

CHROM. 4232

CALIBRATION OF GAS CHROMATOGRAPHIC DETECTORS USING THE MASS DETECTOR

S. C. BEVAN, T. A. GOUGH* AND S. THORBURN

Chemistry Department, Brunel University, London, W. 3 (Great Britain)

(Received June 16th, 1969)

SUMMARY

The mass detector was used to confirm the predictability of response of the Martin gas density balance, to calibrate a katharometer, and to measure limits of detection. The mass detector was operated in parallel with two destructive detectors, the flame thermocouple and flame ionisation detectors, and response curves were constructed for several different compounds.

INTRODUCTION

It has been established that the response of the mass detector is species independent, and that its response is linear over a wide operating range¹. The detector thus offers an excellent, rapid and reliable means of calibrating other detectors². It is not necessary to prepare carefully weighed-out mixtures, and the amount of material injected into the chromatograph need not be accurately known. Calibration errors arising from effects such as irreversible adsorption on the column are eliminated, and the only precaution necessary is to ensure that there is no leakage or condensation of material between the detector undergoing calibration, and the mass detector. A detector may be calibrated using either a single substance, or a number of components simultaneously. A detector may be calibrated absolutely, since the absolute adsorption efficiency of the mass detector at any flow rate is readily determined, or it may be calibrated relative to a pure standard material. The response of the Gow-Mac gas density detector toward a number of materials has been studied by this technique^{3,4}. Several other detectors have been calibrated with the aid of the mass detector, and the results are presented herein. The Martin gas density balance was calibrated to confirm that response is a function of molecular weight. A katharometer was calibrated to demonstrate the value of the technique for use with a detector of completely unpredictable response. Destructive detectors must be operated in parallel with the mass detector. The flame thermocouple detector was calibrated by this means. Detectors such as the flame ionisation detector, whose sensitivities differ significantly from that of the mass detector, must also be calibrated in parallel, the major portion of the split effluent stream being fed to the less sensitive detector.

* Present address: Laboratory of the Government Chemist, Stamford Street, London, S.E.1.

The mass detector is of value in the determination of limits of detection, since the amount of material present in the region of the detection limits is readily obtained from the mass detector response.

EXPERIMENTAL

The Martin gas density balance

The absolute and relative responses, and linear dynamic range of the Martin gas density balance towards a number of compounds were determined in a manner analogous to that previously described for the Gow-Mac gas density detector³. Operating conditions are given in Table I.

TABLE I

OPERATING CONDITIONS FOR CALIBRATION OF THE MARTIN GAS DENSITY BALANCE

Apparatus	Shandon KG 2
Column	Ref. E ^a
Column temperature	101°
Carrier gas	Nitrogen
Analytical gas flow rate	50 ml min ⁻¹
Reference gas flow rate	50 ml min ⁻¹
Sample sizes	0.2-5 μ l
Gas density balance	
filament current	1.9 A
sensitivity	$\times 10^3, \times 500$
Mass detector	
ranges	1-5 mg
temperature	24°

^a Column details are given in Table XIII.

For each component of a mixture, a graph was plotted of response of the gas density balance (corrected peak area) against the mass detector response (weight adsorbed). In all cases a straight-line relationship was found, *i.e.* the Martin gas density balance gave a linear response at least over the range investigated (about 10^2). In addition the slopes of the lines were identical for all components of a mixture, they passed through the origin and the response per unit weight (the sensitivity) was identical at all sample sizes (see *e.g.*, Table III). There were, however, small variations in response per unit weight from one mixture to another, but these can be attributed to the day-to-day fluctuation of conditions (temperature, flow, rate, etc.). This is borne out by the observation that a given compound, analysed at different times, gave a slightly different response per unit weight. The results are shown in Figs. 1-6 for all the mixtures containing more than two components. The coefficient of variation of the absolute response factors ($\text{cm}^2 \mu\text{g}^{-1}$) for 137 determinations was 5.1%.

The mean percentage weight of each component in the mixture \bar{x}_D over a wide mass range was found and compared with that obtained from the mass detector (\bar{x}_M). These values, together with the true percentage weight (at injection), x_0 , are given in Table II.

Excellent quantitative results were obtained for all samples. The standard deviations of the relative response factors were 2.2×10^{-2} for R_{DO} and 1.8×10^{-2} for

