

**“New Boron Procedure:  
A Technical Discussion”**

**by**

**Scientific Staff  
Balazs Analytical Laboratory**



## **NEW BORON PROCEDURE: A TECHNICAL DISCUSSION**

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1990

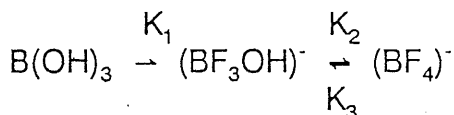
To meet the ever pressing need to turn around QC data more rapidly with greater sensitivity and accuracy, Balazs Laboratory through the years has spent considerable effort on upgrading its procedures. Consequently, in the past two years we have altered several procedures to take advantage of the swiftness in analysis and great sensitivity of such tools as ICP or ICP-MS. Although not as reliable as colorimetric procedures, the spectroscopic tools more readily meet client needs for immediate results. These tools, however, have more matrix interferences than the slower colorimetric procedures. It is these interferences that led us to conduct an in-depth research study on all of our procedures that contain F<sup>-</sup> ion to determine matrix effects and kinetic reactions. These procedures involved phosphorous, boron, silicon, aluminum and manganese measurements using both colorimetric and spectroscopic measuring techniques.

In general our findings indicated that there are matrix interferences in measuring these elements in both colorimetric and spectroscopic procedures. We also found that in most of our procedures we had adequately handled these matrix effects and therefore had lost no accuracy in our measurements. However, in one procedure, namely the measurement of boron in BPSG, we found an error caused by the way our standards were being made up.

Prior to 1988, using our colorimetric procedure the wafers were stripped with sodium hydroxide and the boron measured as a borate ion for which there were no interferences. This procedure required the BPSG film to be deposited on a silicon nitride film. In our newer ICP-AES procedure, the wafers are stripped with HF which allows for the deposition of BPSG directly on a silicon wafer thus eliminating the need for a nitride layer. This led to a faster and more convenient procedure for us and our clients. However, an error occurred in the way the standards were made up for the procedure with HF stripping.

When doing solution chemistry it is important that the matrix of your standards be as similar to that of your samples as possible. Our samples which are BPSG films on silicon substrates are stripped with a 25% HF solution. The resulting solution is quantitatively transferred, manganese is added as an internal standard and the combination diluted to a known volume with water. The final concentration of HF is 0.1%. When making our standards, we start with a certified NBS boric acid solution, add our manganese internal standard, and dilute to volume using a 0.1% HF solution. All standards are freshly prepared in the morning. The resulting solutions were measured 1-3 hours later using ICP-AES. The internal standard was used to insure consistency between the standards and the samples as well as an accurate way to standardize the signal from ICP-AES.

It was our belief that the conversion of the boric acid  $B(OH)_3$  to boron tetrafluoride ( $BF_4^-$ ) was a relatively fast reaction. Our kinetic study has revealed, however, that the conversion from  $B(OH)_3$  to  $BF_4^-$  is not a rapid one. The first three exchanges of  $F^-$  are very fast but the last one is not. The final substitution converting  $(BF_3OH)^-$  to  $(BF_4)^-$  is dependent on the concentration of the  $F^-$  and can be rapid for  $F^-$  concentrations over 2% but very slow for  $F^-$  concentration of 0.1% which takes more than one day for full conversion.



$K_1$  - very fast  
 $K_2$  - dependent on  $F^-$  conc.  
 $K_3$  - very slow

Our experiments also showed that the emission signal of  $BF_4^-$  is ~ 20% larger than that of the  $B(OH)_3$  of the same boron concentration. Our samples which were dissolved in a higher HF concentration solution were practically totally converted from  $B_2O_3$  to  $BF_4^-$  on dissolution. The standards, however, which were boric acid solutions diluted and adjusted to 0.1% HF concentration went through a very slow conversion and thus at the time of measurement contained considerable amount of unconverted  $BF_3OH^-$ . The  $BF_3OH^-$  form gives a lower signal than the  $BF_4^-$  form. This condition caused our standards to give lower signal for the same amount of boron than our samples and thus, caused an error in our calculated results. (See Table 1 and Fig. 1) This error has been measured to be  $9\% \pm 5\%$  (two standard deviations). (See Fig. 2) The lack of precision is caused by the fact that the standards were measured in a time span of 2-6 hours after they were made up. During this time a continuous conversion of  $BF_3OH^-$  to  $BF_4^-$  was occurring causing inconsistency in the standards which resulted in an error in the calculation of %B in the samples.

Now that this study has revealed an error in the standards, a new procedure for making up standards has been put into place. This procedure insures that the reaction to  $BF_4^-$  is completed prior to measurement in the standard as well as in the samples. Table 2 shows the accuracy and precision of results using 2 NBS glass standards to make five boron sample solutions. It also shows the stability of these solutions over time and the excellent long period reproducibility of the measurement. The reproducibility test of the method from the same wafer sample is shown in Table 3 and Figure 3. As these data show, 2% precision or reproducibility is achievable by the present method.

