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Determination of Boron in Boron-Pyrolytic Graphite

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Prepared by F.M. WACHI, D.E. GILMARTIN, and K.G. JEFFERSON
Materials Sciences Laboratory

Prepared for BALLISTIC SYSTEMS AND SPACE SYSTEMS DIVISIONS
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LOS ANGELES AIR FORCE STATION
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~~Prepared by~~

(10) F. M. Wachi, D. E. Gilmartin, and K. G. Jefferson,
~~Materials Sciences Laboratory~~

AEROSPACE CORPORATION
El Segundo, California

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DETERMINATION OF BORON IN BORON-PYROLYTIC GRAPHITE

Prepared

F. M. Wachi

D. E. Gilmartin

K. G. Jefferson

Approved

J. I. Slaughter, Head
Re-Entry Effects Department

J. E. Hove, Director
Materials Sciences Laboratory

This technical documentary report has been reviewed and is approved for publication and dissemination. The conclusions and findings contained herein do not necessarily represent an official Air Force position.

For Space Systems Division
Air Force Systems Command

James F. Hoelscher
Captain, USAF

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ABSTRACT

An analytical technique for determining boron in boron-pyrolytic graphite in the concentration range from 0.03 to 3.5 percent by weight is described. Its chief attributes are simplicity of operation, high accuracy, and excellent precision.

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I. INTRODUCTION

Recently, there has been considerable confusion as to the boron content in boron-pyrolytic graphite. Three analytical techniques[1] have been used: spectrographic analysis, measurement of residual ash content, and fast neutron activation analysis. Large discrepancies have been found in the results obtained by these three methods, especially when the boron content is less than 1 percent by weight.

This report demonstrates the applicablility of a fourth analytical method based on the pyrohydrolytic separation of boron and the quantitative determination of the liberated boron by potentiometric titration of the mannitol-boric acid complex with standard sodium hydroxide solution. Although this technique has not been used for the analysis of boron in pyrolytic graphite, it has been successfully used for the quantitative determination of boron in other materials (Refs. 1, 2, 3, 4). This pyrohydrolytic separation technique has also been successfully employed in the determination of other volatile elements. A fairly comprehensive bibliography on this subject may be found in the articles by McKinley and Wendt (Ref. 1), Williams et al. (Ref. 2), and Morgan (Ref. 4).

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[1] Dr. P. D. Gorsuch (Missile & Space Division, General Electric Co.) Letter to Aerospace Corporation. (Attn: Dr. J. I. Slaughter) 31 August 1965.

II. EXPERIMENTAL

A. APPARATUS AND MATERIALS

The apparatus (Fig. 1) is a typical pyrohydrolysis setup. It is constructed from high purity quartz except for the 1-liter, 3-neck, round-bottom, Pyrex flask and the 800-ml Pyrex beaker. The wall thickness of all the quartz tubing is 1.5 mm.

The reactor or combustion tube is fabricated from a 23-mm-o.d. tube and is terminated with standard taper 24/40 male joints at both ends. Each male joint is fitted with 0.5-mil gold foil sleeves 2.5 cm in width. The reactor tube including the joints is 80 cm long. One end of the reactor tube is connected through a T-connection to the delivery tube of the steam generator and to a quartz window cap through a standard taper 24/40 female joint. The steam delivery tube is made from 12-mm-o.d. tube 70 cm in length and is terminated with a standard taper 24/40 male joint which is fitted with a Teflon sleeve (A. H. Thomas Company). The other end of the reactor tube containing a wad of coarse quartz wool is connected to the condenser by a standard taper 24/40 joint. The position of the quartz wool is such that it is located immediately ahead of the sample boat during pyrohydrolysis to prevent any particles from being blown out of the hot reaction zone.

The water condenser consists of a 12-mm-o.d. inner tube 70 cm in length and a 23-mm-o.d. outer tube forming the shell of the water-jacket 46 cm in length. The top of the water-jacket is located 10 cm below the horizontal plane of the reactor tube. The end of the delivery tube is positioned in the 800-ml beaker that is immersed in the ice bath.

