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A COMPARISON OF THE MASS DETECTOR AND GAS DENSITY DETECTOR FOR QUANTITATIVE ANALYSIS

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SUMMARY

A gas chromatograph was equipped with a gas density detector and mass detector in series. A comparison was made between the repeatability of response of the two detectors over a wide gas flow rate range, and at a fixed flow rate. The linear dynamic range, limit of detection and response time of the gas density detector were measured. The value of the gas density detector for relative composition analyses, assuming a response based on molecular weight, was assessed and compared with results obtained using the mass detector.

INTRODUCTION

The use of the mass detector for quantitative analysis has recently been demonstrated¹. It has been shown that quantitative results can be obtained with a precision of 1%.

A gas density balance designed for use as a chromatographic detector was introduced by MARTIN AND JAMES in 1956². Since only a few papers have subsequently been published on this type of detector, it is pertinent to discuss the device in detail. The gas density balance is a non-destructive detector and by passing column effluent first into this detector and then into a mass detector, a direct comparison of the performance of the two detectors is possible. The results of this work are described below.

DISCUSSION

The original Martin gas density balance was constructed from a solid copper block. Other workers³ have constructed skeletal types of balance from copper tubing, and have compared some of the characteristics of the two models. The overall conclusions were that the original block detector gives less noise, but has a smaller

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linear dynamic range than the skeletal model. However, both detectors have a linear dynamic range greatly in excess of that required for gas chromatography.

The skeletal gas density balance is far easier to construct. Other minor modifications to the original MARTIN AND JAMES design have been proposed by several workers³⁻⁷, but these concern mainly the construction of the detector and do not substantially alter the performance characteristics. A gas density balance for use at high temperatures has also been described⁸.

The sensitivity of the detector will depend on the volume of the main conduits, the power dissipated by the heater, and the nature of the carrier gas. A gas of low thermal conductivity will increase the temperature gradient along the wire, and for this reason nitrogen is generally used as carrier gas. However, for the analysis of materials of molecular weight similar to that of nitrogen, a different gas should be used, in order to maintain reasonable sensitivity. The detector is temperature sensitive and excellent thermostating is required. For a correctly balanced detector, the response is completely flow insensitive. The constituents of mixtures under analysis do not come into contact with the heated filament of the detector. The response of the detector is predictable from a knowledge of molecular weights. By correcting the peak areas corresponding to each of the constituents of a mixture, using the expression:

$$f = \frac{M_X}{M_X - M_C} \quad (1)$$

where M_X and M_C are the molecular weights of the constituent X, and of the carrier gas, respectively, the percentage composition of the mixture by weight, is obtained directly:

$$\% \text{ w. of component X} = \frac{A_X f_X}{\sum_1^j A_f} \cdot 100 \quad (2)$$

where A = peak area.

Thus no experimental calibration of the detector is required, and the response should be linear for all materials^{9,10}. Clearly the gas density balance has many of the properties of an ideal detector for quantitative analysis.

Although the Martin gas density balance is not commercially available, a simplified version based on a design by NERHEIM¹¹ is manufactured by the Gow-Mac Instrument Company*. GUILLEMIN AND AURICOURT have published several papers¹²⁻¹⁵ on the performance of the Gow-Mac gas density detector.

These authors set out to define the optimum operating conditions for quantitative analysis. The effect of the ratio of the reference and analytical gas flow rates on sensitivity was studied. The performance of the detector was examined using several different carrier gases, both permanent gases, and those of high molecular weight such as the halogenated alkanes. The effect of temperature on detector sensitivity was studied. The linearity of the detector was briefly examined, but no definitive study was undertaken. Results of the quantitative analyses of a number of mixtures of low boiling halogenated hydrocarbons, calculated using eqn. 2, were in good agreement with the true mixture compositions. Each mixture was analysed

* Gow-Mac Instrument Company, New Jersey.

three times, at one sample size only. Useful data may be found in a paper by WALSH AND ROSIE¹⁶. The effect of changing various parameters on the detector output was studied. Several two-component mixtures, and one five-component mixture were analysed, and the bias of the results varied between 1.1 and 2.2%. No information is given on the precision of the determinations. In the present work the effect of gas flow rate on detector response, the repeatability of response, and the reliability of the detector as a quantitative device is assessed.

