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QUANTITATIVE ANALYSIS BY MASS DETECTION

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SUMMARY

The mass detector has been used for the analysis of a wide range of materials embracing low boiling and high boiling liquids. Some low boiling materials were quantitatively detected without calibration by operating the detector below room temperature. The quantitative analyses of a wide variety of mixtures of normal and high boiling liquids were carried out and satisfactory results obtained without the necessity for calibration. The response of the detector toward gases has been studied.

INTRODUCTION

Recently the absolute and linear response of the mass detector has been demonstrated over a variety of operating conditions and the results of the analyses of a number of simple acetate mixtures have been presented[1]. The purpose of the present work is to cover a wider range of materials, and thereby demonstrate the value of the mass detector for the quantitative analysis of mixtures. A wide variety of species has been analysed, and it is convenient to divide the results into several sections, relating to the boiling ranges of the materials under analysis. This is not a consequence of any peculiarity of the mass detector, but arises from the conditions under which the chromatograph itself must be operated to give a satisfactory performance. In general, it is convenient to place materials for chromatographic analysis into the following categories: (i) materials boiling over approximately the range 50° to 200°; (ii) high boiling materials: liquids boiling over 200° (including those which are solids at room temperature); (iii) low boiling materials (0 – 50°); (iv) gases.

The mass detector was used to analyse materials in all these categories, and the results are presented below. Any requirements associated with a particular boiling range are described in the appropriate section.

NORMAL BOILING MATERIALS

The majority of experiments were carried out using a Shandon KG2 chromatograph fitted with a mass detector as previously described[1]. The column effluent was fed

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by means of a resistively heated 1/8 in. O.D. stainless steel tube into a mass detecting element attached to the arm of an electromicrobalance (Research and Industrial Instruments Company, model EMB I). The detecting element was enclosed in a metal box about 2.5 in. cubed, attached to the underside of the balance case. Some experiments were carried out using a Pye Panchromatograph, also fitted with a mass detector. In this work the detecting element was housed within the balance case proper.

Mixtures for analysis were prepared by weighing directly into sample bottles which were filled almost to the limit. Samples were removed with a syringe via a septum. No mixture was kept for more than a few hours. A number of different sample sizes of each mixture were analysed covering the mass range from 10 μg to 1 mg per component of a mixture. Usually this amounted to a total of about ten determinations. A wide variety of mixtures was analysed: homologous series mixtures, mixtures containing compounds of a similar chemical nature, and mixtures containing different chemical species, covering saturated and unsaturated hydrocarbons and halogenated and oxygenated compounds.

The operating conditions under which the analyses were carried out are given in Tables I, V, VII, X, XII, and XIV. For each mixture the mean observed percentage weight of the components ($\bar{x}$) was calculated, and the standard deviations (σ) and coefficients of variation (V) of these values were found. The mean detector response ($\bar{R}$) defined as the ratio of the mean observed percentage weight and the true percentage weight ($\bar{x}/x_0$) is given. Bias values represent the discrepancy between the mean observed composition and the true composition and were calculated using expressions:

$$\text{Bias} = \bar{x} - x_o \tag{1}$$

$$\text{(Absolute) \% Bias} = \frac{\bar{x} - x_o}{x_o} \times 100 \tag{2}$$

For each mixture, the components are listed in order of increasing retention time.

The results presented in Table II were obtained using the KG2 chromatograph under the conditions given in Table I. The results in Table III were obtained using the