The complete study of the spectroscopic measurement of elements of BPSG films in the presence of fluoride ion is being presented for publication. The details of this study and the kinetic modeling showing the correlation between data of kinetic calculations and actual measurements are a part of this paper. The complete paper is expected to be available after January 1, 1991.

**Table 1. Change of the boron ICP signal with time for a 5ppm boron standard with different HF concentrations. 100% is the signal of standard with 2% HF concentration.**

HF % Concentration	Time After Preparation of Solution			
	0.5 Hour	2 Hours	1 Day	3 Days
0%		82.54	82.68	82.90
0.05%	85.97	83.13	92.57	96.68
0.1%	85.56	84.66	97.05	99.74
0.2%	89.16	89.33	98.49	100
0.4%	94.80	95.56	98.74	99.60
0.8%	98.10	98.16	99.44	99.24

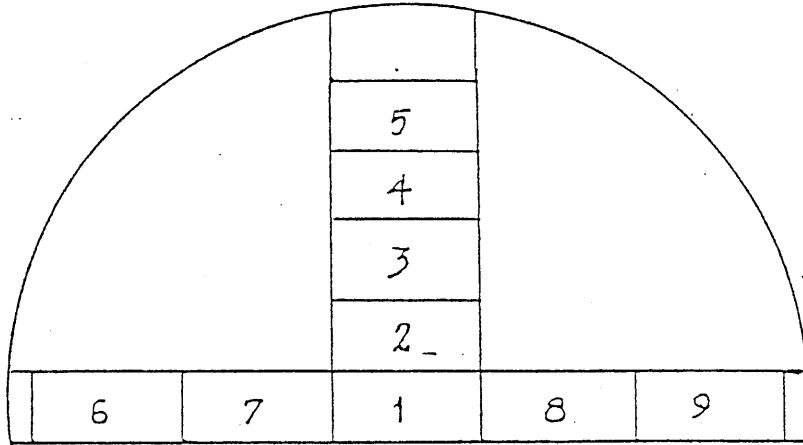
Note: A slight decrease in the ICP signals were observed for the standards containing 0.05% and 0.1% HF at two hours due to a small change in the ICP parameters during this experiment.

**Table 2. Measured boron concentration of samples prepared from NBS glass standards.**

Date & Time of Series	NBS 93a Glass		NBS 1411 Glass		
	#1	#2	#3	#4	#5
	Expected Value				
	4.328	2.627	4.358	2.949	4.08
08/09 9:57	4.356	2.660			
08/09 15:31	4.361	2.673			
08/09 18:02	4.200	2.626			
08/27 11:01	4.298	2.646	4.328	2.928	4.036
	4.337	2.628	4.294	2.962	4.020
08/28 8:47	4.385	2.670	4.360	2.927	4.092
08/29 9:45	4.333	2.633	4.326	2.980	4.112
08/31 10:46	4.342	2.676	4.368	2.965	4.081
10/05 14:18			4.407	2.992	4.143
Mean value	4.327	2.651	4.347	2.959	4.081
No. of Measurements	8	8	6	6	6
SD=Standard Deviation	0.057	0.021	0.040	0.027	0.046
RSD=Relative Standard Deviation	1.316%	0.788%	0.910%	0.902%	1.132%

Sample Patterns for Study in Table 3

Wafer No. 1



Wafer No. 2

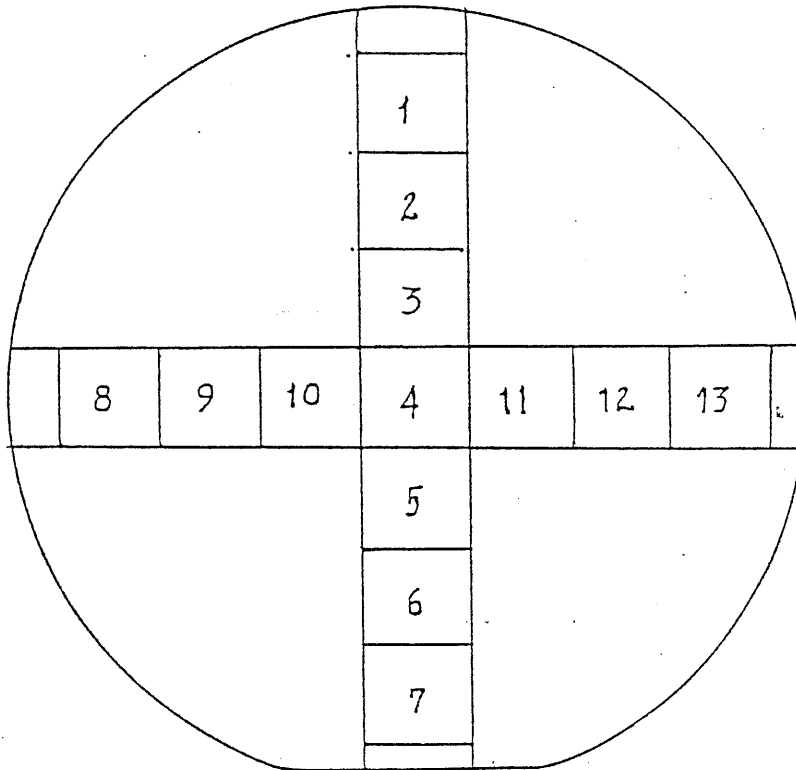


Figure 1.