EXPERIMENTAL

A Shandon KG 2 chromatograph was fitted with a Gow-Mac gas density detector Model 091. The gas outlet of the gas density detector was connected with a short length of $\frac{1}{8}$ in. O.D. stainless steel tubing to a mass detector, situated outside the chromatograph oven. The tube was heated resistively. A detailed description of the mass detector has previously been published¹⁷. The responses of the detectors were monitored with a Honeywell dual pen potentiometric recorder. The mass detector output was fed to the 10 mV channel, and the gas density detector to the 1 mV channel. Two chromatograms were thus obtained for each analysis. The chromatograms were not completely superimposed due to the finite time taken for a component to traverse the distance between the two detectors. This is illustrated in Fig. 1.

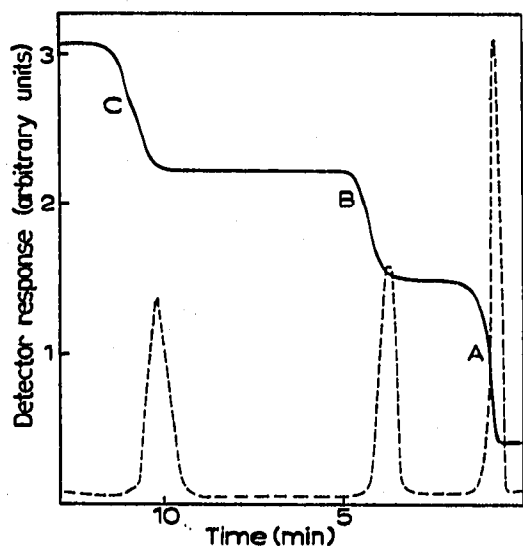


Fig. 1. Chromatogram from mass detector-gas density detector system. A = ethyl acetate; B = *n*-propyl acetate; C = *n*-butyl acetate; —, mass detector response; - - - -, gas density detector response.

Preparation of samples

Prior to use, all compounds were checked for impurities by conventional gas chromatographic techniques. The majority of aliphatic hydrocarbons were found to be of high purity, and minor amounts of branched alkanes in normal alkanes were removed by treatment with molecular sieve. The acetates, ketones, and aromatics, which were in general better than 98% pure, were distilled before use. In addition,

TABLE I

OPERATING CONDITIONS

Column	Ref. E
Carrier gas	Nitrogen
Injection temperature	154°
Column temperature	104° ± 0.1°
Delivery tube temperature	34° ± 1°
Nominal sample size	1.2 µl
Gas density detector	
Bridge current	150 mA
Sensitivity	× 200
Mass detector range	1 mg f.s.d.

impurities in several of these compounds were removed by preparative scale chromatography, using a Wilkens Autoprep chromatograph. The lower alcohols and ketones were dried by standing over molecular sieve, and the water content checked using a Martin gas density balance. Mixtures were prepared by weighing directly into sample bottles, which were completely filled, and stored in a refrigerator when not in use. Samples for analysis were withdrawn with a syringe through a septum fitted to the bottles.

The effect of flow rate on the relative response of the gas density detector was measured by varying the total flow rate through the detector (*i.e.* the flow rate to the mass detector) over the range 15–250 ml min⁻¹. The requirement that there must be a substantially greater flow rate through the reference arm of the detector than through the analytical arm was met over the whole flow rate range. The same three-component acetate mixture was analysed three times at each of 24 different flow rates. The conditions of analysis are given in Table I.

Column Ref. E is 4 m × 4 mm I.D. stainless steel containing 20% PEGA on 72–85 mesh Chromosorb G.

The percentage composition of the mixture was calculated at each flow rate from the chromatograms. The results from the mass detector were calculated directly from step height measurements. The gas density detector results were calculated from peak area measurements, corrected using eqn. 2. Mean percentage compositions embracing the whole flow rate range are quoted in Table II.

Comparison of the results obtained using the two detectors reveals a similar trend in bias, although the values are significantly greater on the gas density detector.

TABLE II

QUANTITATIVE RESULTS (WIDE FLOW RATE RANGE)

x_0 = true % composition; \bar{x} = mean % weight of n determinations; σ = standard deviation; V = coefficient of variation (%).