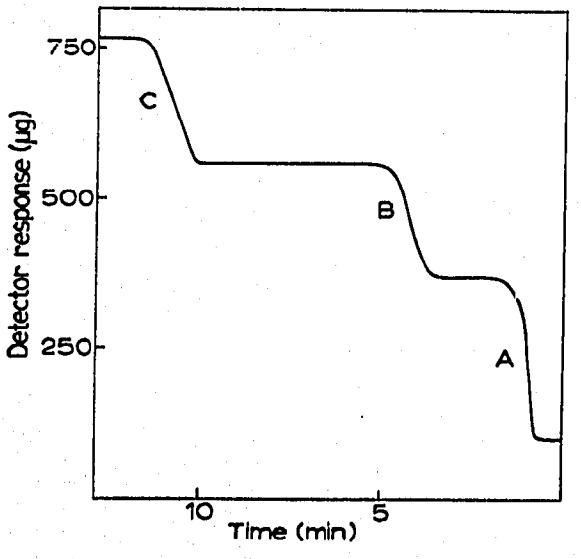


Fig. 1. Chromatogram of ketone mixture. A = ethyl acetate, B = *n*-propyl acetate, C = *n*-butyl acetate.

TABLE I

OPERATING CONDITIONS

Column temperature	101°
Detector temperature	22–24°
Carrier gas	nitrogen
Carrier gas flow rate	51 ml min^{-1}
Sample sizes	0.1 – 5 μl
Mass detector ranges	100 μg – 5 mg f.s.d.
Columns[a]: KG 2	Ref. E
Panchromatograph	Ref. A

[a] A key to columns is given in Table XIX.

TABLE II

Compound	$\bar{x}$	σ	V	x_0	$\bar{R}$	*Bias*
Benzene	39.71	1.32	3.32	39.20	1.01	+0.51
Toluene	29.97	0.91	3.04	30.25	0.99	−0.28
Ethyl benzene	30.32	1.03	3.32	30.55	0.99	−0.23
Methyl ethyl ketone	38.75	1.84	4.75	37.56	1.03	+1.19
Methyl *n*-propyl ketone	29.84	1.73	5.70	29.77	1.00	+0.07
Methyl *n*-butyl ketone	31.41	0.54	1.72	32.67	0.96	−1.26
Ethyl acetate	41.45	0.73	1.74	40.36	1.03	+1.09
n-Propyl acetate	31.63	0.66	2.08	31.58	1.00	+0.05
n-Butyl acetate	26.92	1.06	3.95	28.06	0.96	−1.14
n-Heptane	17.72	0.40	2.26	17.82	1.00	−0.10
n-Octane	17.30	0.56	3.24	17.50	0.99	−0.20
Ethyl acetate	21.38	0.79	3.70	21.73	0.98	−0.35
Methyl ethyl ketone	16.39	0.55	3.36	16.09	1.02	+0.30
Benzene	27.22	0.33	1.21	26.86	1.01	+0.36
Cyclohexane	22.63	0.67	2.96	22.86	0.99	−0.23
n-Octane	15.52	0.97	6.27	15.46	1.00	+0.06
Carbon tetrachloride	35.95	0.50	1.39	35.02	1.03	+0.93
Dichloroethylene	25.90	0.72	2.78	26.65	0.97	−0.75
2,2,4-Trimethyl pentane	44.27	0.61	1.37	43.97	1.01	+0.30
n-Octane	28.47	1.34	4.70	27.86	1.02	+0.61
1-Octene	27.26	0.84	3.07	28.16	0.96	−0.90
n-Octane	35.79	0.74	2.06	34.28	1.04	+1.51
Butylene oxide	32.91	0.55	1.67	32.03	1.03	+0.88
Dioxan	31.30	0.91	2.90	33.69	0.93	−2.39

TABLE III

Compound	$\bar{x}$	σ	V	x_0	$\bar{R}$	*Bias*
Methyl propionate	33.05	0.60	1.81	33.51	0.99	−0.46
Toluene	30.35	0.41	1.35	30.41	1.00	−0.06
Chlorobenzene	36.59	0.44	1.20	36.08	1.01	+0.51
Ethyl alcohol	54.25	0.55	1.01	53.63	1.01	+0.62
n-Propyl alcohol	45.75	0.57	1.24	46.37	0.99	−0.62

Panchromatograph under similar conditions. A chromatogram of the ketone mixture is shown in Fig. 1.

