Journal of Chromatography, 150 (1978) 329–338
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CHROM. 10,560

DIRECT QUANTITATIVE ANALYSIS USING THE FLAME-IONIZATION DETECTOR

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(Received August 8th, 1977)

SUMMARY

It has been generally accepted that the use of the flame-ionization detector (FID) in the quantitative determination of differing types of solute in gas chromatographic eluents necessitates prior detector calibration for each species in question.

Methods of operating the FID using hydrogen-rich flames with oxygen as the supporter of combustion have been evaluated, which permits the direct quantitative determination of the solutes investigated on both a molar and a weight mode basis and which therefore enables estimates of molecular weights to be calculated. It has also been shown that the detector response to carbon can be minimized while allowing an enhanced selective response for chlorine.

INTRODUCTION

The flame-ionization detector (FID) is probably the most widely used "sensitive" detector in chromatography on account of its relative ease of construction, its robustness and, more important, because it possesses a linear response and a wide dynamic range. Since it was first proposed as a detection principle for gas chromatography independently by McWilliam and Dewar[1] and Harley *et al.*[2] in 1958, it has been the subject of numerous studies and many variations upon the basic design have been used in an attempt to improve its response characteristics. The response of the FID to organic compounds has been widely investigated[3–9] and it has been demonstrated that the presence of elements other than carbon and hydrogen in the eluting solutes leads to a reduction in response. This unfortunate property necessitates calibration of the detector for each species under investigation when quantitative studies are to be performed.

It has also been widely accepted that the FID shows little or no response to various compounds, *e.g.*, inorganic gases and carbon tetrachloride. Recently, Russev *et al.*[10] demonstrated that inorganic gases could be detected, often to the same level as methane, by using a hydrogen-rich flame with oxygen as the combustion medium.

Other workers have investigated the use of oxygen to support combustion[11,12]

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and demonstrated an enhanced sensitivity when the FID is operated in this mode, but the detection of inorganic gases or other species was not noted.

It is clear from the work of Russev *et al.*[10] that the FID operated in the manner described possesses unusual properties which have not been previously observed. Accordingly, a collaborative exercise has been arranged between Russev and co-workers and the authors to investigate the properties of the FID operated under conditions of a hydrogen-rich flame using oxygen as the supporter of combustion. The results given in this paper relate to the response characteristics of some halogenated aromatic hydrocarbons.

EXPERIMENTAL

A Pye Unicam Series 104 gas chromatograph equipped with a standard Series 104 FID and amplifier was used. The collector was slightly modified by drilling holes round the bottom as previously described[10]. High-purity hydrogen, nitrogen and oxygen were obtained from Air Products (New Malden, Great Britain). All gases were purified and dried by passage through activated molecular sieve (5 Å). Peak area measurements were obtained using an Infotronics CRS201 digital integrator. Standard test solutions were prepared by accurately weighing the test solutes (benzene, chlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene; BDH, Poole, Great Britain) into vials fitted with a septum head (Precision Sampling, Baton Rouge, La., U.S.A.). A 1520 × 4 mm I.D. glass column packed with 5% Bentone 34 and 5% Silicone Fluid MS 550 on 80–100-mesh silanized Chromosorb G and maintained at 159° with 42.1 ml/min of nitrogen as carrier gas was used for most experiments. The detector oven temperature was maintained at 300°. Hydrogen and oxygen flow-rates were accurately set using a soap-bubble flow meter and continuously monitored using Rotameter flow meters. Results are expressed in terms of the ratio of observed to true weight percentages or molar percentages and in absolute terms in coulombs per gram or coulombs per mole where applicable and are the means of eight replicate injections of 0.1 μl with a standard deviation of < 0.3.

RESULTS AND DISCUSSION

The choice of test solutes stemmed from the data presented by Maggs[13] in his evaluation of the Pye-Unicam Series 104 FID. Maggs showed that the series benzene, chlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene underwent a substantial reduction in absolute response in terms of coulombs per gram and coulombs per mole as the number of chlorine atoms in the compounds increased.

In this work, the responses of the above solutes in the FID were obtained under conditions of various fixed oxygen flow-rates and varying hydrogen flow-rates. The response of the various compounds was obtained in two forms: (i) correction factors (on both a weight and a molar basis) for the individual test solutes by which the observed percentage compositions should be divided to obtain the true percentage compositions, and (ii) absolute response in terms of coulombs per gram or coulombs per mole.

