



Designation: **C809 – 94 (Reapproved 2007) C809 – 13**

Standard Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Aluminum Oxide and Aluminum Oxide-Boron Carbide Composite Pellets¹

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 (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover procedures for the chemical, mass spectrometric, and spectrochemical analysis of nuclear-grade 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	7 to 13
Boron by Titrimetry and ICP OES	7 to 16
Separation of Boron for Mass Spectrometry	14 to 19
Separation of Boron for Mass Spectrometry	17 to 22
Isotopic Composition by Mass Spectrometry	20 to 23
Isotopic Composition by Mass Spectrometry	23 to 26
Separation of Halides by Pyrohydrolysis	24 to 27
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Fluoride by Ion-Selective Electrode	28 to 30
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Chloride, Bromide, and Iodide by Amperometric Microtitrimetry	31 to 33
Chloride, Bromide, and Iodide by Amperometric Microtitrimetry	34 to 36
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Trace Elements by Emission Spectroscopy	37 to 49
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1.3 The values stated in SI units are to be regarded as the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* (For specific precautionary statements, see Section 5.)

2. Referenced Documents

2.1 *ASTM Standards:*²

[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](#)

[D1193 Specification for Reagent Water](#)

[E115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis \(Withdrawn 2002\)](#)³

[E116 Practice for Photographic Photometry in Spectrochemical Analysis \(Withdrawn 2002\)](#)³

¹ 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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² 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.

³ The last approved version of this historical standard is referenced on www.astm.org.

3. Significance and Use

3.1 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**.

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

3.2 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**.

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

3.2.2 Determination of the isotopic content of the boron is made to establish whether the ^{10}B concentration is in compliance with the purchaser's specifications.

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

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.⁴ 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, reference to water shall be understood to mean reagent water conforming to Specification **D1193**, Type III.

5. Safety Precautions

5.1 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.

6. Sampling

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

6.2 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. Summary of Test Method

8.1 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 manniboric 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.

9. Interferences

9.1 *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 CO₂ shall be removed by heating the sample solution or by purging the sample solution with nitrogen.

9.2 *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

⁴ *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.

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.

10. Apparatus

10.1 See Test Methods [C791](#), Section 20.

11. Reagents

11.1 See Test Methods [C791](#), Section 21.

12. Precautions

12.1 See Test Methods [C791](#), Section 22.

13. Sampling and Sample Preparation

13.1 See Test Methods [C791](#), Section 23.

14. Procedure

14.1 See Test Methods [C791](#), Section 24.

15. Titrimetric Determination of Boron

15.1 See Test Methods [C791](#), Section 25.

16. ICP OES

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

SEPARATION OF BORON FOR MASS SPECTROMETRY

17. Scope

17.1 This test method covers the ~~determination~~separation of boron in ~~aluminum oxide-boron carbide composites~~. As an alternative, the procedure for total boron by titrimetry detailed in Test Methods ~~from aluminum and other impurities~~. The isotopic composition of the separated boron is measured using mass spectrometry. The ~~C791 may be used~~ 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. Summary of Test Method

18.1 The sample is crushed, passed through a 100-mesh screen, weighed in a glass boat, and introduced into a heavy-wall glass tube. Nitric acid is added to the tube and the contents mixed using a vortex mixer. The tube is sealed, placed into a safety container, heated for 6 h, cooled to room temperature, opened, and the contents washed into a beaker. Boron is put into solution using a sealed-tube dissolution method. It is separated from aluminum and other impurities by solvent extraction. The solution is adjusted to pH 9.0 and filtered, then adjusted to pH 3.5 and boiled to remove CO₂ and ion exchange. Substantially, a pure boric acid is obtained which can be titrated in the presence of mannitol with a standard solution of sodium hydroxide.

19. Interferences

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

20. Apparatus

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

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

20.3 *Sieve*, No. 100 (150- μ m) U.S. Standard Sieve Series, 76-mm diameter, brass or stainless steel.

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

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

20.6 *Mixer*, vortex type.

20.6 *Glass Blower's Torch*.

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

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

20.9 *pH Meter, Separatory Funnel*, with pH electrodes and magnetic stirrer, 60-mL with TFE-fluorocarbon stopcock.

20.10 *Steam Bath, Mixer*, vortex type.

~~9.12 Hot Plate.~~

20.11 *Filter Paper*, 41 cm, ashless-ashless, slow filtering for fine precipitates.

20.12 *Buret, Ion Exchange Column, Class A*, 25-mL, borosilicate glass, 5-mm inside diameter, 100-mm long with a TFE-fluorocarbon stopcock.

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

21. Reagents

~~10.1 Boric Acid~~, NIST SRM 951 or its replacement.

~~10.2 Hydrochloric Acid (HCl)~~, 1 N.

~~10.3 Hydrochloric Acid (HCl)~~, 0.1 N.

~~10.4 Mannitol.~~

21.1 *Nitric Acid* (sp gr 1.42) ~~—1.42~~—Concentrated Concentrated Nitric Acid (HNO₃).

21.2 *Cation Exchange Resin*,⁵80 to 100 mesh. Prepare the resin by treatment with 3 N HCl followed by water wash until the effluent is neutral to pH paper.

21.3 *Chloroform (CHCl₃)*.

21.4 *2-Ethyl-1,3Hexanediol Solution*, 5 volume % in chloroform.

