



Designation: **C809—13 C809 – 19**

# Standard Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Aluminum Oxide and Aluminum Oxide-Boron Carbide Composite Pellets<sup>1</sup>

This standard is issued under the fixed designation C809; 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 ( $\epsilon$ ) 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 aluminum oxide and aluminum oxide-boron carbide composite pellets to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

|   | Sections |
|---|----------|
| Boron by Titrimetry and ICP OES                               | 7 to 16  |
| Boron by Titrimetry and ICP OES                               | 8 to 17  |
| Separation of Boron for Mass Spectrometry                     | 17 to 22 |
| Separation of Boron for Mass Spectrometry                     | 18 to 23 |
| Isotopic Composition by Mass Spectrometry                     | 23 to 26 |
| Isotopic Composition by Mass Spectrometry                     | 24 to 27 |
| Separation of Halides by Pyrohydrolysis                       | 27 to 30 |
| Separation of Halides by Pyrohydrolysis                       | 28 to 31 |
| Chloride and Fluoride by Ion-Selective Electrode              | 31 to 33 |
| Chloride and Fluoride by Ion-Selective Electrode              | 32 to 34 |
| Chloride, Bromide, and Iodide by Amperometric Microtitrimetry | 34 to 36 |
| Chloride, Bromide, and Iodide by Amperometric Microtitrimetry | 35 to 37 |
| Trace Elements by Emission Spectroscopy                       | 37 to 49 |
| Trace Elements by Emission Spectroscopy                       | 38 to 50 |
| Keywords  | 50       |
| Keywords  | 51       |

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

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use. (For specific precautionary statements, see Section 56.)*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

[C784 Specification for Nuclear-Grade Aluminum Oxide-Boron Carbide Composite Pellets](#)

[C785 Specification for Nuclear-Grade Aluminum Oxide Pellets](#)

[C791 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Boron Carbide](#)

[C799 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Uranyl Nitrate Solutions](#)

[C859 Terminology Relating to Nuclear Materials](#)

[C1128 Guide for Preparation of Working Reference Materials for Use in Analysis of Nuclear Fuel Cycle Materials](#)

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and are the direct responsibility of Subcommittee C26.03 on Neutron Absorber Materials Specifications.

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<sup>2</sup> 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.

**D1193** Specification for Reagent Water

**E115** Practice for Photographic Processing in Optical Emission Spectrographic Analysis (Withdrawn 2002)<sup>3</sup>

**E116** Practice for Photographic Photometry in Spectrochemical Analysis (Withdrawn 2002)<sup>3</sup>

### 3. Terminology

3.1 *Definitions*—For definitions of terms relating to nuclear materials, see Terminology **C859**.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *analytical or emission line*—the particular wavelength of electromagnetic radiation used in determining the presence or concentration of an element.

3.2.2 *calibration*—the act, process, or result of establishing the relationship between the response of an instrument and the amount of analyte present.

3.2.3 *calibration samples or solutions (standards)*—samples or solutions with known analyte contents or analyte concentrations, respectively, to establish the relationship between the response of an instrument and the amount of analyte.

3.2.4 *certified reference material (CRM)*—a reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence.

3.2.5 *DCArc OES*—optical emission spectrometry (OES) with direct current arc (DCArc) as excitation source.

3.2.6 *ICP MS*—mass spectrometry (MS) with inductively coupled plasma (ICP) as ionization source.

3.2.7 *ICP OES*—optical emission spectrometry (OES) with inductively coupled plasma (ICP) as excitation source.

3.2.8 *matrix*—all components of a material except the analyte.

3.2.9 *method*—instructions used to produce a numerical result, which are detailed in a document referred to as “the method.”

3.2.10 *optical emission spectrometry (OES)*—pertaining to emission spectrometry in the ultraviolet, visible, or infrared wavelength regions of the electromagnetic spectrum.

3.2.11 *sample*—a portion of a material selected and processed to render its composition representative of the composition of the whole.