Weight response characteristics

A series of weight response curves were generated under the conditions indicated, an example of which is shown in Fig. 1, which also includes the effect on weight response of varying the hydrogen flow-rate at a fixed air flow-rate, *i.e.*, normal FID operation. These results show the unusual, and previously unobserved, effect that all of the test solutes exhibit substantially unit weight response (under the definition proscribed) at hydrogen and oxygen flow-rates of 83 and 64 ml/min, respectively. The responses shown under normal FID operating conditions are as normally observed.

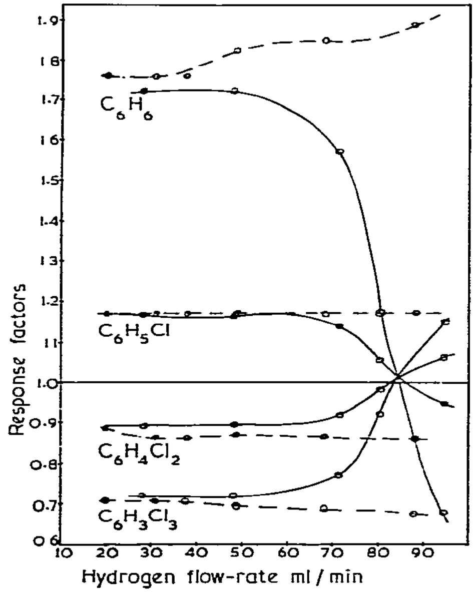

Fig. 1. Variation in weight response correction factors for the FID operated in the hydrogen-rich mode (full lines) and normal operation (dashed lines). Test solutes: benzene, chlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene. Oxygen flow-rate, 64.25 ml/min.

A further unusual characteristic demonstrated in Fig. 1 is that at high hydrogen flow-rates the responses of the four test solutes are reversed, benzene decreasing from a high response factor of 1.7 to 0.65 while 1,2,4-trichlorobenzene increases from a response factor of 0.7 to 1.15. It appears that under conditions of high hydrogen flow-rate, carbon response is being suppressed and the detector is responding principally to the number of chlorine atoms present.

Fig. 2 gives the locus of the zone in which equivalent weight response correction factors for the test solutes can be obtained within the range ± 5% of the true value. This zone is limited in the operating flow-rates of hydrogen and oxygen and arises principally from the rapid decrease in the response of benzene shown in Fig. 1. The unusual shape of the curve between oxygen flow-rates of 40 and 50 ml/min probably arises through difficulties experienced in maintaining precise control of the oxygen flow.

Table I compares the absolute weight response characteristics of the test

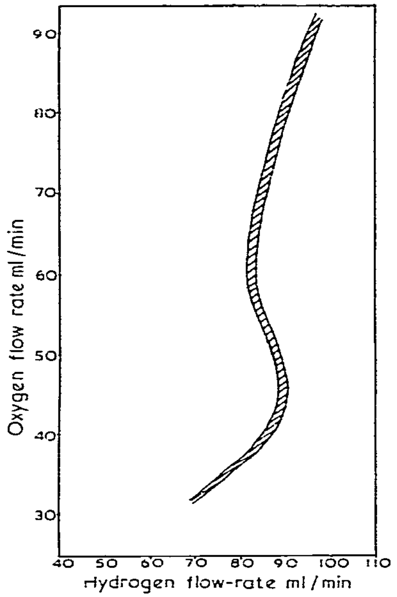

Fig. 2. Locus of conditions for equivalent weight response correction factors of the test solutes to give ± 5% of the true values.

solutes under conditions of unit response correction factor with the absolute weight response for these substances in the same detector optimally operated as a normal FID. The equivalent data obtained by Maggs[13] are also included.

The data show that the absolute weight responses for the test solutes obtained under normal FID operation compare well with those reported by Maggs, which indicates that the minor modification made to the collector has no effect on normal FID operation, and indeed confirms Maggs' findings.

