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Chemistry

MASTER

DETERMINATION OF NITROGEN
IN BORON NITRIDE

L. D. Keele

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the **ATOMIC ENERGY COMMISSION** under **U. S. GOVERNMENT** Contract W-7405 eng 26

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Nuclear Division

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ABSTRACT

High-fired boron nitride reacts with six-molar sulfuric acid and potassium perchlorate when the mixture is heated in a sealed glass tube for four hours at 350° C. The resulting ammonium-type nitrogen is contained in a clear solution that is suitable for analysis using a modified Kjeldahl apparatus.

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SUMMARY

Boron nitride can be effectively decomposed to ammonium-type nitrogen by heating the nitride with six-molar sulfuric acid plus an oxidizer (KClO_4)⁽¹⁾ sealed in a glass tube.⁽²⁾ The clear solution can then be transferred from the glass tube to a modified Kjeldahl apparatus. The resulting distillate is trapped in a boric acid solution and titrated with one-tenth normal hydrochloric acid using a mixed indicator. In 11 determinations on a commercial boron nitride, the nitrogen content found by this procedure was 56.1 ± 0.16 percent.

INTRODUCTION

Determination of nitrogen in high-fired boron nitride has always presented difficulties to the analyst. Two methods of decomposing the compound were initially proposed: (1) by boiling the nitride with mixed acids under a reflux condenser, or (2) by a prolonged Kjeldahl digestion with a catalyst. However, with both methods a residue remained that had to be filtered, ignited, and fused in order to complete the decomposition.

Because these procedures were found to be unreliable or inadequate, variations of the sealed-tube method were considered.^(1,2) One variation was effected by placing a quantity of low-fired boron nitride (50 mgs) into a glass tube with some six-molar hydrochloric acid (4 mls), then the glass tube was sealed and placed in an oven for two hours at 190° C. Under these conditions, a clear solution was obtained.

High-fired boron nitride was found to be unreactive with four, six, or even nine-molar hydrochloric acid in the temperature range from 190 to 350° C. But, subsequent investigation revealed that a clear solution could be obtained using six-molar sulfuric acid with an oxidant (KClO_4).

DETERMINING NITROGEN IN BORON NITRIDE

GENERAL PROCEDURE

After the nitride-sulfuric acid-oxidant mixture was heated in a sealed glass tube for four hours at 350° C, the sample was cooled to room temperature, the tube opened, and the sample transferred to a boiling flask. The flask was then connected to a modified Kjeldahl distillation apparatus (Figure 1), the solution was made alkaline with sodium hydroxide, heat was applied to the 500-milliliter round-bottom boiling flask, and the ammonia distillate allowed to react with a boric acid solution containing two indicators. (a) This solution was titrated with a standard hydrochloric acid solution (0.1 N) to a faint pink end point. In 11 determinations on a commercial boron nitride, the nitrogen content found by this procedure was 56.1 ± 0.16 percent.

Figure 1. MODIFIED KJELDAHL APPARATUS.

- (a) The boric acid solution was made by dissolving 40 grams of boric acid in 1,960 milliliters of distilled water, adding two milliliters of a 0.1 percent methyl red solution and 10 milliliters of a 0.1 percent bromcresol green solution. The final volume was then made to two liters. (3)

REAGENTS AND EQUIPMENT

Reagents

Sulfuric Acid - Six-molar solution.

Hydrochloric Acid - One-tenth normal solution.

Methyl Red - One-tenth percent solution.

Bromcresol Green - One-tenth percent solution

Sodium Hydroxide - Fifty-percent solution.

Boric Acid - Two-percent solution. (a)

Helium Gas - Sweep gas.

Equipment

Muffle - Range to 1,200° C.

Iron Pipe - One-half-inch ID; 5/8-inch OD (Figure 2).

Glass Tubing - Heavy-wall Pyrex; 5-millimeter ID and 9-millimeter OD (Figure 3).

Boiling Flask - Five-hundred milliliters with a 24/40 ground glass fitting.

Variac - Control for heating mantle.