TABLE II

QUANTITATIVE ANALYSIS USING THE MARTIN GAS DENSITY BALANCE

$$R_{DM} = \bar{x}_D/\bar{x}_M; R_{DO} = \bar{x}_D/x_0.$$

Compound	Composition			Response		
	x_0	\bar{x}_M	\bar{x}_D	R_{DO}	R_{DM}	Fig.
Benzene	38.45	38.90	39.05	1.02	1.00	1
Toluene	33.22	33.14	33.11	1.00	1.00	
Ethylbenzene	28.33	27.96	27.84	0.98	1.00	
Methyl ethyl ketone	35.88	36.72	37.16	1.04	1.01	2
Methyl <i>n</i> -propyl ketone	38.21	38.93	38.30	1.00	0.98	
Methyl <i>n</i> -butyl ketone	25.92	24.34	24.54	0.95	1.01	
Ethyl acetate	39.33	39.71	40.34	1.03	1.02	3
<i>n</i> -Propyl acetate	31.32	31.18	30.54	0.98	0.98	
<i>n</i> -Butyl acetate	29.36	29.11	29.12	0.99	1.00	
<i>n</i> -Heptane ^a	22.79	23.33	23.30	1.02	1.00	4
<i>n</i> -Octane	15.38	15.38	15.40	1.00	1.00	
Ethyl acetate	21.54	21.00	21.76	1.01	1.04	
Methyl ethyl ketone	16.10	15.74	15.47	0.96	0.98	
Benzene	24.19	24.55	24.07	1.00	0.98	
Cyclohexane	21.17	20.57	21.07	1.00	1.02	5
<i>n</i> -Octane	16.65	16.17	16.71	1.00	1.03	
Carbon tetrachloride	34.54	35.34	34.94	1.01	0.99	
Dichloroethylene	27.64	27.92	27.28	0.99	0.98	
<i>n</i> -Octane	26.74	27.63	27.44	1.02	1.01	6
Butylene oxide	28.80	28.56	27.01	0.94	0.95	
Dioxan	44.45	43.81	45.55	1.03	1.04	
Benzene	52.51	52.31	52.02	0.99	0.99	
Toluene	47.49	47.69	47.98	1.01	1.01	
<i>n</i> -Butyraldehyde ^b	39.80	39.24	38.96	0.98	0.99	
Methyl ethyl ketone	60.20	60.76	61.05	1.02	1.01	
Isopropyl alcohol	40.12	42.40	42.18	1.06	1.00	
Nitromethane	59.88	57.60	57.82	0.94	1.00	
Water ^c	54.02	47.30	47.29	0.88	1.00	
Ethyl alcohol	45.98	52.70	52.71	1.12	1.00	
Ethyl alcohol ^d	53.63	54.25	53.68	1.00	0.99	
<i>n</i> -Propyl alcohol	46.37	47.75	46.32	1.00	1.01	
<i>n</i> -Propyl alcohol ^d	52.83	54.91	54.59	1.04	1.00	
<i>n</i> -Butyl alcohol	47.17	45.09	45.41	0.94	1.00	
<i>n</i> -Butyl alcohol ^d	52.95	53.42	51.74	0.98	0.97	
<i>n</i> -Amyl alcohol	47.05	46.58	48.26	1.02	1.03	
<i>n</i> -Propyl alcohol ^d	44.94	45.36	45.57	1.02	1.00	
Methyl <i>n</i> -propyl ketone	55.06	54.64	54.43	0.98	1.00	

^a See also Table III.^b Column temperature, 66°.^c Column Ref. D at 70°.^d Column Ref. D at 140°.

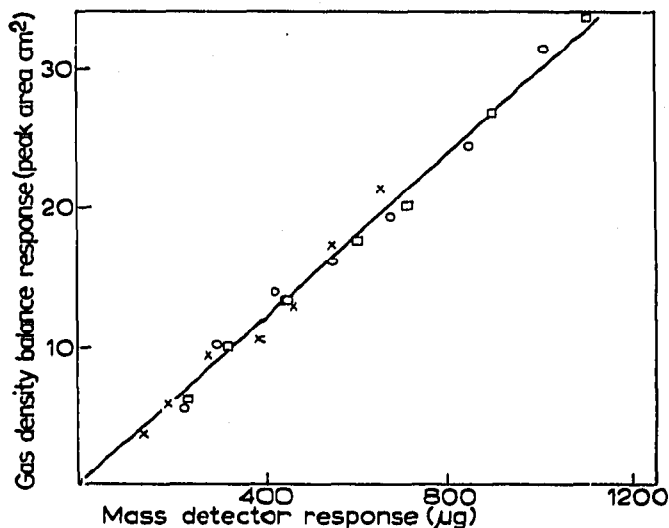
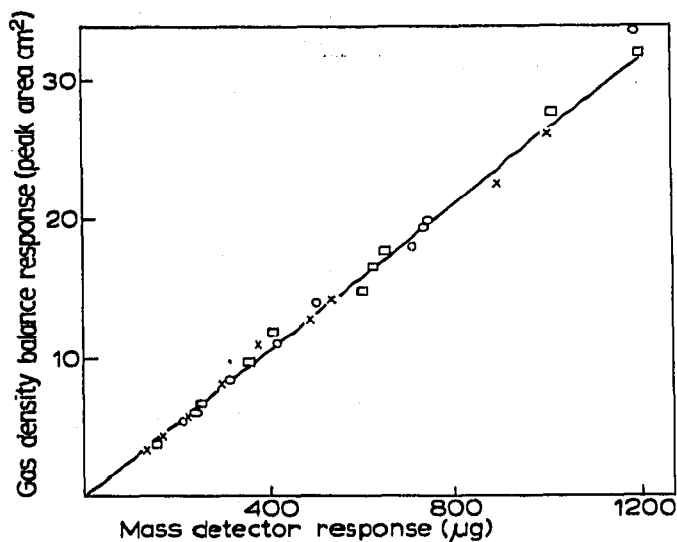


Fig. 1. Response curve for the gas density balance. ○, Benzene; □, toluene; ×, ethylbenzene.

Fig. 2. Response curve for the gas density balance. ○, Methyl ethyl ketone; □, methyl *n*-propyl ketone; ×, methyl *n*-butyl ketone.

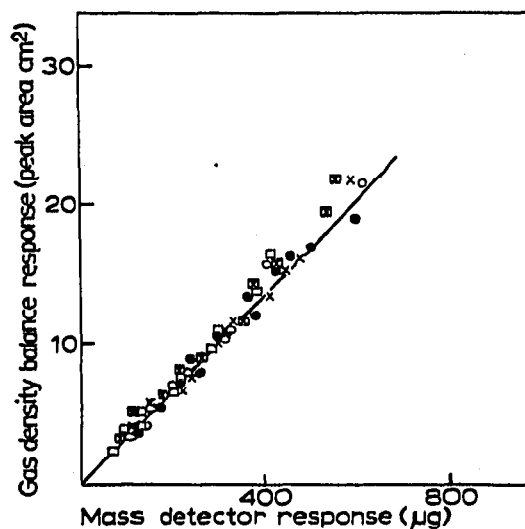
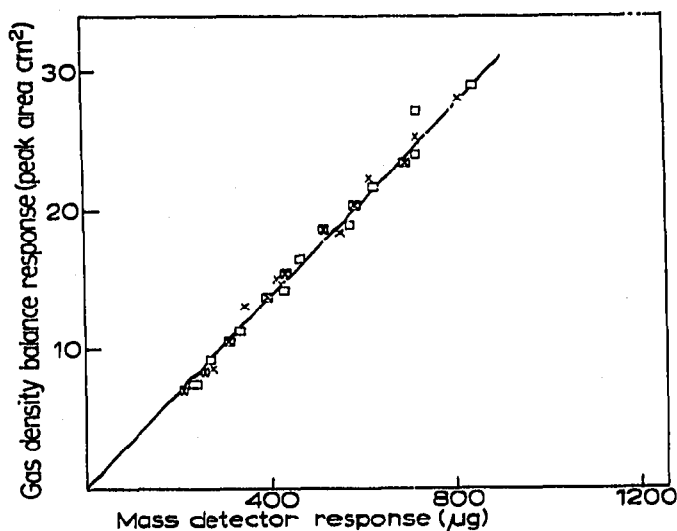


Fig. 3. Response curve for the gas density balance. ×, Ethyl acetate; □, *n*-propyl acetate; ⊠, *n*-butyl acetate.