Many analyses of similar mixtures were carried out at a flow rate of 105 ml min^{-1}, on the Shandon KG2 chromatograph, under the conditions given in Table I where appropriate. Variations in conditions are noted at the foot of Table IV, which summarises these results.

TABLE IV

RESULTS — NORMAL BOILING MATERIALS (RAPID FLOW RATE)

Compound	$\bar{x}$	σ	V	x_0	$\bar{R}$	*Bias*
n-Pentane[a]	22.30	0.66	2.95	22.50	0.99	−0.20
n-Hexane	18.40	0.71	3.86	17.57	1.05	+0.83
n-Heptane	15.16	0.59	3.85	14.67	1.03	+0.49
n-Octane	16.46	0.64	3.87	16.45	1.00	+0.01
n-Nonane	27.69	0.89	3.23	28.82	0.96	−1.13
Benzene	41.35	0.70	1.70	41.33	1.00	+0.02
Toluene	30.94	0.69	2.23	31.00	1.00	−0.06
Ethyl benzene	27.72	0.60	2.16	27.67	1.00	+0.05
Methyl ethyl ketone	43.05	0.57	1.32	42.20	1.02	+0.85
Methyl *n*-propyl ketone	25.75	0.84	3.28	25.69	1.00	+0.06
Methyl *n*-butyl ketone	31.20	1.32	5.58	32.10	0.97	−0.90
Methyl acetate	21.46	0.83	3.85	23.72	0.90	−1.26
Ethyl acetate	25.50	0.81	3.17	23.47	1.09	+2.03
n-Propyl acetate	23.03	1.01	4.38	22.82	1.01	+0.21
n-Butyl acetate	30.02	0.46	1.53	29.99	1.00	+0.03
n-Heptane	18.61	0.20	1.08	18.44	1.01	+0.17
n-Octane	13.81	0.34	2.46	13.77	1.00	+0.04
Ethyl acetate	23.92	0.31	1.30	23.68	1.01	+0.22
Methyl ethyl ketone	16.28	0.36	2.21	16.49	0.99	−0.21
Benzene	27.37	0.31	1.13	27.63	0.99	−0.26
Cyclohexane	19.39	0.59	3.04	19.30	1.00	+0.09
n-Octane	16.14	0.43	2.68	15.87	1.02	+0.27
Carbon tetrachloride	34.79	0.63	1.81	34.92	1.00	−0.13
Dichloroethylene	29.68	—	—	29.92	0.98	−0.24
2,2,4-Trimethyl pentane	38.25	0.72	1.88	38.03	1.01	+0.22
n-Octane	35.52	0.71	2.00	35.59	1.00	−0.07
1-Octene	26.23	2.00	7.65	26.38	0.99	−0.15
n-Octane	27.63	0.47	1.71	26.74	1.03	+0.89
Butylene oxide	28.56	0.59	2.06	28.80	0.99	−0.24
Dioxan	43.81	0.82	1.87	44.45	0.99	−0.64
n-Butyraldehyde[a]	39.24	1.03	2.62	39.80	1.00	−0.56
Methyl ethyl ketone	60.76	1.06	1.74	60.20	1.00	+0.56
n-Butyl alcohol[b]	53.42	1.05	1.97	52.95	1.01	+0.47
n-Amyl alcohol	46.58	1.05	2.26	47.05	0.99	−0.47
n-Propyl alcohol[b]	45.36	0.28	0.62	44.94	1.01	+0.42
Methyl *n*-propyl ketone	54.64	0.52	0.96	55.06	0.99	−0.42

[a] Column temperature 66°.
[b] Column Ref. D, Table XIX.