Component	Mass detector					Gas density detector				
	x_0	\bar{x}	σ	V	% bias	\bar{x}	σ	V	% bias	
Ethyl acetate	33.49	33.04	0.63	1.93	-1.37	32.68	2.4	7.34	-2.42	
<i>n</i> -Propyl acetate	31.64	31.38	0.28	0.90	-0.85	31.05	1.8	5.80	-1.86	
<i>n</i> -Butyl acetate	34.87	35.57	0.67	1.89	+1.99	36.26	2.0	5.52	+3.84	
				1.57	1.40			6.62	2.34	

TABLE III

QUANTITATIVE RESULTS (FIXED GAS FLOW RATE)

Component	Mass detector					Gas density detector			
	x_0	\bar{x}	σ	V	% Bias	\bar{x}	σ	V	% Bias
Ethyl acetate	33.29	33.07	0.414	1.25	-0.66	34.04	1.42	4.43	+2.25
<i>n</i> -Propyl acetate	30.92	30.66	0.158	0.52	-0.87	30.21	0.76	2.52	-2.33
<i>n</i> -Butyl acetate	35.78	36.26	0.404	1.11	+1.34	35.75	1.44	3.85	-0.08
				0.96	0.96			3.60	1.55

The standard deviations of the gas density detector results are all of the same order and are much greater than those obtained using the mass detector. Repeatability can be defined numerically in terms of the coefficient of variation. If the coefficient of variation is $n\%$ then the repeatability of 19 out of 20 results is $\pm n\%$. The repeatability of the mass detector response is $\pm 1.6\%$ and the Gow-Mac gas density detector $\pm 6.6\%$. The very much higher value obtained with the latter detector may result from the difficulty of precisely assessing peak areas by peak height and width measurements. The precision of area measurements by this method was measured in a different series of experiments. The coefficient of variation was 2.9% for 31 analyses. For the mass detector the change in bias with flow rate was $5 \times 10^{-30}\%$ per ml min⁻¹. For the gas density detector the value was $1 \times 10^{-20}\%$ per ml min⁻¹, and although this value is greater than that for the mass detector, for practical purposes the relative responses of both detectors are flow independent.

A similar acetate mixture was analysed 15 times under the conditions given in Table I, at a single gas flow rate (analytical gas flow 49 ml min⁻¹ and reference gas flow 77 ml min⁻¹). The results are summarised in Table III.

Comparison with Table II shows that the performance of both detectors is much improved. Coefficients of variation have been halved and the bias of the results considerably decreased. Repeatability of response of the gas density detector is $\pm 3.6\%$, whereas it is $\pm 1\%$ for the mass detector.

TABLE IV

OPERATING CONDITIONS

Column	Ref. E
Carrier gas	Nitrogen
Injection temperature	154°
Column temperature	101°
Delivery tube temperature	34°
Analytical gas flow rate	45 ml min ⁻¹
Reference gas flow rate	60 ml min ⁻¹
Sample sizes	0.1-5 μ l
Gas density detector	
Filament current	125 mA
Sensitivity	$\times 500$ to $\times 50$
Temperature	101°
Mass detector	
Ranges	100 μ g-5 mg
Temperature	24°

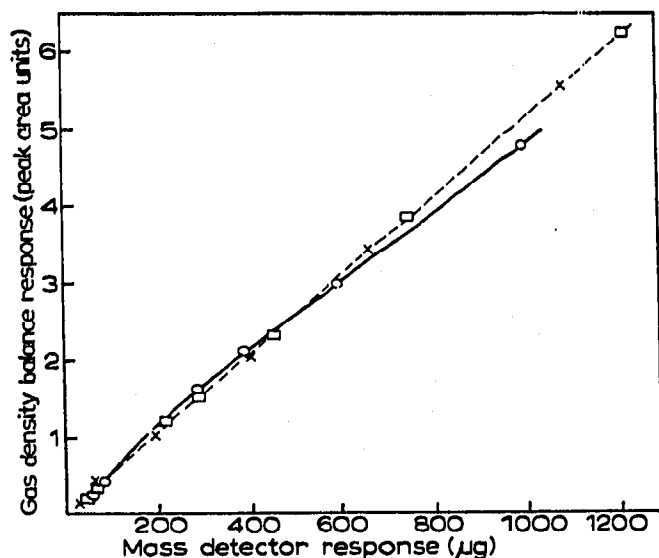


Fig. 2. Gas density detector calibration curve. ○, benzene; □, toluene; ×, ethylbenzene.

The response of the gas density detector to a variety of organic compounds, over a range of sample sizes, was measured under the conditions given in Table IV. Conditions were chosen such that the mass detector was operated within the range known to give a linear response, and the gas density detector to give optimum behaviour.

