PERFORMANCE CHARACTERISTICS OF THE BRUNEL MASS DETECTOR

S. C. BEVAN, T. A. GOUGH* AND S. THORBURN
Chemistry Department, Brunel University, London, W.3 (Great Britain)
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SUMMARY

The mass detector comprises a microbalance, to the arm of which is attached a small cylindrical chamber containing active charcoal. Response, which is integral, is a function of the weight of materials adsorbed by the charcoal. Under a wide range of operating conditions complete adsorption of materials is achieved, and quantitative data are obtained without the need for qualitative information. Data on the performance of the detector are presented from which it is shown that the device is satisfactory for quantitative analysis and that it possesses advantages over existing detectors.

INTRODUCTION

There is available to the gas chromatographer a wide selection of detectors[1]. In general, the choice of detector depends upon the particular problem in hand. For routine qualitative work, most of the non-selective detectors are satisfactory. For the qualitative analysis of minor constituents the choice is more limited, and for the detection of compounds containing specific functional groups, a detector whose response is selective to these materials alone is used[2,3]. For quantitative analysis the choice of detectors is very limited, and no commercially available detector fulfils all the requirements of an ideal quantitative detector. In particular, a detector suitable for quantitative analysis should give a response directly proportional to some fundamental physical property to avoid the necessity for the calibration of all materials at all concentrations. The flame ionisation detector has a linear response over six orders of magnitude[4], but response is not always predictable, for example, on the number of carbon atoms present[5]. The response of the Martin gas density balance is a function of molecular weight, and the detector has a wide linear dynamic range, but even with this detector, which in some respects is ideal, a qualitative knowledge of the sample under analysis is required before quantitative results can be calculated. A detector whose response is directly related to the weight of components emerging from a gas chromatograph offers outstanding advantages over even the best available detectors: quantitative data are obtained without a knowledge of the nature of the

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

sample, and since response is integral the weight of each component is obtained directly from step height measurements without the need for integration. A gas chromatographic detector based on the measurement of weight changes has been devised by BEVAN AND THORBURN[6] and the present work gives details of the performance of this detector.

DISCUSSION

Column effluent is fed by means of a resistively heated tube into a small cylindrical vessel containing an adsorbent, which is suspended from the arm of an automatically recording electromicrobalance.

Choice of adsorbent

For a completely non-selective detector a material is required which will adsorb, to the same extent and preferably completely, all materials in the vapour phase, irrespective of their physical and chemical nature. In addition, conditions must be chosen such that the carrier gas does not interfere with the process, and that desorption of sample does not follow adsorption to any appreciable extent. The capacity of the adsorbent must be such that continual adsorption of materials is possible for a reasonable period of use, without deterioration of the efficiency of adsorption. If these conditions can be fulfilled, a detector will be obtained which responds directly on a weight basis and which requires no calibration against standard adsorbates. The only material which is likely to satisfy these conditions is activated charcoal. Provided that adsorption is carried out at a suitable temperature and pressure, physical adsorption on the charcoal will predominate, and hence the detector will be non-selective. The continuous passage of carrier gas into a charcoal detector will at first give rise to a weight change, which becomes progressively less as equilibrium is approached, until finally a constant weight is reached. The maximum amount of any given material which active charcoal can adsorb is related to the critical temperature (and hence the boiling point) of the adsorbate. By using a permanent gas as carrier the extent to which this is adsorbed by the charcoal is negligible compared with the adsorption of a compound, boiling say above room temperature. In effect, therefore, no interference in the adsorption of organic molecules should be caused by the presence of the carrier gas.

For a linear detector response it is essential that adsorbate uptake increases linearly with concentration in the carrier gas. This condition can only be fulfilled up to a given amount of adsorbate, determined from the adsorption isotherm: the concentrations met in gas chromatographic analysis are well within these limits. The capacity of the adsorbent toward a given adsorbate under fixed conditions is directly proportional to the weight of adsorbent present, so that the upper limit of detection of a gas chromatographic detector may be increased simply by increasing the amount of charcoal.

Design of detecting elements

A practical detecting element must be sufficiently light to be within the capacity of the microbalance, and must be simple to construct. The adsorption process itself must be rapid and the detector must have a small effective dead volume to minimise

resolution losses, response time, and step distortion. At the same time a large surface area for adsorption is required. A suitable element is described below.