There was a negligible difference between the precision and accuracy of the results at 51 and 105 ml min^{-1}. The overall standard deviation (σ) was 0.75%, and the coefficient of variation (V) 2.5%, for 180 analyses. The corresponding values for runs carried out at a single sample size on a single mixture were 0.4% and 1.0% respectively. Values for a single mixture over a wide flow rate range were 0.6% and 1.6%. The accuracy of the results is expressed in terms of bias, and the mean value of the runs in Tables II–IV is 0.54% (absolute bias 1.8%); the value for 15 replicate analyses of a three component mixture at a single sample size (1 μl) was 0.32% (absolute bias 0.96%). Response factors are very similar for all materials, and for practical purposes can be taken as unity. In order to assess the reliability of the mass detector for the analysis of minor constituents and to detect any trends in bias and precision with respect to percentage composition, a number of mixtures of heptane and hexane were prepared, in which the proportion of one compound was progressively increased from 2% to 100%. Experimental conditions are given in Table V. Results were calculated solely on the basis of the weight of heptane present and not on the proportion of heptane in the mixture. The results, given in Table VI, were used only to determine the bias of the measurements, and not the precision of the measurements for each mixture.

TABLE V

OPERATING CONDITIONS

Chromatograph	Shandon KG2
Column	Ref. E
Column temperature	64°
Carrier gas	nitrogen
Carrier gas flow rate	32–36 ml min^{-1}
Sample size	1 μl
Mass detector range	100 μg to 1 mg
Detector temperature	24°

TABLE VI

RESULTS— MINOR CONSTITUENTS

Heptane (%)	*Bias*		*Heptane* (%)	*Bias*	
	μg	%		μg	%
2.3	+2.1	+15.8	18.0	−4.9	−4.7
3.6	−0.8	− 4.0	21.9	−0.9	−0.7
7.2	−0.9	− 2.2	21.9	+1.3	+1.0
8.2	−4.1	− 8.7	24.0	−5.1	−3.6
8.2	−3.1	− 6.4	24.0	−3.5	−2.5
9.9	−6.0	−10.5	25.9	+2.6	+1.7
9.9	−5.5	− 9.6	26.3	−7.8	−5.2
9.9	+2.1	+ 3.5	26.3	−2.6	−1.7
10.0	−1.4	− 2.5	48.3	+6.0	+2.1
11.1	−0.5	+ 0.8	67.5	+5.6	+1.4
11.1	+1.5	+ 2.4	76.3	−8.2	−1.8
15.6	−2.3	− 2.6	100.0	−5.5	−0.9

The percentage bias values show a slight improvement when the proportion of heptane exceeds about 10%. The mean value of the (absolute) bias is 4%. Using a similar series of hexane–heptane mixtures, and carrying out ten determinations per

mixture, a measure of the precision of the detector at each heptane composition was obtained. All values were calculated on a percentage weight rather than on an absolute basis, and the results are given in Table VIII in the same manner as Table II, with which they may be compared. Experimental conditions are given in Table VII.

TABLE VII

EXPERIMENTAL CONDITIONS

Chromatograph	Panchromatograph
Column	Ref. G
Column temperature	100°
Carrier gas flow rate	40 ml min^{-1}
Sample size	1 μl, 3.5 μl
Mass detector range	1 mg – 5 mg
Detector temperature	24°