The results are expressed graphically, by plotting the weight of each compound detected by the mass detector against the (corrected) peak area obtained from the gas density detector. Peak areas were in general measured with a digital integrator, but for comparison some areas were in addition calculated from peak height and

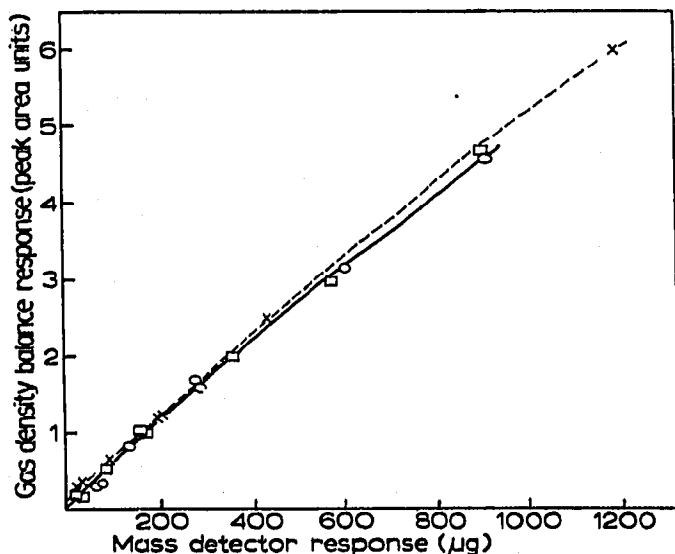


Fig. 3. Gas density detector calibration curve. ○, methyl ethyl ketone; □, methyl *n*-propyl ketone; ×, methyl *n*-butyl ketone.

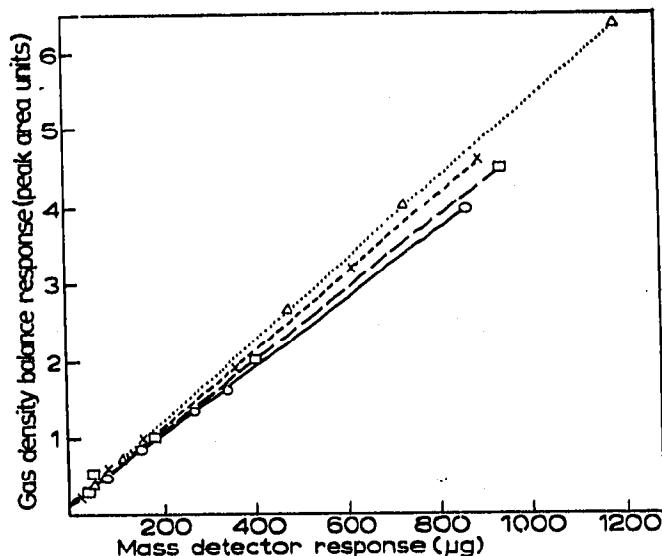


Fig. 4. Gas density detector calibration curve. ○, methyl acetate; □, ethyl acetate; ×, *n*-propyl acetate; △, *n*-butyl acetate.

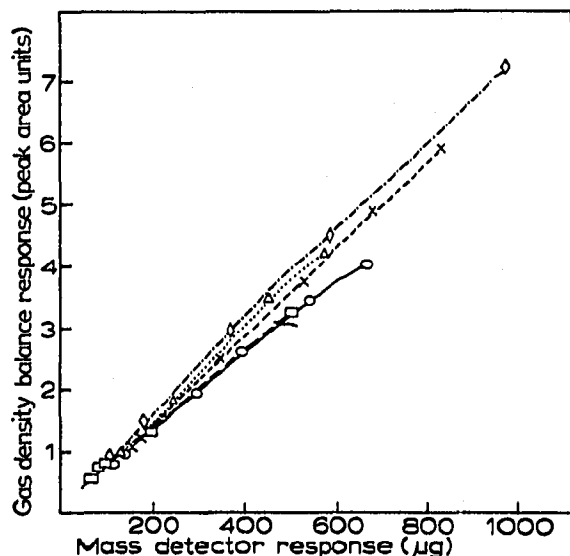


Fig. 5. Gas density detector calibration curve. \circ , *n*-heptane; \square , *n*-octane; \times , ethyl acetate; \triangle , methyl ethyl ketone; \diamond , benzene.

