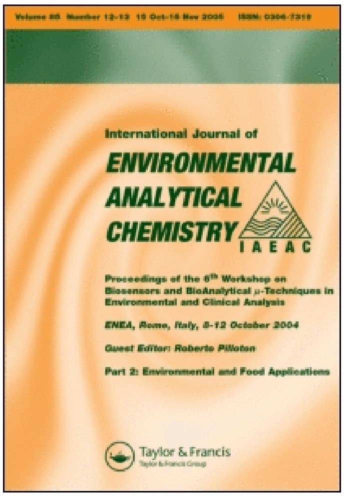

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The Determination of Boron by Inductively Coupled Plasma Atomic Emission Spectroscopy. Part 1: Method Development

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The use of inductively coupled plasma atomic emission spectroscopy (ICP-AES) for trace determination of boron was investigated. Usable spectral lines occur both in the normal air and vacuum ultraviolet regions of the spectrum. Optimization of instrumental parameters and a study of interferences were carried out. Good sensitivities were achieved, however, an unexpected memory effect in the torch-nebulizer system and calibration drifts were experienced. These problems, together with line and background interferences emphasize the need for careful investigation when developing new analytical schemes with ICP-AES.

KEY WORDS: Boron, inductively coupled plasma atomic emission spectroscopy, method development.

INTRODUCTION

In the past, detailed studies of boron levels in environmental samples have been hampered by the lack of fast, simple, sensitive and precise analytical techniques. Methods used for the determination of this element have been reviewed by Gladney *et al.*[1] and included are colorimetry, atomic absorption and emission spectroscopy, selective ion electrodes, mass spectrometry and neutron-prompt γ-ray spec-

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trometry. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is increasingly becoming a widely used technique and methods for the determination of boron in various samples have been developed, for example: boron in steels;[2,3] geological materials;[4] soil extracts[5] and plants.[6] ICP-AES is a relatively new technique and since analytical results may be severely biased by numerous, often unpredictable interferences, great care is required when developing analytical methods, especially when dealing with complex samples like rocks, coal and coal ashes, or liquid samples containing high dissolved salt concentrations. In this report an account of preliminary investigations made is given, including the problems and interferences experienced.

EXPERIMENTAL

Instrumentation

At the beginning of the study, samples were analysed with an IL Plasma-100 ICP spectrometer fitted with two standard monochromators. Subsequently an IL Plasma-200 ICP spectrometer fitted with both a standard monochromator and a scanning vacuum monochromator was used. A line printer (IL) was used to record the analytical data and a video printer (Axiom Ex-850) to record video displays. The IL Plasma-100 ICP has been described by Smith *et al.*[7] Details of the operating conditions appear in Table I.

Investigations of operating conditions

The general steps for developing an analytical method using ICP-AES are outlined in Table II. Aqueous boron standards were prepared by dissolving high purity boric acid ("Aristar" grade, BDH Chemicals Ltd., England) in water, from a Milli-Q-system (Millipore Corporation).

Boron has a relatively high ionization potential and has a simple spectrum with only a few neutral atom lines when excited in the ICP.[2] The following lines have been identified and spectral scans near these wavelengths are shown in Figure 1.

TABLE I

ICP operating conditions (IL Plasma-200)

RF power supply	27.12 MHz, 1–1.6 kW, selectable in six steps 1 to 6 corresponding to 1.0, 1.1, 1.2, 1.2, 1.4 and 1.6 kW respectively
Optical system	
(a) Standard monochromator	
Primary monochromator	$\frac{1}{3}-m$ Ebert–Fastie configuration
Premonochromator	$\frac{1}{6}-m$ Ebert–Fastie configuration
Operating range: 1st order	190–365 nm
2nd order	365–900 nm
Resolution	0.02 nm (2nd order)
(b) Vacuum monochromator	
Operating range	160–300 nm
Resolution	0.02 nm (1st order)
Peak search window width	0.033, 0.067, 0.100 nm (user selectable)
Observation height	0 to 48 mm above RF coil for air monochromator, selectable for each elemental line. For vacuum monochromator, fixed observation height for each analytical program
Torch and sample introduction system	
Torch (three concentric quartz tubes)	
Plasma coolant gas flowrate	$13\,l\,min^{-1}$ for power settings 1 to 3 and $18\,l\,min^{-1}$ for power settings 4 to 6
Polypropylene spray chamber and cross-flow nebulizer with synthetic sapphire capillaries	
Carrier gas flow rate	0.35 to $0.45\,l\,min^{-1}$
Sample feed rate	0.1 to $2.2\,ml\,min^{-1}$ (peristaltic pump)