Fig. 4. Response curve for the gas density balance. ×, *n*-Heptane; □, *n*-octane; ○, methyl ethyl ketone; ⊠, ethyl acetate; ●, benzene.

R_{DM} . Absolute response values for *n*-heptane, for a variety of sample sizes, are given in Table III.

Comparison with the Gow-Mac gas density detector results³, obtained under similar conditions, reveals that the Martin gas density balance used is the less sensitive, by a factor of about 30. However, the absolute response of the Martin gas density balance is constant whereas the Gow-Mac detector response depends on sample size. The Martin detector will therefore give reliable relative composition data over a wide

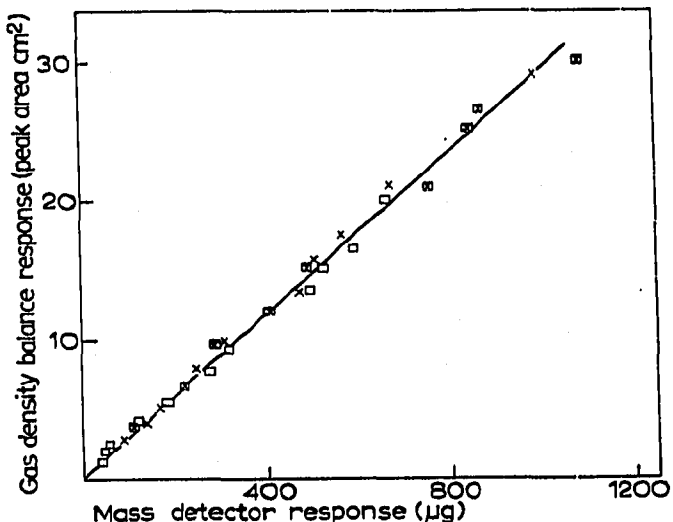
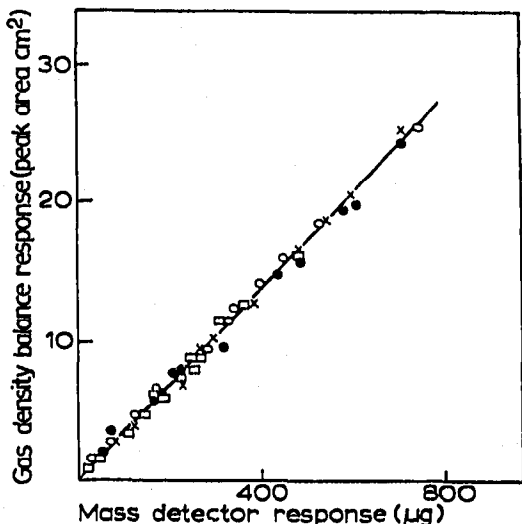


Fig. 5. Response curve for the gas density balance. ○, Cyclohexane; □, *n*-octane; ×, carbon tetrachloride; ●, dichloroethylene.

Fig. 6. Response curve for the gas density balance. ×, *n*-Octane; □, butylene oxide; ⊠, dioxan.

sample size range, but the Gow-Mac detector will only give accurate results within a limited range.

The repeatability of the relative composition results was determined over the whole sample size range used: the coefficient of variation of 165 determinations was 2.1%. The same value was obtained for the mass detector repeatability. A similar calculation for the Gow-Mac detector is meaningless, since response is concentration dependent; even the result for single sample size was significantly greater, at 3.6%. The overall bias of the Martin gas density balance results was 0.5%, *i.e.* 1.5% absolute bias. Very similar values were obtained for the mass detector bias. Bias values for the Gow-Mac detector increased as sample size increased. Bias values for a single sample size are similar to the Martin and mass detector values quoted above.

TABLE III

ABSOLUTE RESPONSE VALUES FOR *n*-HEPTANE

GDB = gas density balance; MD = mass detector. $x_0 = 22.79$.

Weight of material detected (µg)	GDB response (cm ² µg ⁻¹)	% heptane detected	
		MD	GDB
124	0.0241	22.95	23.78
175	0.0251	23.20	23.88
213	0.0239	23.38	23.59
254	0.0251	23.51	21.43
300	0.0246	23.50	23.74
338	0.0249	22.69	23.26
411	0.0235	23.57	24.29
436	0.0246	23.02	22.72
479	0.0240	23.47	22.95

TABLE IV

OPERATING CONDITIONS FOR CALIBRATION OF A GOW-MAC KATHAROMETER

Apparatus	Shandon KG2
Column	Ref. E
Column temperature	101°
Carrier gas	Nitrogen
Analytical gas flow rate	51 ml min ⁻¹
Reference gas flow rate	51 ml min ⁻¹
Sample sizes	0.1-1 μ l
Katharometer	
filament current	150 mA
sensitivity	$\times 500$ to $\times 50$
temperature	101°
Mass detector	
ranges	100 μ g-1 mg
temperature	24°

The lower limit of detection was determined by the procedure previously described³. The lower limit of detection was 6.3×10^{-6} mmole ml⁻¹, representing a mass limit of detection of 8 μ g. The Gow-Mac detector exceeds this value by a factor of 10, although it is more sensitive by a factor of 30. The discrepancy is a result of the lower noise level on the Martin detector. The upper limit of detection exceeds that normally required for gas chromatography.