21.5 *Sodium Hydroxide (NaOH) Solution, Nitric Acid* ~~1~~ (HNO₃), 2 N, *M.* carbonate-free.

21.6 *Sodium Hydroxide (NaOH) Solution, carbonate* 0.1 N, (Na₂CO₃ carbonate-free.), powder.

21.7 *Sodium Hydroxide (NaOH) Solution, 0.025* (NaOH) *Solution*, 0.1 N, carbonate-free, standardized against NIST SRM 951 ~~carbonate-free~~. Store in a plastic bottle.

22. Procedure

22.1 Crush the aluminum oxide/boron carbide composite pellet using a diamond mortar until all the sample is passed through a No. 100 (150-µm) screen.

22.2 Weigh a 250-mg sample into a glass boat. [ASTM C809-13](#)

22.3 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.

22.4 Introduce 0.5 mL of concentrated HNO₃ into the glass tube.

22.5 Mix the sample and acid using the vortex mixer.

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

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

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

22.7.2 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.

22.8 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.

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

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

22.11 Allow the assembly to cool to room temperature.

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

NOTE 3—~~Contents~~ Contents of the tube may be under pressure.

⁵ Dowex 50 × 8 (or equivalent).

22.13 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.

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

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

22.16 Wash the contents from the glass tube into paper with 15-mL of 2 *M* 250-mL HNO₃ beaker; however, if the aluminum oxide is stuck to the walls of the tube, shake on a vortex mixer. Catch the wash in the separatory funnel.

NOTE 2—The matrix Al₂O₃ does not completely dissolve, but all of the boron is in solution.

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

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

22.19 Repeat 22.17 and 22.18.

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

22.21 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.

22.22 Precipitate the iron and the aluminum by using 1 *N* sodium hydroxide solution to adjust the pH to 9.0.

22.23 Place the beaker on a steam bath and digest for Wash the aqueous phase with two 5-mL portions of CHCl₃ 1 hr. Discard the organic wash.

22.24 Filter the sample through the filter paper (9.13) and wash the precipitate with several portions of hot deionized water. Transfer the aqueous phase containing the boron to a 50-mL quartz or TFE-fluorocarbon beaker.

22.25 Adjust the pH between 3.5 and 4.0 using Evaporate the solution to a volume of about 1 NmL. HCl.

22.26 Cover the solution with a flat watch glass, then place the beaker on a hot plate and boil for about 5 min to remove carbon dioxide. Add 0.5 mL of ion exchange resin to the beaker and swirl.

NOTE 4—Addition of the resin to the beaker prevents formation of CO₂ bubbles on the resin column in the subsequent step.

22.27 Remove the sample from the hot plate and cool to room temperature in a water bath. Transfer the slurry to a prepared resin column containing a 10-mm depth of resin.

22.28 Adjust the pH of the sample to 5.6 to 5.7 using 0.1 *N* HCl. Elute the boron with an amount of water calculated to yield a *N*-NaOH solution and 0.1 containing *N* HCl. Add 1 to 3 g of mannitol. 1 mg B/mL.

11.22 Titrate the sample to pH 8.0 using a 0.025 *N* NaOH solution.

22.29 Determine Add solid Na₂CO₃ a blank by performing 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 11.3-11.22 without spectrometry (see 23-26 the sample.).

12. Calculation

12.1 Calculate the percent boron in the sample as follows:

$$B, \% = \frac{(V - B)(N)(A)(100)}{W} \quad (1)$$

where:

V = millilitres of NaOH solution used in titration of the sample;

B = millilitres of NaOH solution used in titration of the blank;

N = normality of the NaOH solution;

A = atomic weight of boron computed for the sample based upon the measured isotopic composition, and

W = milligrams of sample weight.

13. Precision

13.1 The limit of error at the 95 % confidence level for a single determination is ±0.10 % absolute.

SEPARATION OF BORON FOR MASS SPECTROMETRY

14. Scope

14.1 This test method covers the separation of boron from aluminum and other impurities. The isotopic composition of the separated boron is measured using another test method found herein.

15. Summary of Test Method

15.1 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.

16. Interferences

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

17. Apparatus

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

17.2 *Mixer*, vortex type.

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

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

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

18. Reagents

18.1 *Cation Exchange Resin*,⁸80 to 100 mesh. Prepare the resin by treatment with 3 *N* HCl followed by water wash until the effluent is neutral to pH paper.

18.2 *Chloroform* (CHCl₃).

18.3 *2-Ethyl-1,3Hexanediol Solution*, 5 volume % in chloroform.

18.4 *Nitric Acid* (HNO₃), 2 *M*.

18.5 *Sodium carbonate* (Na₂CO₃), powder.

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

19. Procedure

19.1 Prepare an aliquot of sample by following 11.1-11.13.

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

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

19.4 Wash the paper with 15-mL of 2 *M* HNO₃. Catch the wash in the separatory funnel.

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

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

19.7 Repeat 19.5 and 19.6.

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

19.9 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.

19.10 Discard the organic phase.

19.11 Wash the aqueous phase with two 5-mL portions of CHCl₃. Discard the organic wash.

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

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

19.14 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 CO₂ bubbles on the resin column in the subsequent step.

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

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

19.17 Add solid Na₂CO₃ to give a Na/B ratio of 0.9 to 1.0. Transfer the solution to a plastic bottle.

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.