$$\left.\begin{array}{ll}249.77, & 249.68\,\mathrm{nm}\\ 208.96, & 208.89\,\mathrm{nm}\end{array}\right\}\mathrm{uv}$$

$$\left.\begin{array}{ll}182.64, & 182.59\,\mathrm{nm}\\ & 181.84\,\mathrm{nm}\end{array}\right\}\mathrm{vacuum\ uv}$$

The vacuum monochromator resolution is seen to be lower than that of the standard monochromator.

TABLE II
Method development

(1) Sample preparation
    grinding, drying, sieving, dissolution or fusion-dissolution, filtration

(2) ICP-AES analytical programme
    —Preparation of suitable aqueous standards
    —Choice of spectral line(s)
    —Choice of instrumental parameters (optimization)
    —Determination of analytical characteristics
      (e.g., detection limits, upper concentration limits, sensitivities)
    —Interference studies
    —Precision of analytical instrumental procedures

(3) Evaluation of the complete method (accuracy)
    —Calibration of instrument
    —The use of standard reference material
      (e.g., National Bureau of Standards)
    —Studies of possible contamination or losses of analyte

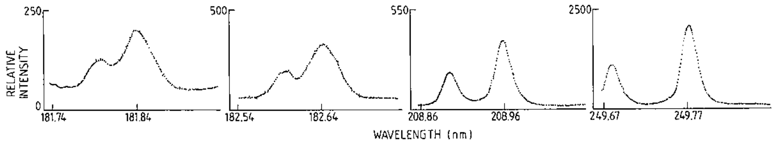

FIGURE 1 Spectral scans near boron lines.

Boron standard solutions were used to optimize instrumental conditions. The effects of varying the RF power, the carrier gas flow rate, the sample feed rate and the observation height in the plasma were studied and some of the effects are illustrated in Figures 2 to 5. These parameters are interdependent and changing one may well affect the optimal conditions for the others. Figure 2 shows plots of the peak at 249.77 nm when the RF power is changed keeping the other parameters constant. A background shift is seen to occur, however, the line to background ratio increases more rapidly with increasing power.

Figures 3 and 4, show the variation of the line-to-background ratio (I_N/I_B) and the blank signal (from water) with the carrier gas flow rate and the sample feed rate respectively.

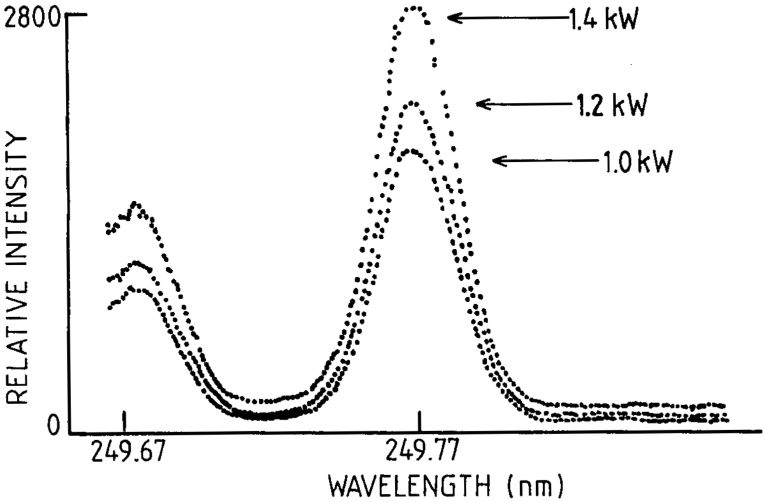

FIGURE 2 Effect of the RF power (carrier gas flow rate 0.40 l min^{-1}, sample feed rate 1 ml min^{-1}, observation height 14 mm).

