Comparative Evaluation of Inductively Coupled Plasma–Atomic Emission Spectroscopy and Colorimetric Methods for Determining Hot-Water-Extractable Boron in Soils

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Abstract: Boron (B) deficiency frequency is increasing in rainfed systems and hence the need to diagnose the deficiency. Colorimetric methods are still widely used in soil testing laboratories in India for measuring B. Little information is available on the comparative evaluation of the colorimetric and inductively coupled plasma (ICP) methods for determining extractable B in soils. We describe results on the comparative evaluation of these methods for measuring extractable B in 57 soil samples with pH ranging from 5.0 to 9.5. There was a significant correlation between B values determined by the two methods and the correlation coefficient was higher for soil samples with pH in the neutral to alkaline range. Interaction between soil samples and methods (ICP or colorimetric) was significant except for soil samples in the pH range of 8.0 to 9.5. Precision for B determination was greater with the ICP than with the colorimetric method.

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INTRODUCTION

The deficiency of boron (B) as a constraint to crop productivity in intensified, irrigated systems has long been recognized (Keren and Bingham 1985; Gupta 1993; Shorrocks

1997; Singh 2004; Rashid et al. 2009). The deficiency of B has been reported especially on light-textured soils, in soils with acidic pH, in soils containing a high amount of calcium carbonate or iron and aluminum oxides and hydroxides, and in soils low in organic carbon (Biggar and Fireman 1960; Okazaki and Chao 1968; Elrashidi and O'Connor 1982; Keren and Bingham 1985; Bloesch et al. 1987; Mandal et al. 2004; Sahrawat et al. 2007; Sarkar et al. 2008).

The review of literature also indicates that in general the deficiency of B can be suspected on coarse-textured soils with low organic matter content, on soils with a pH above 6.0 and on over limed soils (soil pH > 7.0). The availability of B to plants decreases with increasing soil pH, especially soil pH > 6.5. Strongly acid soils (pH < 5.0) also tend to be low in B. Moisture regime, especially wetting and drying has a significant effect on B adsorption and desorption by soils and clay minerals. Also, soil properties, especially exchangeable ion composition, ionic strength of soil solution and temperature have significant effect on B adsorption and availability (Biggar and Fireman 1960; Elrashidi and O'Connor 1982; Keren and Gast 1981, 1983; Keren and Bingham 1985; Bloesch et al. 1987; Mandal et al. 2004; Sarkar et al. 2008)

Little research has been conducted in diagnosing B deficiency in the rainfed systems of the semi-arid tropical India. However, recent survey of farmers' fields in the Indian semi-arid tropics showed a widespread deficiency of B (Rego et al. 2007; Sahrawat et al. 2007). The results showed that several field crops grown on soils having less than 0.58 mg kg^{-1} soil hot water-extractable B, responded to the application of B (Rego et al. 2007).

At the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT), Patancheru, Andhra Pradesh, India) analytical laboratory, we use inductively coupled plasma- atomic emission spectroscopy (ICP-AES) for determining extractable B in soil samples. We have observed that in almost all soil testing laboratories of the national programs in India, the colorimetric method such as azomethine-H colorimetric method (Keren 1996; Sah and Brown 1997) is used for determining extractable B in soils. However, there is little information on the comparative evaluation of ICP and colorimetric methods for determining extractable (available) B in soils. The objective of the present study therefore was to compare the efficacy of ICP-AES method with that of colorimetric method for determining hot water-extractable B in diverse soil samples with a wide range in pH and organic carbon.

MATERIALS AND METHODS

Soil Samples

A total of 57soil samples were selected from a large number of samples for the study to have a wide range in pH (5.0 to 9.5) and organic carbon (0.10 to1.96 g $100g^{-1}$, Table 1). The soils samples generally belonged to Alfisols and Vertisols and associated soils. To enhance the pH range, a few soil samples belonging to Entisols and Ultisols orders were also included. The soil samples were air-dried and pulverized to pass a 2-mm sieve before analysis. For organic carbon (C) analysis, the soil samples were ground to pass a 0.25-mm sieve.

For the soil analysis reported in Table 1, pH was determined in a soil to water ratio of 1: 2; organic C was determined by using the Walkley-Black method (Nelson and Sommers 1996).