3.2.12 *standardization*—the experimental establishment of the concentration of a reagent solution.

3.2.13 *TIMS*—thermal ionization mass spectrometry.

3.2.14 *titrimetry*—a method of quantitative chemical analysis that is used to determine the concentration of an identified analyte.

### 4. Significance and Use

4.1 Aluminum oxide pellets are used in a reactor core as filler or spacers within fuel, burnable poison, or control rods. In order to be suitable for this purpose, the material must meet certain criteria for impurity content. These test methods are designed to show whether or not a given material meets the specifications for these items as described in Specification **C785**.

4.1.1 Impurity content is determined to ensure that the maximum concentration limit of certain impurity elements is not exceeded.

4.2 Aluminum oxide-boron carbide composite pellets are used in a reactor core as a component in neutron absorber rods. In order to be suitable for this purpose, the material must meet certain criteria for boron content, isotopic composition, and impurity content as described in Specification **C784**.

4.2.1 The material is assayed for boron to determine whether the boron content is as specified by the purchaser.

4.2.2 Determination of the isotopic content of the boron is made to establish whether the <sup>10</sup>B concentration is in compliance with the purchaser’s specifications.

4.2.3 Impurity content is determined to ensure that the maximum concentration limit of certain impurity elements is not exceeded.

### 5. Reagents

5.1 *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.<sup>4</sup> 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.

<sup>3</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

<sup>4</sup> *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.

5.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification **D1193**, Type III.

## 6. Safety Precautions

6.1 Many laboratories have established safety regulations governing the use of hazardous chemicals and equipment. The users of these test methods should be familiar with such safety practices.

## 7. Sampling

7.1 Criteria for sampling aluminum oxide pellets are given in Specification **C785**.

7.2 Criteria for sampling aluminum oxide-boron carbide composite pellets are given in Specification **C784**.

## BORON BY TITRIMETRY AND ICP OES

### 7. Scope

~~7.1 For the determination of boron in aluminum oxide-boron carbide composites by titrimetry and ICP OES the procedures detailed in Test Method **C791**, Sections 17–26 shall be used.~~

### 8. Scope

8.1 For the determination of boron in aluminum oxide-boron carbide composites by titrimetry and ICP OES the procedures detailed in Test Method **C791**, Sections 18 – 27 shall be used.

## 9. Summary of Test Method

9.1 Powdered aluminum oxide-boron carbide composite is mixed with alkaline reagents and this mixture is fused to decompose the aluminum oxide-boron carbide. The melt is dissolved in diluted hydrochloric acid and heated or purged with nitrogen to remove carbon dioxide. The boron as boric acid is titrated with standardized sodium hydroxide solution, using the mannitoboric acid procedure. Alternatively, the boron in the samples solution is measured using ICP OES.

NOTE 1—Sodium carbonate or a mixture of sodium carbonate and potassium carbonate (1:1) is normally used as alkaline reagent to decompose the aluminum oxide-boron carbide composite.

## 10. Interferences

10.1 *Titrimetry*—Because metallic impurities in high concentrations may distort the inflection points of the titration aluminum should be precipitated from the sample solution using barium carbonate. No distortion was found for concentrations of Fe < 2 %, Ti < 1 %. Interferences by dissolved CO<sub>2</sub> shall be removed by heating the sample solution or by purging the sample solution with nitrogen.

10.2 *ICP OES*—Interference effects depend primarily upon the resolving power of the spectrometer and the selection of the analytical lines. In practice, line interferences (spectral interferences) and non spectral interferences are critical. Non spectral interferences are caused primarily by different chemical composition of calibration solution and sample solution, resulting in an alteration of nebulization and excitation properties. Also memory-effects can play a role. The best way to minimize non spectral interferences is the use of calibration samples with the same composition of matrix, ideally certified reference materials. When certified reference materials are not available, consider Guide **C1128** for preparation of working reference materials.

