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DIRECT QUANTITATIVE ANALYSIS USING THE FLAME-IONIZATION DETECTOR

SOME OPERATING PARAMETERS AND THE FIDOH DETECTOR

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SUMMARY

The effect of varying carrier gas (nitrogen) flow-rate on the absolute molar and weight responses of a flame-ionization detector operated under conditions of a hydrogen-rich flame using oxygen as the supporter of combustion has been investigated and shows that a considerable degree of flexibility is available for achieving these detector responses. Selective detection of chlorine has been shown to depend upon high hydrogen and low nitrogen flow-rates with intermediate to high oxygen flow-rates. Additional compounds have been shown to respond equally to carbon content in the molar mode of operation.

INTRODUCTION

It has recently been demonstrated by Karagözler and Simpson[1] and Gough *et al.*[2] that the flame-ionization detector (FID) possesses properties that have not previously been observed when operated in a hydrogen-rich mode and using oxygen to support combustion. For example, it has been shown that direct quantitative analyses are obtainable, on both a molar and a weight basis, provided that suitable oxygen and hydrogen flow-rates are used[1]. It has also been demonstrated that the detector can respond equally on a molar basis to a number of different species and, most important, the detector responds only to the carbon content of the solute in question, heterogeneous atoms do not alter the response and indeed the detector appears to count the carbon atom content of molecules[2]. Finally, the detector can be operated so that carbon response is substantially suppressed and it responds principally to the heterogeneous atoms present in the solute molecules[1].

Clearly, it is important that the parameters controlling these unusual but desirable responses are thoroughly evaluated and this paper describes the effect of the nitrogen carrier gas flow-rate on the response together with an investigation into the responses of other solute types.

In the light of the above, a new detector has been designed that can more readily exploit the facets outlined above, and some preliminary details are given. In order to distinguish between the new detector design and a conventional FID it has been designated the flame-ionization detector/oxygen/hydrogen (FIDOH).

EXPERIMENTAL

Evaluation of the effect of nitrogen flow-rates on detector response

A conventional Pye Unicam Series 104 FID was installed in a Pye Panchromatograph, substantially modified in order to provide a means of controlling and measuring all gas flow-rates independently. All flow-rates were measured using a soap-bubble flow meter at the operating conditions of the column and detector. Hydrogen, oxygen and nitrogen were supplied by Air Products (New Malden, Great Britain) and were purified before use by passage through activated (300°) Linde 5Å molecular sieve (BDH, Poole, Great Britain).

A Mark II Pye Unicam Type 12304 ionization amplifier was used, its output being monitored with an Oxford Instruments 3000 potentiometric recorder and an Infotronics (Stone, Great Britain) CRS 304 computing integrator.

The analytical column was designed to permit rapid analysis of the four test solutes chosen, viz., benzene, chlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene (BDH), and consisted of a 5 ft. $\times$ 2 mm I.D. stainless-steel column, deactivated by silanization and packed with 1 % (w/w) OV-17 on silanized 120–150-mesh (64–87 μm) Chromosorb G. The column was operated at 140° with a nitrogen flow-rate of *ca.* 8.0 ml min^{-1}, which constituted the basic nitrogen flow investigated. Provision was made for varying the total nitrogen flow-rate through the detector by installing a nitrogen make-up line immediately after the column and just prior to entry into the detector. Under the conditions specified, a resolution of at least 1.5 was obtained between the four test solutes and the analysis was completed within 3 min.

As in a previous paper[1], the choice of test solutes was made on the basis of their wide variation in detector response exhibited in the conventionally operated FID[3]. A blend was prepared containing approximately equal proportions by weight, and was used in the subsequent evaluations.

Samples of 0.1 μl of the test mixture were reproducibly injected into the analytical column and response data were obtained at a variety of fixed hydrogen and oxygen flow-rates chosen to provide a four by four matrix with flow-rates ranging from 40 to 100 ml min^{-1} at 20 ml min^{-1} increments of the two gases. Nitrogen flow-rates were varied between the basic column flow-rate (*ca.* 8.0 ml min^{-1}) to about 70 ml min^{-1} using the make-up gas flow stream. The quantitative data presented represent the mean of ten replicate injections at a given gas flow composition.

Determination of absolute molar responses of various test solutes

A Pye Unicam Series 104 Model 64 gas chromatograph was used. The FID had been modified as previously described[4] by incorporating a number of 1-mm-diameter holes in the detector collector near its base. CP-grade hydrogen (British Oxygen, Morden, Great Britain) was used as the flame gas, using oxygen instead of air to support combustion, and nitrogen was the carrier gas. The flow-rates of

the combustible gases were set so as to give similar molar responses to the *n*-alkanes as obtained under normal FID operation. Flow-rates under molar response conditions are not critical and, as will be seen, cover a wide range of oxygen and hydrogen flow-rates.