Determination of Hot Water-Extractable B in Soil Samples

For determining extractable B in soil samples, 20 g soil sample was refluxed with 40 ml hot water (boiling) for a period of 5 min. One aliquot from the filtered extract was used for measuring B using ICP-AES and a second aliquot was used to determine B using the azomethine-H colorimetric method (Keren 1996). All the analyses were made in three replications (three independent samples were used for each soil sample) and the results reported are mean of three replications.

RESULTS AND DISCUSSION

The soil samples used in the study (Table 1) had a wide range in pH (5.0 to 9.5) and organic C (0.10 to 1.96 g $100g^{-1}$). The results on extractable B in the 57 soil samples analyzed by ICP-AES (ICP-B) and colorimetric (Color-B) methods (Table 2) showed that they had a range in extractable B. There was a highly significant interaction ($p<0.001$) between soil samples and the method used for soil samples with pH in the acidic to neutral range, but the interaction was not significant for the soil samples with pH in the alkaline range (pH 8.0 to 9.5, $n = 21$). These results suggest that soil pH influenced the relationships between ICP-B and color-B; and the correlation coefficient between the values of extractable B by the two methods increased with increase in soil pH (Figures 1, 2 and 3). However, the correlation coefficient (R^2) of extractable B with soil pH was low

($R^2 = 0.2538$, n = 57). The correlation between extractable B and soil organic C was not significant ($R^2 = 0.0518$, n = 57).

The correlation between ICP-B and color-B was highly significant ($R^2 = 0.9701$, n = 57, Figure 4) for all 57 soil samples and the regression equation showing the relationship between Color-B and ICP-B for all the 57 soil samples was as follows:

Color-B = -0.3694 + 1.2331 ICP-B, $R^2 = 0.9701$ (n = 57) (1)

The regression equations for various soil pH groups were as given below.

For soil samples with pH ranging from 5.0 to 6.5, the regression equation was

Color-B = 0.1572 + 0.5477 ICP-B, $R^2 = 0.7655$ (n = 9) (2)

The regression equation for soil samples with pH ranging from 6.5 to 7.9 was

Color-B = -0.3013 + 1.1319 ICP-B, $R^2 = 0.955$ (n = 27) (3)

The regression equation between color-B and ICP-B for 21 soil samples with pH ranging from 8.0 to 9.5 was

Color-B = - 0.4920 + 1.2919 ICP-B, $R^2 = 0.9643$ (n = 21) (4)

These regression equations (1 to 4) can be used to calculate the ICP-B values from the color-B values in soil samples for extractable B. Such results are also useful and required for the calibration of soil tests using ICP-B results in field and greenhouse studies for various crops.

A summary of the results showing the range, mean and SD (standard deviation) for extractable B by the two methods for different soil pH groups (Table 3) showed that the SD was generally lower for the ICP-AES method than the colorimetric method.

It has been indicated that a drawback in the azomethine-H method for soils is the error resulting from suspended or dissolved material which imparts a yellow color to the extract (for review see Keren 1996). To overcome this problem, Wolf (1974) and Gupta (1979) have proposed the use of charcoal to decolorize soil extracts. We also tested the effect of activated charcoal (obtained from Bio-Rad Laboratories, Richmond, CA, USA) addition (0.1 or 0.5 g per sample) on the recovery of added B in the extracts. It was found that the addition of activated charcoal decreased the recovery of B from the solution and the decrease in the recovery of B decreased with increase in the amount of charcoal added from 0.1 to 0.5 g. The recovery of added B without adding charcoal by the azomethine-H colorimetric method ranged from 96.8 to 98.7% (Table 4).

To determine precision in the determination of extractable B by the two methods, two soil samples with extractable B in the low and high range were analyzed in four replications. The results showed that the ICP-AES method provided a better precision than the colorimetric method. The CV for the determination of B for the two samples was greater for the colorimetric method as compared to the ICP-AES method (Table 5).

In summary, the results of our study on the determination of hot water-extractable B in diverse soil samples by the azomethine-H colorimetric and ICP-AES methods suggest that there is a significant interaction between the method and soil samples used for determining B. There was a high correlation between the values of B determined by the two methods and the value of correlation coefficient increased with soil pH. The ICP-AES method provided a better precision than the colorimetric method for the determination of hot water extractable B in the soil samples.