## 11. Apparatus

11.1 See Test Methods **C791**, Section ~~20~~21.

## 12. Reagents

12.1 See Test Methods **C791**, Section ~~21~~22.

## 13. Precautions

13.1 See Test Methods **C791**, Section ~~22~~23.

## 14. Sampling and Sample Preparation

14.1 See Test Methods **C791**, Section ~~23~~24.

## 15. Procedure

15.1 See Test Methods **C791**, Section ~~24~~25.

## 16. Titrimetric Determination of Boron

16.1 See Test Methods [C791](#), Section [25-26](#).

## 17. ICP OES

17.1 See Test Methods [C791](#), Section [26-27](#).

## SEPARATION OF BORON FOR MASS SPECTROMETRY

### 17. Scope

~~17.1 This test method covers the separation of boron from aluminum and other impurities. The isotopic composition of the separated boron is measured using mass spectrometry. The test method for isotopic composition is found in this standard.~~

~~NOTE 2—Alternatively, the separation of boron can be performed by pyrohydrolysis. A stream of moist oxygen is passed over the powdered sample at 1100 °C. The pyrohydrolytic reaction releases boric acid and boron oxide from the sample, which volatilize and collect in the condensate (see Test Methods [C791](#), Section 40). The condensate is used for measurement of isotopic composition by ICP-MS (see Test Methods [C791](#), Section 32).~~

### 18. Scope

18.1 This test method covers the separation of boron from aluminum and other impurities. The isotopic composition of the separated boron is measured using mass spectrometry. The test method for isotopic composition is found in this standard.

18.2 Alternatively, the separation of boron can be performed by pyrohydrolysis. A stream of moist oxygen is passed over the powdered sample at 1100°C. The pyrohydrolytic reaction releases boric acid and boron oxide from the sample, which volatilize and collect in the condensate (see Test Methods [C791](#), Section 41). The condensate is used for measurement of isotopic composition by ICP-MS (see Test Methods [C791](#), Section 33).

### 19. Summary of Test Method

19.1 Boron is put into solution using a sealed-tube dissolution method. It is separated from aluminum and other impurities by solvent extraction and ion exchange.

### 20. Interferences

20.1 There are no known interferences not eliminated by this separation test method.

### 21. Apparatus

21.1 *Analytical Balance*, capable of weighing to  $\pm 0.1 \pm 0.1$  mg.

21.2 *Mortar*, diamond (Plattner) (or equivalent).

21.3 *Sieve*, No. 100 (150- $\mu$ m) U.S. Standard Sieve Series, 76-mm diameter, brass or stainless steel.

21.4 *Glass Boats*, borosilicate, 4-mm wide, 3-mm deep, 40-mm long.

21.5 *Glass Tubing*, heavy-wall borosilicate, 5-mm inside diameter by 250-mm long, sealed at one end.

21.6 *Glass Blower's Torch*.

21.7 *Iron Pipe*, 12.7 by 254-mm long with threaded end caps.

21.8 *Muffle Furnace*, capable of operation at 300°C. The heated area must be of sufficient size to hold the capped iron pipe.

21.9 *Separatory Funnel*, 60-mL with TFE-fluorocarbon stopcock.

21.10 *Mixer*, vortex type.

21.11 *Filter Paper*, ashless, slow filtering for fine precipitates.

21.12 *Ion Exchange Column*, borosilicate glass, 5-mm inside diameter, 100-mm long with a TFE-fluorocarbon stopcock.

21.13 *Beaker*, 50-mL, quartz or TFE-fluorocarbon.

### 22. Reagents

22.1 *Nitric Acid* (sp gr 1.42)—Concentrated Nitric Acid (HNO<sub>3</sub>).

22.2 *Cation Exchange Resin*,<sup>5</sup>80 to 100 mesh. Prepare the resin by treatment with 3 N HCl followed by water wash until the effluent is neutral to pH paper.

22.3 *Chloroform* (CHCl<sub>3</sub>).