Test mixtures of a variety of test solutes were prepared containing 1000 μg ml^{-1} of the various *n*-alkanes studied with *n*-hexane or *n*-heptane as the diluent. Similar samples were prepared containing various aliphatic alcohols (C_7, C_8, C_9 and C_{10}) and aliphatic and aromatic halogenated species containing chlorine, bromine and iodine.

Aliquots of 2 μl of these mixtures were reproducibly injected on to the chromatographic column, which was chosen to provide a reasonable retention time of the test solute with complete separation ($R_s > 2$) from the solvent. The aliphatic alcohols were chromatographed on a 12 ft. $\times$ 2 mm I.D. column packed with 15% (w/w) Carbowax 20M on Gas-Chrom W (80–100 mesh), with a nitrogen flow-rate of 40 ml min^{-1} at appropriate column operating temperatures. The halogenated compounds were chromatographed on a 5 ft. $\times$ 4.5 mm I.D. column packed with 5% (w/w) Apiezon L on diatomite CLQ (80–100 mesh), again at appropriate column operating temperatures to produce reasonable elution times.

The detector was maintained at 150° throughout this work as detector temperature has been shown to affect the performance of the hydrogen-rich flame (the precise nature of this effect has yet to be evaluated and is at present being studied). The response of the detector to each solute under study was calculated in absolute terms (coulombs per mole) from the peak area (calculated on a height times half-height basis corrected for the error of measurement using 94.34% of the true area for a Gaussian peak).

RESULTS AND DISCUSSION

Effect of nitrogen flow-rate on detector response

As indicated in a previous paper[1], the nitrogen carrier gas flow-rate appears to change the zones in which equivalent molar and weight responses to the test solutes occur. Accordingly, a programme was developed as outlined above to investigate this variable. The results of this investigation are expressed in two ways:

$$\text{(i) Percentage response correction factors} = \frac{\text{Observed percentage composition}}{\text{Actual percentage composititon}}$$

where the observed percentage composition is the percentage composition of a given solute calculated directly from the peak areas of the sum of the elution peaks (obtained from the digital integrator).

$$\text{(ii) Absolute response ratio} = \frac{\text{Absolute area count under test conditions}}{\text{Absolute area count for normal FID operation}}$$

under equivalent conditions of carrier gas flow-rate.

Conventional FID operation. In order to assess the effect of gas flow composition a base-line is necessary. In this investigation, the response of a normally operated

FID was chosen to distinguish between variations in response occurring from variations in oxygen, hydrogen and nitrogen flow-rates. Fig. 1 shows how a conventionally operated Pye Unicam Series 104 FID responds to the four test solutes chosen under varying conditions of nitrogen carrier gas flow-rate at the recommended air and hydrogen flow-rates of 500 and 50 ml min^{-1}, respectively. Responses are expressed in terms of percentage response correction factors as defined above on both a molar (Fig. 1A) and weight basis (Fig. 1B). The molar responses (Fig. 1A) show the effect of varying carrier gas flow-rate for the four test solutes and demonstrate an inversion in molar response as the carrier gas flow-rate increases, with a point of equivalent molar response at a nitrogen flow-rate of about 35 ml min^{-1}, which is a previously unreported event. The weight responses (Fig. 1B) under conditions of increasing carrier gas flow-rate show a diminution in benzene response with an overall increase in response of the chlorinated aromatic hydrocarbons. However, no point of equivalent weight response was observed under the test conditions used.
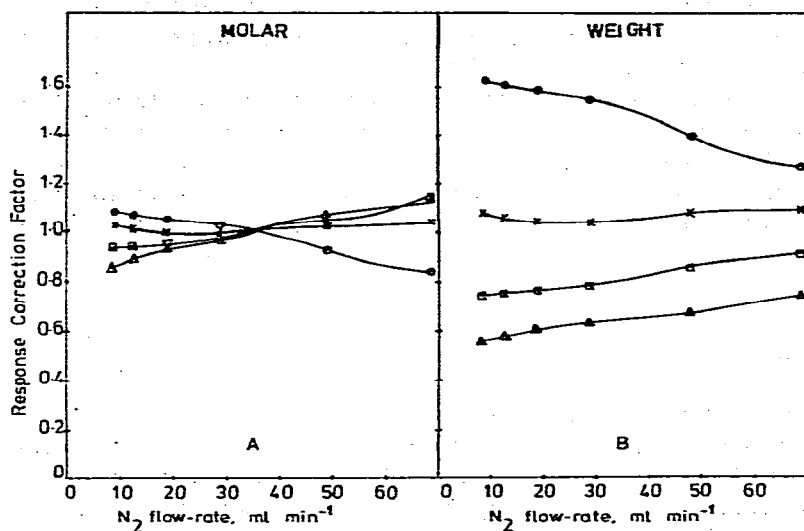