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Table1. Chemical properties of the soil samples used for comparing the colorimetric and ICP-AES methods for determining extractable boron in soils

S.No.	pH	Organic C ($g100g^{-1}$)	S.No	pH	Organic C ($g100g^{-1}$)
1	5.7	0.90	30	7.4	1.13
2	5.3	0.87	31	7.8	0.83
3	5.5	0.85	32	7.6	0.29
4	5.6	1.09	33	6.0	0.27
5	5.7	1.13	34	6.3	0.62
6	5.7	0.57	35	6.4	0.66
7	6.0	1.05	36	6.6	0.49
8	5.6	0.86	37	6.7	0.63
9	5.8	0.66	38	8.2	0.20
10	6.5	0.77	39	8.0	0.10
11	6.9	0.49	40	8.7	0.32
12	7.0	0.34	41	8.5	0.41
13	7.0	0.36	42	8.1	0.77
14	6.8	0.74	43	8.1	0.51
15	6.9	0.40	44	8.2	0.56
16	7.0	0.48	45	9.1	0.39
17	6.8	0.43	46	9.0	0.44
18	6.9	1.07	47	9.4	0.37
19	7.0	0.87	48	8.9	0.31
20	6.7	0.94	49	9.0	0.22
21	7.1	0.37	50	9.0	0.23
22	6.6	0.52	51	9.4	0.30
23	6.8	0.35	52	9.0	0.10
24	7.8	0.34	53	9.5	0.11
25	7.8	0.63	54	9.2	0.46
26	7.3	0.56	55	8.9	0.37
27	7.5	1.46	56	8.9	0.18
28	7.1	1.96	57	8.5	0.33
29	7.4	2.5			

Table 2. Comparative evaluation of colorimetric (Color-B) and ICP-AES (ICP-B) methods for determining extractable boron in 57 soil samples. The values given are mean of three replications± standard deviation.

Sample No.	ICP-B	Color-B	Sample No.	ICP-B	Color-B
	(mg kg^{-1})			(mg kg^{-1})	
1	0.69±0.01	0.66±0.04	30	2.52±0.01	2.90±0.09
2	1.20±0.19	0.78±0.06	31	1.09±0.01	0.80±0.02
3	0.29±0.02	0.19±0.03	32	0.47±0.01	0.38±0.01
4	0.59±0.01	0.57±0.05	33	0.45±0.05	0.31±0.18
5	0.52±0.01	0.49±0.02	34	0.66±0.21	0.51±0.33
6	0.49±0.01	0.37±0.01	35	0.50±0.02	0.30±0.02
7	0.72±0.01	0.58±0.02	36	0.55±0	0.30±0.02
8	0.50±0.01	0.44±0.07	37	4.13±0.02	4.96±0.05
9	0.97±0.06	0.59±0.03	38	2.47±0.01	2.68±0.02
10	0.49±0.03	0.31±0.00	39	1.66±0.02	1.87±0.02
11	0.48±0.00	0.33±0.02	40	1.23±0.02	1.23±0.18
12	0.73±0.04	0.46±0.01	41	2.93±0.01	3.37±0.03
13	0.44±0.08	0.27±0.01	42	2.09±0.02	2.47±0.04
14	0.57±0.03	0.51±0.09	43	1.31±0.07	1.23±0.12
15	0.75±0.04	0.41±0.02	44	3.20±0.01	3.27±0.22
16	0.59±0.01	0.37±0.01	45	2.01±0.04	2.02±0.12
17	1.43±0.05	0.97±0.02	46	1.79±0.03	1.23±0.03
18	0.66±0.01	0.48±0.01	47	3.40±0.03	4.20±0.18
19	0.63±0.07	0.54±0.03	48	5.11±0.29	6.11±0.01
20	2.73±0.07	2.79±0.05	49	0.69±0.29	0.69±0.01
21	3.30±0.09	3.79±0.04	50	3.84±0	4.98±0.02
22	0.64±0.09	0.67±0.05	51	1.36±0.08	1.24±0.15
23	0.82±0.07	0.47±0.16	52	4.36±0.05	5.21±0.05
24	0.90±0.05	0.45±0.13	53	1.39±0.04	1.40±1.39
25	0.61±0.38	0.62±0.03	54	1.82±0.02	1.72±1.82
26	2.32±0.02	2.05±0.01	55	2.91±0.02	2.55±2.91
27	1.63±0.02	1.31±0.50	56	0.80±0.03	0.81±0.80
28	1.03±1.19	0.72±0.23	57	1.95±0.01	1.61±1.95
29	1.50±0.16	1.07±0.09			