TABLE VIII

RESULTS— MINOR CONSTITUENTS

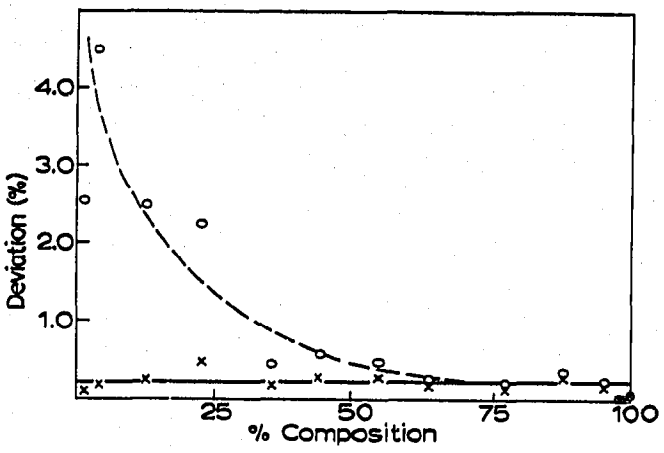
$\bar{x}$(%)	σ	V	x_0(%)	*Bias*	*Bias*(%)
0.34	0.05	14.7	0.29	+0.05	17.2
1.51	0.04	2.65	1.38	+0.13	9.4
4.17	0.20	4.80	4.39	−0.12	2.7
12.16	0.32	2.63	12.65	−0.49	3.9
22.19	0.51	2.29	22.45	−0.26	1.2
35.87	0.18	0.50	35.94	−0.07	0.19
44.68	0.29	0.65	44.79	−0.11	0.24
55.33	0.29	0.52	55.21	+0.12	0.22
64.13	0.18	0.28	64.06	+0.07	0.11
77.82	0.17	0.22	77.55	+0.27	0.35
87.85	0.33	0.38	87.36	+0.49	0.56
95.80	0.21	0.22	95.61	+0.19	0.20
98.49	0.00	—	98.62	−0.11	0.11
99.66	0.05	0.05	99.71	−0.04	0.04

All runs were carried out using 1 μl samples on the 2 mg range of the balance except those samples of percentage composition less than 2% and greater than 98%. For these runs 3.5 μl samples were used, with the 5 mg range for the major constituent and the 1 mg range for the minor constituent.

The changes in standard deviation and coefficient of variation with sample composition are shown on Fig. 2. The coefficient of variation is less than 1% for all sample compositions over 30% and even at 5% composition has only increased to about 4%. The standard deviation remains sensibly constant throughout the whole range of sample compositions, at about 0.25%. The overall mean bias is 0.2% (absolute bias 2.6%).

HIGH BOILING MATERIALS

It is to be expected that a number of experimental difficulties, not present to any significant extent at normal operating temperatures, will become apparent when analysing high boiling materials. For example, the temperature of the carrier gas



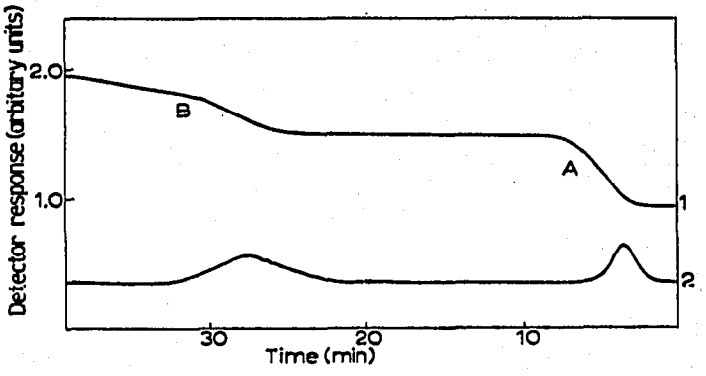


Fig. 2. Variation of precision with percentage composition. × = standard deviation, ○ = coefficient of variation.

Fig. 3. Chromatogram of some *n*-alkanes showing the effect of condensation. A = *n*-docosane, B = *n*-tetracosane, 1 = mass detector response curve, 2 = differential detection response curve.

emerging from the chromatographic column may be sufficiently high to create disturbances by convection within the mass detector chamber. Condensation of materials in the delivery tube prior to reaching the mass detector is more likely, and could lead to erroneous results, in particular with samples containing materials covering a wide boiling range. Experiments were designed to measure any decrease in stability of the detector as the carrier gas temperature was increased, and to determine the extent to which condensation within the delivery tube occurred. On the basis of these experiments the mass detection system was modified to be suitable for high temperature analysis.

To prevent condensation of high boiling materials in the detector delivery tube it was essential to heat the tube along its whole length. It was not satisfactory to allow that part of the tube within the detector chamber to be heated only by conduction. However, by heating the delivery tube within the chamber, the noise level increased significantly. By lagging the chamber the effect was minimised and for a delivery tube at 180° the noise level on the 1 mg range was 0.5% f.s.d. At a given temperature there is an increasing tendency towards condensation, the lower the vapour pressure of the solute. The result is an increase in distortion of the steps, as a homologous series is ascended, the points of inflexion becoming progressively more difficult to locate. An example of this effect is shown in Fig. 3. The effect on a quantitative analysis is shown in Table IX.