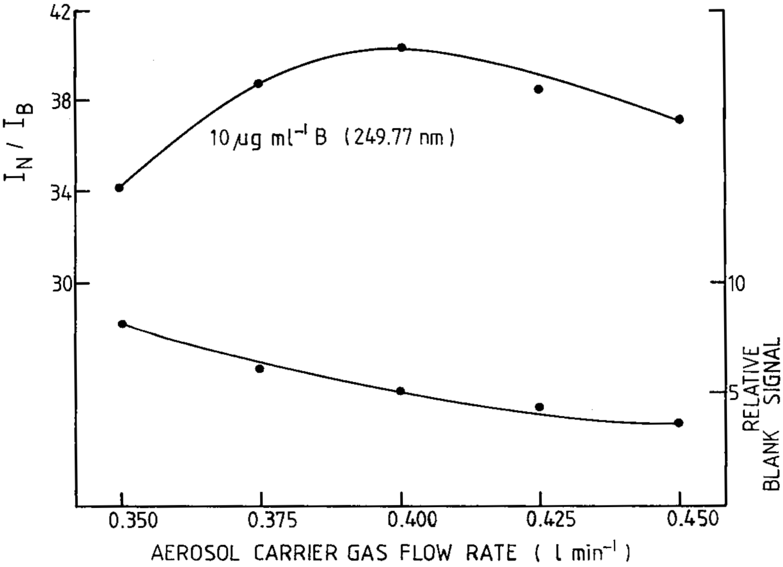

FIGURE 3 Effect of carrier gas flow rate (RF power 1.2 kW, sample feed rate 1 ml min^{-1}, observation height 14 mm).

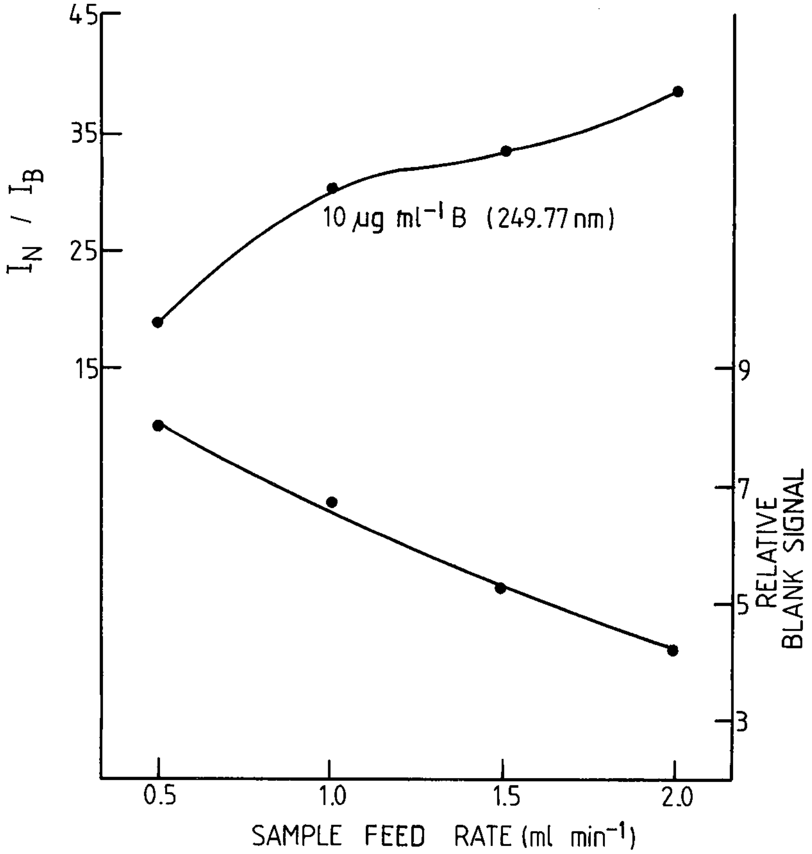

FIGURE 4 Effect of sample feed rate (RF power 1.2 kW, carrier gas flow rate 0.40 l min^{-1}, observation height 14 mm).