The microbalance. A microbalance must be able to weigh accurately sample components of a size which is compatible with the column, to avoid overloading, loss of resolution etc. For conventional packed columns this is of the order of 10 μg. The balance output must be automatically recorded; the balance must be robust, stable, and have a capacity of at least 1 g, to exceed the weight of the detecting element. Automatic recording electromicrobalances have been described in the literature and are available commercially. The new detector would offer a further advantage if the cost were of the same order as a conventional commercial detector. Since the original work of BEVAN AND THORBURN, such balances have become available, and the present work was carried out using an RIIC electromicrobalance*.

EXPERIMENTAL

Detecting elements are constructed from aluminium foil, the inside of which is lined with charcoal. A sheet of aluminium about 0.0015 in. thick is cut to the appropriate size, lightly coated with an epoxy resin adhesive, and granular charcoal evenly scattered over the surface. The prepared aluminium is wrapped round a cylindrical former and the adhesive cured. The closed end of the cylinder (usually the top) is similarly prepared, and the completed detecting element is suspended from a microbalance using fine wire (42 SWG). The most suitable particle size range of charcoal, compatible with a light detector and high capacity is 60–80 BS mesh (*ca.* 200 microns). A typical detecting element 5 cm in length and 1.5 cm diameter contains about 250 mg of charcoal and weighs a total of about 600 mg. Suitable charcoal is available under the name "charcoal activated for gas analysis", the sample used in this study had a surface area of 1300 m^2g^{-1} by nitrogen adsorption at $-196°$. The surface area available for adsorption on a mass detecting element, measured *in situ*, using benzene as adsorbate and nitrogen as carrier gas was 600 m^2g^{-1}.

An RIIC microbalance model EMB1 was used in conjunction with a Honeywell 10 mV potentiometric recorder. Calibration of the microbalance–recorder system was carried out using ASA class M weights. Linearity of the recorder response was confirmed using a decade potential divider and 1.5 V cell. The precision of the resistors in the decade box was ± 0.1%, and the maximum observed error on the recorder was 0.2% full scale deflection (f.s.d.). The most suitable balance range gave a 1 mg f.s.d. on the recorder *i.e.* 1 μg was represented by 0.1% f.s.d. (0.3 mm). Several modifications were made to the basic balance. A means of backing off weight increases electrically was added by applying a small current across the balance coil. The current was supplied by a mercury cell and was continuously variable up to 750 μA, using a helical potentiometer and resistance network. The linearity of the backing off device was satisfactory up to a current equivalent to a weight of 5 mg. Additional ranges were built into the balance to give recorder full scale readings of 250 and 100 μg. This was achieved by using the existing range switch and replacing the appropriate resistors within the balance control unit. In view of the small weights involved calibration could not be conveniently carried out with standard weights. The backing off unit

has a linear response and was used to calibrate these ranges. The repeatability of response of the balance–recorder system to a given weight (688 μg) was measured by weighing the same piece of wire 14 times over a period of 8 h, using the 1 mg range. The coefficient of variation of the values was 0.3%. The stability of the balance was measured over a period of 16 h. Drift was 0.02%/h on the 1 mg range. Noise levels and limits of detection are given in Table I.

TABLE I

STABILITY OF THE MICROBALANCE

Range (μg)	Noise level (% f.s.d.)	Limit of detection (μg)
1000	not detectable	4
250	not detectable	1
100	0.2	0.4
25	0.5	0.25