The reactor tube is heated in a tubular furnace (Marshall Products Company) that is 2.54 cm in bore diam and 36 cm in length. The power is supplied by a stepdown transformer (60 volt, 40 amp) and is monitored with a voltmeter and an ammeter (Weston, Model 904). The core temperature of the furnace is maintained at 1300°C so that the temperature on the quartz reactor tube is at least 1200°C during pyrohydrolysis. The temperature is

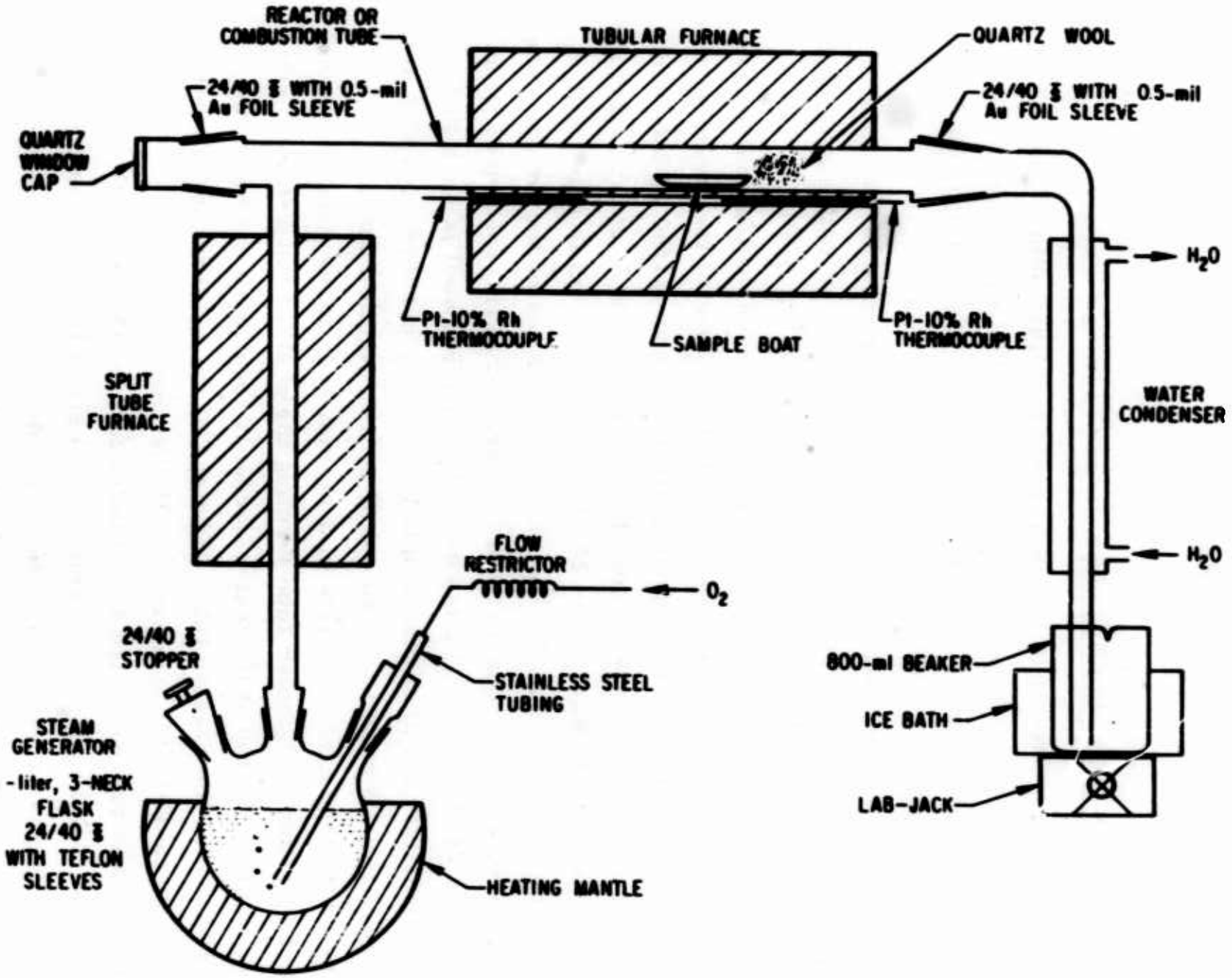

Fig. 1. Pyrohydrolysis Apparatus

monitored with two thermocouples (platinum-10 percent rhodium). No attempt was made to determine the temperature of the interior of the reactor tube during pyrohydrolysis.

