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Note

Response of a hydrogen-rich flame ionisation detector to some chlorinated hydrocarbons

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The flame ionisation detector (FID) is widely used in gas chromatography (GC) due to its simplicity of construction, a linear response and its ability to be operated over a wide dynamic range. The response of the FID to different organic compounds has been the subject of numerous studies[1–7] and it has been established that the molar response of the *n*-alkanes is proportional to the number of carbon atoms[4,7] present in the molecule. Organic compounds which contain other elements in addition to carbon and hydrogen are found to have a lower molar response than the corresponding *n*-alkane, although a predictable molar response is still maintained within any given homologous series. Minor variations in the value of the molar response can result from parameters such as column effects, design effects, *e.g.* jet size and non-optimisation of hydrogen and air flow-rates. However, these differences are negligible compared with species differences which cannot be attributed to these factors.

The response of the FID when operated in a conventional manner is low or negligible to many inorganic gases and several attempts have been made to improve the response by the use of carefully selected conditions[8,9]. It was recently found in this laboratory that a slightly modified FID, operated in a hydrogen-rich mode with oxygen to support combustion, can exhibit a greatly enhanced response to some inorganic gases[10]. For some gases the response was as high as that observed for *n*-alkanes using a conventional FI[illegible]ollowing this work the response of the FID operated in a hydrogen-rich mode [illegible]as now been investigated with regard to some halogenated hydrocarbons.

EXPERIMENTAL

The gas chromatograph was a Pye 104 fitted with a normal FID which had been modified as previously described[10] by incorporating a number of 1-mm diameter holes in the detector collector electrode near its base. CP grade hydrogen (British Oxygen Company) was used as the flame gas, oxygen instead of air to support combustion and nitrogen as carrier gas. The flow-rates were optimised to give similar molar responses to the *n*-alkanes as obtained by normal FID operation and were 60 ml/min hydrogen, 40 ml/min oxygen and 20 ml/min nitrogen. Flow-rates are not however critical, although at very high flow-rates it has been found that at least for the chlorobenzenes the detector will respond on a weight rather than a molar basis.

These observations are reported by Karagözler and Simpson[11]. Mixtures were prepared containing 1000 μg/ml of the various *n*-alkanes with hexane or heptane as diluent and also of the various chloroalkanes or chlorobenzenes with benzene as diluent. 2-μl Aliquots of these mixtures were injected on to the gas chromatograph. For all the solutes except the penta- and tetrachlorobenzenes the column was 2 m × 1.8 mm I.D. stainless steel containing 15% Apiezon L on Diatomite CLQ, 80–100 mesh, at a temperature to give reasonable retention times. For the other chlorobenzenes the column was 2.5 m × 1.8 mm containing 3% Dexil 300 on the same support, at 220°. The detector was maintained at 150° throughout this work, as detector temperature has previously been shown to effect the performance of the hydrogen-rich flame. The response of the detector to each solute was calculated from the peak area (height times width at half height).

RESULTS AND DISCUSSION

The molar responses of the hydrogen-rich FID were measured for the C_5 to C_9 *n*-alkanes and gave values in agreement with those published using a Pye 104 conventionally. Table I lists these values and the corresponding relative response values based on hexane. The linear relationship between molar response and carbon number for the homologous series is maintained with this mode of operating the detector as shown on Fig. 1. Moreover, experimentally determined molar response values for tetrachloroethane and pentachloroethane were found to be the same as our extra-

TABLE I

RESPONSE OF THE FLAME IONISATION DETECTOR

Compound	*Hydrogen-rich FID*		*Conventional FID*	
	Molar response (C/mole)	*Relative response (hexane = 1.00)*	*Molar response (C/mole)*	*Relative response (hexane = 1.00)*
n-Pentane	1.57	0.83	1.44*	0.84
n-Hexane	1.89	1.00	1.71*	1.00
n-Heptane	2.11	1.12	2.02*	1.18
n-Octane	2.48	1.31	2.26*	1.33
n-Nonane	2.86	1.51	2.69	1.57
Methane	0.32***	0.17	0.31	0.18
Carbon tetrachloride	0.35	0.19	0.14	0.08**
Ethane	0.64***	0.34	0.55	0.32**
1,1,2,2-Tetrachloroethane	0.64	0.34		
Pentachloroethane	0.63	0.33		
Benzene	1.87	0.99	1.69*	0.99
Chlorobenzene	1.87	0.99	1.63*	0.96
1,2-Dichlorobenzene	1.88	1.00	1.54*	0.85
1,2,4-Trichlorobenzene	1.88	1.00	1.34*	0.79
Pentachlorobenzene	1.88	1.00		
Hexachlorobenzene	1.88	1.00		

* From ref. 2.