In Figure 5 the boron emission intensity is plotted against the observation height measured above the RF coil in the plasma at two different carrier gas flow rates (0.40 l min^{-1} and 0.45 l min^{-1}). As with most elements, the highest emission intensities are usually found between 12 and 20 mm above the coil depending on the power used and the carrier gas flow. The alkali metals, however, emit strongly lower in the plasma.

Using the best conditions for boron determination in aqueous solutions (sample feed rate 1 ml min^{-1}, RF power 1.2 kW, carrier gas

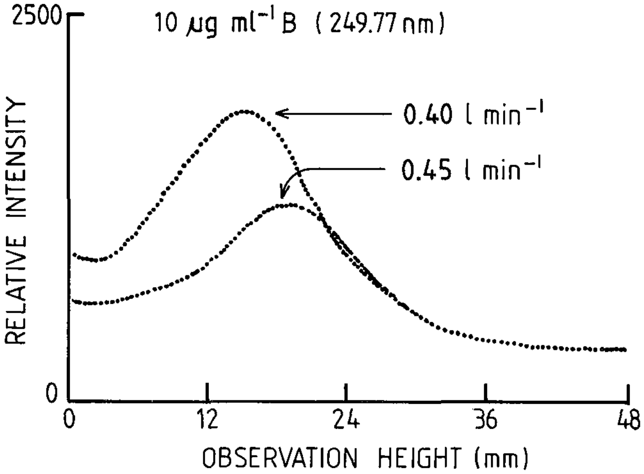

FIGURE 5 Intensity profile in the plasma at carrier gas flow rate of 0.40 and 0.45 l min^{-1} (RF power 1.2 kW, sample feed rate 1 ml min^{-1}).

flow rate 0.40 l min^{-1}, viewing height 14 mm for all lines used in the standard monochromator while in the vacuum monochromator, the viewing heights were adjusted manually by moving the monochromator for maximum sensitivity), the analytical characteristics i.e., the detection limit, (C_L) and the line to background ratios were established. Results are listed in Table III. The background intensities were taken as the signals obtained when aspirating the blank (water). It must be noted that the values (Table III) are substantially

TABLE III

Line-to-background ratio (I_N/I_B) and 3σ detection limits (C_L) for prominent ICP boron lines

Wavelength (nm)	I_N/I_B (for 10 μg ml^{-1})	C_L μg ml^{-1}
249.77	40.8	0.005
249.68	29.6	0.007
208.96	25.9	0.009
208.89	14.1	0.012
182.64	15.8	0.008
181.84	4.6	0.05

affected by the type of sample analysed, for example those containing high concentrations of dissolved salts, relatively high concentrations of easily ionizable elements like sodium and potassium which enhance or depress signals depending on the instrumental parameters used and high acid concentrations which can also cause signal depressions.

From Table III, boron determination appears to be relatively sensitive and in principle its determination at low levels should be both accurate and precise. However, many problems were encountered. Apart from spectral interferences discussed below, background interferences, drift and memory effects in the nebulizer-torch system required detailed investigations before satisfactory analytical schemes could be obtained.

One unexpected problem was persistently high boron signals from blank solutions following the aspiration of more concentrated boric acid solutions (up to 5% w/v dissolved H_3BO_3). Aspiration of water and dilute hydrofluoric acid (to complex the boron) for long periods of time only partially removed this "memory" effect. The problem was finally resolved by soaking the entire assembly (nebulizer and torch) in 10% (v/v) aqueous detergent ("Contrad", Hickman and Kleber, South Africa) for 48 hours. Cleaning was accelerated with an ultrasonic bath. A white material was present on the tip of the sample injection tube. Traces of a crystalline material were also present in the region where the torch was connected to the spray chamber. It is possible that these deposits contained boron and released the element continuously in the plasma. These findings emphasize the importance of regular disassembly and cleaning of the torch/nebulizer; simple aspiration of a blank does not always suffice.

