

# Determination of Boron in Fertilizers by Atomic Absorption Spectrophotometry

Steve J. Weger, Jr., Lloyd R. Hossner,<sup>1</sup> and Louis W. Ferrara

A procedure for the determination of small amounts of boron in fertilizers and related compounds by atomic absorption spectrophotometry is described. The boron is complexed and extracted from aqueous acid solution with 2-ethyl-1,3-hexanediol in chloroform. This separation decreases the amount of interferences common to atomic absorption and

increases the sensitivity of the boron determination. The detection limit is 1 p.p.m. boron with a good signal-to-noise ratio. The working concentration range in solution is 0 to 100 p.p.m. boron with a sensitivity of 1.5 p.p.m. per 1% absorption at 2497.7 Å. Interfering ions were considered and their effects were found to be negligible.

Several general methods for the determination of boron described by Boltz *et al.* (1958) and Nemodruk and Karalova (1965) were investigated by this laboratory. More specific procedures as those of Jackson (1958), Borland *et al.* (1967), and the Association of Official Agricultural Chemists (1965) were also explored. None of the above methods, however, proved as versatile and reproducible for our purposes as the atomic absorption method described below. An earlier form of a hollow-cathode boron source lamp was described by the Perkin-Elmer Corporation, but this lamp did not prove satisfactory for concentrations of boron less than 50 p.p.m. Recently, however, Perkin-Elmer introduced an improved hollow-cathode boron lamp which produced a more stable signal. This boron tube allowed a detection limit of 10 p.p.m. at a 10× scale expansion in aqueous solutions. Because of possible refractive complexes similar to those described by Perkin-Elmer (1966), and low boron content of our compounds, we found it necessary to employ an organic solvent system to increase sensitivity and decrease refractive interferences.

This paper describes the procedures for preparing and analyzing fertilizers which contain varying amounts of boron.

## EXPERIMENTAL

**APPARATUS AND OPERATING CONDITIONS.** The Perkin-Elmer Atomic Absorption, Model 303, Spectrophotometer was used for all tests. The shielded form of the hollow-cathode source lamp (Perkin-Elmer Corp. lamp number 303-6015) for boron was employed at 30 mA of source current. A wavelength setting of approximately 2500 Å in the ultraviolet region of the spectrum and a slit setting of four were used. A 2-inch nitrous oxide burner head was mounted in the conventional assembly. Burner height and alignment to the signal beam were adjusted to give maximum absorption with a 100-p.p.m. boron standard solution. Optimum sensitivity was obtained with a nitrous oxide flow of 21 liters per minute and an acetylene flow of approximately 12 liters per

minute. When the organic solvent system was employed, the fuel flow had to be reduced appropriately to maintain the inner cone of the flame at a height of approximately 2 inches.

**EXTRACTION SOLUTION.** Several organic systems for extracting boron from aqueous solution have been described by Agazzi (1967), Dean (1960), and Maeck *et al.* (1963). A 5% solution of 2-ethyl-1,3-hexanediol in chloroform proved most effective for use with atomic absorption.

**REAGENTS.** The chemicals used for this analysis were obtained from commercial sources. A 6*N* hydrochloric acid solution was prepared from reagent grade concentrated acid and double deionized water. Reagent grade sodium carbonate was used for all fusions. The 5% 2-ethyl-1,3-hexanediol in chloroform solution was prepared on a volume-to-volume basis from reagent grade chemicals. The aqueous standards containing 5, 10, 25, 50, 75, and 100 p.p.m. boron were prepared from a primary boric acid standard solution.

**PREPARATION OF STANDARD CURVES.** Aliquots of the standards listed above were extracted in a ratio of 1 to 1 with 5% 2-ethyl-1,3-hexanediol by shaking in a closed Nalgene bottle for 20 minutes. The boron-containing organic layer was allowed to separate completely prior to analysis. A working standard curve was obtained from these standards with reference to base line established for the 5% 2-ethyl-1,3-hexanediol in chloroform solution.

## SAMPLE PREPARATION

**Acid Soluble Boron.** Weigh a 2-gram fertilizer sample into a boron-free 300-ml. flask fitted with a ground glass joint. Add 30 ml. of 6*N* HCl to the flask and attach it to a water-cooled condenser. Reflux the digestion solution for 4 hours at 80–90° C. (Do not allow the solution to boil because boron tri-chloride is extremely volatile at temperatures in excess of 100° C.) Transfer the solution to a 100-ml. volumetric flask, filtering if necessary, and dilute to volume with double deionized water. Extract an appropriate aliquot of this solution with 5% 2-ethyl-1,3-hexanediol in a ratio of 2 to 1 (aqueous to organic) and analyze for boron.

