Short Communication

Comparative Evaluation of ICP-AES and Turbidimetric Methods for Determining Extractable Sulfur in Soils

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The deficiency of sulfur (S) as a constraint to crop productivity in irrigated, intensified systems has long been recognized (Kanwar 1972; Pasricha and Fox 1993; Singh 2001). A recent survey of farmers' fields in the Indian semi-arid tropics (SAT) demonstrated that the deficiency of S, as a constraint to crop production and productivity, is also equally widespread in the rainfed production systems (Rego *et al.* 2007; Sahrawat *et al.* 2007). The results of this research further showed that soil testing was effective in diagnosing S deficiency; and the crops grown on farmers' fields with calcium chloride extractable-S levels of less than 8-10 mg kg^{-1} soil responded positively to the application of sulfur (Rego *et al.* 2007).

At the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT) central analytical services laboratory at Patancheru, Andhra Pradesh, we determine the extractable (available) S in soil samples by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). However, because of cost consideration in procuring an ICP-AES and also the cost involved in the conduct of analysis, the turbidimetric method of S determination in soil, water and plant samples (Jackson 1958; Beaton *et al.* 1968) is still widely used in laboratories especially in the developing countries including India. There is no information on the comparative evaluation of the turbidimetric method with ICP-AES for determining extractable S in soil samples. The objective of this research therefore, was to compare the values of extractable (available) S measured by ICP-AES and turbidimetric methods using diverse soil samples having a wide range in pH.

To compare the efficacy of turbidimetric method with that of ICP-AES method, a total of 80 soil samples were selected (Sahrawat *et al*. 2009). The surface soil samples (0-15 cm layer) were collected from fields under diverse crop production systems in India. The soil samples had a wide range in pH (5.0 to 8.3) and extractable S.

To measure extractable (available) S, the soil samples (10 g) were extracted with 50 mL of 0.15% calcium chloride ($CaCl_2$) by shaking the contents in Nalgene bottles for 30 min. The filtered extracts were analyzed for sulfur by ICP-AES (Tabatabai 1996) and turbidimetry (Subba Rao 1993). In the turbidimetric method, sulfate in the extract was measured by converting it to barium sulfate suspension by using barium chloride fine crystals (<20-30 mesh); and the resulting turbidity was measured at 340 nm on a spectrophotometer (Subba Rao 1993). All the soil samples were analyzed in triplicate and the mean values of three replications are reported.

Regression analysis was carried out to establish relationship between the values of extractable S obtained by ICP-AES (ICP-S) and turbidimetric (Turbid-S) methods for all the 80 samples, and also for soil samples grouped according to pH in the acidic, neutral and alkaline range.

The results of analysis of 80 soil samples for S extracted by 0.15% calcium chloride solution (sulfate-S) and determined by ICP-AES (ICP-S) and turbidimetric (Turbid-S) methods showed that the ICP-S values varied from 1.2 to 32.6 mg kg^{-1} of soil, while the Turbid-S values ranged from 4.2 to 32.5 mg kg^{-1} soil. In general, the Turbid-S values were high than the ICP-S values in soil samples with different pH (5.0-5.9, 6.0-6.9, 7.0-7.9 and >8.0) groups (Table 1).

The regression analysis between the ICP-S and Turbid-S values for all the 80 samples (Fig. 1) showed that there was a significant (R^2=0.621 p<0.01,

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Table 1. Results of analysis of 80 soil samples for extractable S by ICP-AES and turbidimetric methods. The values presented are mean of three replications± SD