Fig. 1. Effect of nitrogen flow-rate on the response of a conventionally operated FID. Percentage response correction factors on (A) a molar and (B) a weight basis. ○, Benzene; ×, chlorobenzene; □, 1,3-dichlorobenzene; △, 1,2,4-trichlorobenzene.

Hydrogen–oxygen FID. Typical graphs taken from the complete series prepared in this investigation are shown in Figs. 2 and 3. These show the changes in detector response with respect to both molar (Fig. 2) and weight (Fig. 3) response correction factors when the nitrogen carrier gas flow-rate was increased from 7.5 to 70 ml min^{-1} at four different flow-rates of hydrogen. During these experiments, the oxygen flow-rate varied between 40 and 100 ml min^{-1}. Fig. 2 shows that at a constant oxygen and an increasing hydrogen flow-rate, a substantial zone of equivalent molar response exists, and this decreases as the hydrogen and nitrogen flow-rates increase. At a high hydrogen flow-rate (100 ml min^{-1}) it is impossible to achieve equivalent molar response with the nitrogen flow-rate investigated, although by extrapolation the nitrogen
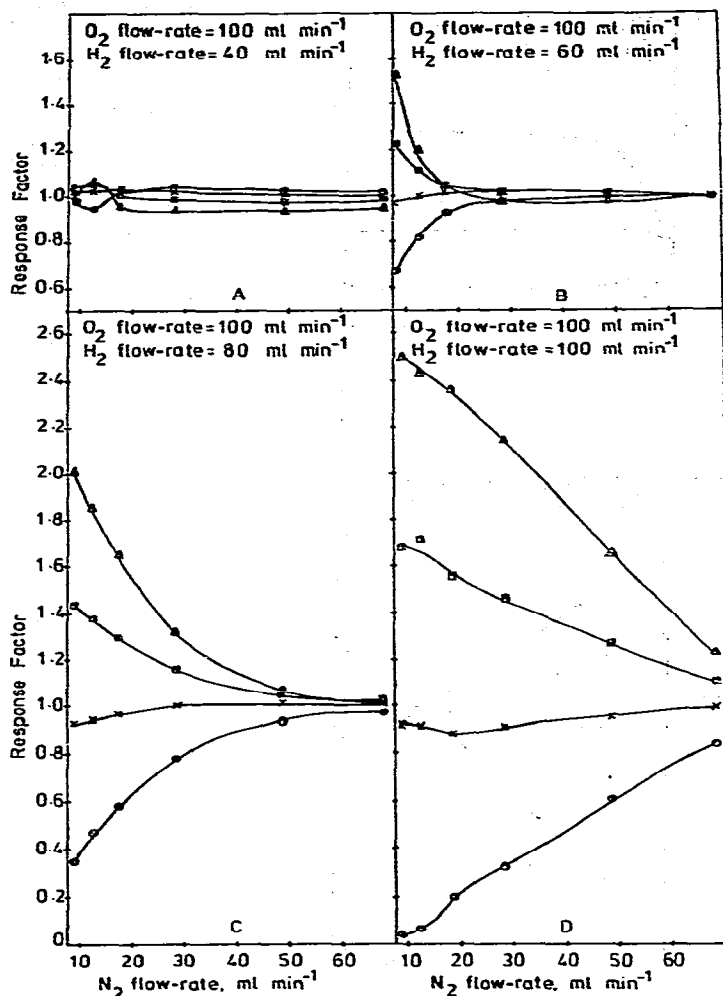
Fig. 2. Effect of nitrogen flow-rate on the molar response of the hydrogen-rich FID at various constant hydrogen and oxygen flow-rates. Symbols as in Fig. 1.

flow-rate for equivalent response would be in excess of 70 ml min^{-1}. Nevertheless, at lower hydrogen fllow-rates substantial areas exist where the nitrogen flow-rate has little or no effect on the equivalent molar responses obtainable with a precision of $\pm 5\%$ of the true values, a level of accuracy that is acceptable for ad hoc analyses of unknown mixtures, particularly when no standard compounds are required for calibration purposes (see below).