The effect of progressively increasing the total load on the balance was measured by increasing the weight on each pan in 50 mg increments and weighing a standard weight (430 μg) after each addition. Balance response was constant up to a load of 0.5 g after which it fell progressively. Provided that the balance is calibrated with a detecting element in position, the small weight increases caused by effluent adsorption will not effect the calibration. The results are exhibited in general form on Fig. 1. Repeatability of weighing at various total loads decreases as load increases (see Fig. 2). Errors due to changes in ambient temperature after calibration constitute a source of error. The temperature coefficient of the balance is 1 μg/°C, so that a 4° temperature change will result in a 0.4% f.s.d. error using the 1 mg range. Errors in measuring the step heights using a good quality ruler are not likely to exceed 0.1% f.s.d. The overall balance behaviour was satisfactory and it was regarded as suitable for use with a gas chromatograph.
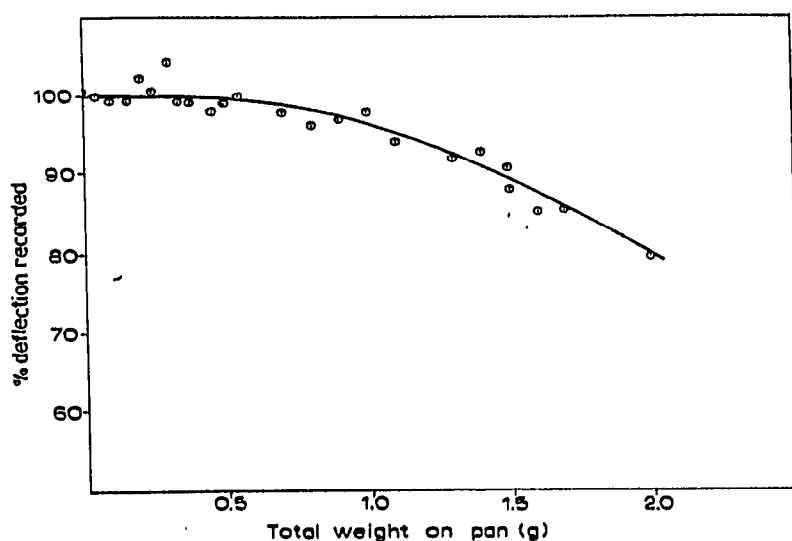

Fig. 1. The effect of total load on balance response.

The suspension of a mass detecting element from the microbalance, and the continuous flow of hot carrier gas from a gas chromatographic column would be expected to increase the noise level of the balance. Noise levels and lower limits of detection are given in Table II. Detection limits are quoted in absolute weight units since the detector response is integral. For the purpose of comparison with differential detectors the limit of detection was calculated in terms of concentration for a compound of mol. wt. 100 (heptane), having an elution time of 2 min at a carrier gas flow rate of 30 ml min^{-1}. The value (10^{-7} mmoles ml^{-1}) is of the same order for conventional hot wire detectors.
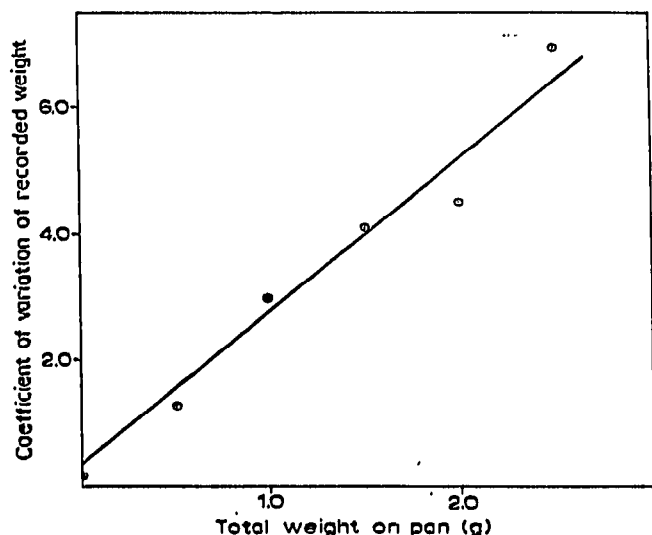

Fig. 2. The effect of balance load on precision.

TABLE II

STABILITY OF THE MASS DETECTOR

Range (μg)	Noise level (% f.s.d.)	Limits of detection	
		μg	$mMml^{-1}$
1000	not detectable	4	6.6×10^{-7}
250	negligible	2	3.3×10^{-7}
100	0.25	0.5	8×10^{-8}
25	2	1	1.7×10^{-7}

The major contribution to mass detector drift is desorption of materials from the detecting element, which will increase as the total sample loading increases. Drift, measured over a period of 15 h using a detector containing a total sample load of 17 mg of n-butyl acetate (b.p. 124°), was 2 $\mu g/h$ (i.e. 0.2% f.s.d./h). No significant decrease in the precision of the result occurs as drift increases.

