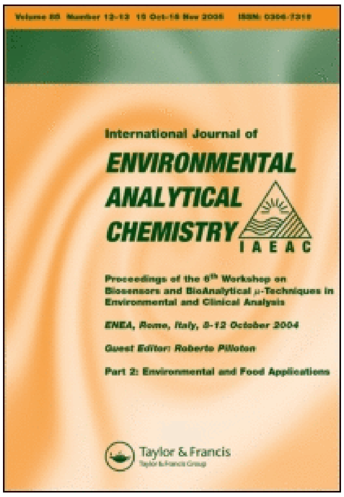

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Flame Photometric Determination of Submicrogram Quantities of Boron

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A procedure for the determination of submicrogram amounts of boron in aqueous solutions is described. The method is based on measuring the chemiluminescence of the molecular species BO_x in either an air/hydrogen or air/acetylene flame. Detection limits obtained with these flames were 0.004 and 0.06 ppm, respectively. Potential interferences may be removed by ion-exchange chromatography. The procedure is applicable to the determination of boron in potable waters.

The quantitative analysis of boron by classical techniques involves the distillation of methyl borate and is very time-consuming.[1] To provide a more rapid method for analyses, Dean and Thompson developed a flame photometric method by which the intensity of the boron oxide (BO_x) band head emission was measured using an oxyacetylene flame.[2] The procedure, however, is relatively insensitive. A detection limit of 1–3 ppm was reported with the optimum range of applicability being 50–200 ppm. Boron may also be determined by atomic absorption spectroscopy; however, the sensitivity of this procedure is also not as great as could be desired. A detection limit of

6 ppm has been reported with a sensitivity (concentration required to produce 1% absorption) of 35 ppm.[3]

Our present studies concern the flame photometric determination of boron using air/acetylene and air/hydrogen flames. Sensitivities and detection limits were improved at least two orders of magnitude over previous experiments in which the hotter oxyacetylene flame was used.

EXPERIMENTAL

Apparatus

The equipment used was a modified Aminco-Bowman spectrophotofluorometer. The sample compartment was removed to provide room for the burner system which was aligned so that the radiation from the flame fell on the entrance slit of the emission monochromator. The signal from the photomultiplier was amplified with a Hewlett-Packard 2470A amplifier and the output was displayed on a Sargent-Welch S.R.L.G. recorder. A Perkin-Elmer nebulizer and mixing chamber were used in conjunction with the standard single slot burner.

To reduce the noise and high background caused by stray light entering the monochromator a light baffle was placed around the flame.

Procedure

The burner was aligned with the slot parallel to and in line with the entrance slit. The height was adjusted so that the burner head was just below the level of the slit. The sample solutions were aspirated directly into the mixing chamber and the intensity of the emission was measured in the normal manner.

RESULTS AND DISCUSSION

Two flames were investigated in this study, the air/acetylene flame and the air/hydrogen flame. With both flames the characteristic band head emission spectra of the BO_x species were observed and are shown in Figure 1.

The band head at 518 nm was slightly more sensitive than the one at 546 nm with the instrument used. However, the higher background at 518 nm (with both flames) resulted in a lower signal to noise ratio than at 546 nm and so all further measurements were made at the latter wavelength.

The use of organic solvents generally results in an enhancement of the analytical signal in both atomic absorption and flame spectroscopy.[4] Such enhancement is usually attributed to the lowering of the surface tension of the solution to be nebulized which increases the rate of aspiration and results in the formation of smaller droplets.

In the case of boron, however, the volatility factor must be considered. If a boric acid or sodium borate is dissolved in methanol, methyl borate is formed quite readily and is very volatile. This can readily be demonstrated by placing a container of a solution of boric acid in methanol in the vicinity of a flame: the trimethyl borate formed is sufficiently volatile to vaporize from the surface of the solution and to become entrained in the flame, producing the green glow characteristic of the emission of BO_x species.