The corresponding curves depicting equivalent weight response (Fig. 3) show considerably more restricted zones of operation. Under the conditions prescribed only certain oxygen, hydrogen and nitrogen flow-rates will provide equivalent weight response data for the test solutes and these vary at constant oxygen content with increasing hydrogen and nitrogen flow-rates.
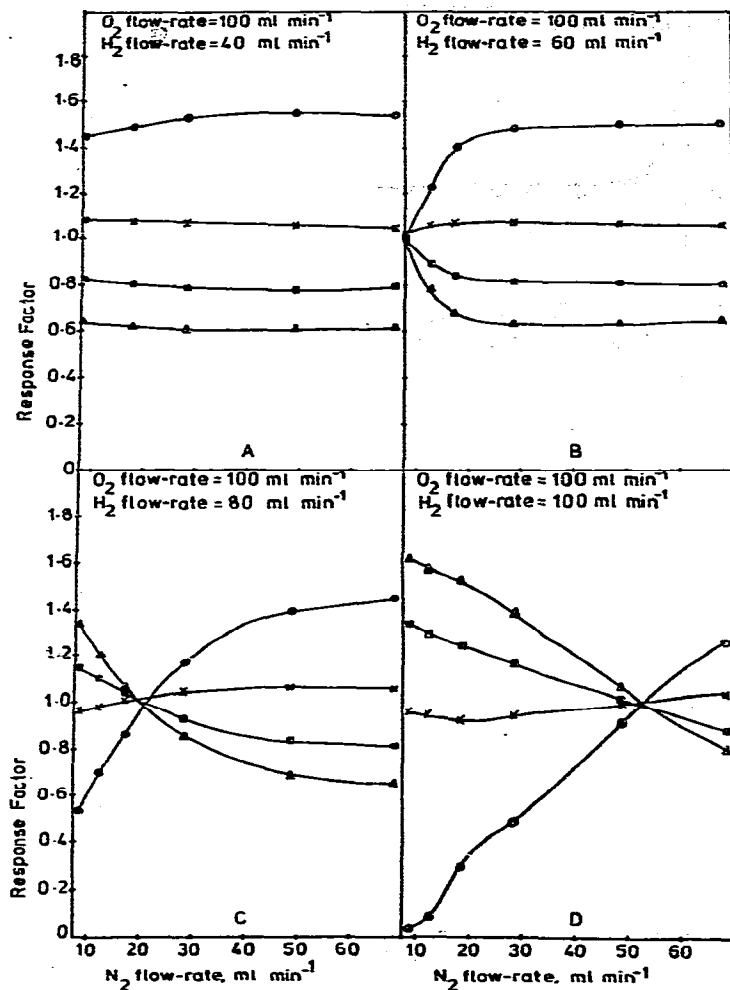
Fig. 3. Effect of nitrogen flow-rate on the weight response of the hydrogen-rich FID at various constant hydrogen and oxygen flow-rates. Symbols as in Fig. 1.

Figs. 4 and 5 show the zones of equivalent molar responses and loci of equivalent weight responses, respectively, for the varying conditions of oxygen, hydrogen and nitrogen flow-rates investigated, and are derived from a series of curves of which those represented in Figs. 2 and 3 are typical. They are derived from different flow-rates of oxygen and hydrogen but under equivalent conditions of nitrogen flow-rate. Although the areas where equivalent molar response (Fig. 4) will be seen to diminish as hydrogen flow-rate increases, they are sufficiently large to be of practical use and can accommodate the range of carrier gas flow-rates required for good chromatography of all packed columns. For capillary columns, provision of make-up gas will be necessary to satisfy the flow-rate criteria for equivalent molar response operation.
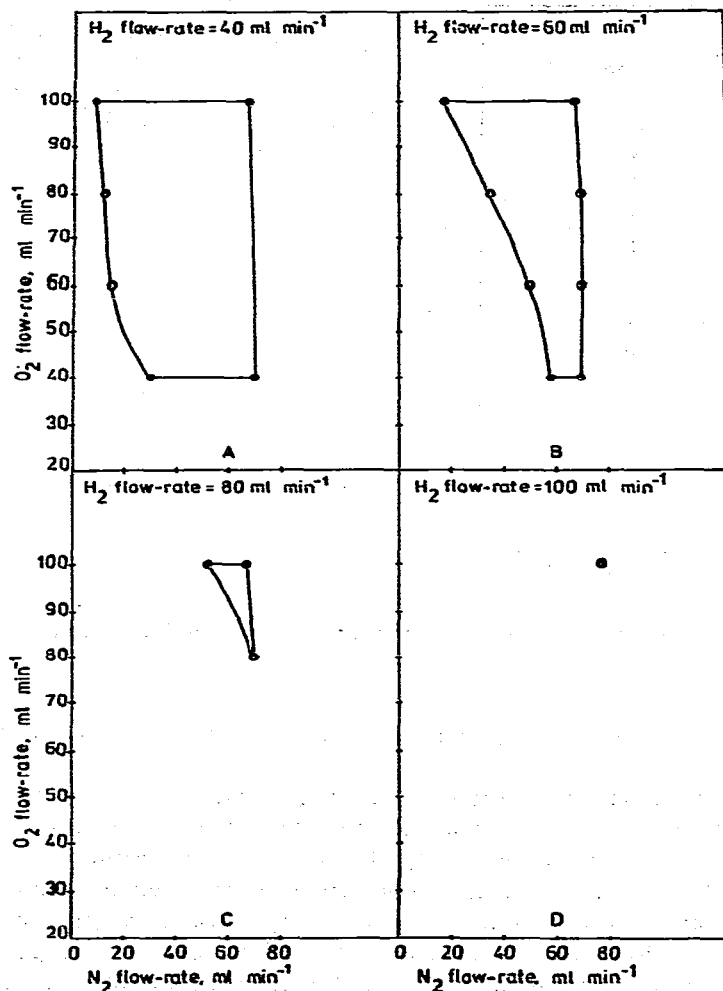
Fig. 4. Zones of equivalent molar response at constant hydrogen flow-rate and varying oxygen and nitrogen flow-rates.

