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Note

The detection of boron and the response of some boronate derivatives of carbohydrates with an alkali flame ionization detector*

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The use of boronic acids for the derivatization of compounds containing a diol moiety has been reported by Brooks and MacLean[1]. Preliminary reports[2,3] suggested a potential for butylboronates as derivatives for some carbohydrates and alditols. These esters can be chromatographed by gas chromatography (GC) and detected by flame ionization (FID) or specifically by flame photometric detectors (FPD)[4]. In addition, it has now been found that they can be detected by an alkali flame ionization detector (AFID).

Although the AFID is considered to be a specific detector for phosphorus and nitrogen, it is known to respond to other elements such as bromine, chlorine and iodine[5], sulphur[6] and lead, silicon and tin[7]. For each element, the detector parameters, such as the jet diameter, electrode spacing, alkali salt and flame conditions required for optimum response are different. This paper describes the flame conditions most suitable for the detection of boron.

The GC analyses were performed on a Pye 104 Model 154 gas chromatograph fitted with a three-electrode AFID and a CsBr annulus. The compounds were chromatographed on a 3 ft. $\times$ $^1/_4$ in. glass column, packed with 100–120 mesh Gas-Chrom Q coated with 3% OV-17, which was conditioned after the manner of Bowman and Berosa[8]. A column flow of 40 ml/min was used throughout. The decaborane was purchased from ICN Research Prods., and the phenylboronic acid anhydride (triphenylboroxole) was synthesized by dehydration of phenylboronic acid (Alfa Inorganics Inc.) and crystallised from isopropyl ether/petroleum ether. The boronate derivatives of fucose, xylose and arabinose were prepared by the method of Wood and Siddiqui[9]. The purity and elemental composition were established by carbon and hydrogen analysis and by mass spectrometry.

In the AFID, the temperature of the flame and the stability of the detector are dependent on a very precise hydrogen flow-rate. Variation of this flow is the

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most common method employed to change the flame conditions in order to optimize the response to a particular element. A plot of the response (peak height) against hydrogen flow with this detector is shown in Fig. 1 for ethion (S,S'-methylene *o,o,o',o'*-tetraethyl phosphorodithioate) and phenylboronic acid anhydride.

The maximum response to boron occurs at a higher hydrogen flow-rate than for phosphorus, enabling some specificity to be obtained from the other elements to which the detector is sensitive. Higher hydrogen flow results in a hotter flame, which in turn gives a higher standing current and noise level; possibly a greater sensitivity (*S/N* value) and a lower noise level would be obtained by the use of a higher melting alkali salt like rubidium chloride.