Adsorption efficiency

The effect of changing various parameters on the efficiency of adsorption of the element was studied. Using a mixture of acetates, the relative percentage composition
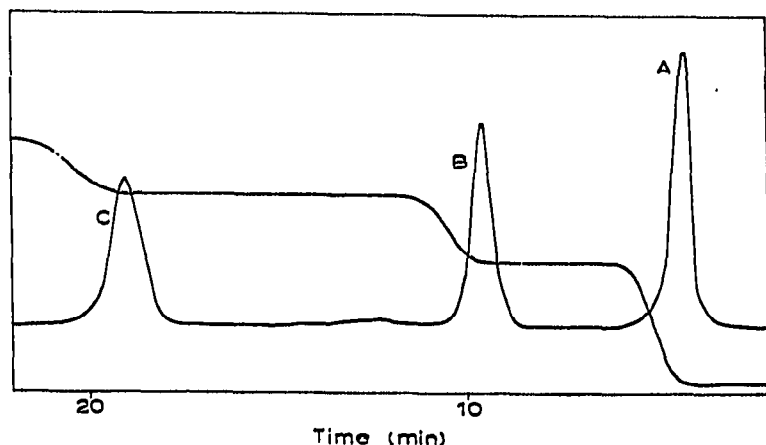
Fig. 3. Chromatogram of acetate mixture. Integral response: mass detector. Differential response: gas density balance. Experimental details: Shandon KG2 chromatograph fitted with 4 m × 4 mm (I.D.) column containing 20% PEGA on 72-85 mesh Chromosorb G. Injection temperature 154°. Column temperature 104°. Sample size 1.2 μl. Components, A = ethyl acetate; B = n-propyl acetate; C = n-butyl acetate.

of the sample was determined at a number of different carrier gas flow rates covering the range 15 to 250 ml min^{-1}. A typical chromatogram is shown in Fig. 3. Satisfactory quantitative results do not depend on complete adsorption of all materials, only on an equal adsorption efficiency toward each component of the mixture. To be more generally applicable, the results are expressed in terms of % bias, calculated as follows:

$$\% \text{ bias} = \left(\frac{\bar{x} - x_0}{x_0}\right) \times 100$$

where $\bar{x}$ = mean experimentally determined % composition;
x_0 = true percentage composition.

The change in bias with flow rate was 5×10^{-3}%/ml min^{-1} for each material. This represents such insignificant changes in relative response that it is reasonable to assume that the relative response of the detector is independent of flow rate at least over the range 15 to 250 ml min^{-1}. Bias values and relative composition values, embracing the whole flow rate range, for 51 analyses, are given in Table III. Repeatability of the determinations is quoted in terms of the coefficient of variation (V).

A similar mixture was analysed repeatedly (15 times) at a single carrier gas flow rate and a significant improvement in precision and accuracy was observed.

TABLE III

BIAS VALUES AND RELATIVE COMPOSITION VALUES (WIDE FLOW RATE RANGE)

Component		$\bar{x}$	σ	V	x_0	Bias	% Bias	$\bar{R}$[a]
Ethyl acetate		33.04	0.634	1.93	33.49	−0.45	−1.37	0.99
n-Propyl acetate		31.38	0.282	0.90	31.64	−0.26	−0.85	0.99
n-Butyl acetate		35.57	0.671	1.89	34.87	+0.70	+1.99	1.02
	Mean			1.57		| 0.47 |	| 1.40 |	

[a] The response factor $\bar{R} = \bar{x}/x_0$.

TABLE IV

BIAS VALUES AND RELATIVE COMPOSITION VALUES (FIXED FLOW RATE)

Component		$\bar{x}$	σ	V	x_0	Bias	% Bias	$\bar{R}$
Ethyl acetate		33.07	0.414	1.25	33.29	−0.22	−0.66	0.99
n-Propyl acetate		30.66	0.158	0.52	30.93	−0.27	−0.87	0.99
n-Butyl acetate		36.26	0.404	1.11	35.78	+0.48	+1.34	1.01
	Mean			0.96	.	| 0.32 |	| 0.96 |	