     In contrast, conditions whereby weight responses can be obtained for the solutes under investigation are severely restricted; the loci (Fig. 5) where equivalent weight responses can be obtained are strictly dependent on the oxygen, hydrogen and nitrogen flow-rates. Nevertheless, the loci present a reasonable degree of flexibility with respect to nitrogen carrier gas flow-rate for different column dimensions to enable the equivalent weight responses to be obtained. Chromatographic conditions for separation are initially obtained and the appropriate hydrogen and oxygen flow-rates can then be determined from the loci presented. It must be emphasized that these conditions will probably vary according to detector design but, for a given design, (Pye Unicam Series 104 FID) the loci will produce weight responses at least for the solutes prescribed within $\pm 5\%$ of the true value.
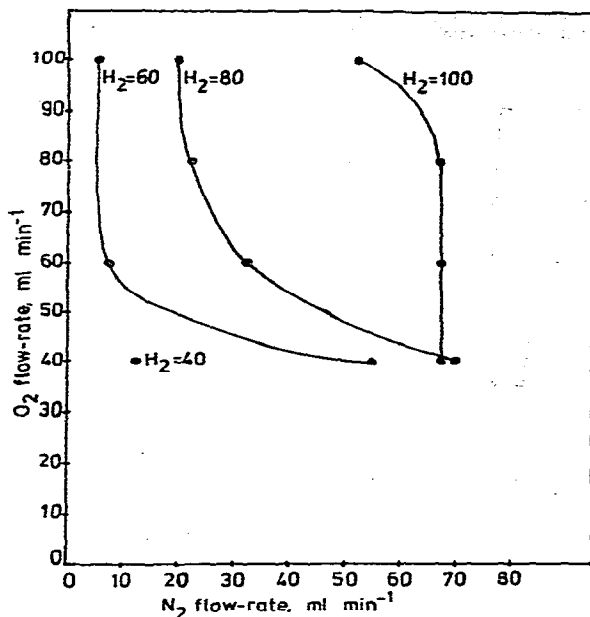
Fig. 5. Loci of equivalent weight response at constant hydrogen levels and varying oxygen and nitrogen flow-rates.

Variation in absolute detector response in the Hydrogen–oxygen FID versus normal FID operation

Data representing the change in absolute detector response of the four test solutes using the oxygen–hydrogen flame compared with their responses in a conventionally operated FID were obtained by taking the ratio of the absolute area counts for the four test solutes under equivalent conditions of nitrogen flow-rate. These data are shown in part in Fig. 6 and illustrate the effect of increasing the combined oxygen and hydrogen flow-rates in a 1:1 ratio with various constant nitrogen flow-rates. Fig. 6 shows that at low combined oxygen and hydrogen flow-rates, there is little difference in absolute response ratio between any of the test solutes. However, as the combined oxygen and hydrogen flow-rate increases so a marked variation in absolute response ratio is observed. The change in response is inversely proportional to nitrogen flow-rate and confirms the previous observation[1] that the oxygen–hydrogen flame can be made selective to heterogeneous atoms, in this instance chlorine, and indeed shows that response to carbon can be effectively suppressed. The detector thus responds principally to the chlorine content of the molecule (cf., Figs. 2 and 3). This is in distinction to operation of the detector in the molar response mode, when response is effectively controlled by the carbon content of the molecules[2] (see below).