Heating Mantle - Five-hundred-milliliter size.

Distillation Apparatus - Modified Kjeldahl design (Figure 1) with condenser.

Burette - Fifty milliliters.

Figure 2. ONE-HALF-INCH IRON PIPE SAFETY CONTAINER.

Torch - Seal glass tips.

Erlenmeyer Flask - Five-hundred milliliters.

Glass Boat - Dimensions: four millimeters wide, three millimeters deep, and 40 millimeters long.

Figure 3. HEAVY-WALL GLASS REACTION TUBE.

PROCEDURAL STEPS

Detailed steps in the analytical procedure are as follows:

1. Weigh a 50-milligram sample of boron nitride into a glass boat.
2. Introduce the glass boat containing the sample into the heavy-wall glass tube. Be very careful to prevent any of the sample from adhering to the wall of the tube within one inch of the open end of the tube. (Particles adhering near the top will be decomposed during sealing of the tube and cause low results.)
3. Add 40 milligrams of potassium perchlorate to the tube.
4. Introduce four milliliters of six-molar sulfuric acid into the glass tube.
5. Seal the glass tube. There are two methods available:
 - a. Sealing may be accomplished by constriction, then drawing off a short piece of tube, then working down the sealed tip with a torch.⁽³⁾
 - b. 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 seal is red with heat, the tube is warmed enough to blow out the seal to a rounded shape.⁽³⁾
6. Place the glass tube into a safety container which is a one-half-inch black iron pipe with screw caps on each end (Figure 2). The caps can be tightened with finger-tip control.
7. Insert the assembly into a 350° C muffle and heat for three to four hours or until the solution is clear.

8. Remove the assembly from the muffle, place it in a tray with one end elevated, and allow the assembly to cool to room temperature.
9. Withdraw the glass tube from the safety container and file a notch about one-half inch from one end of the tube.
10. Heat a glass rod to red heat, then place the rod on the filed notch. This action should crack the glass tube; a light tap may be needed to complete the break.
11. Wash the solution from the glass tube with distilled water into a 500-milliliter boiling flask having a 24/40 ground glass fitting.
12. Dilute the sample to 250 milliliters with distilled water.
13. Connect the flask and condenser to a modified Kjeldahl apparatus (Figure 1).
14. Place the condenser tip about one-fourth inch beneath the surface of the boric acid solution.
15. Add 20 milliliters of the 50 percent sodium hydroxide solution to the boiling flask through a stopcock.
16. Apply heat to the boiling flask with a heating mantle, controlled with a Variac.
17. Introduce a flow of inert gas (helium) at a rate of 60 to 80 bubbles per minute into the system as a sweep gas.
18. Increase the temperature of the solution to the boiling point.
19. Collect about 150 milliliters of condensate in the 40 milliliters of boric acid solution.
20. Titrate the solution to a mixed-indicator⁽⁴⁾ end point with the one-tenth-normal hydrochloric acid.
21. Analyze a blank containing all reagents for percent nitrogen by this procedure and correct the results from the total volume in titrating the sample. Use the equation given in the next step.
22. Calculate the percent nitrogen by the equation:

$$\% \text{ N} = \frac{(\text{milliliters HCl} - \text{blank}) \times \text{normality} \times \text{milliequivalent weight of nitrogen} \times 100}{\text{weight of sample in grams}}$$

RESULTS

In eleven determinations on a commercial high-fired boron nitride having a purity level of 99.5% boron nitride, the nitrogen content of each sample, determined by this method, was:

<u>Sample Number</u>	<u>Percent Nitrogen</u>	<u>Sample Number</u>	<u>Percent Nitrogen</u>
1	56.0	7	56.4
2	56.3	8	56.2
3	55.6	9	56.4
4	56.1	10	56.2
5	56.1	11	56.3
6	55.9		

These accumulated data for the 11 determinations were statistically evaluated and yielded an absolute limit of error of 0.16 percent (0.95), which is equivalent to an absolute limit of error of ± 0.53 percent (0.95) for a single determination.

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