Absolute adsorption efficiencies, defined as the ratio of the amount of material adsorbed by the detector and the amount introduced into the detector, were measured. The experiment was designed to eliminate the need to know the quantity of sample injected and the possibility of loss of sample between the injection port and the detector, which would lead to erroneous values of adsorption efficiency. Column effluent, after passing through a short column in an oven at 100° was passed to a small cylindrical chamber at room temperature, and then back into the oven to a gas density balance. The chamber could contain either a mass detecting element or an empty cylinder of the same dimensions. To determine the absolute adsorption efficiency of the mass detector at any flow rate, a sample was injected in the normal manner, a proportion of which was adsorbed by the mass detecting element. The remainder of the sample was detected by the gas density balance. By repeating the experiment in the absence of the detecting element the proportion of material adsorbed, and hence the adsorption efficiency, was found. In both experiments all conditions were identical, so that any losses of material due to leakage or irreversible adsorption on the column were equal, and did not affect the results. Adsorption efficiencies were measured over the flow rate range 15–250 ml min^{-1}, with nominal sample sizes of 0.25, 0.5, 1 and 2 μl of chloroform or nonane. Results are displayed on Fig. 4. Adsorption efficiency decreases as flow rate increases, which is of no consequence in the determination of the proportions of components in a mixture, assuming the determination is carried out at a constant flow rate. For flow rates up to about 75 ml
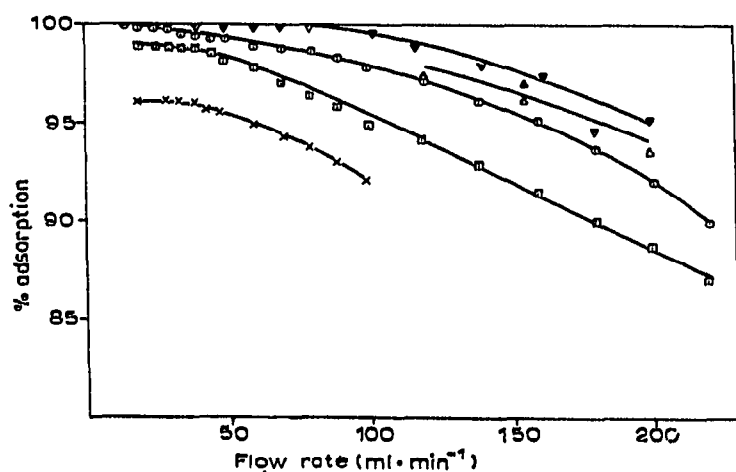

Fig. 4. The effect of flow rate and sample size on the adsorption efficiency of the mass detector. Key: △, 0.25 μl chloroform; ⊙, 0.5 μl chloroform; □, 1.0 μl chloroform; ×, 2.0 μl chloroform; ▽, 0.5 μl n-nonane.

min^{-1} (linear gas velocity of 62 cm sec^{-1}) adsorption was sensibly complete. Above this value the absolute weight of material present may be determined from the quotient of the observed step height and the adsorption efficiency. A potentially more serious effect, illustrated in Fig. 4, is that adsorption efficiency decreases as sample size increases, so that for a mixture containing materials in widely differing proportions, the observed composition may not agree with the true composition.

The efficiency experiment described above was conducted under conditions which gave very short retention times (about 1 min), so that the adsorbates were reaching the detecting element in the concentrated state. This effect was further studied by measuring adsorption efficiencies at a single flow rate for a number of different sample sizes of n-octane, introduced into the detecting element at varying concentrations with respect to the carrier gas (see Fig. 5). The more dilute the sample, the smaller was the effect of sample size on adsorption efficiency. The most dilute sample gave an efficiency of over 99.5% for all sample sizes injected. The maximum sample size was 8 μl and the maximum concentration at the detector 120 μg ml^{-1}. On the other hand, the most concentrated sample never attained complete adsorption even for a 1 μl injection: in this case the minimum concentration was 1 mg ml^{-1}. The remaining samples were all totally adsorbed up to a concentration of about 130 mg ml^{-1}. Since the decrease in efficiency occurs to an appreciable extent at high flow rates and very short retention times, in practice under normal operating conditions, there will be no adverse effect on the quantitative results.
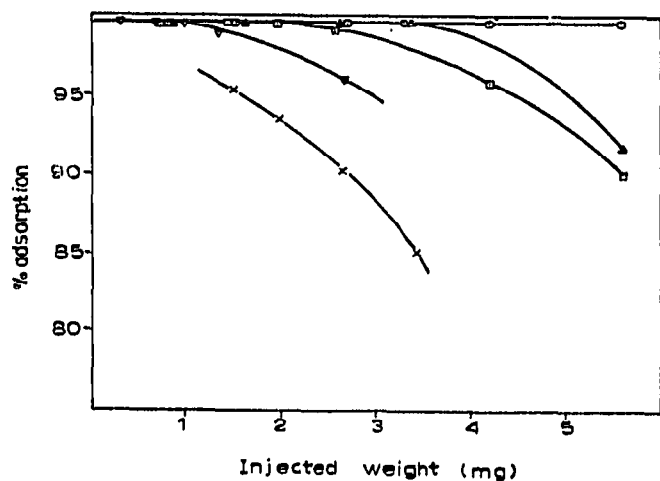

Fig. 5. Effect of sample size and concentration on adsorption efficiency of the mass detector. Increasing sample concentration → $\odot$, $\triangle$, $\square$, ∇, $\times$.