This mode of operation of the detector, *i.e.*, selectivity to heterogeneous atoms, could provide a useful adjunct to the electron-capture detector (ECD) in that it does not respond, or at least only to a low level, to aromatic nuclei, while responding to electron-capturing species. This is a potentially useful property in that the ECD does respond to aromatic nuclei.
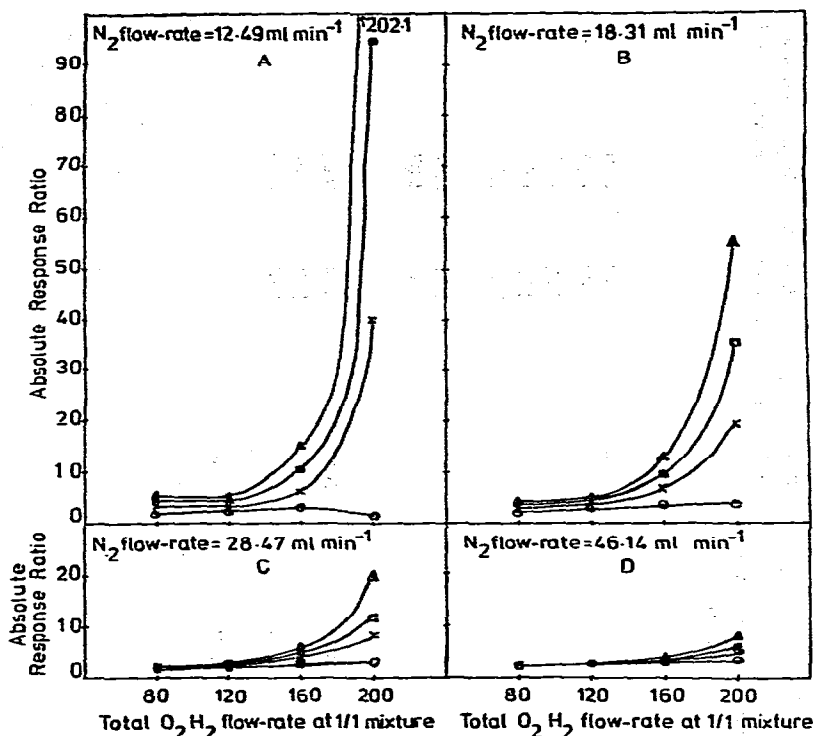
Fig. 6. Variation in the ratio of absolute responses (hydrogen-rich *versus* normal FID) with total oxygen and hydrogen flow-rate (at a 1:1 ratio) at various constant nitrogen flow-rates. Symbols as in Fig. 1.

A further useful property of the oxygen–hydrogen FID is in the enhancement of the response to the four test solutes if the oxygen level is high[5]. Indeed, the oxygen level appears to control the degree of absolute response until the hydrogen flow-rate exceeds 80 ml min^{-1} when the detector response changes to a selective mode.

In the selective mode of operation, the maximum increase in absolute response against a conventionally operated FID is about 300 (for 1,2,4-trichlorobenzene). Concomitant increases for chlorobenzene and dichlorobenzene that are proportional to the chlorine content of the molecule are observed.

A further feature derived from Fig. 6 and illustrated in detail in Fig. 7 is the effect of nitrogen flow-rate at intermediate oxygen and hydrogen flow-rates. The absolute response level increases to a maximum of about 6 above normal FID operation as the nitrogen flow-rate increases to about 20 ml min^{-1} and then diminishes to approximately twice normal FID response for all of the test solutes. This effect is probably due to the diverse combined effect of the thermal conductivity of nitrogen and its decreased residence time in the vicinity of the flame as the flow-rate increases. A study of the effect of argon and helium on this variation in response is being made in order to confirm the reasons for this effect.

Absolute molar responses of various test solutes

Previous work[2] has shown that for some *n*-alkanes and aromatic hydrocarbons

TABLE I

ABSOLUTE MOLAR RESPONSES OF VARIOUS TEST SOLUTES

Flow-rates: series I, oxygen = 40, hydrogen = 40, nitrogen = 40 ml min⁻¹; series II, oxygen = 40, hydrogen = 60, nitrogen = 25 ml min⁻¹.