TABLE IX

ANALYSIS OF *n*-ALKANES

Delivery tube temperature 26°.

Compound	$\bar{x}$	x_0	*Bias*	*Bias* (%)
n-Nonane	56.77	54.86		
n-Dodecane	43.23	45.14	−1.91	4.2

Using a heated delivery tube and lagged detector chamber, replicate analyses of high boiling mixtures, including materials solid at room temperature, were carried out. The results are given in Table XI, and operating conditions in Table X. In some samples of the higher alkanes one member much lower in the series was included; (i) to act as a solvent; (ii) to eliminate the possibility that all materials within a small boiling range were condensing to the same extent, and thus giving a false impression of satisfactory performance.

Before injection, samples were warmed to ensure complete mixing and liquefaction, and the syringe was warmed before use.

TABLE X

OPERATING CONDITIONS

Samples	*n*-Alkanes	Aromatics
Chromatograph	KG2	KG2
Column	Ref. H	Ref. H
Column temperature	232°	155°
Carrier gas flow rate	108 ml min^{-1}	35 ml min^{-1}
Delivery tube temperature	196°	112°
Detecting element temperature	51°	35°

TABLE XI

RESULTS — HIGH BOILING MATERIALS

Compound	$\bar{x}$	σ	V	x_0	$\bar{R}$	*Bias*
n-Dodecane	24.44	0.82	3.4	24.92	0.99	−0.48
n-Tetradecane	14.90	0.47	3.1	15.61	0.96	−0.71
n-Hexadecane	32.98	0.63	1.9	32.44	1.02	+0.54
n-Octadecane	27.68	1.26	4.5	27.03	1.02	+0.65
n-Dodecane	26.12	0.57	2.2	27.11	0.96	−0.99
n-Hexadecane	14.96	1.00	6.7	14.86	1.01	+0.10
n-Octadecane	17.72	0.85	4.8	18.32	0.97	−0.60
n-Nonadecane	4.28	0.41	9.6	3.84	1.12	+0.44
n-Eicosane	36.92	0.96	3.1	35.88	1.02	+1.04
n-Dodecane	35.33	0.64	1.8	33.92	1.04	+1.41
n-Eicosane	27.47	0.60	2.2	28.18	0.98	−0.71
n-Docosane	27.80	1.07	3.9	28.57	0.97	−0.77
n-Tetracosane	9.40	1.30	13.8	9.33	1.01	+0.10
n-Eicosane	42.45	2.09	4.9	42.65	1.00	−0.20
n-Docosane	42.99	1.48	3.4	43.24	1.00	−0.25
n-Tetracosane	14.57	1.71	11.7	14.12	1.03	+0.45
n-Hexadecane	40.16	2.91	7.2	40.05	1.00	+0.11
n-Eicosane	41.85	2.78	6.6	41.57	1.00	+0.28
n-Docosane	18.00	2.19	12.2	18.38	0.98	−0.38
Cumene	15.01	0.29	1.9	15.26	0.98	−0.25
Mesitylene	20.98	0.74	3.5	21.68	0.97	+0.30
p-Cymene	12.81	0.47	3.7	13.06	0.98	−0.25
Iodobenzene	51.20	2.13	4.2	49.99	1.02	+0.21
n-Nonane	27.71	0.74	2.7	27.56	1.00	+0.15
p-Cymene	53.53	0.36	0.7	53.44	1.00	+0.09
Iodobenzene	18.76	0.79	4.2	19.00	0.99	−0.24

A chromatogram, showing the analysis of some hydrocarbons between n-C_{16} and n-C_{20} is shown in Fig. 4. Retention distances, obtained from the alkane mixtures listed in Table XI were plotted against carbon number (Fig. 5) and a straight line relationship was obtained embracing the normal alkanes dodecane and tetracosane.