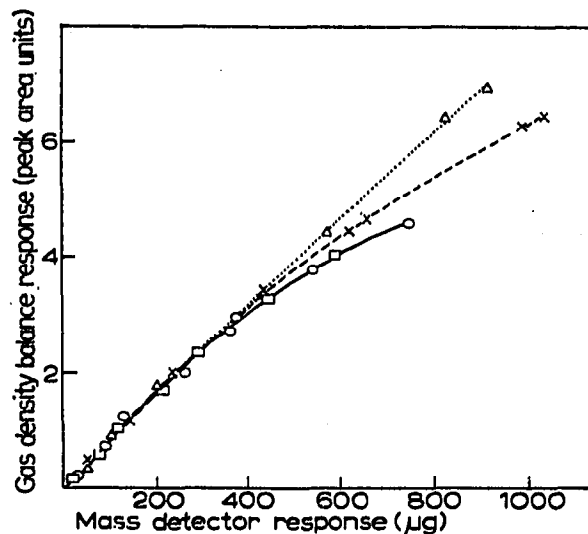


Fig. 6. Gas density detector calibration curve. \circ , cyclohexane; \square , *n*-octane; \times , carbon tetrachloride; \triangle , dichloroethylene.

width measurements. These results are discussed below. Although each compound formed part of a mixture, the results are absolute in the sense that response is expressed in terms of detected weight and not percentage composition. The composition of the mixtures in no way affects the results, and all components were well resolved. Each Fig. (2-8) shows the response of the detector to each of the components of a mixture. Since corrected peak areas were used, all curves on all figures should be coincident and linear, assuming an ideal detector response. In practice it is difficult

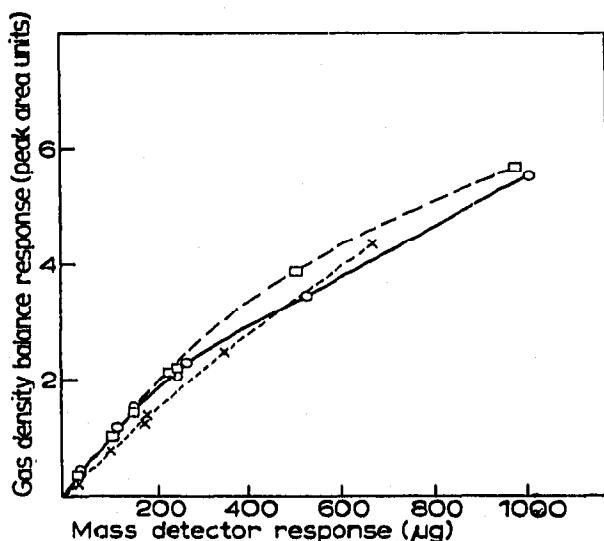


Fig. 7. Gas density detector calibration curve. \circ , 2,2,4-trimethylpentane; \square , *n*-octane; \times , 1-octene.

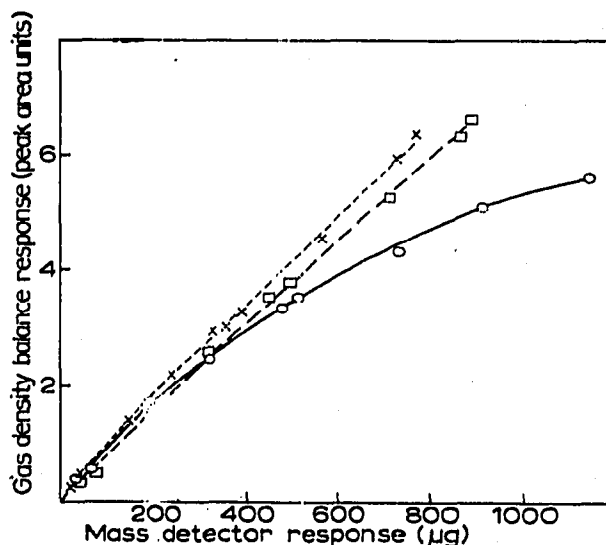


Fig. 8. Gas density detector calibration curve. \circ , *n*-octane; \square , butylene oxide; \times , dioxan.