Instrumental drift is frequently reported causing poor accuracy and precision. The precision is governed by the stability of the different components of the instrumentation, viz. the optical system, the RF generator and the sample introduction system. The latter is considered to be critical for determining precision in ICP analyses. Samples containing high concentrations of dissolved salts e.g. 5% w/v, give signals with much fluctuation and which decrease with increasing aspiration times, until finally the nebulizer or the injector tip orifice becomes blocked. Addition of a surfactant (about 0.05% w/v Triton X-100) to the sample solution reduces these problems, probably by enhancing aerosol formation and transport of fine droplets to the torch. It is therefore common practise in our laboratory to add this surfactant to all solutions prepared for ICP-AES analysis. A method to improve analysis when drift or memory is experienced is that of an "alternating blank routine".[8] The average blank concentrations measured before and after each sample are subtracted from the measured concentration of the sample. Although time consuming, the advantages of this procedure are: (a) Reduction of errors due to carry-over from previous samples (memory); (b) Reduction of background drift errors; (c) Reduction of the importance of the calibration blank.

Instrumental drift is illustrated in Figure 6. The instrument was calibrated with a 1 μg ml^{-1} boron standard and a blank and these were analysed alternately over a period of one hour. The systematical decrease in both the blank and the 1 μg ml^{-1} standard could be caused by: (i) an improperly stabilized plasma; (ii) a boron contaminated system; (iii) by gradual blocking of the nebulizer. The apparent drift (Figure 6) appeared to be due to a small memory effect during calibration since high boron solutions were aspirated prior to calibration and the washing time before the blank was aspirated was too short. Our system requires about 50 sec washing time at 2.2 ml min^{-1} when determining boron. The plasma is allowed to stabilize for about 10 minutes prior to analysis and after making changes e.g. in power levels or carrier gas flow.

Interferences

The choice of spectral lines is often limited by interferences especially

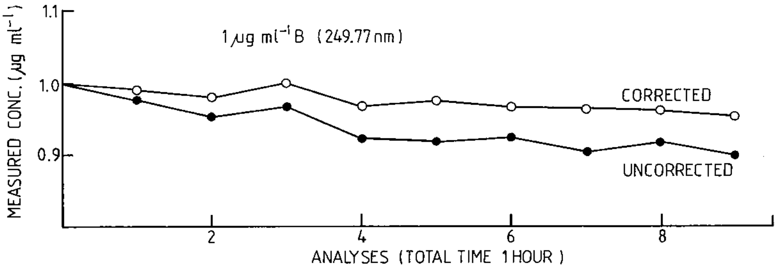

FIGURE 6 Calibration drift observed after successive alternate analyses of a water blank and a 1 μg ml^{-1} B standard. The use of the "alternating blank" routine is shown to decrease the errors of measurements.

for trace element determination in complex matrices therefore these interferences must first be investigated and evaluated for each analyte in each type of sample. Some of the interferences identified with the boron spectral lines are illustrated below.

From Table III, the 249.77 nm line appears to be the most suitable for trace boron determination, however, there is a serious spectral interference from iron, which has an intense and complex spectrum in the region. This is illustrated in Figure 7. For samples with high iron concentrations, the use of this spectral line would require correction for the spectral overlap and background shift. This interference was found to be linear over a large concentration range thus allowing a correction factor to be calculated and used. The correction factor (CF) was calculated using:

$$\mathrm{CF}=\frac{\text{measured apparent B concentration at B analysis wavelength}}{\text{concentration of Fe}}$$

CF values vary with changes of other parameters, e.g., observation heights, RF power and the use of background correction or after any adjustments of the instrument, these factors have to be recalculated. The iron concentration in the sample $[\mathrm{Fe}]_s$ is first measured at