<sup>5</sup> Dowex 50 × 8 (or equivalent).

22.4 2-Ethyl-1,3Hexanediol Solution, 5 volume % in chloroform.

22.5 Nitric Acid (HNO<sub>3</sub>), 2 M.

22.6 Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), powder.

22.7 Sodium Hydroxide (NaOH) Solution, 0.1 N, carbonate-free. Store in a plastic bottle.

### 23. Procedure

23.1 Crush the aluminum oxide/boron carbide composite pellet using a diamond mortar until all the sample is passed through a No. 100 (150- $\mu$ m) screen.

23.2 Weigh a 250-mg sample into a glass boat.

23.3 Introduce the boat and sample into a heavy-wall glass tube, being very careful to prevent any of the sample from adhering to the wall of the tube near the open end.

23.4 Introduce 0.5 mL of concentrated HNO<sub>3</sub> into the glass tube.

23.5 Mix the sample and acid using the vortex mixer.

23.6 Flame the glass tube to remove the moisture from the walls.

23.7 Seal the glass tube. There are two methods available:

23.7.1 Sealing the glass tube may be accomplished by constriction, then drawing off a short piece of the tube, then working down the sealed end.

23.7.2 A seal can be made by allowing the open end of the tube to flow together by heating and revolving the tube slowly. While the tube is red with heat, the tube is warmed enough to blow out the seal to a rounded ~~shape~~ shape.

23.8 Place the glass tube into a safety container which consists of a 12.7-mm inside diameter black iron pipe with screw caps on each end. The caps can be tightened with finger tip control.

23.9 Insert the assembly into a 300°C muffle furnace with the top end of the assembly elevated and heat for 6 h.

23.10 Remove the assembly from the muffle furnace and place into a tray, keeping the same end of the assembly elevated.

23.11 Allow the assembly to cool to room temperature.

23.12 Withdraw the glass tube from the safety container and file a notch about 13 mm from one end of the tube.

NOTE 2—Contents of the tube may be under pressure.

23.13 Heat a glass rod to red heat, then place the rod on the notch. This action should crack the glass tube; however, a light tap may be needed to complete the break.

23.14 Pipet 4 mL of water into the glass tube and mix using a vortex mixer.

23.15 Filter the solution through filter paper (15.3). Catch the filtrate in a 60-mL separatory funnel.

23.16 Wash the paper with 15-mL of 2 M HNO<sub>3</sub>. Catch the wash in the separatory funnel.

23.17 Add 10 mL of 5 % 2-ethyl-1,3 hexanediol solution to the separatory funnel and shake for 2 min.

23.18 Drain the organic (lower) layer into a clean 100-mL beaker.

23.19 Repeat ~~22-17~~ 23.17 and ~~22-18~~ 23.18.

23.20 Transfer the 2-ethyl-1,3 hexanediol solution to a clean 60-mL separatory funnel.

23.21 Extract the boron by shaking for 2-min with a NaOH solution containing the amount of sodium calculated to give a B/Na ratio of two and a volume sufficient to give 1 mg B/mL.

23.22 Discard the organic phase.

23.23 Wash the aqueous phase with two 5-mL portions of CHCl<sub>3</sub>. Discard the organic wash.

23.24 Transfer the aqueous phase containing the boron to a 50-mL quartz or TFE-fluorocarbon beaker.

23.25 Evaporate the solution to a volume of about 1 mL.

23.26 Add 0.5 mL of ion exchange resin to the beaker and swirl.

NOTE 3—Addition of the resin to the beaker prevents formation of CO<sub>2</sub> bubbles on the resin column in the subsequent step.

23.27 Transfer the slurry to a prepared resin column containing a 10-mm depth of resin.

23.28 Elute the boron with an amount of water calculated to yield a solution containing 1 mg B/mL.

23.29 Add solid Na<sub>2</sub>CO<sub>3</sub> to give a Na/B ratio of 0.9 to 1.0. Transfer the solution to a plastic bottle. The solution is used for measurement of isotopic composition by mass spectrometry (see ~~2324~~ 2624 – ~~2627~~).