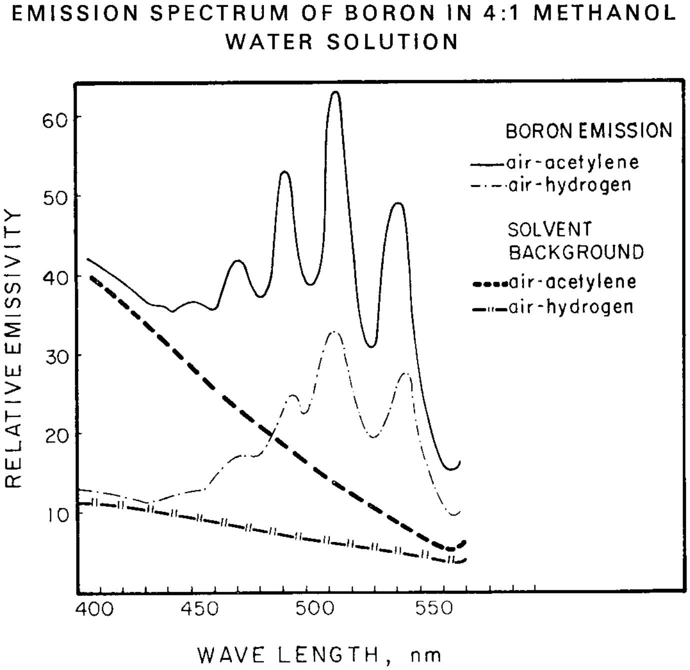

FIGURE 1 Emission spectrum of boron in 4:1 methanol-water solution.

To determine the effect of the volatility of the trialkyl borate on the intensity of the boron emission a number of alcohols were used as solvents and, as expected, the intensity of the emission decreased as the volatility of the trialkyl borate decreased. The results are summarized in Table I.

The signal obtained when aqueous solutions of boron are used is about 100-fold less than that obtained when using methanol as a solvent. However, the signal can be significantly enhanced by diluting the aqueous solution with methanol. Although the overall concentration of boron is lowered, the enhancement obtained more than compensates for this, as shown in Figure 2. A maximum sensitivity is obtained when the aqueous solution is diluted about four to six-fold with methanol, although higher dilutions can be used without major reduction in the overall sensitivity.

The considerable enhancement of the emission of the boron species caused by the addition of methanol to the solvent, coupled with the high sensitivity

TABLE I

Correlation between emissivity and the volatility of the trialkyl borate

Solvent	b.p. of the corresponding trialkyl borate[5] $(RO)_3B$	Relative emissivity
Methanol	68.7	85
Ethanol	117.4	39
Propyl alcohol	175.0	23
Isoamyl alcohol	255.0	7

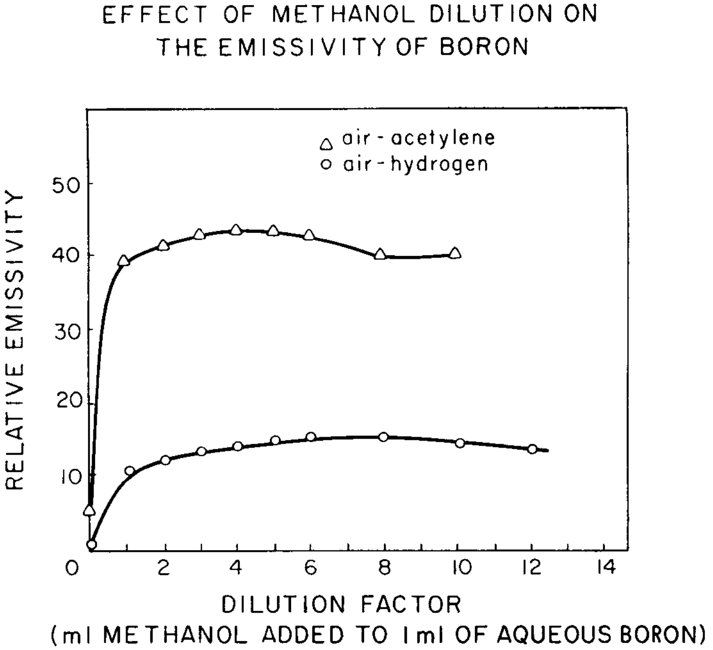

FIGURE 2 Effect of methanol dilution on the emissivity of boron.

that was obtained with the relatively cool air/hydrogen flame, indicates that the emission is not purely thermal in origin; it is probable that it is partially due to the chemiluminescence of the trimethyl borate species.

Range of Applicability and Detection Limit

With the same slit width and amplification settings, the air/acetylene flame was slightly more sensitive than the air/hydrogen flame, which may be a result of the slightly higher temperature of the former. The intensity of the background radiation is considerably higher for the air/acetylene flame (Figure 1) and thus the detection limit is not as low as that obtained with the air/hydrogen flame (0.004 ppm of boron for air/hydrogen flame and 0.06 ppm for air/acetylene flame). The relative luminosity of boron at 546 nm after subtraction of the blank is proportional to the boron concentration over a wide range. Linear calibration curves were obtained from 0.04 ppm to at least 1000 ppm for air/hydrogen flame, and from 0.4 to at least 1000 ppm for air/acetylene flame (Figure 2).