Change of measured boron concentration with time for 2ppm B standard in 0.5 and 1% HF

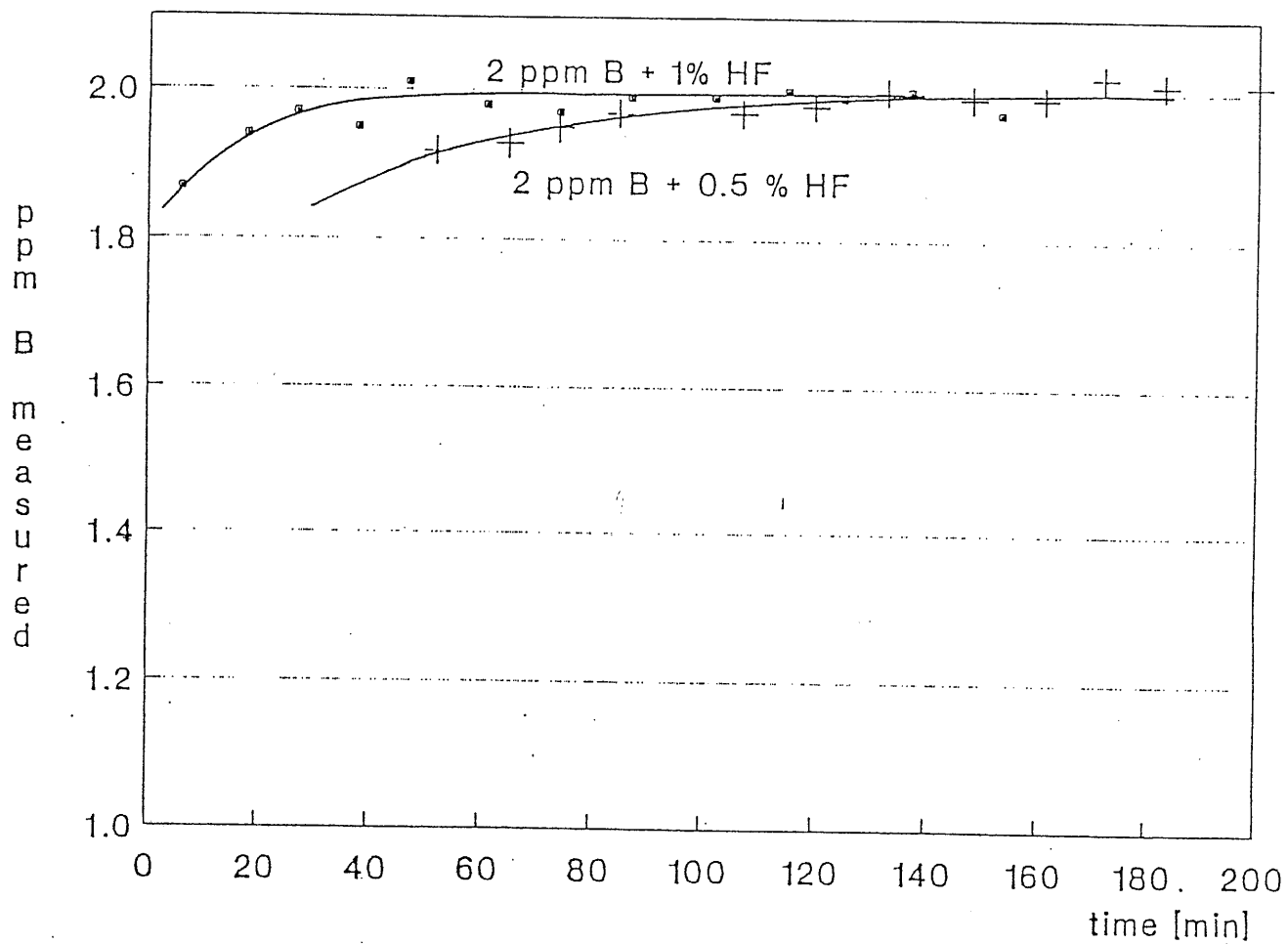


Figure 2.  
Relationship Between Standards and Samples  
Old Vs. New Standard