Adsorption capacity

A knowledge of capacity is required to predict the frequency with which the element must be regenerated. Capacity is defined as the weight of a given material which the element can hold under given conditions before desorption of that material is detected. In a typical experiment a 1 μl charge of n-butyl acetate (b.p. 124°) was repeatedly injected into the apparatus. 25 mg of material ($\equiv$ 33 1 μl injections) was adsorbed before desorption was detected. The experiment was repeated for n-octane (b.p. 125°) and n-butyl alcohol (b.p. 118°) and for several different sample sizes.

There were no significant differences in the capacity values. Adsorption efficiency is not affected by the degree of saturation of a detecting element. The mean adsorption efficiency was 99.2% with a standard deviation of 0.7% for 104 1 μl injections of n-butyl acetate. The variation of capacity with temperature was measured by keeping the detector temperature constant and adsorbing materials of different boiling point, using a homologous series of alkanes (see Fig. 6). The effect of carrier gas flow rate on capacity is shown on Fig. 7. It was concluded that capacity is increased by increasing the temperature difference between the boiling point of the adsorbate and the detecting element, and decreased as carrier gas flow rate is increased. In general the adsorption capacity of an element is sufficient for many analyses and regeneration may be conveniently carried out overnight.
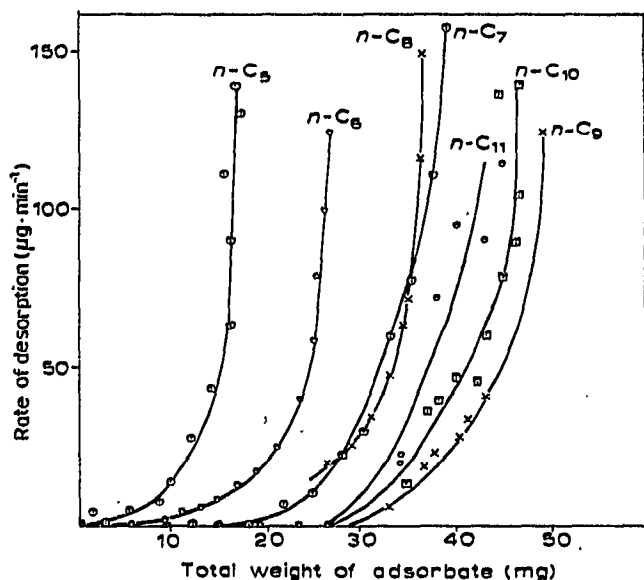

Fig. 6. Adsorption capacity of the mass detector toward a homologous series of alkanes.
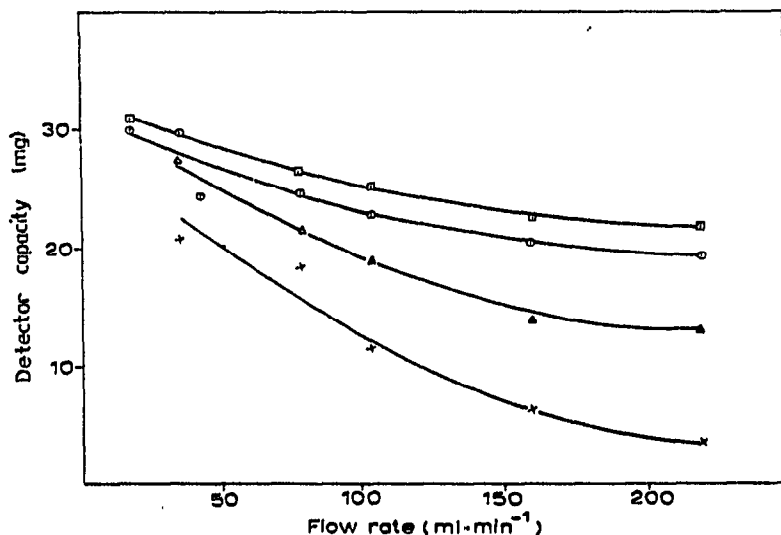

Fig. 7. The effect of flow rate on the adsorption capacity of the mass detector. Desorption rate: $\times$, 10 μg min^{-1}; $\triangle$, 50 μg min^{-1}; $\odot$, 100 μg min^{-1}; $\square$, 150 μg min^{-1}.