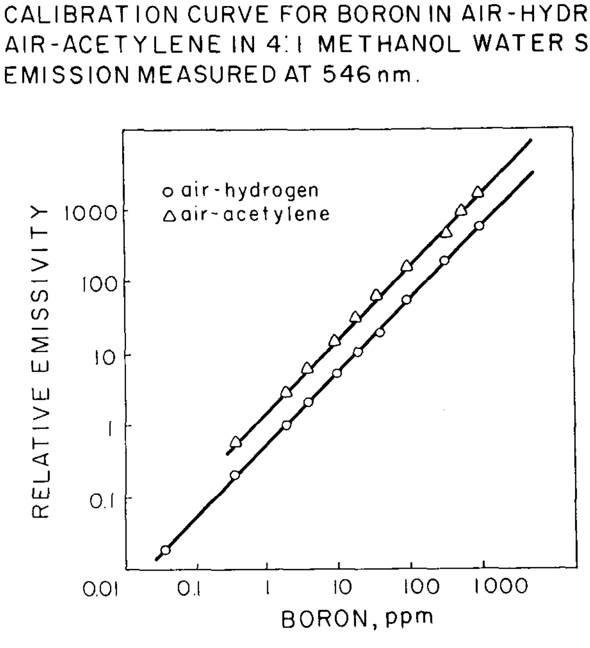

FIGURE 3 Calibration curve for boron in air/hydrogen and air/acetylene in 4:1 methanol-water solution. Emission measured at 546 nm.

Interferences

A number of elements were investigated as potential sources of interference. For each element tested a methanol-water solution was prepared containing known concentrations of the element and 100 ppm boron. The effects of the various metals examined are summarized in Table II. As shown, a number of cations caused interference due to emission of radiation in the vicinity of the band head emission of boron species at 546 nm. For some elements, *e.g.* calcium, this interference was overcome by measuring at either the 518 or 492 nm peak. These measurements, however, caused a decrease in sensitivity and necessitated investigation of the removal of interferences with an ion-exchange column.

TABLE II

Effect of diverse ions in determination of boron by flame photometry. Boron concentration 100 ppm.

		% Boron found					
		492 nm		518 nm		546 nm	
Metal ion	Conc. (ppm)	A-H	A-A	A-H	A-A	A-H	A-A
Ba	200	390	220	290	170	270	170
Ca	200	100	100	100	100	>500	>300
	1000	100	100	100	100	—	—
Co	1000	150	120	120	110	120	110
Cr	1000	250	140	220	140	240	180
Cu	1000	260	110	280	120	310	120
Na	1000	180	110	140	110	200	120
Ni	1000	230	130	180	120	180	120
Li	1000	100	100	100	100	100	100
Cd	1000	100	100	100	100	100	100
Al	1000	100	100	100	100	100	100
Zn	1000	100	100	100	100	100	100
Mg	1000	100	100	100	100	100	100
K	1000	>400	>200	300	130	210	120
NH_4	1000	100	100	100	100	100	100
Ag	1000	100	100	100	100	100	100
Pb	1000	100	100	100	100	100	100
Cl^-	1000	100	100	100	100	100	100
NO_3^-	1000	100	100	100	100	100	100
$SO_4^=$	1000	100	100	100	100	100	100

A-H: Air/Hydrogen Flame.
A-A: Air/Acetylene Flame.

Other workers have used a variety of ion-exchange resins to separate boron from various cations and anions, for example: Amberlite IR-120,[6] Dowex-50,[7] Amberlite IR-45 and Nalcite HCR mixed bed resin.[8] We confined our investigations to Dowex-50 resin; the procedure used follows.

A Dowex-50 (8% DVB) column (1 cm diameter, 16 cm long) in the acid form was first eluted with methanol to remove any trace amount of water left from the regeneration process. A 10-ml aliquot of an aqueous solution 100 ppm in boron and 1000 ppm in the interfering ion was added to the column. After all the sample solution had been added to the column, it was eluted immediately with about 40 ml of methanol. The effluent was collected in a 50-ml volumetric flask, and diluted to volume with methanol. The resulting solution contained 10 ml of water and 40 ml of methanol. With this procedure all the interfering cations were removed.

With the less interfering cations such as cobalt or when the overall concentration of interferences is low it is possible to remove the interfering ions by shaking a 10-ml aliquot of the aqueous solution with about 2 g of the Dowex-50 resin (acid form). The solution is then filtered and the resin is washed with sufficient methanol to bring the methanol to water ratio to 4:1 by volume.

CONCLUSION

Boron may be determined flame photometrically in submicrogram amounts using an air/hydrogen or air/acetylene flame. Interferences may be removed prior to the determination with an ion-exchange column.

The high sensitivities obtained when using the relatively cool air/hydrogen flame indicate that the emission may not be entirely thermal but that it may be due partially to chemiluminescence of the trimethyl borate species.

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