Table 3. Comparison of colorimetric (Color-B) and ICP-AES (ICP-B) methods for determining extractable B in 57 soil samples grouped according to soil pH

No of samples	pH	ICP-B			Color-B		
		Range	Mean	SD	Range	Mean	SD
9	5.0-6.4	0.29-1.20	0.66	1.16	0.19-0.78	0.52	1.46
27	6.5-7.9	0.44-3.30	0.97	0.27	0.30-3.79	0.81	0.17
21	8.0-9.5	0.69-5.11	2.12	0.79	0.69-6.11	2.25	0.91
57	5.0-9.5	0.29-5.11	1.49	1.23	0.69-6.11	1.47	1.62

Table 4. Recovery of extractable B with and without the addition of activated charcoal as determined by the azomethine-H colorimetric method. The results reported are means of three replications

B added (mg L^{-1})	Charcoal added (g)	B recovered	
		mg L^{-1}	%
0.32	0	0.31	96.8
	0.1	0.13	40.6
	0.5	0.08	25.0
0.80	0	0.79	98.7
	0.1	0.50	62.5
	0.5	0.34	42.5

Table 5. Precision in the determination of extractable B in two soil samples low and high in B by the ICP-AES (ICP-B) and colorimetric (Color-B) methods. Each soil sample was analyzed in four replications

	Color-B	ICP-B
	(mg kg^{-1})	
Sample No. 1		
Range	0.26-0.31	0.20-0.22
Mean	0.28	0.21
SE	0.01	0.01
CV (%)	6.38	5.50
Sample No. 2		
Range	5.06-5.15	6.07-6.15
Mean	5.10	6.11
SE	0.01	0.01
CV (%)	0.85	0.61

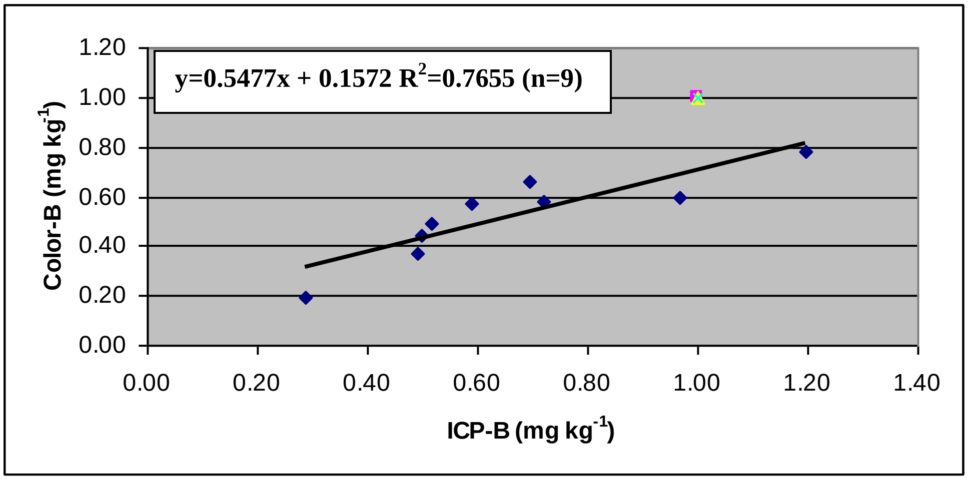

Figure 1. Relationship between ICP-B and Color-B in 9 soil samples with pH ranging from 5.0 to 6.5