Under conditions of a hydrogen-rich flame with oxygen as the supporter of combustion, the absolute responses of the test solutes, although equivalent, do vary

TABLE I

ABSOLUTE RESPONSES FOR TEST SOLUTES FOR THE FID OPERATED UNDER THE HYDROGEN-RICH AND NORMAL MODES

Gas flow-rates (ml/min)				*Absolute response (C/g)*			
Air	H_2	O_2	H_2/O_2	C_6H_6	C_6H_5Cl	$1,3\text{-}C_6H_4Cl_2$	$1,2,4\text{-}C_6H_3Cl_3$
—	71.5	32.75	2.18	$1.16 \cdot 10^{-3}$	$1.16 \cdot 10^{-3}$	$1.16 \cdot 10^{-3}$	$1.16 \cdot 10^{-3}$
—	83.0	38.0	2.18	$2.51 \cdot 10^{-3}$	$2.51 \cdot 10^{-3}$	$2.51 \cdot 10^{-3}$	$2.51 \cdot 10^{-3}$
—	87.0	51.75	1.68	$1.44 \cdot 10^{-2}$	$1.44 \cdot 10^{-2}$	$1.44 \cdot 10^{-2}$	$1.44 \cdot 10^{-2}$
—	83.0	64.25	1.29	$2.66 \cdot 10^{-2}$	$2.66 \cdot 10^{-2}$	$2.66 \cdot 10^{-2}$	$2.66 \cdot 10^{-2}$
—	97.0	91.0	1.065	$3.93 \cdot 10^{-2}$	$3.93 \cdot 10^{-2}$	$3.93 \cdot 10^{-2}$	$3.93 \cdot 10^{-2}$
475*	32.0	—		$2.23 \cdot 10^{-2}$	$1.53 \cdot 10^{-2}$	$1.11 \cdot 10^{-2}$	$0.81 \cdot 10^{-2}$
500**	30.0	—		$2.17 \cdot 10^{-2}$	$1.45 \cdot 10^{-2}$	$1.05 \cdot 10^{-2}$	$0.74 \cdot 10^{-2}$

* This study.

** From ref. 13.

as the hydrogen to oxygen ratio decreases from 2.18 to 1.065 with a concomitant approximate doubling of the combined oxygen and hydrogen flow-rates. This variation in absolute response ranges from a distinctly inferior response to a significantly enhanced response, which is just under a factor of 2 better for all of the test solutes as is benzene under normal FID operation.

To ascertain whether unit response to all test solutes occurred at different ratios of hydrogen to oxygen flow-rates from those used in the initial evaluations, an arbitrary composition was chosen from the locus given in Fig. 2. Four blends containing varying proportions of the test solutes were evaluated; the results are given in Table II and show that most of the observed percentages lie within ± 5% of the true values. Two results are slightly above this level. Variation in composition had no apparent effect on the results and no significant bias occurred, with the exception that 1,2,4-trichlorobenzene exhibited mainly a small negative percentage error. The observed compositions are an acceptable quantitative analysis of the four test mixtures, particularly as they did not involve the use of correction factors.

TABLE II

COMPARISON OF TRUE AND OBSERVED COMPOSITIONS OF THE TEST SOLUTES USING THE FID OPERATED UNDER UNIT RESPONSE CONDITIONS

Flame composition: hydrogen, 88 ml/min; oxygen, 56.5 ml/min; H_2/O_2 ratio, 1.56.

Solute	*True composition (wt.-%)*	*Observed composition (wt.-%)*			*Error (%)*
		Mean[*]	*Standard deviation*	*Coefficient of variation*	
Benzene	14.05	14.78	0.124	0.84	5.19
Chlorobenzene	20.91	21.40	0.084	0.39	1.87
1,3-Dichlorobenzene	26.21	26.27	0.117	0.44	0.23
1,2,4-Trichlorobenzene	38.83	37.55	0.114	0.30	−3.29
Benzene	7.44	7.66	0.237	3.09	2.96
Chlorobenzene	17.54	18.28	0.122	0.67	4.22
1.3-Dichlorobenzene	23.35	23.72	0.117	0.49	1.58
1,2,4-Trichlorobenzene	51.66	50.33	0.252	0.50	−2.57
Benzene	51.05	51.62	0.216	0.42	1.12
1,3-Dichlorobenzene	9.55	8.92	0.081	0.91	−6.59
1,2,4-Trichlorobenzene	39.41	39.45	0.172	0.43	0.10
Chlorobenzene	17.09	17.75	0.078	0.44	3.86
1,3-Dichlorobenzene	45.90	46.08	0.113	0.24	0.39
1,2,4-Trichlorobenzene	37.01	36.17	0.137	0.38	−2.27

[*] Mean of five replicate determinations.