The response time of the Martin detector, at a flow rate of 50 ml min⁻¹ was 3.5 sec. The value quoted by SCHMAUCH⁵ is 3 sec.

Calibration of a katharometer

A Gow-Mac katharometer type 9285D fitted with tungsten-rhenium filaments was placed in series with the mass detector. The operating conditions are given in Table IV.

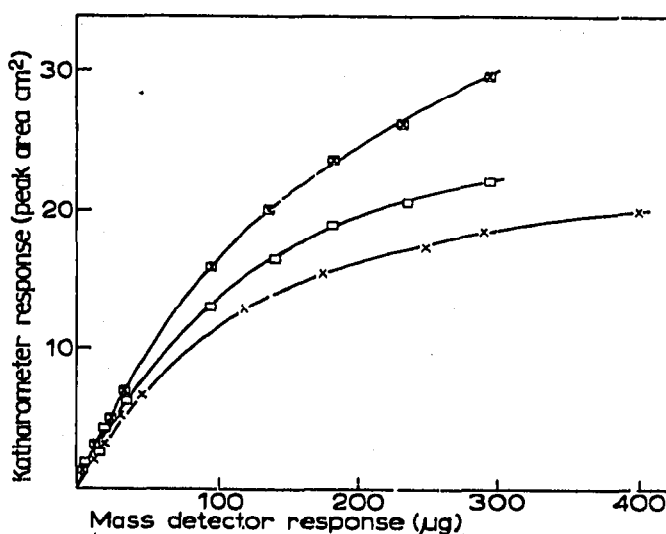


Fig. 7. Response curve for a katharometer. \times , Benzene; \square , toluene; \boxtimes , ethylbenzene.

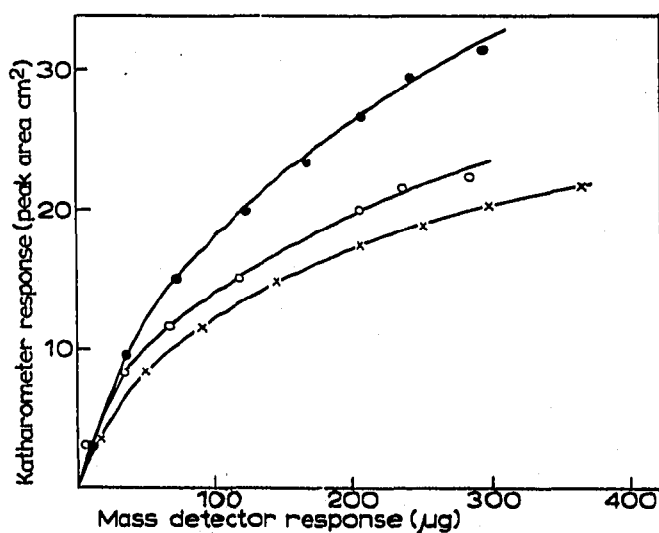


Fig. 8. Response curve for a katharometer. \times Methyl ethyl ketone; \circ , methyl *n*-propyl ketone; \bullet , methyl *n*-butyl ketone.

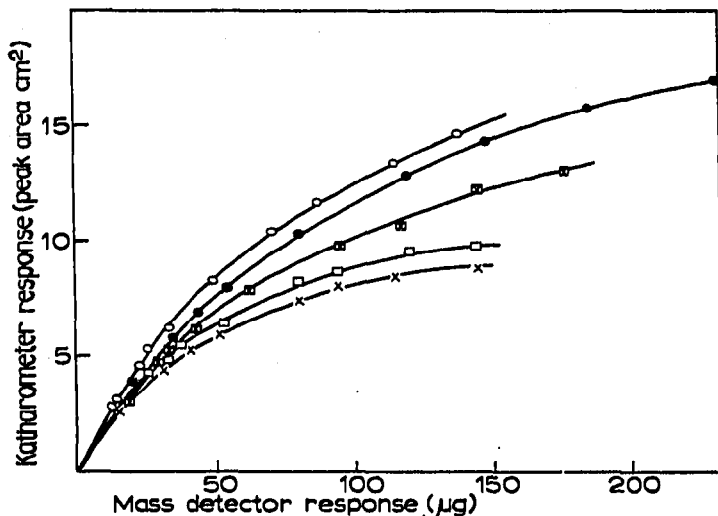
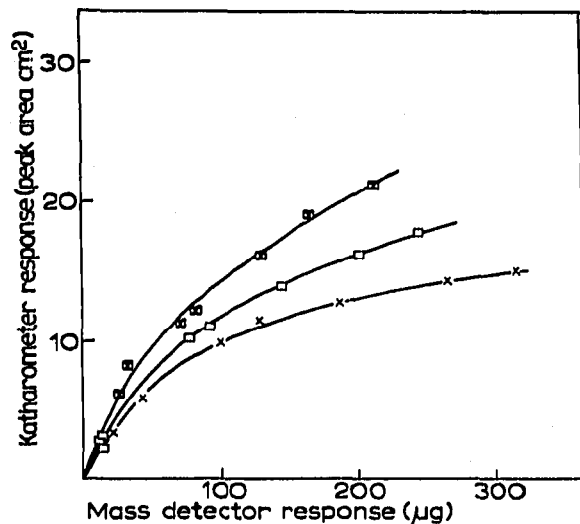


Fig. 9. Response curve for a katharometer. \times , Ethyl acetate; \square , *n*-propyl acetate; \boxtimes , *n*-buty acetate.

Fig. 10. Response curve for a katharometer. \times , *n*-Heptane; \square , *n*-octane; \boxtimes , ethyl acetate; \circ , methyl ethyl ketone; \bullet , benzene.