Compound evaluated	Series I			Series II			Conventional FID[*]	
	Molar response (C/mole)		Relative response (n-hexane = 1.00)	Molar response (C/mole)		Relative response (n-hexane = 1.00)	Absolute response (C/mole)	Relative response (n-hexane = 1.00)
	Determined	Calculated from n-C₆ response		Determined	Calculated from n-C₆ response			
Ethane[**]	0.66	0.65	0.34					
n-Butane[**]	1.30	1.30	0.67					
n-Hexane	1.95	—	1.00	1.31		1.00	1.72	1.00
n-Heptane							2.02	1.17
n-Octane							2.26	1.31
n-Decane	3.23	3.23	1.66				2.83	1.64
n-Butanol	1.24[**]	1.30	0.64				1.02	0.59
n-Hexanol	1.86	1.95	0.95					
n-Heptanol							1.61	0.94
n-Octanol	2.47	2.60	1.27				1.85	1.07
n-Nonanol	2.79	2.92	1.43					
n-Decanol	3.11	3.25	1.59					
1-Bromopropane				0.65	0.65	0.49	0.74	0.43
1-Bromobutane				0.84	0.87	0.64	1.05	0.61
Bromobenzene				1.27	1.31	0.97	1.63	0.95
Chlorobenzene				1.38	1.31	1.05		
Iodobenzene				1.40	1.31	1.06		

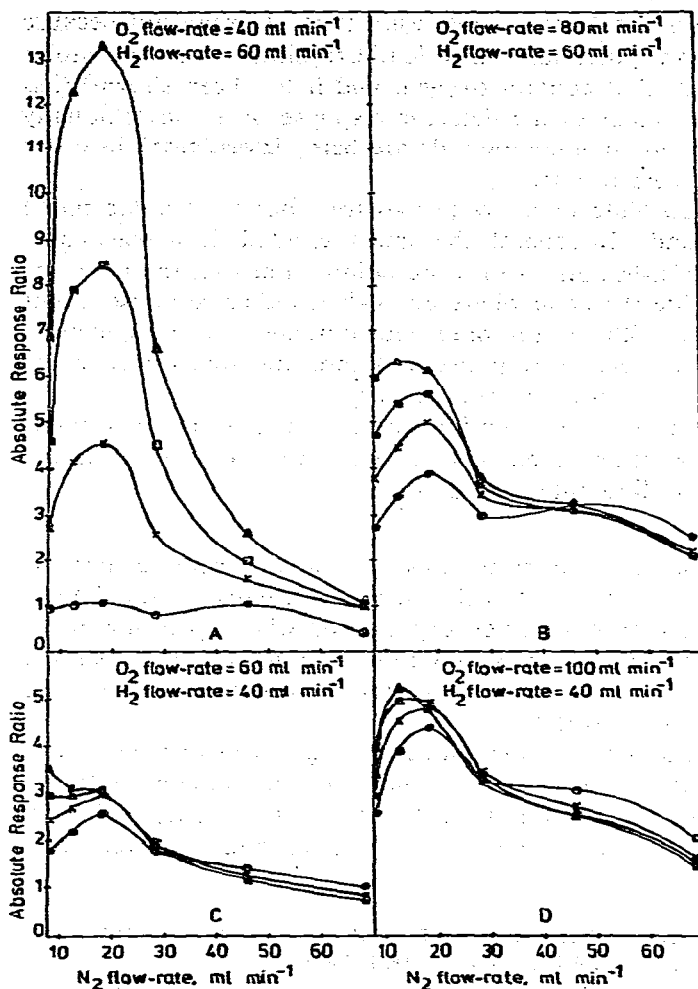[*] Taken from ref. 3.
[**] Extrapolated values.

Fig. 7. Variation in absolute response ratio (hydrogen-rich *versus* normal FID) with nitrogen flow-rate at various intermediate hydrogen and oxygen flow-rates. Symbols as in Fig. 1.

and their chlorinated analogues absolute molar responses are obtained that show a linear relationship with the carbon content of the test solutes. Even compounds such as carbon tetrachloride and hexachlorobenzene, which have a low response on a conventionally operated FID, obey this relationship in a hydrogen-rich flame.

Clearly, this ability to count carbon atoms is important, and further, the ability to predict response or have constant response even when heterogeneous atoms are present in solutes is particularly important in quantitative analysis.

Two series of absolute molar response data on some different solute types are presented in Table I, and are compared with absolute molar response data obtained on a conventionally operated FID.

Series I compares the absolute molar responses of some *n*-alkanes and aliphatic alcohols. The data show a substantially constant response on a carbon number basis;

the deviations are within experimental error. This result is most important because it extends the range of compounds potentially capable of exhibiting equivalent molar responses to include compounds that contain oxygen, and it has been shown[3] that the presence of oxygen severely changes the detector response in a conventionally operated FID. Other oxygen-containing compounds are being investigated in order to confirm the applicability of these results.

