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SIMPLEX OPTIMIZATION OF INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY FOR DETERMINATION OF BORON IN WATER

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1. Introduction

The curcumin (U.S.EPA 212.3) method has been used for years for the determination of boron in water samples. But, this analytical procedure, due to considerable interferences of diverse elements, is quite complex. Therefore, another approach which gained wide acceptance as an alternative to spectrophotometry, uses inductively coupled plasma atomic emission spectroscopy (ICP-AES) for the determination of boron. In order to achieve the maximum sensitivity in ICP-AES measurements, the operating parameters have to be set up properly.

The optimization procedure consists of varying of the ICP-AES operating parameters until an optimum condition is reached. To conduct the optimization one may resort to the traditional "trial-and-error" approach or a systematic way, such as the implementation of the simplex method [1,2]. Using this method is a fast way to find the optimal values for the experimental variables.

The aim of the present work was to optimize the ICP-AES operating parameters in order to measure boron concentration in water samples.

2. Experimental

All measurements were made directly at 249.678 and 249.773 nm emission lines with a standard configuration of the Perkin-Elmer ICP/6500 system. Milli-Q treated water and chemicals of reagent grade were used throughout the study. The boron concentration was 0.35 mg/L. The following parameters were optimized: forward power (FP), viewing height (H), sample flow rate (VS), nebulizer gas flow rate (VN), auxiliary gas flow rate (VA), and plasma gas flow rate (VP). The algorithm used for the simplex optimization was based on the modified simplex method of Nelder and Mead [3]. All calculations were performed on a Pentium PC using a laboratory-written Mathcad program.

3. Results and discussion

As six ICP-AES parameters were to be varied simultaneously, the initial simplex consisting of the first seven vertices was established by the first design matrix of coordinates. Of a number of different objective functions proposed in ICP-AES, based on the detection limit, the net line signal or signal to background ratio (SBR), SBR was chosen in this study to evaluate the system response. The simplex was moved in the direction given by the rules of the variable-size simplex algorithm, including reflection, expansion and contraction vertices. The obtained data from the sequential simplex procedure are presented in Table 1. The simplex progressed toward the optimum SBR value as shown in Fig. 1. A total of 15 trials was made, and SBR increased from 6.28 in the first simplex to the best value of 10.7 in the last one - an improvement of 59 %. The experiment that gave the best result for the variables of the ICP-AES system used was 9, while the complete procedure was finished with 15 trials.

Table 1. Data obtained from simplex optimization

No.	FP (kW)	VP (psi)	VA (psi)	VN (psi)	VS (ml/min)	H (mm)	T*	SBR
1	0.80	10.0	0.3	0.2	0.65	5.0	I	1.73
2	1.70	11.9	0.7	0.5	0.78	11.8	I	0.00
3	0.99	19.0	0.7	0.5	0.78	11.8	I	0.84
4	0.99	11.9	2.3	0.5	0.78	11.8	I	4.76
5	0.99	11.9	0.7	1.4	0.78	11.8	I	6.28
6	0.99	11.9	0.7	0.5	1.24	11.8	I	5.73
7	0.99	11.9	0.7	0.5	0.78	36.5	I	0.22
8	0.80	13.7	1.1	0.7	0.89	17.8	R	3.36
9	0.80	10.0	1.8	1.1	1.11	8.0	E	10.7
10	0.99	14.9	2.4	1.5	1.28	17.1	R	2.84
11	0.90	12.4	0.7	1.5	1.30	6.8	R	9.43
12	0.87	12.6	2.2	1.5	0.94	5.1	R	8.41
13	0.83	12.8	2.5	1.1	1.30	5.0	R	6.29
14	0.87	12.6	2.2	1.2	1.29	5.1	CR	9.20
15	1.10	12.5	2.5	1.2	1.29	5.1	CW	9.15

*T - vertex type: I = initial; R = reflection; E = expansion; CR = positive contraction; CW = negative contraction.

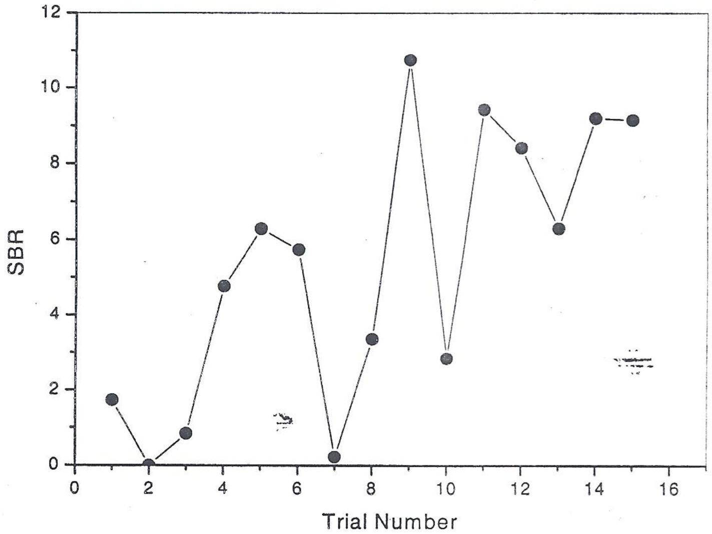

Fig.1. Relationship between SBR and the experiment number during simplex optimization of ICP-AES.

The ICP-AES method gave a linear response for the boron concentration in the range up to 20 ppm (r=0.999). A detection limit (3 SDR) of 0.1 μg/L, with a precision of RSD < 9 %, and typical recoveries of 94 to 108 % from spiked water samples were obtained. The method has been successfully applied to routine analyses of water samples in our Laboratory.

4. Conclusion

It has been shown that the simplex method may provide a viable option for the optimization of an ICP-AES system. The variables were optimized leading to a decrease in viewing height, and an increase in sample uptake rate, and auxiliary and nebulizer gas flow rates. Optimization was achieved with a relatively small number of experiments, therefore, experimentation time was decreased with respect to univariant methods. The optimized method is suitable for the determination of boron in routine water analysis.

5. References

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