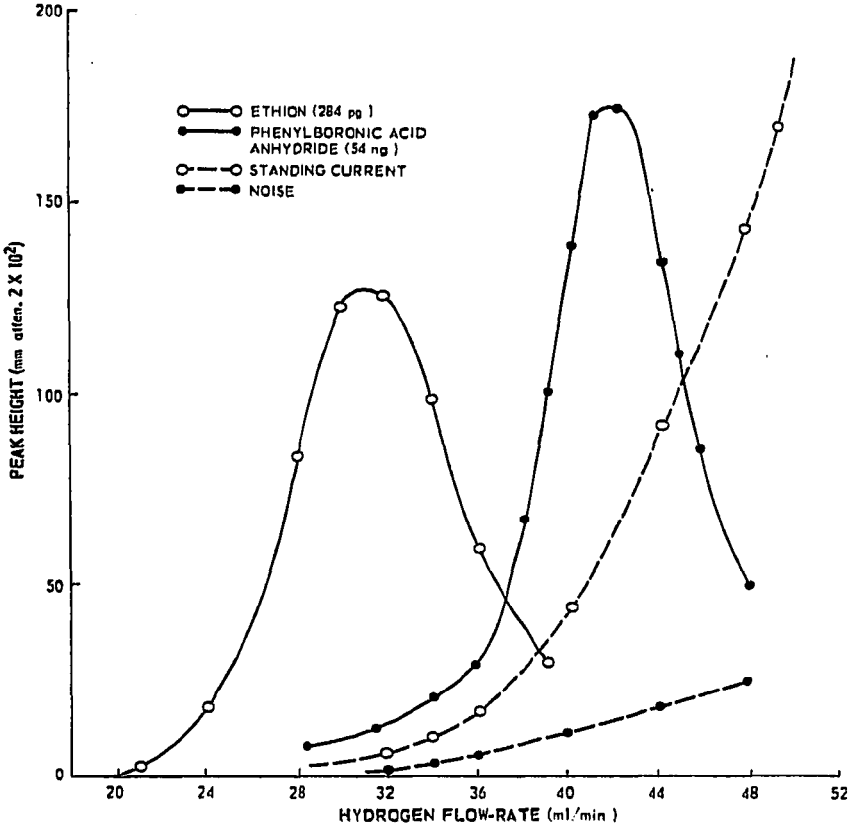

Fig. 1. Response/hydrogen flow-rate profile of the AFID for ethion and phenylboronic acid anhydride: phenylboronic acid anhydride, 54 ng; ethion, 284 pg. Column, 3 ft. × 1/4 in. O.D., 3% OV-17 on Gas-Chrom Q, 100–120 mesh; nitrogen flow-rate, 40 ml/min; column temperature, 256°.

Using the optimum conditions established, the response was determined for seven boron compounds including five boronate derivatives of sugars. The results are given in Table I.

The calculated least detectable amounts (LDA) are of the same order of magnitude, indicating that the response measured is in fact due to boron. The

TABLE I

GC CONDITIONS AND CALCULATED LEAST DETECTABLE AMOUNTS OF SOME BORON COMPOUNDS DETERMINED WITH AN AFID*

Compound	*Column temperature (°C)*	*Retention time (min)*	*Least detectable amount*	
			(10^{-12}g/sec)	*(10^{-12}g B/sec)*
Decaborane	117	3.00	16	14
Phenylboronic acid anhydride	256	3.25	120	12.5
L-Fucose butylboronate	185	3.87	72	5.3
D-Xylose butylboronate	185	2.75	41	3.1
L-Arabinose butylboronate	185	2.62	32	2.4
D-Xylose phenylboronate	268	3.50	165	11.0
L-Arabinose phenylboronate	268	4.00	246	16.5

* Calculated as 2 × noise level.

reason for the apparent low value for butylboronates (av. 3.6×10^{-12}g B/sec) compared with the phenylboronates (av. 13.6×10^{-12}g B/sec) is not clear. The peak shape was symmetrical and similar for all the compounds. Possibly it could be due to the difference in the substitution at the boron, since there are marked differences in the susceptibility to hydrolysis and oxidative cleavage of the C–B bond in alkyl- and aryl-boronic acids[10]. The average LDA for boron is 9.25×10^{-12}g

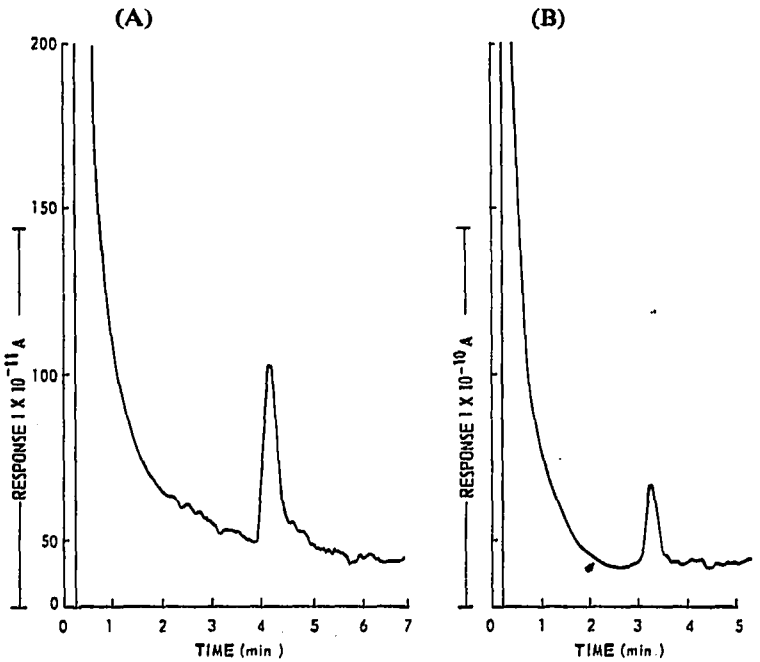

Fig. 2. Chromatograms of decaborane and fucose butylboronate with the AFID. (A) Decaborane, 10 ng. Column temperature, 117°; other parameters as in Fig. 1. (B) Fucose butylboronate, 6 ng. Parameters as in Fig. 1.

