

## A Method for Determining Boron in Cotton Fabric

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### Synopsis

A technique involving radiofrequency-discharged oxygen has been demonstrated in the analysis for boron in cotton fabric as well as preparation of residual ash replicas of identical three-dimensional configuration of the original sample for microscopic studies. The main advantages of this technique lie in its simplicity and fastness.

### INTRODUCTION

There are two general approaches to the determination of boron in boron-containing compounds. In organic esters of boric acid, the procedure consists of hydrolyzing the ester and then titrating the resulting boric acid in the presence of mannitol.<sup>1</sup> However, several limitations exist in this procedure. If the ester is of high hydrolytic stability, long hydrolysis may be required and even then the results may be low.<sup>2</sup> In esters of alkanolamines<sup>3</sup> and aromatic hydroxy compounds, the liberated alkanolamines and phenols interfere with the titration.<sup>2</sup> The other approach is more general and applicable to many types of boron compounds; it consists of first fusion with sodium carbonate in a platinum crucible, and then digestion with hydrochloric acid, neutralization with a base, and titration of the boric acid in the presence of mannitol.<sup>4-6</sup> At best, all the procedures are time consuming and require some experience if reproducible results are to be obtained.

As a result of some of our work with organoboron compounds on cotton fabric, it became imperative that a simple and fast analysis for boron were available. We believe we have developed such an analysis and would like to present some representative data. The technique involves the use of electrodeless radiofrequency-discharged oxygen for the removal of all organic matter from the sample, leaving behind only boric oxide ( $B_2O_3$ ), the amount of which is determined by weighing.

### EXPERIMENTAL

#### Materials

The fabric used in this work was 7.5 oz/y<sup>2</sup> S/423 Twill, obtained from Test Fabrics, Inc. The various boron-containing compounds were used as received and were obtained from the following sources: boric acid, Baker

TABLE I  
Per Cent Boron in Cotton Fabric

Boron compound	Solvent	Concn of solution, %	Wet pickup, %	Calcd boron, %	Boron, <sup>a</sup> %	Wt of sample before ashing, g	Wt of sample after ashing, g	Boron in sample, %
None	—	—	—	—	0.07	0.2273	0.0002	—
Boric acid	water	15	51	1.34	1.02	0.2277	0.0067	0.91
Benzeneboronic acid	benzene	25	44	0.98	1.09	0.2769	0.0097	1.08
Triethanolamine borate	DMF <sup>b</sup>	25	42	0.72	0.85	0.2693	0.0079	0.91
9,10-Dichloro- <i>o</i> -carborane	benzene	5	19	0.95	1.48	0.1860	0.0065	1.08
B-Trichloro- <i>N</i> -triphenylborazine	DMF	25	80	1.57	1.61	0.2320	0.0130	1.74

<sup>a</sup> Determined by Galbraith Laboratories, Incorporated; their procedure consisted of digesting the sample with nitric acid in a sealed tube at 300°C and then determining the boron content volumetrically using the mannitol procedure.

<sup>b</sup> *N,N*-Dimethylformamide.

TABLE II

Per Cent Boron in Various Compounds\*

Compound	Calcd boron, %
Boric oxide ( $B_2O_3$ )	31.03
Boric acid ( $H_3BO_3$ )	17.48
Benzeneboronic acid	8.86
Triethanolamine borate	6.88
9,10-Dichloro- <i>o</i> -carborane	50.70
B-Trichloro-N-triphenylborazine	7.87

\* The compounds were used as received.

Chem. Company; benzeneboronic acid, Aldrich Chem. Company; triethanolamine borate, Aldrich Chem. Company; 9,10-dichloro-*o*-carborane, courtesy of Dr. H. A. Schroeder, Olin Chemical Corporation; B-trichloro-N-triphenylborazine, Aldrich Chem. Company. Oxygen was Linde, commercial grade.

### Fabric Treatment

Samples of fabric were padded with the various solutions through squeeze rolls to a wet pickup, as indicated in Table I. They were then mounted on pin frames at original dimensions and dried in a forced-air oven for a minimum of 5 min at 100°C and then conditioned at 21°C (70°F) and 65% relative humidity for at least 6 hr. The per cent add-on was calculated from the wet pickup of the fabric and the per cent solids in the bath. This procedure was followed, rather than weighing the conditioned sample, in order to eliminate any complications due to possible differential moisture sensitivity of the various boron compounds. The per cent boron was then calculated from the per cent add-on and the per cent boron in the different compounds, as shown in Table II.