A series of mixtures, including the same compounds listed in Table II, was analysed covering the mass range of 10–300 μg per component. Since the response of a katharometer is not predictable when nitrogen is used as carrier gas, the results are most satisfactorily expressed graphically. Response curves are shown as plots of peak area, obtained from the katharometer, against the weight of component, determined by the mass detector. Each figure shows the response of the detector to the constituents of each mixture (Figs. 7–13). All compounds, except carbon tetrachloride, gave a response of similar pattern, namely a gradual fall in sensitivity as sample size was

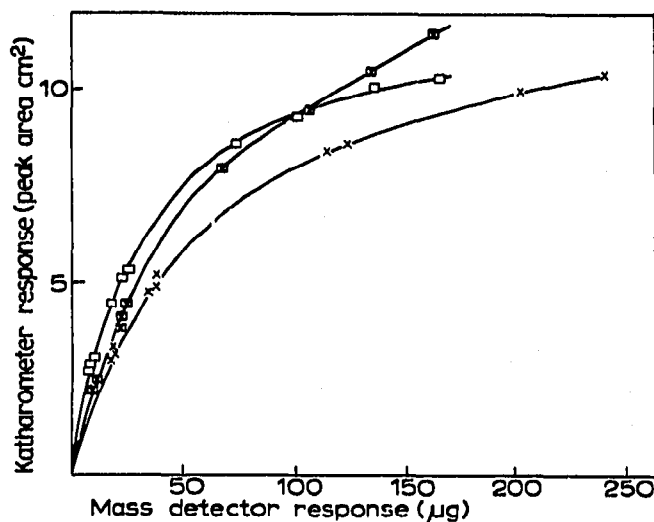
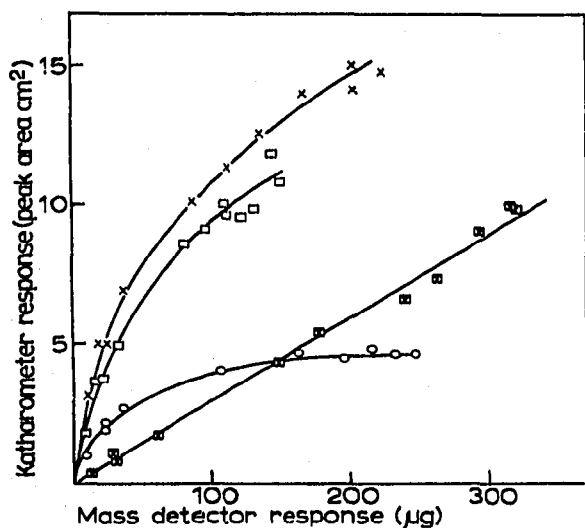


Fig. 11. Response curve for a katharometer. \times , Cyclohexane; \square , *n*-octane; \boxtimes , carbon tetra- chloride; \circ , dichloroethylene.

Fig. 12. Response curve for a katharometer. \times , 2,2,4-Trimethylpentane; \square , *n*-octane; \boxtimes , 1-octene.

TABLE V

RESPONSE FACTORS OF A SERIES OF COMPOUNDS WITH RESPECT TO *n*-HEPTANE

Compound	Area/unit weight ($\text{cm}^2 \mu\text{g}^{-1}$)	Weight response w.r.t. heptane (R_W) ^a	Molar response w.r.t. heptane		Fig.
			<i>R</i>	R_M	
<i>n</i> -Heptane	0.79	1.00	1.00	1.00	15
Benzene	1.11	1.41	1.81	1.24	7
Toluene	1.33	1.69	1.84	1.62	
Ethylbenzene	1.64	2.09	1.97	2.17	
Methyl ethyl ketone	1.28	1.63	2.27	1.38	8
Methyl <i>n</i> -propyl ketone	1.42	1.81	2.11	1.68	
Methyl <i>n</i> -butyl ketone	1.80	2.29	2.30	2.29	
Ethyl acetate	0.98	1.25	1.42	1.17	9
<i>n</i> -Propyl acetate	1.21	1.54	1.51	1.55	
<i>n</i> -Butyl acetate	1.43	1.82	1.57	1.99	
<i>n</i> -Heptane	0.81	1.03	1.03	1.03	10
<i>n</i> -Octane	0.90	1.15	1.01	1.21	
Ethyl acetate	1.01	1.29	1.46	1.21	
Methyl ethyl ketone	1.27	1.62	2.25	1.34	
Benzene	1.18	1.50	1.93	1.39	
Cyclohexane	1.07	1.36	1.62	1.26	11
<i>n</i> -Octane	0.96	1.22	1.07	1.30	
Carbon tetrachlo- ride	-0.30	-0.38	-0.25	-0.62	
Dichloroethylene	0.38	0.48	0.50	0.47	
2,2,4-Trimethyl- pentane	0.77	0.98	0.86	1.04	12
<i>n</i> -Octane	0.93	1.18	1.04	1.24	
1-Octene	0.93	1.18	1.06	1.24	
<i>n</i> -Octane	0.91	1.16	1.02	1.20	13
Butylene oxide	1.13	1.44	2.00	1.31	
Dioxan	1.72	2.19	2.49	2.04	
Benzene	0.57	1.78	—	1.39	—
<i>p</i> -Cymene	1.53	3.60	—	2.04	

^a w.r.t. = with respect to.

increased. Carbon tetrachloride was the only material to give a response linear with concentration, but for all sample sizes the response was negative. A chromatogram of the mixture containing carbon tetrachloride is shown in Fig. 14.

n-Heptane was used as a reference standard, and the response of pure *n*-heptane (99.99%) was measured over the mass range of 50 to 170 μg : the response curve is shown in Fig. 15. The response of any other compound with respect to *n*-heptane can be calculated using the appropriate calibration curve. The following response factors have been calculated and are listed in Table V: area response per unit weight of material ($\text{cm}^2 \mu\text{g}^{-1}$), and response with respect to *n*-heptane by weight (R_W) and in molar proportions (R) for 100 μg of material. The alternative way of expressing molar

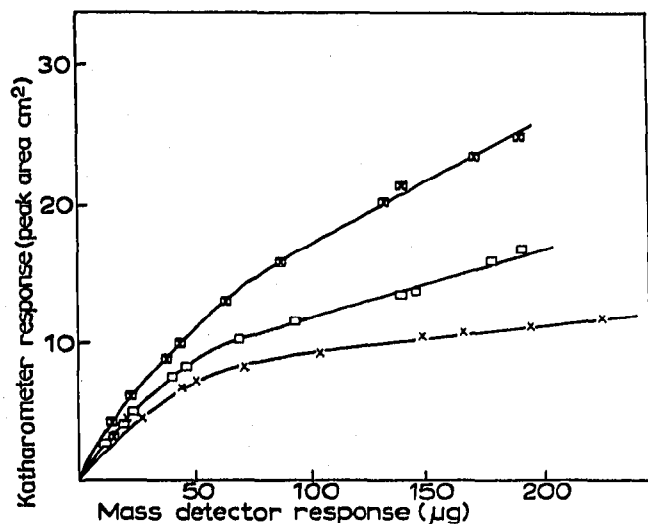


Fig. 13. Response curve for a katharometer. ×, *n*-Octane; □, butylene oxide; ⊠, dioxan.