**Total Boron.** Weigh 1 gram of the fertilizer sample into a platinum crucible which contains 1 gram of Na<sub>2</sub>CO<sub>3</sub>. Mix these materials thoroughly before adding a layer of approximately 4 grams of Na<sub>2</sub>CO<sub>3</sub>. Fuse the sample for 10 to 20

<sup>1</sup> Present address, Department of Soil and Crop Sciences Department of Agriculture, Texas A&M University, College Station, Texas 77843.

Research and Development Division, International Minerals and Chemical Corporation, Libertyville, Ill. 60048.

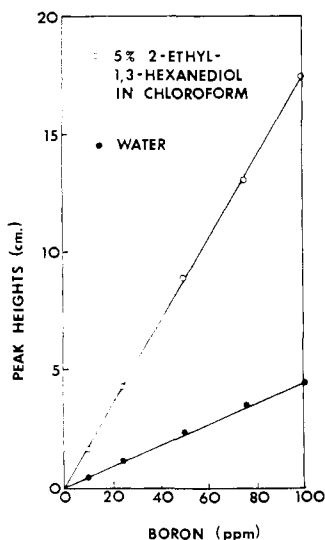


Figure 1. Comparison of the boron standard curve 2-ethyl-1,3-hexanediol in chloroform solutions to that of water solutions

Table I. Operating Conditions for Boron Determination with Perkin-Elmer Model 303 Spectrophotometer

Wave length	B2497.7 Å
Slit setting (mm.)	1 (Position 4)
Lamp current	30 mA
Nitrous oxide	21 liters/minute
Acetylene	~12 liters/minute
Sample uptake	5 ml./min.
Scale expansion	10 ×
Noise suppression	4
Burner height and alignment	adjusted for maximum absorption

Table II. Effects of 1000 P.P.M. of Following Ions on Recovery of 50 P.P.M. Boron

Ion	P.P.M. Boron Recovered
Na <sup>+</sup>	50.0
Ca <sup>2+</sup>	49.1
Fe <sup>3+</sup>	50.0
Mg <sup>2+</sup>	50.0
K <sup>+</sup>	50.5
NH <sub>4</sub> <sup>+</sup>	49.5
Al <sup>3+</sup>	50.0
SO <sub>4</sub> <sup>2-</sup>	50.0
Cl <sup>-</sup>	50.0
PO <sub>4</sub> <sup>3-</sup>	49.8
SiO <sub>3</sub> <sup>2-</sup>	50.0
NO <sub>3</sub> <sup>-</sup>	49.5

Table III. Recovery of Boron from Fertilizers by Atomic Absorption Technique

Fertilizer Grade	Boron, %		Standard Deviation	Standard <sup>b</sup> Addition Recovery, %
	Guarantee <sup>a</sup>	Found		
0-0-60	...	0.000	...	99.7
11-48-0	...	0.000	...	100.5
0-46-0	...	0.006	0.001	101.9
16-8-8	0.02	0.016	0.002	101.8
3-9-18	0.04	0.045	0.002	100.2
6-12-12	0.07	0.075	0.002	101.9
0-20-20	0.56	0.344	0.005	98.1

<sup>a</sup> By manufacturer.

<sup>b</sup> Added 1.260 mg. of B with fertilizer sample prior to fusion with Na<sub>2</sub>CO<sub>3</sub>.

Table IV. Comparison of Data Obtained by Association of Official Agricultural Chemists' Method, Atomic Absorption Spectrophotometric Analysis, and Semiquantitative Emission Spectrographic Analysis

Fertilizer Grade	Guarantee <sup>a</sup>	Boron Content, %		
		A.O.A.C. method	Found by A.A.	Found by emission
0-0-60	...	0.003	0.000	<0.003
11-48-0	...	0.003	0.000	<0.003
0-46-0	...	0.006	0.006	0.01
16-8-8	0.02	0.018	0.016	0.03
3-9-18	0.04	0.038	0.045	0.05
6-12-12	0.07	0.069	0.075	0.09
0-20-20	0.56	0.326	0.344	0.39

<sup>a</sup> By manufacturer.

minutes with an air-natural gas flame, cool, and transfer the resulting fused crystalline mass to a 400-ml. boron-free beaker. Neutralize this mass with 6N HCl and transfer to a 200-ml. volumetric flask and dilute to volume with double deionized water. Extract an appropriate aliquot of the aqueous solution with 5% 2-ethyl-1,3-hexanediol solution and analyze for boron.

**INTERFERING IONS.** Calcium, iron, magnesium, potassium, sodium, ammonium, and aluminum are the main cations present in fertilizers. These ions are usually present as sulfates, chlorides, borates, nitrates, phosphates, or silicates. Solutions containing each of these ions and a known amount of boron were prepared to determine whether they interfered in the boron analysis. For the purposes of this paper, each ion was added at a concentration level of 1000 p.p.m. per 50 p.p.m. of boron in solution. To further test for interferences, fertilizers of varying boron content were analyzed and a per cent recovery was calculated for each fertilizer by the addition of a standard amount of boron.