### Instrumentation

The instrument used in this work was the LTA-600L low-temperature asher developed by Tracerlab, a division of Laboratory for Electronics, Inc. The instrument has five ashing chambers with a capacity of up to four samples per chamber, depending upon the sample size. The rf generator operates at 13.56 MHz and delivers from 0-300 watts of continuously variable power output. The instrument was connected through a cold trap (Dry Ice/acetone) to a Welch Duo-Seal (No. 1402 B) vacuum pump with a free air capacity of 140 liters per min.

### Typical Procedure

About a 0.2-g sample of the conditioned fabric was found to be most convenient for a fast and reproducible analysis. The sample was weighed on an analytical balance and then placed in a weighed open glass boat. The assembly was then transferred to the ashing chamber, and the instrument

was operated at the following conditions: pressure, 0.70 mm; flow rate of O<sub>2</sub>, 15 cc/min; power, 300 watts.

The ashing time required depended upon the sample size and the boron compound involved. However, a very convenient visual indication of the completeness of ashing is possible by simply noting the change in color of the plasma from blue to pink. The blue color of the plasma is due to discharge of CO, and the pink is due to that of O<sub>2</sub>. Thus, when the sample does not contain any more oxidizable material, the discharge color changes from blue to pink. After completion of the ashing, the glass boat is allowed to equilibrate to room temperature and is then weighed again. The gain in weight is the weight of boric oxide which resulted from the oxidation of the boron compound on the fabric. The per cent boron on the fabric is then calculated from the sample weight before and after ashing and the per cent boron in boric oxide.

## RESULTS AND DISCUSSION

Discharged gases have been put to many uses, including surface modification of polymers,<sup>7-9</sup> grafting of natural and man-made fibers,<sup>10</sup> preparation of thin pore-free polymer films,<sup>11</sup> and cleaning of high precision bearings.<sup>12</sup> More specifically, discharged oxygen has been used in a variety of analytical problems, for example, in decomposition of organic substances for trace element analysis,<sup>13,14</sup> ashing of coal,<sup>15</sup> determination of selenium in biologic specimens,<sup>16</sup> and determination of arsenic in food stuffs.<sup>17</sup> Thus, our application of this technique to boron analysis in cotton fabric illustrates further the versatility of ionized gases.

The technique has been used with equal results on many more boron compounds than indicated in Table I. However, the general applicability of the technique should become apparent from the data in the table which represent five different classes of boron compounds, containing anywhere from about 7% to about 51% boron. Furthermore, the compounds were padded onto the fabric from three different solvents in concentrations from 5% to 25%. From the results it can be seen that with one minor exception there is a good agreement in the per cent boron found by the chemical analysis and our plasma technique. The one exception is the 9,10-dichloro-*o*-carborane, which is 0.4% higher according to the chemical analysis. On the other hand, in this particular case the plasma technique agrees with the result from the indirect determination. The greatest advantage of this technique lies in its simplicity and fastness. The determinations reported in Table I required anywhere from 1 to 3 hr of total time, depending upon the boron compound involved.

Earlier in this work a check for the completeness of oxidation was conducted by continuing plasma treatment of the samples up to 48 hr. However, constant weight of the sample (residue) was achieved right after the change in plasma color from blue to pink in all cases. In the initial stages of ashing, the plasma has also a green coloration due to gaseous boron. How-

ever, the boron loss apparently is insignificant, as the data in Table I indicate.

The residue (boric oxide) left behind is actually left as extremely thin fibrils in complete structural integrity of the original fabric sample. The residue was subsequently scanned with an optical microscope for uniformity of deposition of the boron compounds in the fibers. In this connection it should be noted that when the untreated fabric was completely ashed, it too left behind a trace of residue (0.0002 g) which again was left in the form of minute fibrils of structure identical to the original sample. In this case some inorganic residues left from the manufacture of the fabric must have been responsible for the residue.

This technique may also be applied to the determination of boron in crystalline boron compounds. However, some precautions have to be taken as the results tend to be high. Apparently this is due to incomplete ashing as a result of boric oxide crust formation, thus stopping further oxidation. However, pulverizing the material and agitating during the ashing eliminates the problem.

In conclusion, the use of radiofrequency-discharged oxygen has been demonstrated in the analysis for boron in cotton fabric as well as preparation of residual ash replicas of identical three-dimensional configuration of the original sample for microscopic studies. The main advantages of this technique lie in its simplicity and fastness.

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