## ISOTOPIC COMPOSITION BY MASS SPECTROMETRY

### **23. Scope**

~~23.1 This test method covers the determination of the isotopic composition of boron in nuclear-grade aluminum oxide/boron carbide composite pellets containing natural to highly enriched boron.~~

### **24. Scope**

24.1 This test method covers the determination of the isotopic composition of boron in nuclear-grade aluminum oxide/boron carbide composite pellets containing natural to highly enriched boron.

### **25. Summary of Test Method**

25.1 Boron isotopic ratios are measured in aluminum oxide/boron carbide composites by thermal ionization mass spectrometry (TIMS) following chemical separation of boron (see [1718 – 2223](#)). The loaded filament is transferred to the mass spectrometer where boron isotopic ratios are measured using the  $\text{Na}_2\text{BO}_2^+$  ion. When mixing the boron containing sample solution (see [23.29](#)) and sodium hydroxide or sodium carbonate, a Na to B ratio of 1:1 is maintained, which gives a stable ion emission within a few minutes after operational vacuum is attained. There is no apparent bias caused by selective volatilization of  $^{10}\text{B}$ .

25.2 As an alternative method, the boron isotopic ratios are measured in boron carbide by ICP-MS in accordance with Section 33 of Test Methods [C791](#).

### **26. Interferences**

26.1 Impurity elements, at the specification limits usually established for nuclear-grade composites, do not interfere. Strontium is a potential interference and it is an impurity element in the tantalum filament material. At the temperature used to ionize sodium borate, however, the strontium impurity in the filament does not volatilize to cause a high bias at mass 88. This potential interference does not occur in ICP-MS.

NOTE 5—This potential interference does not occur in ICP-MS.

### **27. Procedure**

27.1 Continue with the determination of the isotopic composition by TIMS in accordance with Section 32 of Test Methods [C791](#). If sodium carbonate is used for fusion, pulverized sodium carbonate shall be used instead of sodium carbonate solution.

27.2 Continue with the determination of the isotopic composition by TIMS. Alternatively, the isotopic composition of boron in aluminum oxide-boron carbide composites can be measured by ICP-MS following chemical separation of boron by pyrohydrolysis in accordance with Section 34 Sections 33 and 41 of Test Methods Method [C791](#).

NOTE 6—Alternatively, the isotopic composition of boron in aluminum oxide-boron carbide composites can be measured by ICP-MS following chemical separation of boron by pyrohydrolysis in accordance with Sections 32 and 40 of Test Method [C791](#).

## SEPARATION OF HALIDES BY PYROHYDROLYSIS

### **27. Scope**

~~27.1 This method covers the separation of up to 100  $\mu\text{g}$  of chloride and fluoride per gram of sample. The separated halides are measured using other methods found in this standard.~~

### **28. Scope**

28.1 This method covers the separation of up to 100  $\mu\text{g}$  of chloride and fluoride per gram of sample. The separated halides are measured using other methods found in this standard.

### **29. Summary of Test Method**

29.1 A stream of moist argon is passed over a mixture of powdered sample and  $\text{U}_3\text{O}_8$  or sodium tungstate with tungsten trioxide accelerator heated at 1000 to 1100°C. Alternatively, a stream of moist oxygen is passed over the powdered sample at 1100°C, which requires no accelerators. The pyrohydrolytic reaction releases chloride and fluoride as hydrochloric and hydrofluoric acids as well as boric acid and boron oxide, which volatilize and collect in the condensate.

### **30. Interferences**

30.1 Interferences are not expected. The conditions given in this test method for pyrohydrolysis must be controlled to ensure complete recovery of the halides.

### **31. Procedure**

31.1 Continue with pyrohydrolysis in accordance with Sections ~~33~~34 to ~~39~~40 of Test Methods [C791](#).