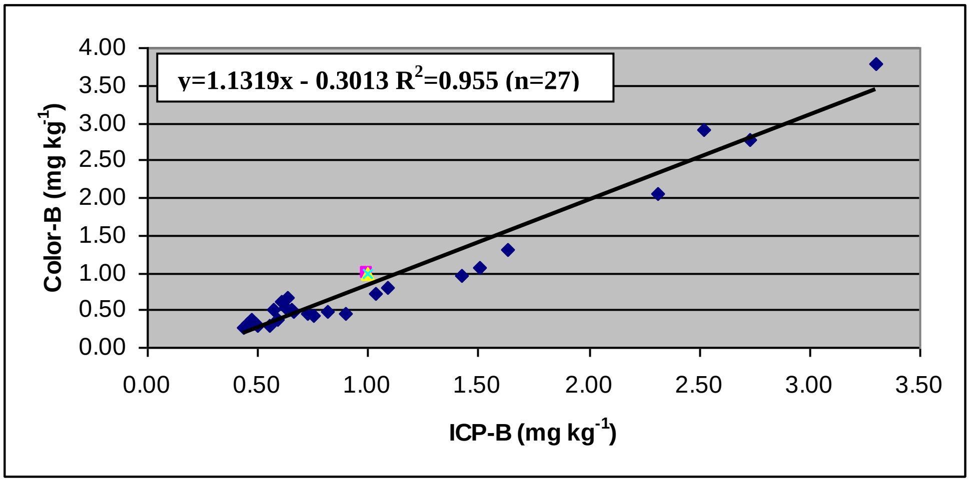

Figure 2. Relationship between ICP-B and Color-B in 27 soil samples with pH ranging from 6.5 to 7.9

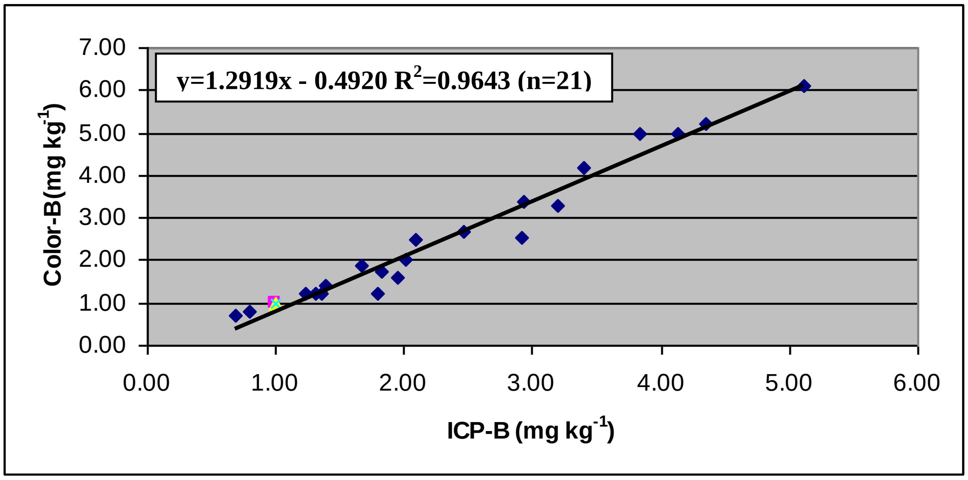

Figure 3. Relationship between ICP-B and Color-B in 21 soil samples with pH ranging from 8.0 to 9.5

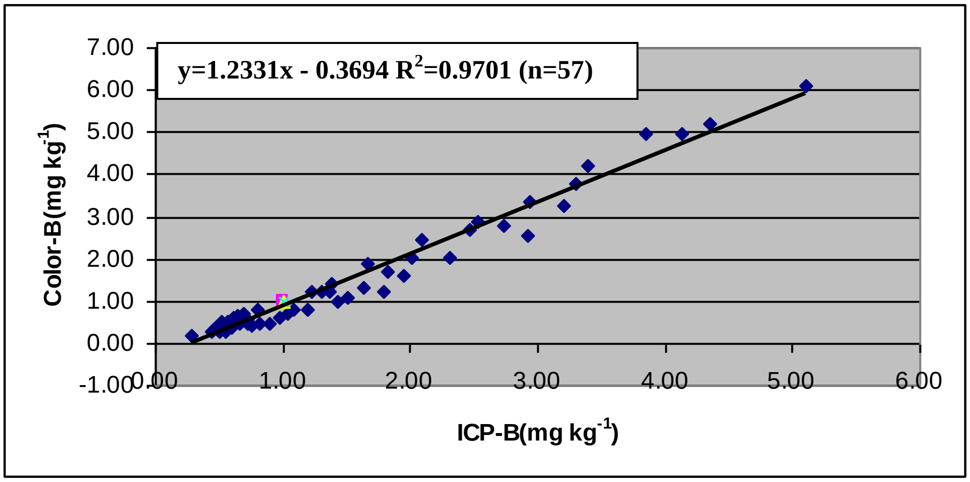

Figure 4. Relationship between ICP-B and Color -B in all 57 soil samples with pH ranging from 5.0 to 9.5.