Molar response characteristics

A second series of curves was generated as described above, an example of which is shown in Fig. 3.

These curves also show the unusual, and previously unobserved, effect that all of the test solutes exhibit substantially unit molar response correction factors, but in this instance over a wide range of hydrogen flow-rates (27–60 ml/min) at a constant oxygen flow-rate. The molar response correction factors again show the unusual

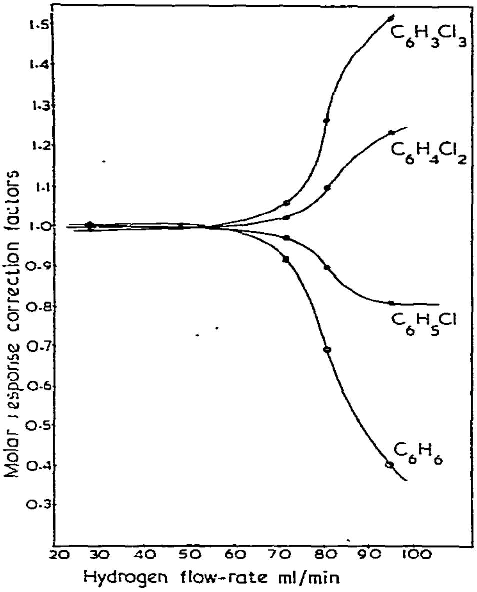

Fig. 3. Variation in molar response correction factors for the FID operated in the hydrogen-rich mode. Test solutes: benzene, chlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene. Oxygen flow-rate, 64.25 ml/min.

property at high hydrogen flow-rates of inversion of normal response (benzene 0.375 and 1,2,4-trichlorobenzene 1.55). This effect supports the conclusion obtained above that carbon response is being suppressed and the FID is responding principally to the chlorine atoms present.

Under conditions of unit molar response correction factor, it appears that the detector is responding solely to the carbon content of the test solutes, a fact which is substantiated by Gough *et al.*[14].

Fig. 4 gives the locus of the zone in which equivalent molar response correction factors for the test solutes can be obtained within the range ± 5% of the true value. This zone is considerably larger than for the corresponding locus for equivalent weight response, and clearly would be the preferred technique of obtaining direct quantitative data if a molar composition is acceptable; alternatively, if the identity of the sample constituents is known, a percentage weight composition can be readily calculated.

Table III gives examples of the percentage molar compositions obtainable under varying conditions of hydrogen and oxygen flow-rates taken from the locus zone of equivalent molar response. The data show good agreement with the true percentage molar composition. All of the observed results lie well within the limits of ± 5% of the true value.

Effect of nitrogen flow-rate

To assess the effect of nitrogen flow-rate upon response, a limited series of experiments was undertaken at a nitrogen flow-rate of 24.5 ml/min. The results of these experiments are given in Table IV and show that at a constant hydrogen

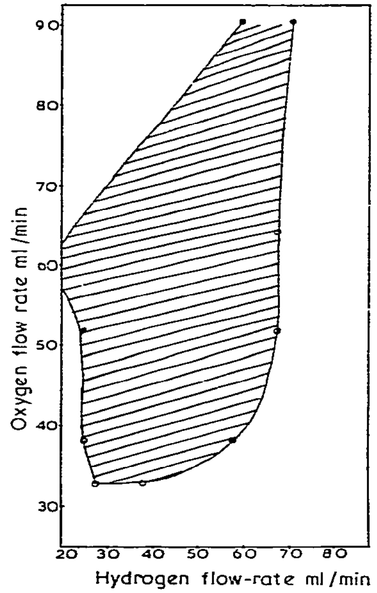

Fig. 4. Locus of conditions for equivalent molar response correction factors of the test solutes to give ± 5% of the true values.

flow-rate of 40 ml/min and varying the oxygen flow-rate between 40 and 100 ml/min direct percentage molar compositions are obtained. It is interesting that the absolute responses of all of test solutes are substantially constant at a given oxygen flow-rate and increase with increasing oxygen flow-rate. All of the absolute responses are considerably greater than for an optimally operated normal FID[11,12].