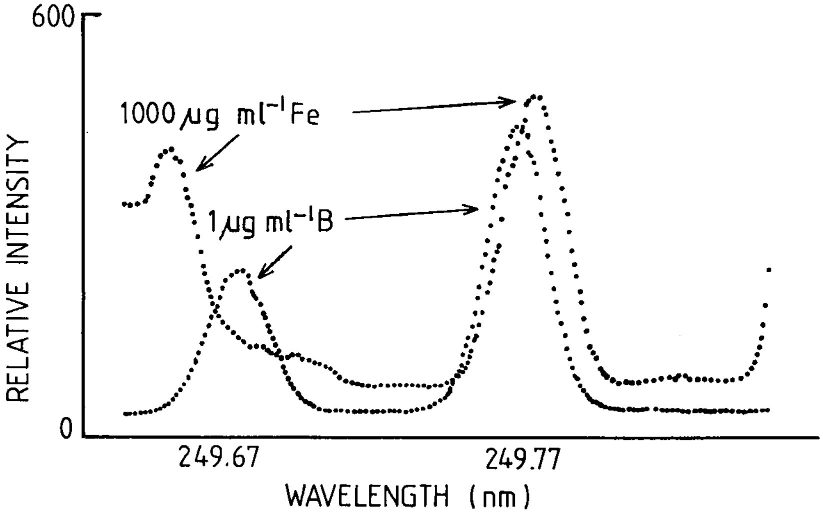

FIGURE 7 Interference by iron at 249.77 nm.

233.28 nm and the correction then applied to the measured B concentration: corrected [B] = measured [B] − CF × $[Fe]_s$. The Fe spectral line at 233.38 nm is used for measuring $[Fe]_s$ because of its suitable sensitivity and its calibration linearity at levels greater than 1000 $\mu g\, ml^{-1}$ ($C_L = 0.02\,\mu g\, ml^{-1}$).

The effect of up to 1000 $\mu g\, ml^{-1}$ Fe on 1 $\mu g\, ml^{-1}$ B at 208.96 nm was not significant and this line can be used without any spectral interference correction when Fe levels in the samples are low. The use of boron lines in the vacuum ultraviolet region has been discussed by Nygaard *et al.*[3] High iron concentrations interfere with the 181.84 nm line and near the 182.64 nm line high background shifts are experienced. At 182.64 nm sulphur emission overlaps directly with the boron line, therefore requiring correction (Figure 8). Large concentrations of aluminium cause background shifts near 208.96 nm and background correction is required, (Figure 9). Since the background on each side of the analyte peak is relatively flat, one point or two point background correction is possible. Molybdenum interferes with the boron lines in the normal ultraviolet region (Figure 10). At 249.77 nm, background correction would be impossible since the background on each side of the analyte peak is not flat. For most analyses, the "medium" size monochromator window (0.067 nm bandpass) can be used satisfactorily, however when partial overlaps from interferents occur the "narrow" window (0.033 nm) is

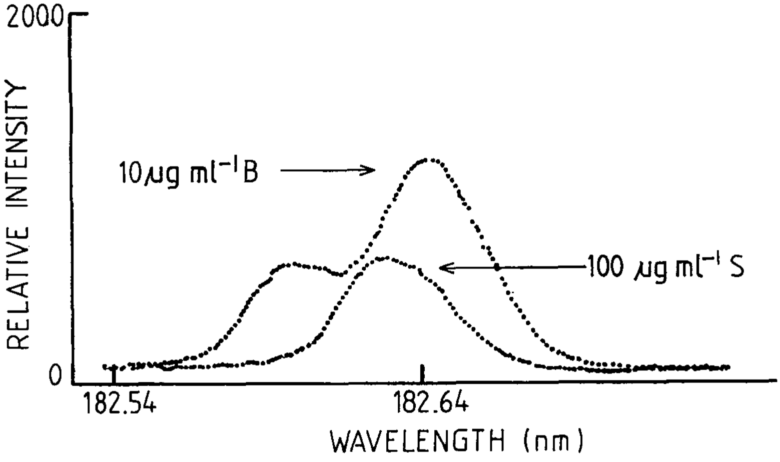

FIGURE 8 Interference by sulfur at 182.64 nm.