to ensure complete reproducibility of operating conditions from day to day, so that it is only reasonable to expect coincidence of the curves obtained from a single mixture, *i.e.*, the curves on any one figure should be coincident, but not necessarily have the same slope as the remaining figures. The only compounds to give a linear response over the whole range investigated were toluene, ethylbenzene, and the acetates. In general all compounds gave a linear response over a fairly limited range (about 10^1). All response curves were virtually coincident at low sample sizes, but became progressively divergent as the sample size increased. 1-Octene gave a significantly lower response, attributed at least in part to the presence of partially resolved impurities. All peaks in all determinations were reasonably symmetrical, so that deviations from linearity as a result of inaccurate area measurement are unlikely. Most figures were constructed from digital integrator results, which were compared with manual peak area measurements: identical response patterns emerged. It is

TABLE V

PERCENTAGE COMPOSITION ANALYSES

Compound	Composition			Response		Fig.
	x_0	\bar{x}_M	\bar{x}_D	R_{DO}	R_{DM}	
<i>n</i> -Pentane ^a	22.50	22.30	21.62	0.96	0.97	—
<i>n</i> -Hexane	17.57	18.40	17.55	1.00	0.96	
<i>n</i> -Heptane	14.67	15.16	15.69	1.07	1.03	
<i>n</i> -Octane	16.45	16.46	16.81	1.02	1.02	
<i>n</i> -Nonane	28.82	27.69	28.32	0.99	1.02	
Benzene	41.33	41.35	40.56	0.98	0.98	2
Toluene	31.00	30.94	31.50	1.02	1.02	
Ethylbenzene	27.67	27.72	27.94	1.01	1.01	
Methyl ethyl ketone	42.20	43.05	42.63	1.01	0.99	3
Methyl <i>n</i> -propyl ketone	25.69	25.75	25.67	1.00	1.00	
Methyl <i>n</i> -butyl ketone	32.10	31.20	31.70	0.99	1.00	
Methyl acetate	23.72	21.46	20.62	0.87	0.96	4
Ethyl acetate	23.47	25.50	24.16	1.03	0.95	
<i>n</i> -Propyl acetate	22.82	23.03	23.58	1.03	1.02	
<i>n</i> -Butyl acetate	29.99	30.02	31.64	1.06	1.05	
<i>n</i> -Heptane	18.44	18.61	18.25	1.00	0.98	5
<i>n</i> -Octane	13.77	13.82	13.45	0.99	0.99	
Ethyl acetate	23.68	23.92	24.43	1.03	1.03	
Methyl ethyl ketone	16.49	16.28	16.29	0.99	1.00	
Benzene	27.63	27.37	27.59	1.00	1.00	
Cyclohexane	19.30	19.39	19.02	0.99	0.99	6
<i>n</i> -Octane	15.87	16.14	16.54	1.04	1.02	
Carbon tetrachloride	34.92	34.79	33.80	0.97	0.97	
Dichloroethylene	29.92	29.68	30.63	1.02	1.03	
2,2,4-Trimethylpentane	38.03	38.25	40.56	1.07	1.06	7
<i>n</i> -Octane	35.59	35.53	37.09	1.04	1.04	
1-Octene	26.38	26.23	22.35	0.85	0.85	
<i>n</i> -Octane	35.64	36.26	37.17	1.04	1.02	8
Butylene oxide	35.71	36.20	33.81	0.95	0.94	
Dioxan	28.65	27.54	29.02	1.01	1.05	

^a Column and gas density detector at 66°.

reasonable to conclude therefore that deviations from linearity are a real effect. A sample chromatogram, which shows the analysis of a 1 μ l sample of a ketone mixture, is shown in Fig. 1.

A linear gas density detector response is not a sufficient criterion for satisfactory quantitative performance. On Fig. 5 for example, all components of the mixture give a linear response to about 500 μ g, but only the *n*-heptane and *n*-octane curves coincided, *i.e.* only these two materials give identical absolute response. This is not the case for the remaining constituents. To obtain satisfactory quantitative results the detector must give a response linear with concentration and equal for all materials, at all sample sizes: even with heptane the absolute response decreases with sample size (see Table VI).

For each mixture, using the linear and coincident portion of the response curves, and for a homologous series of alkanes the mean values of the percentage weights detected by the gas density detector were calculated from the corrected peak areas (\bar{x}_D values). These results are given in Table V. The mean percentage weights of the components in each mixture were also calculated from the mass detector results (\bar{x}_M values) and using these as a standard, the response of the gas density detector with respect to the mass detector was found. The response factor was defined as:

$$R_{DM} = \frac{\bar{x}_D}{\bar{x}_M} \quad (3)$$

All mixtures were of known composition (x_0 values), so that in this particular case, a check could be made on the response factors obtained using the mass detector as standard. The response factor was defined as:

$$R_{DO} = \frac{\bar{x}_D}{x_0} \quad (4)$$

The factors R_{DM} should be the more reliable, since losses due to evaporation of sample before injection, and column adsorption effects, are eliminated.