Series II compares the absolute molar responses for a series of halogenated aliphatic and aromatic compounds. In general, the data presented show reasonable correlation with the response of n-hexane. It must be pointed out that the flow-rate conditions chosen lie just outside the zone where equivalent molar response might be expected (Fig. 4). Compared with the response data obtained on an equivalent FID operated conventionally, the relative response data indicates that direct molar compositions could be obtained with little loss in accuracy.

It will be noted that the responses quoted for n-hexane in series I and II differ. This is due to the different conditions used in their evaluation and confirms the variation in responses at different flow-rates noted above.

The FIDOH

Detector noise when operating under the absolute molar response mode is of the same order of magnitude as or less than that with a normally operated FID. Difficulties arose because of the high noise levels experienced when operating in the selective mode and, to a lesser extent, the absolute weight response mode. This noise is due to thermionic emission from the flame jet as the temperature of the flame increases with increasing fuel gas flow-rates.

A new detector has been designed to exploit the various facets of the oxygen–hydrogen flame detector while eliminating or at least markedly reducing noise levels. This new design has been called the FIDOH to distinguish it from a normal FID. Table II compares the noise levels of the new detector design and a conventional

TABLE II

COMPARISON OF THE STANDING CURRENTS AND NOISE LEVELS OF THE CONVENTIONAL FID, OXYGEN–HYDROGEN FID AND THE FIDOH

Operating conditions: column temperature, $116°$; detector temperature, $300°$; nitrogen carrier gas flow-rate, 40.8 ml min^{-1}.

Flow-rate (ml min^{-1})		Standing current (A)		Noise (A)	
Hydrogen	Oxygen	O_2–H_2 FID	FIDOH	O_2–H_2 FID	FIDOH
40	40	$4.5 \cdot 10^{-10}$	$2.7 \cdot 10^{-11}$	$1.5 \cdot 10^{-13}$	$8.0 \cdot 10^{-14}$
60	60	$6.2 \cdot 10^{-9}$	$1.8 \cdot 10^{-11}$	$1.6 \cdot 10^{-12}$	$8.0 \cdot 10^{-14}$
80	80	$1.5 \cdot 10^{-8}$	$3.0 \cdot 10^{-10}$	— *	$8.0 \cdot 10^{-13}$
125	125	$1.8 \cdot 10^{-7}$	$5.2 \cdot 10^{-9}$	— *	$1.0 \cdot 10^{-12}$**
60	125	$8.5 \cdot 10^{-11}$	$1.1 \cdot 10^{-11}$	$4.0 \cdot 10^{-14}$	$3.0 \cdot 10^{-14}$

Conventional FID

Hydrogen	Air				
50	500	$1.4 \cdot 10^{-11}$		$4.0 \cdot 10^{-14}$	

* It was impossible to obtain a noise level at these flow-rates because the standing current was so high.

** Slightly different operating conditions were used for this determination: column temperature $176°$ and detector temperature $300°$.

FID operated under the conditions indicated in this paper. It can be seen that even at oxygen and hydrogen flow-rates each of 125 ml min^{-1} the noise level has been markedly reduced to nearly acceptable levels, and it is believed that it will be possible to reduce this level still further.

The novel features of this new design of FID which we have called the FIDOH are briefly described below. The fuel gases, hydrogen and oxygen are supplied through two concentric jets. Hydrogen passes through the central jet which is constructed in 0.01-mm-bore stainless-steel capillary of 0.005 mm wall thickness while oxygen passes through the annulus of the two concentric jets. In this manner the hydrogen flame is profiled to give a small, intensely hot flame which is necessary for some of the features of the new modes of operation. Provision is also made to cool the detector by passage of a nitrogen stream through the normal air inlet to the detector.

This stainless-steel construction provided the noise characteristics quoted in Table II; obviously it still gives thermionic emission but this is markedly reduced. It is believed that a similar construction but using concentric quartz jets will reduce the noise level still further. This is being investigated.

Full details concerning the construction and performance characteristics of this new detection design will be reported elsewhere.

CONCLUSIONS

The data presented confirm and extend the results reported previously[1,2]. The nitrogen flow-rate has been shown to exert a considerable effect on the detector responses obtainable under given conditions of oxygen and hydrogen flow-rates and indeed considerably extends the flexibility of the modes of operation presented.

Other types of solute have been investigated, and it has been shown that chloro, bromo and iodo compounds and, most important, alcohols can be determined under the equivalent molar response mode without the need for detector calibration.

ACKNOWLEDGEMENTS

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