At high hydrogen flow-rates (85 ml/min), direct percentage weight compositions are obtained, and the absolute responses are significantly higher than under normal FID operation. A further increase in hydrogen flow-rate (100 ml/min) again demonstrates the unusual effect that the carbon response is reduced and the detector is responding principally to the chlorine content of the compounds, *i.e.*, the FID is

TABLE III

PERCENTAGE MOLAR COMPOSITIONS OBTAINED UNDER VARYING CONDITIONS OF HYDROGEN AND OXYGEN FLOW-RATES

Flow-rate (ml/min)		*Percentage molar composition*							
Hydrogen	*Oxygen*	*Benzene*	*Bias (%)*	*Chloro-benzene*	*Bias (%)*	*1,3-Dichloro-benzene*	*Bias (%)*	*1,2,4-Trichloro-benzene*	*Bias (%)*
27.75	32.75	23.53	−1.01	24.58	+0.28	23.65	+0.59	28.24	+0.11
27.75	64.30	24.18	+1.72	24.42	−0.37	23.40	−0.46	27.95	−0.26
48.90	64.30	24.04	+1.13	24.42	−0.37	23.45	−0.25	28.08	−0.46
60.00	38.00	22.65	−4.71	24.43	−0.33	24.09	+2.46	28.83	+2.23
70.80	91.00	23.32	−1.89	24.00	−2.08	23.63	+0.51	29.05	+2.62
True composition		23.77	—	24.51	—	23.51	—	28.21	—

TABLE IV

PERCENTAGE MOLAR AND PERCENTAGE WEIGHT COMPOSITIONS AND ABSOLUTE RESPONSES FOR TEST SOLUTES AT VARYING OXYGEN AND HYDROGEN FLOW-RATES[**]

Parameter	*Test solute*											
	Benzene[***]						*Chlorobenzene*[§]					
Hydrogen flow-rate (ml/min)	40	40	40	40	85	100	40	40	40	40	85	100
Oxygen flow-rate (ml/min)	40	55	70	100	100	100	40	55	70	100	100	100
Composition taken from integrator (%)	17.72	17.79	17.93	17.98	10.13	3.83	23.25	23.16	23.20	23.13	19.30	16.76
Molar response correction factor	1.002	1.006	1.014	1.017	0.573	0.217	1.001	0.997	0.999	0.996	0.831	0.722
Weight response correction factor	1.767	1.774	1.788	1.793	1.010	0.381	1.225	1.220	1.223	1.219	1.017	0.883
Absolute response (C/mole)	1.85	2.69	3.21	3.75	3.05	2.71	1.84	2.67	3.16	3.68	4.43	9.04
Absolute response (C/g × 10^{-2})	2.37	3.45	4.11	4.81	3.91	3.47	1.64	2.37	2.81	3.27	3.94	8.04
Absolute response, normal FID[*] (C/mole)	1.69						1.63					
Absolute response, normal FID[*] (C/g × 10^{-2})	2.17						1.45					
	1,3-Dichlorobenzene[§§]						*1,2,4-Trichlorobenzene*[§§§]					
Hydrogen flow-rate (ml/min)	40	40	40	40	85	100	40	40	40	40	85	100
Oxygen flow-rate (ml/min)	40	55	70	100	100	100	40	55	70	100	100	100
Composition taken from integrator (%)	27.56	27.71	27.66	27.62	29.54	31.61	31.43	31.35	31.20	31.27	41.01	47.80
Molar response correction factor	0.998	1.003	1.001	1.000	1.069	1.144	0.998	0.996	0.991	0.993	1.303	1.518
Weight response correction factor	0.934	0.939	0.937	0.936	1.001	1.071	0.758	0.756	0.752	0.754	0.989	1.152
Absolute respons (C/mole)	1.84	2.69	3.16	3.69	5.70	14.35	1.80	2.67	3.14	3.68	6.95	19.06
Absolute response (C/g × 10^{-2})	1.25	1.83	2.15	2.51	3.88	9.76	0.99	1.47	1.73	2.03	3.83	10.50
Absolute response, normal FID[*] (C/mole)	1.44						1.34					
Absolute response, normal FID[*] (C/g × 10^{-2})	1.05						0.74					

[*] Taken from ref. 13.