From Table XI, the mean value for the standard deviation of the results was 1.2%, and the coefficient of variation 5.2%. The bias of the results was 0.6% (2% absolute). The precision of the results is poorer than that obtained under normal operating temperatures (Tables II–IV), but nevertheless is still acceptable: bias values, on the other hand, are identical with those obtained for normal boiling materials.

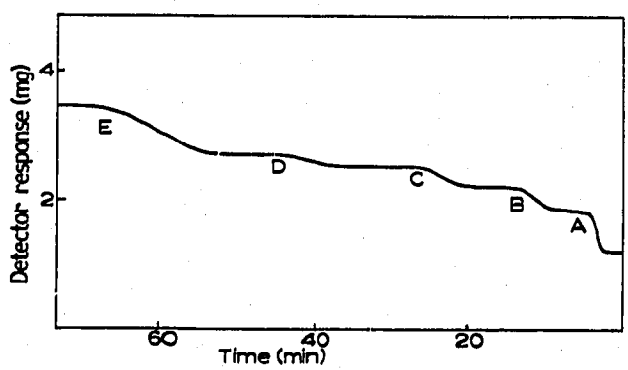


Fig. 4. Chromatogram of n-alkane mixture. A = n-dodecane, B = n-hexadecane, C = n-octadecane, D = n-nonadecane, E = n-eicosane.

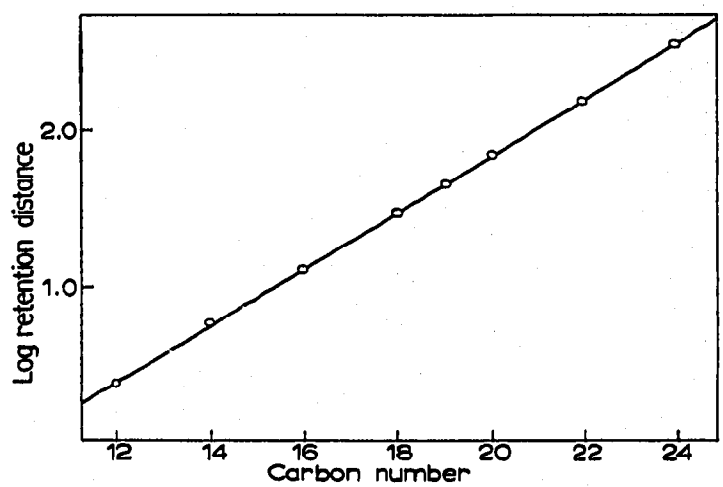


Fig. 5. Retention data for n-alkanes.

LOW BOILING MATERIALS

Previous work on adsorption capacity showed that the capacity of the detector decreases as the boiling point of the adsorbate approaches that of the detecting element temperature. The adsorption capacity of a typical detector is only about 4 mg when this difference is 12°. It is then advisable to operate the mass detector below room temperature to obtain a reasonable adsorption capacity, and to decrease the frequency with which the detector must be regenerated.

An electrothermal cooling unit, manufactured by Frigistor Ltd.* was used. The unit comprised a block of aluminium faced with cooling modules. The centre of the block was drilled, such that a detecting element fitted snugly, without touching the sides. The cooling unit was lagged with expanded polystyrene and placed in the detector chamber. The temperature of the cooling unit was monitored in the centre of the block, this being the temperature of the atmosphere within the detecting element. Noise measurements at various detecting element temperatures were taken, both in the absence of carrier gas, and with a gas flow rate of 55 ml min^{-1}. The noise level remained at 0.25% f.s.d. (12 μg) over the temperature range 10° to —6° and the introduction of carrier gas had no measurable effect. During each temperature decrease the

*De La Rue Frigistor, Ltd., Langley, Bucks., Great Britain.