Sample No.	ICP-S	Turbid-S	Sample No.	ICP-S	Turbid-S
	(mg kg⁻¹)			(mg kg⁻¹)	
1	1.9±0.30	6.7±0.09	41	13.1±1.03	15.0±2.07
2	1.7±0.09	6.0±0.15	42	9.2±0.29	14.4±0.09
3	9.1±0.35	12.0±0.23	43	11.1±0.24	16.9±0.23
4	7.4±0.20	9.6±0.26	44	6.8±0.48	11.3±0.43
5	1.3±0.06	5.3±0.09	45	11.0±0.15	15.6±0.17
6	2.6±0.25	6.6±0.23	46	8.8±0.38	13.6±0.34
7	4.9±0.12	8.4±0.09	47	7.3±0.36	12.7±0.39
8	1.6±0.06	5.4±0.45	48	11.1±0.09	15.7±0.15
9	2.9±0.68	6.4±0.09	49	15.1±0.03	21.3±0.09
10	1.4±0.03	4.7±0.00	50	10.9±0.25	17.2±0.60
11	5.7±0.52	12.3±0.60	51	9.6±0.20	14.6±0.61
12	1.2±0.33	6.1±0.09	52	10.2±1.55	16.2±0.60
13	3.5±0.05	8.8±0.53	53	3.0±0.24	5.9±0.43
14	5.5±0.85	11.6±0.00	54	4.4±0.40	6.0±0.00
15	11.0±0.25	14.5±0.00	55	2.9±0.13	5.1±0.31
16	3.4±0.48	8.4±0.31	56	6.7±0.32	10.1±0.00
17	11.4±0.19	15.6±0.17	57	8.2±0.28	14.2±0.15
18	16.2±0.20	19.8±0.77	58	32.6±0.26	32.5±0.17
19	5.2±0.44	11.1±0.09	59	18.6±0.64	21.8±0.60
20	3.0±0.14	8.4±0.31	60	9.0±0.10	11.9±0.53
21	23.6±1.30	23.2±0.59	61	3.0±0.21	11.1±0.39
22	3.9±0.02	8.9±0.98	62	3.6±0.38	11.5±0.31
23	15.5±0.34	16.3±0.17	63	3.3±0.26	11.1±0.37
24	3.1±0.38	6.8±0.64	64	3.1±0.30	12.2±0.82
25	4.6±0.16	7.1±0.00	65	2.5±0.16	11.9±0.26
26	9.6±0.20	12.8±0.94	66	2.7±0.07	11.7±0.23
27	10.9±0.26	15.3±0.60	67	2.8±0.08	13.5±0.23
28	6.5±0.31	9.4±1.15	68	3.3±0.06	12.7±0.15
29	4.0±0.46	7.1±0.97	69	3.1±0.11	13.1±0.09
30	4.6±0.28	7.1±0.39	70	3.3±0.13	12.3±0.17
31	4.6±0.26	8.7±0.17	71	3.0±0.23	15.1±0.23
32	4.7±0.29	7.8±0.44	72	3.2±0.12	12.9±0.15
33	3.2±0.57	5.2±0.67	73	3.9±0.09	15.7±0.17
34	5.8±0.31	8.1±0.15	74	3.3±0.06	15.9±0.23
35	3.8±0.24	4.2±0.68	75	3.4±0.09	16.6±0.09
36	3.2±0.69	5.2±0.43	76	2.9±0.07	15.7±0.00
37	3.7±0.61	8.2±1.71	77	3.4±0.09	16.6±0.09
38	5.2±0.49	7.6±0.39	78	2.5±0.16	11.9±0.26
39	5.5±0.54	7.1±0.74	79	3.3±0.26	12.9±0.26
40	3.7±0.36	6.4±0.60	80	3.0±0.23	15.1±0.55
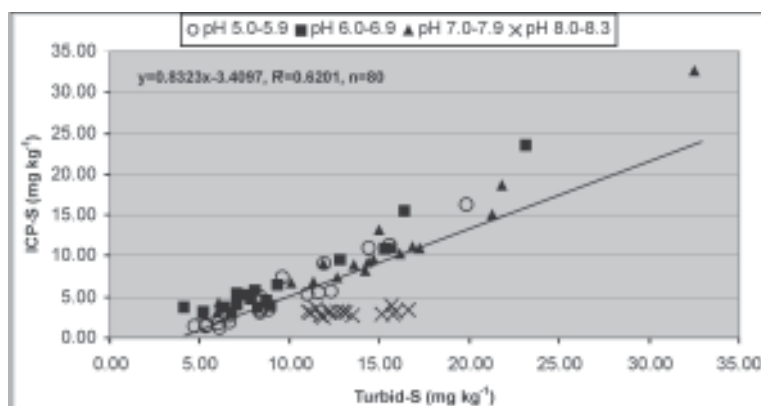
Fig.1. Relationship between ICP-S and Turbid-S in 80 soil samples with pH ranging from 5.0-8.3.