The relative composition analyses given by the gas density detector operated within the linear and coincident portion of the response curve, were satisfactory. The standard deviations of the response factors were 4.8×10^{-2} for R_{DO} and 4.2×10^{-2} for R_{DM} .

The effect of calculating the relative amounts of the various components of a

TABLE VI

EFFECT OF SAMPLE SIZE ON DETECTOR RESPONSE

Weight of material detected (μ g)	GDD response ($cm^2\mu g^{-1}$)	% heptane detected	
		MD	GDD
129	0.779	18.71	18.54
143	0.768	18.93	18.35
259	0.695	18.29	17.98
400	0.657	18.65	17.20
523	0.651	18.70	16.69
670	0.597	18.77	16.31

mixture when response curves are not coincident is shown in the following example (Table VI). The absolute response of the gas density detector is the ratio of the gas density detector (GDD) and mass detector (MD) responses, *i.e.*, is area per unit weight. The table gives the response for maximum sensitivity. The true percentage weight of the component (*n*-heptane) was 18.44%.

The absolute response of the gas density detector to *n*-heptane decreased as sample size was increased. Similar effects occurred for the remaining constituents of the mixture, but to different extents. As a result the proportion of *n*-heptane detected by the gas density detector changed with sample size.

The lower limit of detection, Q_0 , of the gas density detector was calculated using the YOUNG equation¹⁸.

$$Q_0 = \frac{2R_n M}{PF} \quad (5)$$

where

R_n = noise level (mV)

M = amount of component (mmole)

P = peak area (mV min)

F = flow rate (ml min⁻¹)

The noise level (R_n) of the detector was measured on the maximum sensitivity. The response to very small amounts of *n*-octane (in terms of peak area, P) was measured, and the absolute masses of the samples (in mmoles) were obtained from the mass detector. It is reasonable to assume that the response of the gas density detector is linear and predictable over a small range in the region of the limit of detection, and hence by using eqn. 5 a value for the lower limit of detection was

TABLE VII

SOME GAS DENSITY DETECTOR CHARACTERISTICS

Type of detector	Response time (sec)	Limit of detection (mmole ml ⁻¹)	Compound	Reference
MARTIN	3	4×10^{-6}	Pentanol	19
NERHEIM filament	8	1×10^{-6}	Butane	11
NERHEIM thermistor	8	2×10^{-7}	Butane	11
Gow-Mac filament	—	3×10^{-8}	Carbon tetrachloride	12
Pneumatic bridge	—	5×10^{-6}	—	20

calculated. The lower limit of detection = 6.4×10^{-7} mmole ml⁻¹. Under the conditions of the experiment this represents a mass limit of detection of 0.6 μ g. The upper limit of detection exceeds that normally required for gas chromatography, and certainly exceeds the capacity of column Ref. E.

The response time of the gas density detector was measured by the SCHMAUCH procedure¹⁹. The value was determined at room temperature for benzene and ether, with an analytical gas flow rate of 51 ml min⁻¹ and reference flow of 75 ml min⁻¹.

The response time was 11 sec, a value which can be obtained from the following equation:

$$\tau = \frac{V_D}{F} \quad (6)$$

where V_D is the detector dead volume and F the carrier gas flow rate. For the gas density detector $V_D = 8$ ml and hence at 51 ml min^{-1} , the response time is 9.5 sec.

Literature values for limits of detection and response time for some gas density detectors are given in Table VII and agree well with those quoted above.

CONCLUSIONS

For all materials examined the gas density detector gave a response close to the calculated value, over a small concentration range. Provided that the detector is used within this range excellent quantitative results can be obtained. It is however not obvious when this limit is exceeded. The linear dynamic range of the detector does not approach the dynamic range, and is species dependent. The detector is very stable and has a reasonable lower limit of detection. Response time is rather long, although satisfactory for most packed column analyses. Notwithstanding these limitations the detector is one of the most suitable commercially available devices for quantitative work. The precision and accuracy of the results obtained from the mass detector under the same conditions were significantly better.

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