisfactory results. The criterion for satisfactory results is the absence of significant additional carbon release upon recombustion of the specimen.

27.2 *Carbon Dioxide and Moisture Absorbents*—Sodium hydroxide (NaOH) on asbestos,⁸ and Mg(ClO₄)₂

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.

27.3 *Carbon Standard Materials*—National Bureau of Standards SRM 131b Low-Carbon Steel (0.0018% carbon) and SRM 336 Steel (0.567% carbon) or their replacements.

27.4 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfuric acid (H₂SO₄) used in the oxygen purification train.

28. Preparation of Apparatus

28.1 Follow the operating instructions for the specific equipment used. After having properly set the operating controls of the instrument system, condition the apparatus by combustion of several blanks prepared with sample crucible and accelerator in the amount to be used with the test specimen analyses. Successive blanks should approach a constant value, allowing for normal statistical fluctuations. Adjust the instrument for a 2-min combustion period.

29. Calibration

29.1 *Preparation of Standards for Combustion*—Mix a weighed portion of accelerator such as 0.5 g of tin and 1 g of CuO and a weighed portion of approximately 1 g of NBS 131b or similar low-carbon steel in each of three sample crucibles. Weigh 30 to 40 mg of a standard steel, such as NBS 336 (0.567% C), and add to each crucible.

29.2 *Combustion of Standards*—Load and combust the standards and record the results. Adjust the calibration controls in such a way as to produce the correct readout value on the direct readout meter. Combust additional standards as required to produce the correct direct readout. As an alternative, consider the readout digits as arbitrary numbers and plot a calibration curve of known micrograms carbon versus the readout value.

30. Procedure

30.1 Disintegrate the pellet samples for 15 s in the stainless steel capsule of the sample pulverizer.

30.2 Weigh a sample crucible containing the required amount of accelerator. Reweigh the crucible.

30.3 Transfer the sample powder, not to exceed 1 g or of such size as to contain less than 200 μg of carbon, to the crucible with the aid of a stainless steel spatula. Weigh the crucible and its contents to the nearest 0.01 g and get the specimen weight by difference.

30.4 Mix the specimen powder and accelerator with the stainless steel spatula.

30.5 Load the crucible into the furnace and combust the specimen for 2 min. Afterwards record the carbon found.

30.6 Remove the sample crucible and examine it for evidence of incomplete combustion. The crucible contents shall be a uniformly fused mass.

31. Calculation

31.1 Calculate the carbon content as follows:

$$C, \mu\text{g/g} = (C_s - C_b) / W \quad \text{C0696-93E01_6} \quad (6)$$

where:

C_s = micrograms of carbon in test specimen;

C_b = micrograms of carbon in a blank run, and

W = grams of UO₂ test specimen.

32. Precision and Accuracy

32.1 *Precision*—The standard deviation for a single measurement is on the order of 10 μg/g carbon.

32.2 *Accuracy*—Results obtained by experienced operators indicated recoveries of carbon in the range from 95 to 100% of the amount present.

TOTAL CHLORINE AND FLUORINE BY PYROHYDROLYSIS ION-SELECTIVE ELECTRODE METHOD

33. Scope

33.1 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 μg/g of chlorine and 1 to 200 μg/g of fluorine are determined without interference.

34. Summary of Test Method

34.1 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).

35. Apparatus

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

35.1.1 *Gas Flow Regulator and Flowmeter*.

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

35.1.3 *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.

35.1.4 *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.

35.1.5 *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).

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

35.2 *Ion-Specific Electrodes*—A fluoride-specific activity electrode; chloride-specific electrode.

35.3 *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.

35.4 *Magnetic Stirrer*.

35.5 *Beakers*, 50-mL polyethylene.

36. Reagents

36.1 *Accelerator*, U_3O_8 halogen-free, can be used but a flux of sodium tungstate (Na_2WO_4) with tungsten trioxide (WO_3) may be used to advantage (10, 11). Special preparation of the mixture is necessary.