** From ref. 3.

*** Extrapolated from Fig. 1.

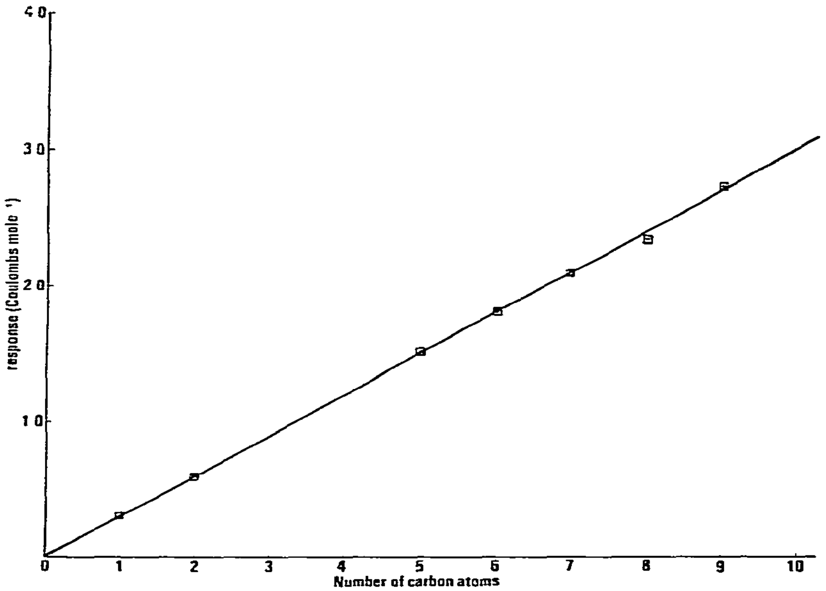

Fig. 1. Linearity of molar response with carbon number using the hydrogen-rich FID. Ordinate: response (coulomb mole^{-1}); abcissa: number of carbon atoms.

polated value for ethane using Fig. 1. This is in contrast to the effects well known with a normal FID in which the substituted analogue has a lower molar response than the corresponding unsubstituted compound. An internal standard of *n*-octane was incorporated with the mixture of chloroethanes to show that the detector response was unchanged since the measurements were made on the *n*-alkanes.

Using the normal FID, carbon tetrachloride gives a small response compared with the alkanes (Table I). But in the hydrogen-rich mode an enhanced response was obtained, which was equal to the value for methane derived from Fig. 1.

The same predictable molar responses were obtained for benzene and some chlorobenzenes including the fully substituted hexachlorobenzene. Table I compares these values with literature values for the normal FID. For the hydrogen-rich FID the molar responses were unchanged despite increasing chlorine substitution, whereas for the normal FID increasing substitution results in a decreasing molar response.

A plot such as shown in Fig. 1 prepared using hydrocarbons can thus be used to predict the response of the chlorosubstituted analogues of these compounds.

The values of molar response for the chloroethanes given in Table I for the hydrogen-rich FID are the mean of seven 2-μl injections and have a standard deviation of 0.03. For the chlorobenzenes the results are the mean of ten 2-μl injections which have a standard deviation of 0.05.

CONCLUSIONS

These results demonstrate that the FID operated in the hydrogen-rich mode gives a response which is both predictable and unaffected by chlorine substitution. A linear relationship between molar response and carbon number is maintained.

We are now continuing investigations on the response to other halogenated compounds such as the fluorocarbons and to other classes of compounds. Initial results indicate that a similar behaviour is to be observed.

This work forms part of a study of the hydrogen-rich FID being carried out jointly with C. F. Simpson of the University of Sussex, Great Britain.

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