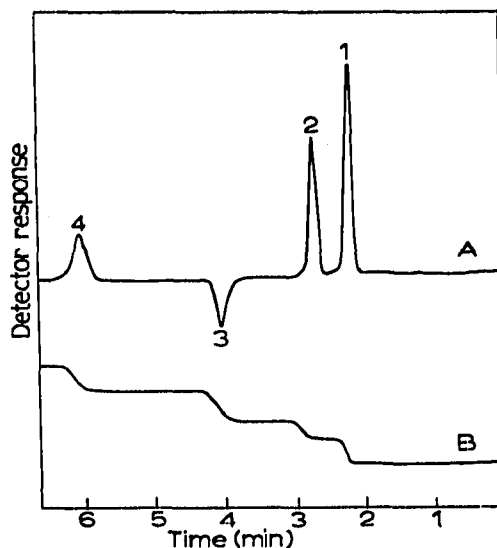


Fig. 14. Chromatogram of a four-component mixture. A = response of katharometer; B = response of mass detector. 1 = cyclohexane; 2 = *n*-octane; 3 = carbon tetrachloride; 4 = dichloroethylene.

response is to read directly, from the response curve, the response per mole and express this value relative to one mole of the standard material (R_M values).

The weight response factors do not follow any trends. Molar response factors are about unity for simple paraffins; simple aromatics approach two, and halogenated compounds give very low values. The difference between benzene and *p*-cymene is striking.

A response curve in the region of the lower limit of detection was constructed. The limit of detection in terms of peak area was estimated from the point at which the extrapolated response curve cut the noise level of the detector: the weight, and hence the concentration of material represented by this peak area was estimated from the mass detector response. The lower limit of detection for *n*-heptane was 8×10^{-8}

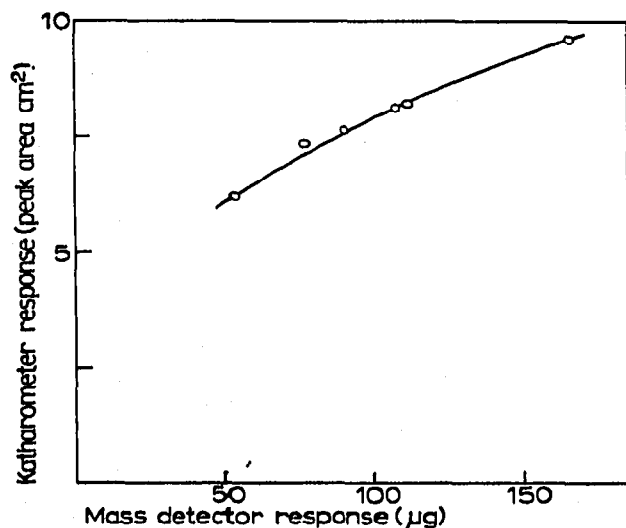


Fig. 15. Response curve for a katharometer. *n*-Heptane.

mmole ml⁻¹ (0.5 μ g). The upper limit of detection was estimated from Fig. 15 and was 1×10^{-4} mmole ml⁻¹ (150 μ g).

Although the sensitivity of the detector (cm² μ g⁻¹) is species and concentration dependent, it is similar to, and a little greater than that of the Gow-Mac gas density detector for many materials.

Calibration of a flame thermocouple detector

The calibration of a destructive detector can be carried out by placing the detector in parallel with the mass detector. The flame thermocouple detector has a sensitivity the same order as the mass detector, so that by splitting the column effluent in approximately equal proportions, a reasonable response will be obtained from each detector. Ideally the ratio of the amounts of material reaching the two detectors will

TABLE VI

OPERATING CONDITIONS FOR CALIBRATION OF THE FLAME THERMOCOUPLE DETECTOR

Apparatus	Pye Panchromatograph
Column	Ref. A
Column temperature	50°
Carrier gas	Nitrogen
Flow rate	
major stream	60 ml min ⁻¹
minor stream	33 ml min ⁻¹
Sample sizes	0.3-3.5 μ l
Flame thermocouple	
thermocouple	Pt-Pt/Rh
cold junction	23°
Hydrogen flow rate	50 ml min ⁻¹
Air flow rate	250 ml min ⁻¹
Mass detector	
ranges	1-5 mg
temperature	23°

be in the ratio of the flow rates at the detectors. However, it may arise that the split ratio is dependent on gas viscosity and hence will be different for different materials; it may also depend on the concentration of material. Such variations in split ratio will interfere with the calibration of the detector if it is to be used subsequently in the absence of a stream splitter. Using approximately equally split streams, and small concentrations of material in the carrier gas, and for materials of a similar nature, variations in split ratio should be negligible compared with the errors resulting from peak area measurements. The linearity of a flame thermocouple detector was determined using a 2:1 splitter, and the quantitative analysis of a two-component mixture was carried out.

A Pye Panchromatograph flame ionisation detector chamber was modified to take a flame thermocouple detector. The cold junction of the detector was maintained at room temperature, and placed in a large block of expanded polystyrene to minimise random temperature fluctuations. The output of the detector was fed directly to a 10 mV potentiometric recorder, without amplification. The standing thermocouple, emf, was backed off with a simple potential divider driven by a 1.5 V battery. Operating conditions are given in Table VI.