The steam generator consists of a 1-liter, 3-neck, round-bottom, Pyrex flask heated by a variac-controlled Glas-Col heating mantle. The flask is attached to the steam delivery tube by a standard taper joint. The steam is superheated by heating approximately 25 cm of the steam delivery tube to 800°C by a split tube furnace (Hevi-Duty Heating Equipment Company). The top of the furnace is located 3 cm from the reator tube. Boiling chips of micro-porous carbon (Todd Scientific Company) are used to promote smooth boiling. In addition, oxygen is introduced into the steam generator at a constant flow rate of 45 cc/min through a 0.476-cm-o.d. stainless steel tubing to promote smooth and steady flow of superheated steam through the reactor tube. The presence of oxygen also enhances the oxidative degradation of the graphite sample. A constant oxygen flow rate is achieved with a flow restrictor fabricated from a 0.254-mm-i.d. stainless steel capillary tube 30 cm long.

The sample boat is a zirconia boat lined with a 2-mil platinum sheet. The boat is approximately 9 cm long, 0.6 cm deep, and 0.8 cm wide.

A pH meter (Beckman, Model 76) equipped with a glass-calomel electrode pair is used for the potentiometric titration of the mannitol-boric acid complex.

Solutions of 0.1N and 0.05N sodium hydroxide were prepared from concentrated carbonate-free sodium hydroxide and carbon dioxide-free demineralized water by the procedure described by Kolthoff and Sandell (Ref. 5) and standardized with potassium hydrogen phthalate. Approximate 0.1N hydrochloric acid solution was prepared by appropriate dilution of concentrated hydrochloric acid (Baker and Adamson, Reagent, A.C.S.).

Mannitol was purchased from Eastman and had a melting point of 167-169°C. Boron carbide was purchased from Plasmadyne (a subsidiary of Giannini Corporation) and had a boron content of 74.95 percent by weight. Spectroscopic graphite rods used in preparing standard boron/graphite mixtures were obtained from United Carbon Products Company.

B. GENERAL PROCEDURE

The furnace is initially heated to 1150°C; this temperature is maintained at all times when there is no steam flowing through the reactor tube to prolong the life of the quartz tube. The power to the steam superheater furnace is adjusted so that the temperature of the delivery tube is about 800°C. When the mixture of superheated steam and oxygen begins to flow, the furnace temperature is raised to the operating temperature of 1300°C. The steam flow rate is then adjusted so that the distillation rate is 5 ml of distillate per minute. The end of the condenser tube is immersed in about 50 ml of water contained in a 800-ml Pyrex beaker. Both the beaker and its contents are kept cold by immersion in the ice bath. The standard taper 24/40 stopper is removed from the flask, and the steam/oxygen mixture is allowed to escape into the atmosphere. The standard taper female joint equipped with the quartz window is removed, and the platinum-lined zirconia boat containing a carefully weighed amount of powdered sample is quickly introduced into the heated zone of the reactor tube with a 3-mm-o.d. quartz rod. The quartz window cap and the stopper are quickly replaced to initiate the flow of steam and oxygen to prevent excessive heating of the quartz tube. As the distillate collects, the beaker is gradually lowered to prevent excessive back pressure on the system. The pyrohydrolytic separation is permitted to continue until 550 ml of distillate have been collected.

The distillate is acidified with 4 ml of 0.1N hydrochloric acid solution, and the acidified solution is gently boiled for 15 min to remove any dissolved carbon dioxide. The solution is cooled to 25°C in an ice bath under a nitrogen atmosphere and subsequently titrated potentiometrically with either 0.1N or 0.05N sodium hydroxide solution, depending upon the anticipated boron content of the sample, to a pH of 5.64 (Ref. 1). Thirty grams of mannitol are added to the solution, and the titration is continued under a nitrogen atmosphere to a pH of 8.50 by the addition of equal incremental volumes of standard sodium hydroxide solution. The end point is determined by the second derivative method (Ref. 6). The volume of sodium hydroxide solution used in titrating the solution to the end point after the addition of mannitol is

the quantity of sodium hydroxide used in titrating the mannitol-boric acid complex.