n = 80) positive relationship between the values of extractable S by the two methods. However, the scatter of the points (Fig. 1) with various pH groups of soils clearly showed that soil samples with pH > 8.0 were the outliers. The correlations between ICP-S and Turbid-S for soil samples with pH ranging from 5.0-5.9, 6.0-6.9 and 7.0-7.9 pH groups were highly significant (p< 0.01). However, the correlation between ICP-S and Turbid-S was not significant (R^2=0.12, NS, n=20) for a group of 20 soil samples with pH >8. The regression analysis of ICP-S on Turbid-S for all the 80 samples showed that the correlation (R^2=0.62 p<0.01, n=80) was significant. The correlation coefficient (R^2) between ICP-S and Turbid-S improved from 0.62 to 0.92 (n=60) when the soil samples with pH >8.0 were excluded in the regression analysis. For the 20 soil samples with pH>8.0, the mean value of extractable S by the turbidimetric method (13.5 mg kg^{-1} soil) was over three times greater than that obtained by the ICP-AES method. The results were confirmed by a repeat-replicated analysis of the soil samples.

The regression equations between the two methods for different groups of soil samples were as follows:

Samples with pH 5.0-5.9, ICP-S = 0.986 Turbid-S – 4.226 (R^2=0.92, p<0.01, n=20)   …(1)

Samples with pH 6.0-6.9, ICP-S = 1.075 Turbid-S – 3.3097 (R^2=0.93, p<0.01, n=20)   …(2)

Samples with pH 7.0-7.9, ICP-S = 1.007 Turbid-S – 4.2280 (R^2=0.92, p<0.01, n=20)   …(3)

Samples with pH 5.0-7.9, ICP-S = 0.989 Turbid-S - 3.579 (R^2=0.91, p<0.01, n=60)   …(4)

Samples with pH 8.0-8.3, ICP-S = 2.313 Turbid-S + 0.0596 (R^2=0.12, NS, n=20)   …(5)

For all 80 samples, ICP-S = 6.96 + 0.745 Turbid-S (R^2=0.62, p<0.01)   …(6)

For comparing the accuracy of the ICP and turbidimetric methods of determining extractable sulfate-S, the recovery of added sulfate-S in wide range of concentrations to the extracts was studied. The results showed that the recovery of the added sulfate-S by the ICP method varied from 90 to 105% with a mean vale of 99%. The recovery of the added sulfate-S by the turbidimetric method ranged from 93 to 108% with a mean value of 101%. The recovery of the added sulfate was near complete when added in the range of 5-10 mg L^{-1}.

The precision (evaluated by testing the repeatability of the analysis in lower and higher range of sulfate-S) showed that the two methods were comparable and equally precise as measured by mean, SE

and CV, but in the case of soil samples with extractable S in the lower range, the turbidimetric method was less precise than the ICP-AES method (results not presented). However, in general both methods were less precise in the lower than in the higher extractable S range (Table 1). These results show that the best results are obtained especially by the turbidimetric method when the extractable S values in the extract are not in the lower range. In such situations, perhaps higher amounts of soil can used to bring the concentration of sulfate-S in the extract in the optimum range. Even the ICP-AES method gave a lower precision for extractable S in the lower than in the higher concentration range (Table 1). This observation is important as a number of soils in the semi-arid tropical regions of India are low to very low in the extractable or available S (Sahrawat *et al.* 2007).

We observed interference in the determination of sulfate-S by the turbidimetric method in calcareous soils and this needs further investigation. Probably, during the estimation of sulfate-S in the extracts by the turbidimetric method in soil samples with pH > 8 results in the formation of barium sulfate and barium carbonate, resulting in the over-estimation of extractable (available) sulfate by the turbidimetric method.

In conclusion, this study on the comparative evaluation of ICP-AES and turbidimetric methods for extractable-S (sulfate) determination showed that the results obtained by the two methods were in close agreement for soil samples with pH varying from 5.0 to 7.9. However, the correlation between the values obtained by the two methods was not significant for soil samples with pH 8.0 or higher. And the ICP-S and Turbid-S were comparable in precision for soil samples relatively high in extractable S, but ICP-AES method gave a better precision than that obtained by the turbidimetric method for soil samples very low in extractable S.

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