Detector linearity

The linearity of the detector response was determined by the following methods. For small sample sizes a 10 μl syringe calibrated for the 1 μl setting using *n*-heptane, was used to deliver 1 μl charges of mixtures of *n*-hexane as solvent and pure (99.9%) *n*-heptane as solute. These two compounds form virtually ideal solutions over the whole mole fraction range[7]. By varying the amount of heptane in hexane, the mass range 15 to 700 μg was covered. The response of the detector to each mixture was measured at least three times (on each mass range). Carrier gas flow rate was 36 ml min^{-1}. The results were calculated directly from the weights of heptane adsorbed, and not relative to the total sample injected (see Figs. 8 and 9). A linear response was obtained over the whole mass range. The slope of the curve was unity demonstrating that adsorption was essentially complete.
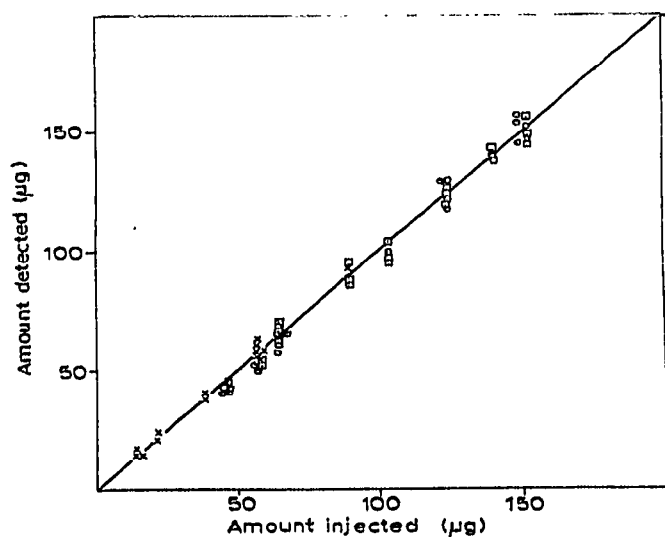

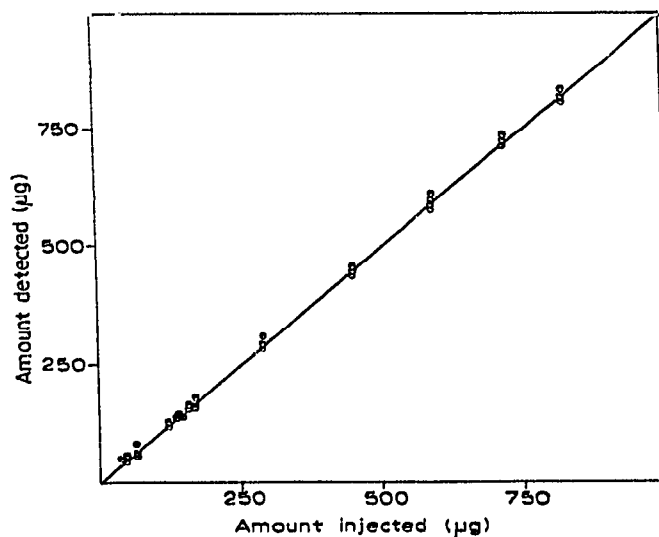Fig. 8. Linearity of response of the mass detector. Range: ×, 100 μg; ☐, 250 μg; ⊙, 1 mg.

Fig. 9. Linearity of response of the mass detector.

For larger sample sizes, in which syringe injection is open to objection, carrier gas containing a known concentration of solute was passed into the detector for measured times, and a comparison of the quantity introduced and detected was made. Complete adsorption was found for sample sizes up to 12 mg, which represented 5% by weight of the total amount of adsorbent present. The coefficient of variation of response over the whole linear range was 2.5% for 28 runs (for determinations of mixtures containing more than 10% heptane in hexane). The adsorption capacity of the detecting element was 10 mg, so that the detector gave a linear response and quantitative adsorption until its capacity was exceeded. Capacity and hence linearity are readily extended by increasing the amount of adsorbent available. The overall linear response of the detector, embracing all balance ranges, is shown on Fig. 10. The line of regression has a slope of 1.02 and an intercept of —0.05. The linearity of response of the detector was also measured at a more rapid flow rate (105 ml min^{-1}).