Blank determinations are conducted between runs to ensure that no boron remains in the apparatus after the conclusion of a run. The average blank correction corresponded to 20 μg of boron per 100 ml of distillate.

C. SAMPLE PREPARATION

Standard samples with boron content in the 3.5 to 0.38 percent by weight range were prepared by mixing weighed amounts of boron carbide and powdered graphite with the aid of the Wig-L-Bug. Samples with boron content of 0.16 percent and 0.032 percent were prepared by diluting the 0.38-percent sample with powdered graphite. Boron carbide was chosen because it is suspected that the boron in pyrolytic graphite exists in this form. Boron-pyrolytic graphite samples supplied by General Electric Company were put into powder form by crushing chunks of the material with the Wig-L-Bug. Sample weight used in the analysis varied from 0.4 to 0.9 g.

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III. RESULTS AND DISCUSSION

The accuracy of this method was evaluated by performing boron analysis on samples of known boron content. The results of the analysis on samples containing from 0.03 to 3.5 percent boron by weight are presented in Table 1. The excellent agreement between the amount of boron present and recovered and between the repetitive samples indicates this method has the dual advantages of high accuracy and excellant precision.

Five boron-pyrolytic graphite samples whose boron content had been ascertained by other analytical techniques were obtained from General Electric Company and were also analyzed using the pyrohydrolysis method. A comparison of the boron content measured by these various techniques is made in Table 2. It is felt that the discrepancies in the results are due to nonuniform samples rather than to the inaccuracies of the respective analytical methods. In order to adjudicate the relative merits of these analytical methods, further studies are required.

Table 1. Boron Analysis on Standard Samples

Sample wt, g	Boron, wt %		Deviation, wt %
	Calculated[a]	Experimental	
0.4785	0.03157	0.03101	-0.00056
0.5210	0.03157	0.03343	+0.00186
0.5837	0.03157	0.03615	+0.00458
0.5650	0.1648	0.1639	-0.0009
0.4380	0.1648	0.1689	+0.0041
0.4955	0.1648	0.1659	+0.0011
0.5793	0.3778	0.3767	-0.0011
0.5155	0.3778	0.3754	-0.0024
0.5374	0.6457	0.6424	0.0033
0.5176	0.6457	0.6348	-0.0109
0.6000	0.6457	0.6450	-0.0007
0.5343	0.9516	0.9431	-0.0085
0.6164	0.9516	0.9534	+0.0018
0.8429	0.9516	0.9546	+0.0030
0.8551	0.9516	0.9536	+0.0020
0.5342	1.459	1.438	-0.021
0.8634	1.459	1.446	-0.013
0.5141	1.459	1.411	-0.048
0.6615	3.431	3.449	+0.018
0.6915	3.431	3.430	-0.001
0.8197	3.431	3.423	-0.008

[a]Based on B_4C purity of 95.77 percent.

Table 2. Comparison of Boron Content Between Various Measurement Techniques

Sample	Sample wt, g	Boron, wt %			
		Pyrohydrolysis	Other Techniques[a]		
			Spectrographic	Residual Ash Content[b]	Fast Neutron Activation
FF-1-0	0.6265	0.0186	0.92	0.92	Not measured
FF-1-0	0.5237	0.0174			
FF-1-0	0.4928	0.0161			
005-1-I	0.7194	0.151	0.16	0.16	Not measured
005-1-I	0.5597	0.169			
005-1-I	0.6321	0.164			
005-5-M	0.4523	0.407	0.46	0.55	0.57
005-5-M	0.5176	0.407			
005-5-M	0.5348	0.413			
005-8-M	0.7853	0.476	0.22	0.76	0.36
005-8-M	0.7311	0.483			
005-8-M	0.9066	0.465			
BOR-3	0.6059	1.04	0.82	Not measured	0.90
BOR-3	0.5910	1.05			
BOR-3	0.6039	1.06			

[a]Data supplied by General Electric Company

[b]Assumes all the ash from a known sample of combusted material is boron oxide.

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