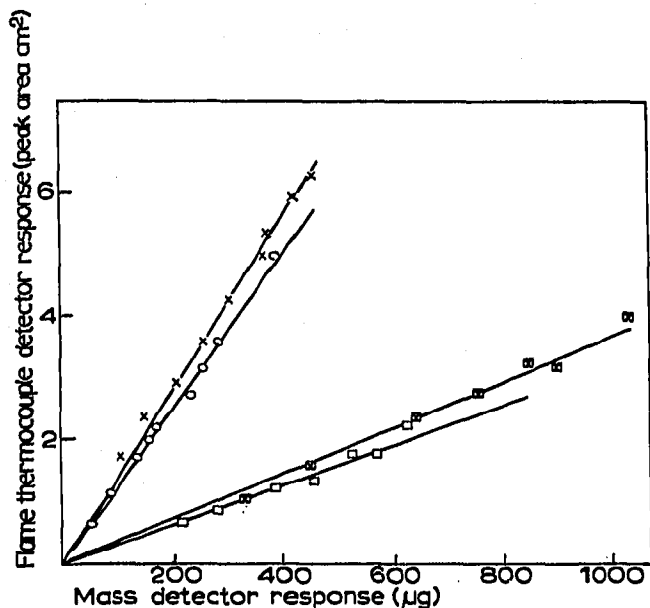


Fig. 16. Response curve for a flame thermocouple detector. Major stream to flame thermocouple detector; \circ , benzene; \times , toluene. Minor stream to flame thermocouple detector; \square , benzene; \boxtimes , toluene.

A two-component mixture was analysed several times covering the mass range of $200\ \mu\text{g}$ – $2\ \text{mg}$ per component, firstly with the major stream, and then with the minor stream to the flame thermocouple detector. For each set of runs a response curve of peak area against weight detected by the mass detector was plotted (Fig. 16). In all cases the response of the flame thermocouple detector varied linearly with sample size. For the materials analysed the heats of combustion were, for practical purposes, identical. The response curves for the two materials at each split ratio should therefore coincide if response is based solely on heats of combustion. The heats of combustion, and the slopes of the response curves, obtained from Fig. 16, are given in Table VII.

Since the streams were split, the slopes of the response curves do not represent absolute sensitivities. An estimate of the split ratio is given by the ratio of the flow rates at the two detectors and is $60/33$, *i.e.* $1.82:1$. The split ratio can be calculated from the ratio of the weight of injected material and the weight of material detected by the mass detector. A $1\ \mu\text{l}$ sample of the mixture will contain $0.30\ \text{mg}$ of benzene. With the major stream to the mass detector $0.20\ \text{g}$ of benzene was detected, *i.e.* the split ratio was $2:1$. The same value was obtained for toluene. This method relies on injection of a known amount of sample and no loss of material within the column.

TABLE VII

FLAME THERMOCOUPLE DETECTOR RESPONSE

Compound	Heat of combustion (kcal g^{-1})	Response ($\text{cm}^2\ \mu\text{g}^{-1}$)	
		Major stream	Minor stream
Benzene	10.02	0.013	0.032
Toluene	10.15	0.014	0.036

Since the detector gives a linear response with respect to concentration, an estimate of the split ratio for each material can be obtained from the response curves. Using Fig. 16, the response of the flame thermocouple detector for each material at the 500 μg level was found, and the split ratio calculated from the differences in response when the major and minor streams were interchanged: *e.g.* for 500 μg of benzene detected by the mass detector, with the major stream to the mass detector, and with a split ratio of $n:1$,

$$\frac{500}{n} = 1.6k \quad (1)$$

where k is a proportionality constant.

For the minor stream to the mass detector:

$$500 = 6.25 \frac{k}{n} \quad (2)$$

from which $n = 1.98$, *i.e.* the split ratio is 1.98:1. For toluene $n = 1.97$, *i.e.* the split ratio is 1.97:1. Thus the absolute sensitivity of the detector was 0.0065 $\text{cm}^2 \mu\text{g}^{-1}$ for benzene and 0.0070 $\text{cm}^2 \mu\text{g}^{-1}$ for toluene. The limit of detection (without amplification of the thermocouple output) was 5.9×10^{-6} mmole ml^{-1} for benzene.

The percentage composition of the mixture of benzene and toluene was calculated directly from the ratios of the peak areas, corrected for heats of combustion (\bar{x} values). The composition of the mixture was also estimated using the experimentally determined response factors (\bar{x}_E values). The results are given in Table VIII.

TABLE VIII

QUANTITATIVE ANALYSIS USING THE FLAME THERMOCOUPLE DETECTOR

Compound	Mass detector			Flame thermocouple detector		
	x_0	\bar{x}	V (%)	\bar{x}	\bar{x}_E	V (%)
Benzene	37.48	37.86	0.8	35.38	36.76	2.9
Toluene	62.52	62.14	—	64.62	63.24	—

More accurate results were obtained using the experimentally determined response factors rather than those based on heats of combustion. The coefficient of variation of the results was significantly greater than the mass detector results.

Calibration of a flame ionisation detector

The use of the mass detector for calibration purposes is not restricted to detectors of comparable sensitivity. It is possible, using a stream splitting device, to calibrate detectors of much greater sensitivity. To demonstrate this, a flame ionisation detector was calibrated. The conditions of operation are given in Table IX.

The response of the detector toward methyl propionate, toluene, and chlorobenzene was determined: the results are illustrated in Fig. 17 as plots of peak area against weight detected by the mass detector. From the slopes of the response curves, the response per unit weight for each compound was found, and hence the response

TABLE IX

OPERATING CONDITIONS FOR CALIBRATION OF A FLAME IONISATION DETECTOR

Apparatus	Pye Panchromatograph
Column	Ref. B
Column temperature	100°
Carrier gas	Nitrogen
Column flow rate	48 ml min ⁻¹
Flame ionisation detector	
voltage	50 V
hydrogen flow rate	50 ml min ⁻¹
air flow rate	250 ml min ⁻¹
sensitivity	10 ⁻⁹ , 10 ⁻⁸
Mass detector	
temperature	23°

relative to one component as standard calculated. These values, together with the coefficients of variation (V) of the response factors, are given in Table XI.