[**] Nitrogen flow-rate = 28.5 ml/min.

[***] True percentage molar composition, 17.68; true percentage weight composition, 10.03.

[§] True percentage molar composition, 23.22; true percentage weight composition, 18.98.

[§§] True percentage molar composition, 27.62; true percentage weight composition, 29.50.

[§§§] True percentage molar composition, 31,48; true percentage weight composition, 41.48.

operating as a selective detector for chlorine and is effectively counting the number of chlorine atoms present in the three halogenated species.

Dropping the nitrogen flow-rate appears to have an effect on the position of the locus of both equivalent weight and molar responses, but only at high oxygen flow-rates. This apparent shift is being investigated in detail. At the lower oxygen flow-rates (40–70 ml/min), however, the locus given in Fig. 4 is followed. This may be fortuitous, and due to the large zone in which equivalent molar response correction factors are obtained.

Determination of molecular weights

The ability of the FID operated under the conditions proscribed to produce direct percentage molar and weight compositions clearly provides a method of estimating molecular weights if one compound is included as standard. Table V gives molecular weights calculated from the percentage compositions given in Table IV, and demonstrates that, using benzene as the standard, good estimates of the molecular weights of the three halogenated compounds are obtained.

TABLE V

CALCULATION OF MOLECULAR WEIGHTS

Test solute	*Composition*		*Wt.-% / Mole-%*	*Molecular weights*			*Bias (%)*	*σ*
	Wt.-%	*Mole-%*		*Ratio*	*Determined*	*True**		
Benzene	10.13	17.72	0.57167	1	—	78.11	—	—
Chlorobenzene	19.30	23.25	0.83011	1.45208	113.42	112.56	+0.76	—
1,3-Dichlorobenzene	29.54	27.56	1.07184	1.87493	146.45	147.01	−0.37	—
1,2,4-Trichlorobenzene	41.01	31.43	1.30480	2.28243	178.28	181.46	−1.75	—
Benzene	10.13	17.79	0.56942	1	—	78.11	—	—
Chlorobenzene	19.30	23.16	0.83333	1.46347	114.31	112.56	+1.5	—
1,3-Dichlorobenzene	29.54	27.71	1.06604	1.87215	146.23	147.01	−0.53	—
1,2,4-Trichlorobenzene	41.01	31.35	1.30813	2.29730	179.64	181.46	−1.11	—
Benzene	10.13	17.93	0.56497	1	—	78.11	—	—
Chlorobenzene	19.30	23.20	0.83189	1.47245	115.01	112.56	+2.17	—
1,3-Dichlorobenzene	29.54	27.66	1.06797	1.89031	147.84	147.01	+0.58	—
1,2,4-Trichlorobenzene	41.01	31.20	1.31442	2.32653	181.72	181.46	+0.14	—
Benzene	10.13	17.98	0.56340	1	—	78.11	—	—
Chlorobenzene	19.30	23.13	0.83441	1.48102	115.68	112.56	+2.77	—
1,3-Dichlorobenzene	29.54	27.62	1.06950	1.89830	148.28	147.01	+0.86	—
1,2,4-Trichlorobenzene	41.01	31.27	1.31148	2.32780	181.82	187.46	+0.20	—
Mean results								
Benzene					—	78.11	—	—
Chlorobenzene					114.60	112.56	+1.81	0.97
1,3-Dichlorobenzene					147.21	147.01	+0.13	1.02
1,2,4-Trichlorobenzene					179.81	181.46	−0.90	1.75

* True molecular weights taken from ref. 15.

CONCLUSION

The results presented indicate that the FID possesses some novel features that have not been reported previously. These features include the ability to obtain direct quantitative analyses on both a molar and a weight basis; the ability to supress carbon response and become selective at least for chlorine; an exclusive response to the carbon content of molecules when the detector is molar responsive; and the provision of a means of estimating molecular weights at least as well as other gas chromatographic detectors.

No attempt is being made at this stage to provide explanations for these effects, other than those briefly indicated above. Further work is progressing on the investigation of these novel ways of operating the detector and will be reported elsewhere.

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