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Precision and Accuracy of Analysis for Boron in ITP Samples

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Summary

Boron, at the 10 mg/L level, in ITP samples can be measured by ICPES with a precision of 6%. A microwave acid digestion is necessary prior to ICPES analysis to eliminate the organic matrix.

Introduction

Inductively Coupled Plasma Emission Spectroscopy (ICPES) has been used by the Analytical Development Section (ADS) to measure boron in catalytic tetraphenylboron decomposition studies performed by the Waste Processing Technology (WPT) section. Analysis of these samples is complicated due to the presence of high concentrations of sodium and organic compounds. Previously, we found signal suppression in samples analyzed "as received". We suspected that the suppression was due to the high organic concentration (up to 0.01 molar organic decomposition products) in the samples. When the samples were acid digested prior to analysis, the suppression was eliminated. The precision of the reported boron concentration was estimated as 10% based on the known precision of the inorganic boron standard used for calibration and quality control check of the ICPES analysis. However, a precision better than 10% was needed to evaluate ITP process operating parameters. Therefore, the purpose of this work was (1) to measure, instead of estimating, the precision of the boron measurement on ITP samples and (2) to determine the optimum precision attainable with current instrumentation.

Experimental

The digestion methods evaluated included a dry ash and a nitric acid-microwave method. The composition of a typical ITP simulant solution (supplied by Mark Barnes of WPT) is listed in Table 1. In addition, Barnes provided a solution of the pure organic compounds (12,500 mg/L each of triphenylborane, diphenylborinic acid, and phenylboronic acid) present as decomposition products in the ITP samples.

The following types of solutions were digested and analyzed using a Leeman PS1000 ICPES:

- Solution 1: 10 mg/L inorganic boron standard prepared from a 1000 mg/L boron standard obtained from High Purity, Inc.
- Solution 2: ITP simulant solution spiked with a known quantity of the organic solution

- Solution 3: ITP simulant solution spiked with a known quantity of NaTPB. Copper and concentrated nitric acid were also added to this solution to cause catalytic decomposition of the NaTPB in an attempt to make an ITP standard.

WSRC-NB-93-225 contains details of the dry ash and nitric acid - microwave digestion methods. The ICPES quality control check standards were required to be within 3% of the calibration standards instead of the 5% normally required under routine operation.

Table 1. Composition of ITP Simulant Solution, Batch # MJB-ITP-Slurry-9/9/97

Component	Concentration
Na^+	4.5 Molar
NO_3^-	0.64 Molar
OH^-	2.6 Molar
NO_2^-	0.69 Molar
$Al(OH)_4^-$	0.17 Molar
CO_3^{-2}	0.17 Molar
SO_4^{-2}	0.009 Molar
Cl^-	0.013 Molar
F^-	0.007 Molar
PO_4^{-3}	0.006 Molar
KTPB (insoluble)	5 wt %
NaTPB (soluble)	~ 200 mg/L
NaTPB (insoluble)	~ 500 mg/L

Results and Discussion

Table 2 lists measured boron concentrations for solutions 1-3 that were dry ashed prior to analysis by ICPES. Recovery of boron in solution 1 was only 84%. The measured boron in solution 2 was greater than expected which is not unreasonable since the amount of boron in the ITP simulant is approximate. Because of this uncertainty, solution 2 could not be used to measure the accuracy of the analysis. Therefore, solution 3, with a known quantity of NaTPB, was prepared and analyzed. Recovery of boron in solution three was only 80%. Precision (95% confidence interval) of the measurements were 2% for solution 3, 4% for solution 2, and 8% for solution 1. Because the data obtained from solutions 1 and 3 indicated a loss of boron, the dry ash was discarded as a digestion method for the determination of boron in ITP samples.

Table 2. Boron Concentration after Ashing Sample 500 °C.

	Measured Boron Conc. (mg/L)							
Solution	**1**	**2**	**3**	**4**	**5**	**Average**	**Standard Deviation**	**Expected Boron Conc. mg/L**
1	7.974	8.166	7.814	7.951	8.603	8.102	0.307	9.616
2	124.7	126.4	130.3	128.1	ND[1]	127.4	2.4	90

3	63.59	64.68	ND[1]	ND[1]	ND[1]	64.14	0.77	80

**[1]ND = no data. Equivalent replicates were not made for each solution.
5 replicates were made for solution 1,
4 replicates were made for solution 2,
duplicates were made for solution 3.**

Table 3 lists measured boron concentrations for solutions 1-3 that were microwave- acid digested. Boron recoveries of 98% and 94% were obtained for solutions 1 and 3 respectively. Good precisions (95% confidence interval) of 1% for solution 3, 6% for solution 2, and 3 % for solution 1 were obtained with this method.