## RESULTS AND DISCUSSION

No attempt was made to maintain a given acid concentration in the sample solutions, but standard solutions of varying acidity were compared and found to be identical with respect to boron content as long as the pH was kept below 6. Boron values determined in water solution are compared to those in 5% 2-ethyl-1,3-hexanediol in chloroform in Figure 1. As seen from this graph, the organic system increases the sensitivity by more than four times that of the water solutions.

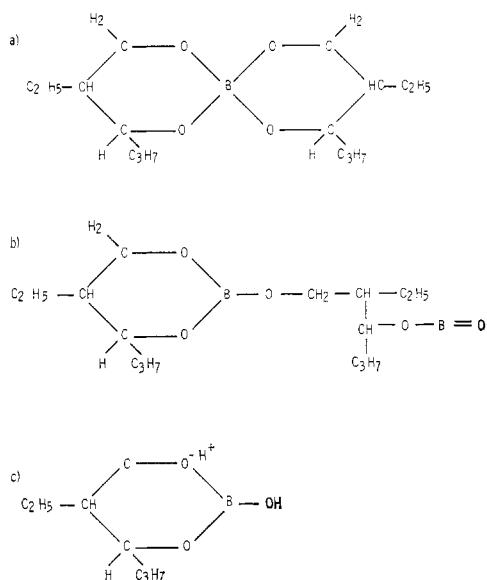
Optimum operating conditions are summarized in Table I; Table II lists interfering ions that might be present in fertilizers and the amount of boron recovered from solutions containing 50 p.p.m. boron and 1000 p.p.m. of the interfering ion. The recovery of boron from seven fertilizers of varying composition is shown in Table III. The data in Tables II and III show that there are no interferences between other ions commonly found in fertilizers and boron. The correlation between this atomic absorption procedure, the standard AOAC acid soluble boron method (1965), and the emission spectrographic technique is shown by the data in Table IV. While the data agree very closely in most instances, deviation is noted in others. This atomic absorption method is in closer agreement with the official AOAC method than is the emission spectrographic technique.

The organic solvent system causes the deposition of carbon on the burner head but this can be removed during operation by occasionally scraping the burner with a spatula.

The sample solutions can be extracted in a 2 to 1 ratio (aqueous to organic) as described in the procedure above or

can be extracted in any ratio from 1 to 1 to 5 to 1 (aqueous to organic) with no observable change in relative concentration values.

Boron is complexed by 2-ethyl-1,3-hexanediol in the following three molecular arrangements:



Nuclear magnetic resonance, low resolution mass spectral analysis, and gas chromatography indicate that all three forms are present to some extent in complexed solution.

Various solvent systems were tried for 2-ethyl-1,3-hexanediol but chloroform gave the highest absorption per p.p.m. ratio for the boron complex.

#### CONCLUSIONS

The method proposed for the atomic absorption determination of boron after its extraction with 5% 2-ethyl-1,3-hexane-

diol in chloroform solution offers a rapid and accurate means of determining boron in fertilizers. This method has no observable interference from the ions commonly found in fertilizers and, as such, should be applicable to all types of fertilizers.

The extraction procedure also eliminates water-soluble salts and refractory complexes which often interfere with atomic absorption spectrophotometry. The low detection limit of 1 p.p.m. boron, as well as the stability of the base line, allows small amounts of boron to be detected. The authors are currently also applying this method to materials outside the fertilizer field.

#### ACKNOWLEDGMENT

The authors are grateful for the technical assistance of Carl Pampel of the Perkin-Elmer Corporation in the development of this method and to Emil Pilior who assisted in the atomic absorption analysis.

#### LITERATURE CITED

- Agazzi, E. J., *Anal. Chem.* **39**, 233-5 (1967).  
 Association of Official Agricultural Chemists, "Official Methods of Analysis," 10th ed., pp. 24-5, 2.092-2.094, 1965.  
 Boltz, D. F., Ed., "Colorimetric Determination of Nonmetals," pp. 339-53, Interscience, New York, 1958.  
 Borland, H., Brownlie I. A., Godden, P. T., *Analyst* **92**, pp. 47-53 (1967).  
 Dean, J. A., "Flame Photometry," McGraw-Hill, New York, 1960.  
 Jackson, M. L., "Soil Chemical Analysis," pp. 370-87, Prentice-Hall, Englewood Cliffs, N. J., 1958.  
 Maeck, W. J., *et al.*, *Anal. Chem.* **35**, 62-7 (1963).  
 Nemodruk, A. A., Karalova, Z. K., "Analytical Chemistry of Boron," Israel Program for Scientific Translations, Jerusalem, 1965.  
 Perkin-Elmer Corp., Norwalk, Conn., "Analytical Methods for Atomic Absorption Spectrophotometry," May 1966.

Received for review March 17, 1969. Accepted July 25, 1969.