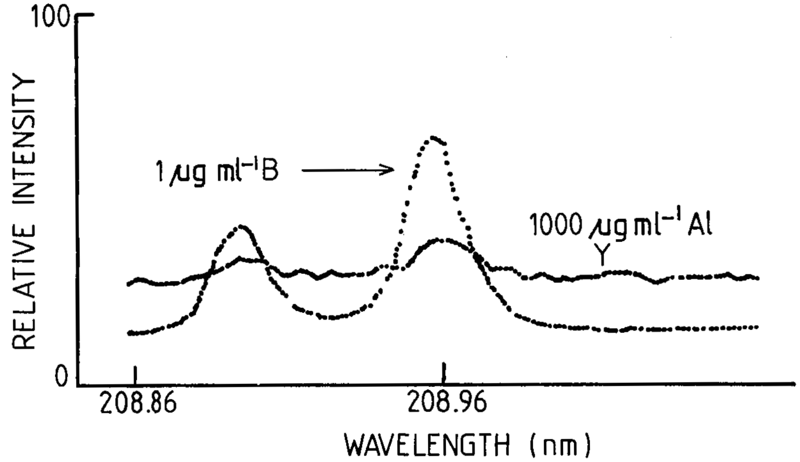

FIGURE 9 Background interference by aluminium at 208.96 nm.

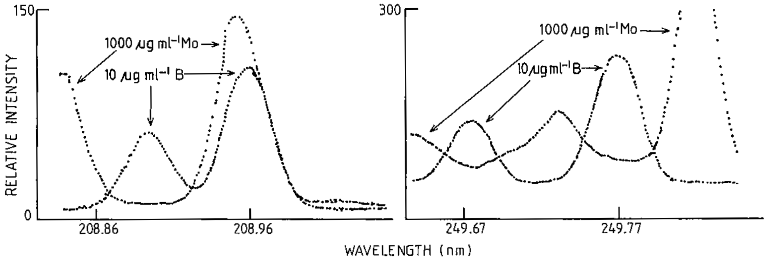

FIGURE 10 Interference by molybdenum at boron spectral lines in the normal UV region.

most useful to exclude or at least diminish the interferences. In low level measurements (near detection limits) and especially when the analyte peak lies on a structured background the small window is used to exclude spurious peaks.

CONCLUSION

Provided the necessary precautions are taken, trace determination of boron is easily achieved by ICP-AES, the sensitivity is good and the availability of several spectral lines is an advantage for circumventing spectral interferences. Unlike major element analysis by ICP-AES trace determinations in complex matrices require careful investigations of possible interferences when developing new analytical methods. Although modern instruments offer automatic spectral overlap and background interference corrections facilities, these have to be first identified and evaluated during the method development. Modern graphic facilities make interference investigations much simpler.

Trace boron determination is certainly not an easy analytical task using conventional routine techniques such as atomic absorption spectroscopy, colorimetry, ion selective electrodes etc. It can be expected that the use of ICP-AES for determining this element in large varieties of samples will increase as ICP spectrometers become available in more and more laboratories. Boren levels in local South African environmental samples were almost unknown and, using ICP-AES, boron has now been measured in our laboratory in a large number of samples such as coal, coal ashes and water[9] as well as in other samples such as minerals, alloys, glasses and some plant material.

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References

1. E. S. Gladney, E. T. Jurney and D. B. Curtis, *Anal. Chem.* **48,** 2139 (1976).
2. G. F. Wallace, *At. Spectrosc.* **2,** 61 (1981).
3. D. D. Nygaard, D. S. Chase and D. A. Leighty, *Research and Development* **Feb.,** 172 (1984).
4. J. W. Owens, E. S. Gladney and D. Knab, *Anal. Chim. Acta* **135,** 169 (1982).
5. J. L. Manzoori, *Talanta* **27,** 682 (1980).
6. R. H. Scott and A. Strasheim, *Anal. Chim. Acta* **76,** 71 (1975).
7. S. B. Smith, Jr., R. G. Schleicher, A. G. Dennison and G. A. McLean, *Spectrochimica Acta* **38B,** 157 (1983).
8. G. F. Larson, R. T. Goodpasture and R. W. Morrow, *Proceedings of International Winter Conference*, San Juan, Puerto Rico, Heyden, January 1980, 611 (R. M. Barnes (ed.)).
9. M. J. Orren and M. A. B. Pougnet, submitted.