TABLE V

MASS DETECTOR RESPONSE

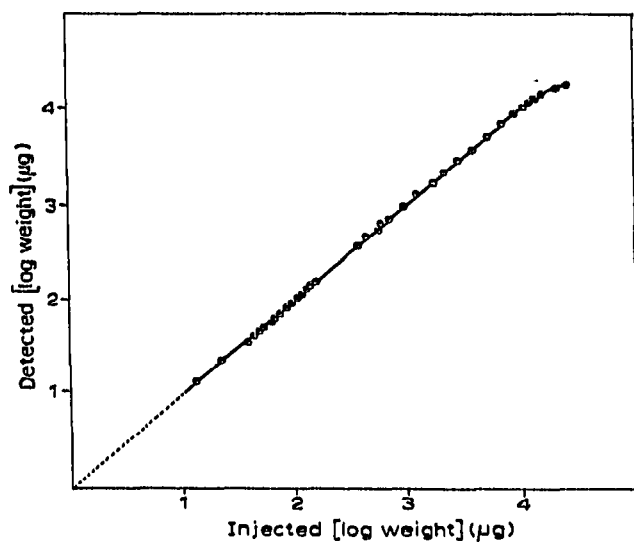| % Heptane in solution	Injected quantity (µg)	Mean detected quantity (µg)	Response
100 µg range			
2.3	13.0	15.1	1.16
3.6	20.8	19.8	0.95
7.2	38.7	37.9	0.98
9.9	56.8	58.8	1.03
10.0	57.9	56.5	0.98
250 µg range			
8.2	47.0	43.9	0.94
9.9	56.8	51.3	0.91
10.0	57.9	53.1	0.92
11.1	64.2	65.7	1.02
15.6	90.2	87.9	0.97
18.0	104.3	99.4	0.96
21.9	126.6	125.7	0.99
24.0	139.2	135.7	0.98
1 mg range			
8.2	47.0	42.9	0.92
9.9	57.2	51.2	0.90
11.1	64.2	64.7	1.01
21.9	126.6	127.9	1.01
24.0	139.2	134.1	0.97
25.9	149.8	152.4	1.02
26.3	152.6	146.8	0.97
48.3	282.1	288.1	1.02
76.3	450.4	442.2	0.98
100.0	595.6	590.1	0.99
100.0	714.7	727.9	1.02
100.0	833.8	839.8	1.01

Fig. 10. Overall linear response of the mass detector.

Response was less than unity (0.96), since adsorption efficiency is less at higher flow rates, but the response was linear over the whole range investigated (50–600 μg). The coefficient of variation of the response for 15 runs was 2%.

It is reasonable to assume therefore that the detector will give a linear response over a wide flow rate range.

The characteristics of the mass detector are given in Table VI.

TABLE VI

CHARACTERISTICS OF THE MASS DETECTOR[a]

Lower limit of (linear) detection	0.5 μg[b]
Upper limit of detection	25 mg[c]
Dynamic range	5×10^4[c]
Linear dynamic range	2×10^4[c]
Baseline drift	2 μg/h (1 mg range)
Response time	$ca.$ 1 sec
Effective volume	<1.5 ml

[a] With reference to the particular system described herein.
[b] Smallest amount of material measured = 0.8 μg.
[c] May be varied by varying the amount of adsorbent.

CONCLUSIONS

The response of the mass detector is predictable on a weight basis. The relative response of the detector is independent of carrier gas flow rate, and repeatability of response at a fixed flow rate is $\pm$ 1%. The absolute response of the detector decreases as flow rate is increased, but is independent of chemical species. The detector has sufficient capacity to adsorb materials from many runs before regeneration is required: the capacity is a function of the amount of adsorbent and the difference between the boiling point of the adsorbate and the temperature of the adsorbent. Detecting elements are simple to construct, and the operating procedure is straightforward. The cost of the detecting element is negligible, and the cost of the complete detector, including the particular microbalance and associated equipment used in this work is of the same order as a katharometer complete with amplifier and control unit. In addition the mass detector functions as its own integrator. The detecting element and microbalance are sufficiently robust to withstand normal careful handling: the detector operates perfectly satisfactorily on an ordinary wooden laboratory bench. The advantages of the mass detector for quantitative analysis, over all other detectors are: (1) The response is predictable and no calibration with respect to sample size or chemical species is required. (2) Since response is a function of mass, no qualitative information is required for a complete quantitative analysis. (3) Peak area measurement is eliminated since quantitative data are obtained directly from step height measurement.

ACKNOWLEDGEMENT

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