NOTE 6—Dehydrate 165 g of Na_2WO_4 in a large platinum dish. Transfer the dried material to a mortar, add 116 g of WO_3 , and grind the mixture to ensure good mixing. Transfer the mixture into a platinum dish and heat with a burner for 2 h. Cool the melt, transfer the flux to a mortar and grind to a coarse powder. Store the flux in an airtight bottle. Mix about 8 g of flux with each portion of sample to be pyrohydrolyzed.

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

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

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

36.5 *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.

36.6 *Compressed Oxygen or Air*.

37. Procedure

37.1 Adjust the pyrohydrolysis system to operating condition as follows:

37.1.1 Heat the furnace to $950 \pm 50^\circ C$.

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

37.1.3 Adjust the gas flow to about 1.5 to 2 litres/min.

37.2 Flush the reaction tube and boat with moist oxygen or according to the pyrohydrolysis procedure in 37.4.

37.3 Run a pyrohydrolysis blank using a halide-free uranium oxide according to the procedure in 37.4. A blank run should be made each day.

37.4 *Sample Pyrohydrolysis*:

37.4.1 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.

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

37.4.3 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.

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

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

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

37.4.7 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.

37.5 Chloride and Fluoride Measurement:

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

37.5.2 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 µg/25 mL to 100 µg/25 mL and the fluoride from 5 µg/25 mL to 100 µg/25 mL.

38. Calculation

38.1 Chlorine—Calculate as follows:

$$Cl, \mu\text{g/g} = (C - B) / WC0696-93E01_7 \tag{7}$$

where:

- C = micrograms of total chlorine in absorber solution;
- B = micrograms of total chlorine in the pyrohydrolysis blank, and
- W = grams of UO₂ specimen pyrohydrolyzed

38.2 Fluorine—Calculate as follows:

$$F, \mu\text{g/g} = (F - B) / WC0696-93E01_8 \tag{8}$$

where:

- F = micrograms of total fluorine in absorber solution;
- B = micrograms of total fluorine in the pyrohydrolysis blank, and
- W = grams of UO₂ specimen pyrohydrolyzed.

39. Precision

39.1 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

40.

7. Scope

40.1 This 7.1 This test method covers the determination of moisture in uranium dioxide samples. Detection limits are as low as 10 µg.

41.8. Summary of Test Method

41.1 The 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 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.

41.2 Precautions 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.

42.9. Apparatus

42.1

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.

42.2

²The boldface numbers in parentheses refer to the list of references at the end of these methods.
⁷A 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, which you may attend.

9.2 *Balance*,⁸ for weighing samples in the range from 1 to 100 mg.

42.3

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

43.

10. Reagents

43.1

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

44.

11. Operation

44.1 ~~Turn~~ 11.1 Turn the main power switch ON.

44.2 ~~Adjust~~ 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.

44.3 ~~11.3~~ Weigh the sample into a small, dry, aluminum boat (~~Note 7~~ Note 1) and insert it into the instrument oven as follows:

~~Note 7~~ 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.

44.3.1 ~~Open~~ 11.3.1 Open the top of the analyzer and remove the TFE-fluorocarbon plug. Do not touch with gloves.

44.3.2 ~~With~~ 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.

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

44.4 ~~Reset~~ 11.4 Reset the counter to 0 μg .

44.5 ~~Set~~ 11.5 Set the timer at 1 h.

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

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

45.

12. Standardization

45.1 ~~Determine~~ 12.1 Determine the blank by processing dry, empty, aluminum boats according to steps 44.3-44.7 11.3-11.7 until constant values are obtained.

45.2 ~~Weigh~~ 12.2 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.

46.

13. Calculation

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

$$Z = (A - B) / 147.2 Y \quad (1)$$

C0696-11_1

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.

46.2 ~~Calculate~~ 13.2 Calculate the percent moisture in the sample as follows:

C0696-11_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

⁸ Ascarite has been found satisfactory for this purpose.

⁸ 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, which you may attend.