B/sec, which when compared with the value for phosphorus, 2.8×10^{-14}g P/sec, calculated from the ethion response, gives a response ratio P:B of 331 : 1.

Chromatograms of fucose butylboronate (6 ng) and decaborane (10 ng) obtained with the AFID are shown in Fig. 2. The response for decaborane is of the same order of magnitude as that obtained by Sowinski and Suffet[4] with an FPD fitted with a 546-nm filter. Using the same GC conditions as for the AFID, the FID response of decaborane was also measured and an LDA of 2.02×10^{-10}g B/sec. was obtained. The signal enhancement (AFID/FID) for boron was 55.

Variation of the response with concentration was determined with both the AFID and FID for fucose butylboronate (Fig. 3). The FID response was linear over a greater concentration range than for the AFID. Even so, the response for boron was linear over a range of 10^3, which is similar to that reported for the AFID with other elements. The sensitivity of the AFID to butylboronate is greater than that for the FID, although not by the same factor as that determined for decaborane, since the AFID discriminates against carbon. The AFID/FID ratio is dependent on the carbon content of the molecule.

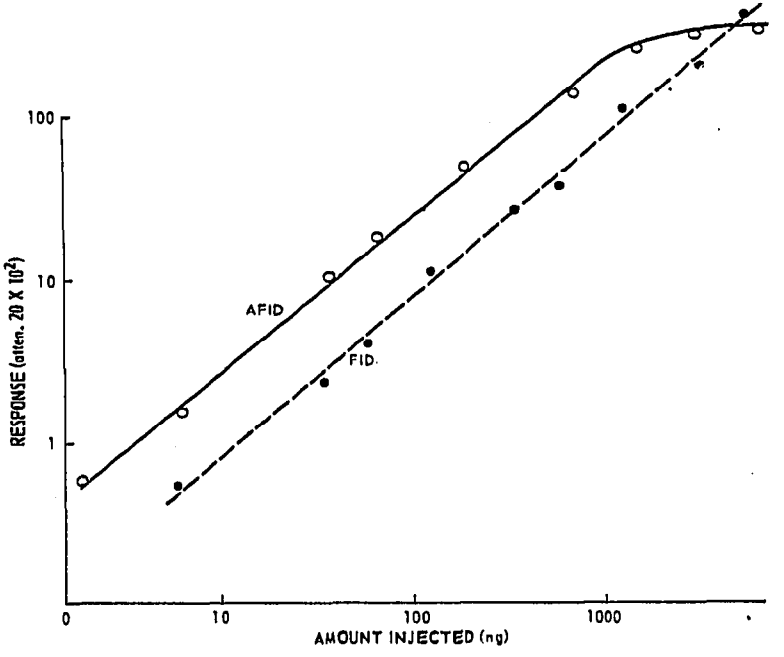

Fig. 3. Response/concentration plot for fucose butylboronate on AFID and FID. Column temperature, 186°; other parameters as in Fig. 1.

In summary, it is suggested that the specificity, sensitivity and linear range of the AFID make it an ideal detector for boron compounds, particularly the boronate esters used in the characterisation of corticosteroids, monoglycerides, amino alcohols and sugars. During this work with boronate derivatives, no adverse effects on the sensitivity of the AFID were observed as compared with the silyl derivatives, which have been reported to contaminate the alkali salt surface[11].

REFERENCES

1 C. J. W. Brooks and I. MacLean, *J. Chromatogr. Sci.*, 9 (1971) 18.
2 F. Eisenberg, *Carbohyd. Res.*, 19 (1971) 135.
3 P. J. Wood and I. R. Siddiqui, *Carbohyd. Res.*, 19 (1971) 283.
4 E. J. Sowinski and I. H. Suffet, *J. Chromatogr. Sci.*, 9 (1971) 632.
5 W. A. Aue, K. O. Gerhard and S. Lakota, *J. Chromatogr.*, 63 (1971) 237.
6 M. Dressler and J. Janák, *J. Chromatogr. Sci.*, 7 (1969) 451.
7 M. Dressler, V. Martina and J. Janák, *J. Chromatogr.*, 59 (1970) 499.
8 M. Bowman and M. Berosa, *J. Ass. Offic. Anal. Chem.*, 53 (1970) 499.
9 P. J. Wood and I. R. Siddiqui, unpublished results.
10 W. Garrard, *The Organic Chemistry of Boron*, Academic Press, New York, 1961, p. 77.
11 R. F. Coward and P. Smith, *J. Chromatogr.*, 61 (1971) 329.