Table 3. Boron Concentration after Microwave Acid Digestion

	Measured Boron Conc. (mg/L)									
Solution	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
1	9.727	9.922	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]
2	8.535	8.132	8.093	8.534	8.760	8.345	8.314	8.358	8.270	8.177
3	74.95	75.81	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]

Solution	**Average**	**Standard Deviation**	**Expected Boron Conc. Mg/L**
1	9.825	0.138	10.0
2	8.352	0.208	6.8 (8.44)*
3	75.24	0.50	80

*** 8.44 is calculated assuming that the measured concentration from dry ashing - ICPES analysis is correct.**

**[1]ND = no data. Equivalent replicates were not made for each solution.
Duplicates were made for solution 1,
10 replicates were made for solution 2,
duplicates were made for solution 3.**

Because a standard of the ITP solution (i.e., solution 2) is not available, the accuracy of the ICPES analysis cannot be determined. Instead, a control sample was submitted and digested with the first batch of samples. The digested control sample was then analyzed with each batch of samples analyzed by the ICPES. The control sample tracks and corrects for any instrument variation, but not digestion variations. When a control sample was about depleted, a new control sample was digested and verified against the old control sample. Table 4 shows the variation of the control standard during the analyses of ITP samples. Figure 1, a plot of the residuals of the data in Table 4, shows a positive bias that ranges from 0.3% to 9%.

Table 4. Boron Concentration of Control Samples

Date	**QC100697**	**% Deviation**	**Date**	**QC100697**	**% Deviation**	**Date**	**QC100697**	**% Deviation**
12/17/97	867.5	0.0	12/29/97	875.3	0.9	12/31/97	919.0	5.9
12/17/97	855.3	-1.4	12/29/97	887.5	2.3	12/31/97	896.3	3.3
12/17/97	861.3	-0.7	12/29/97	884.2	1.9	1/2/98	889.6	2.5
12/17/97	882.3	1.7	12/31/97	876.7	1.1	1/2/98	859.9	-0.9
12/17/97	902.1	4.0	12/31/97	854.1	-1.5	1/2/98	883.7	1.9
12/17/97	873.1	0.6	12/31/97	845.4	-2.5	1/2/98	877.1	1.1
12/17/97	898.4	3.6	12/31/97	870.1	0.3	1/12/98	835.2	-3.7

12/17/97	836.3	-3.6	12/31/97	877.9	1.2	1/12/98	883.6	1.9
12/17/97	859.9	-0.9	12/31/97	891.4	2.8	1/12/98	889.1	2.5
12/22/97	893.6	3.0	12/31/97	858.8	-1.0	1/12/98	872.7	0.6
12/22/97	861.4	-0.7	12/31/97	913.6	5.3	1/12/98	890.1	2.6
12/22/97	846.1	-2.5	12/31/97	925.3	6.7	1/12/98	913.8	5.3
12/22/97	894.9	3.2	12/31/97	926.1	6.8	1/12/98	902.6	4.0
12/22/97	924.3	6.5	12/31/97	936.7	8.0	1/12/98	893.1	3.0
12/22/97	890.2	2.6	12/31/97	935.7	7.9	1/12/98	911.4	5.1
12/22/97	904.6	4.3	12/31/97	944.8	8.9	1/12/98	883.8	1.9
12/22/97	892.7	2.9	12/31/97	902.8	4.1	1/12/98	875.6	0.9
12/22/97	900.3	3.8	12/31/97	909.6	4.9	1/12/98	920.4	6.1
12/29/97	866.3	-0.1	12/31/97	913.6	5.3	1/15/98	897.2	3.4
12/29/97	870.3	0.3	12/31/97	915.9	5.6			
12/29/97	896.3	3.3	12/31/97	896.7	3.4			
						Average	**888.7**	
						STD	**24.9**	
						%RSD	**2.8**	
Date	**QC102491**	**% Deviation**	**Date**	**QC102491**	**% Deviation**	**Date**	**QC102491**	**% Deviation**
1/15/98	702.3	0.0	1/23/98	748.6	6.6	2/5/98	712.9	1.5
1/19/98	696.9	-0.8	1/26/98	711.3	1.3	2/5/98	704.8	0.4
1/19/98	688.6	-2.0	1/26/98	700.4	-0.3	2/5/98	711.4	1.3
1/19/98	699.4	-0.4	1/26/98	738.5	5.2	2/5/98	675.4	-3.8
1/21/98	684.3	-2.6	2/3/98	663.0	-5.6	2/5/98	641.9	-8.6
1/21/98	696.3	-0.9	2/3/98	689.6	-1.8	2/5/98	661.3	-5.8
1/23/98	750.8	6.9	2/3/98	712.9	1.5			
						Average	**695.8**	
						STD	**22.1**	
						%RSD	**3.2**	

Figure. 1 - Control Sample Residuals

Conclusions

A precision of 6% is attainable when measuring boron at the 10 mg/L level by ICPES after a microwave acid digestion. A dry ash digestion results in the loss of boron and, thus, is not recommended. Since an ITP standard is not available, the accuracy of the measurement cannot be determined. Therefore, a control sample should be submitted and analyzed with each day's samples to track any instrumentation variation. A high-pressure microwave acid digestion method may afford a more complete digestion and will be evaluated in future work.