The response factors must be corrected for the contribution of the stream splittings if the detector is to be used in the absence of the splitter. Since the response for each material was linear, it follows that the splitting ratio remained constant over the concentration range covered, but was not necessarily the same for all the components in the mixture. The splitting ratio was determined for each compound individually, under conditions as near as possible to those used in the linearity experiment. The mass detector was connected firstly to the minor stream, and a number of injections of identical size made. The detector was then attached to the major stream and the experiment repeated. The splitting ratio was calculated from the mean value of the step heights in each experiment. The results are given in Table X.

The responses per unit weight obtained from the calibration curves (Fig. 17) were corrected using the values given in Table X, and compared with published response data⁶ (Table XI).

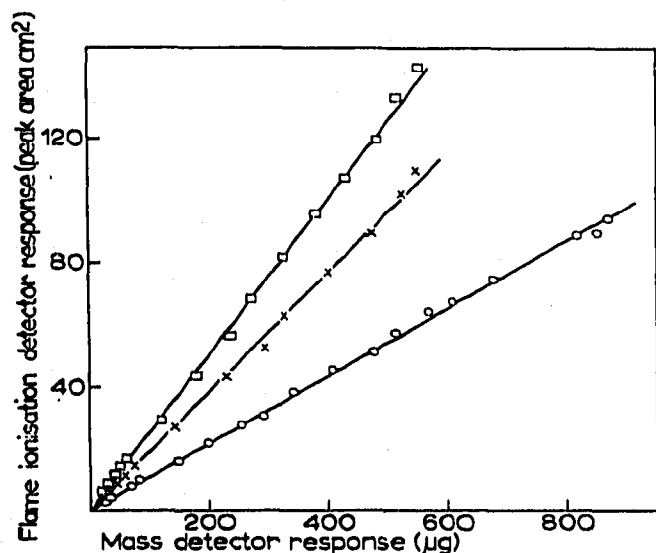


Fig. 17. Response curve for a flame ionisation detector. ○, methyl propionate; □, toluene; ×, chlorobenzene.

TABLE X

SPLITTING RATIOS IN FLAME IONISATION-MASS DETECTOR SYSTEM

Compound	Mean detected weight (mg)		Ratio
	Major stream	Minor stream	
Methyl propionate	6.928	0.1045	66.3:1
Toluene	6.249	0.0946	66.1:1
Chlorobenzene	8.428	0.1178	71.5:1

TABLE XI

FLAME IONISATION DETECTOR RESPONSE

Compound	Response per unit weight		Relative response	Corrected response	Published response
	($\text{cm}^3 \mu\text{g}^{-1}$)	V (%)			
Methyl propionate	0.108	4.2	0.44	0.44	0.40
Toluene	0.247	3.8	1.00	1.00	1.00
Chlorobenzene	0.192	5.1	0.78	0.72	0.69

TABLE XII

QUANTITATIVE ANALYSIS USING THE FLAME IONISATION DETECTOR

Compound	x_0	\bar{x}_N	\bar{x}_{12}	σ	V (%)	Bias
Methyl propionate	33.51	33.05	33.09	0.81	2.45	-0.42
Toluene	30.41	30.35	30.35	0.44	1.45	-0.06
Chlorobenzene	36.08	36.60	36.56	0.66	1.81	+0.48

TABLE XIII

COLUMN DETAILS

Reference	Stationary phase		Inert support	Length and I.D.	Material
	Type	%			
A	Apiezon L	7.5	Chromosorb G 80-100	1.1 m × 3 mm	Stainless steel
B	PEG 20M	15	Chromosorb G 60-80	1.1 m × 3 mm	Stainless steel
D	PORAPAK Q	—	— 100-120	0.56 m × 3 mm	Stainless steel
E	PEGA	20	Chromosorb G 72-85	4.0 m × 4 mm	Stainless steel

Using the response factors obtained from the calibration curves, the mean percentage composition of the mixture was calculated (\bar{x}_E values) and compared with the results obtained from the mass detector (\bar{x}_M values).

The coefficient of variation of the absolute response (area per unit weight) for 45 determinations was 4.4%, and the coefficient of variation of the percentage composition was 1.9%. Very similar values were obtained with the Martin gas density balance.

The specifications of the various columns used in this work are given in Table XIII.

CONCLUSIONS

The Martin gas density balance gives excellent quantitative results over a wide range of sample sizes. No deviations from linearity were observed, and all responses were predictable on a molecular weight basis. Its performance is entirely satisfactory and it may be used with confidence.

When nitrogen is used as carrier gas, a katharometer should be calibrated for all materials at all concentrations. This may be conveniently carried out using the mass detector.

A flame thermocouple detector was calibrated using the mass detector and response was shown to be linear over the concentration range investigated. The linearity of response of a flame ionisation detector toward several compounds was confirmed. Comparison of the response factors with literature values showed good agreement, even though the operating conditions were not identical.

The mass detector is a useful device for rapidly and reliably calibrating both non-destructive and destructive detectors.

ACKNOWLEDGEMENT

One of us (T.A.G.) wishes to thank the M.E.L. organisation for financial assistance given during the period covered by this work.

REFERENCES

- 1 S. C. BEVAN, T. A. GOUGH AND S. THORBURN, *J. Chromatog.*, 42 (1969) 336.
- 2 *Gas Chromatography 1966*, Butterworths, London, 1966, p. 428.
- 3 S. C. BEVAN, T. A. GOUGH AND S. THORBURN, *J. Chromatog.*, 44 (1969) 14.
- 4 P. A. DRABBLE, *Dissertation for B. Tech.*, Brunel University, London, 1969.
- 5 L. J. SCHMAUCH, *Anal. Chem.*, 31 (1959) 225.
- 6 R. J. MAGGS, *Column*, 1, No. 2 (1966) 2.