mass detector gained weight due to increased adsorption of nitrogen at the lower temperature, but reached a new equilibrium after several minutes. At lower temperatures drift due to condensation of water on the element became significant and an enclosed chamber, such as is used for vacuum weighing, would be required for a satisfactory performance. All runs with low boiling materials were carried out with a detecting element temperature of +2.5°. This limited quantitative analysis to materials boiling in the region of 35°, to obtain reasonable adsorption capacity. However, the detection of some amines boiling at much lower temperatures was also accomplished. The following materials (boiling points in parentheses) were detected by the mass detector, under the conditions given in Table XII: *n*-pentane (36°), methylene dichloride (40°), ethyl bromide (38°), methyl iodide (43°), ethylamine, in ethanol (17°), methylamine, in water (—7°).

TABLE XII

OPERATING CONDITIONS

Apparatus	KG2
Column	Ref. H
Column temperature	25°
Flow rate	55 ml min^{-1}
Delivery tube temperature	25°
Detecting element temperature	2.5°

The quantitative preparation of mixtures of low boiling materials is particularly difficult in view of their high volatility. The preparation of *n*-pentane and methylene dichloride mixtures was attempted, but weight loss during preparation was observed. Three analyses of such a mixture, under the conditions quoted in Table XII, yielded the results given in Table XIII.

TABLE XIII

RESULTS—LOW BOILING MATERIALS

Compound	$\bar{x}$	x_0	*Bias*	*Bias* (%)
n-Pentane	17.53	16.95	+0.58	3.4
Methylene dichloride	82.47	83.05	—0.58	0.7

THE ANALYSIS OF GASES

The analysis of gases by the mass detector can be approached in two ways: (1) An extension of the principle described above in which the detecting element is operated at say —100° for the quantitative adsorption of propane and higher boiling materials (using nitrogen as carrier), and at —200° for the detection of methane, ethane and the inorganic gases, using helium as carrier. (2) Operation of the detecting element at room temperature, and observing a combination of buoyancy and adsorption effects.

The first alternative clearly offers a more satisfactory basis from which to obtain quantitative results, but there are additional technical difficulties. The effects of conden-

sation have already been observed, and at very low temperatures the contribution of the carrier gas to the adsorption process may become significant. Detection at room temperature on the other hand, is now an established procedure, and extension to the detection of gases presents little difficulty. This system was therefore adopted with a view to examining its value, at least for the qualitative detection of gases.

Detection will occur as a result of buoyancy changes and adsorption on to the charcoal when a component enters the detecting element. If the adsorption effect predominates, then quantitative estimation based on step heights may be satisfactory, even though the adsorption efficiency of the detector is low, since it may be of the same order for all the components of a mixture. In practice it was observed that desorption was so rapid that peaks rather than steps were observed: the peak height was a measure of the amount of material adsorbed. Partial displacement of carrier gas by sample gas may interfere with the quantitative assessment. If buoyancy effects predominate then detector response is calculable from a knowledge of molecular weights. The peak height at any instant will represent the weight change due to the difference in density between the carrier and sample gas, and hence the peak area will be a measure of the total amount of sample passing through the detector. A combination of adsorption and buoyancy will result in an unpredictable response, but either effect on its own will enable quantitative estimations to be made. Measurements based on buoyancy require a knowledge of the qualitative nature of the sample, but adsorption measurements do not.

Experiments were designed to estimate the contribution of the two effects, by using a standard detecting element, and a cylinder of similar dimensions containing no adsorbent. Experimental conditions are given in Table XIV.

TABLE XIV

OPERATING CONDITIONS

Apparatus	Wilkens Aerograph 1520
Column	Ref.K
Column temperature	80°
Carrier gas	nitrogen
Flow rate	33 ml min^{-1}
Detector range	1 mg, 10 mg
Detector temperature	20°

Gas samples were injected via a stainless steel gas sample valve fitted with sample loops of known volume. Loops of capacities between 0.2 cm^3 and 1.2 cm^3 were used. The volumes do not include the contribution of the gas sampling valve itself, which was estimated from the results obtained (Table XVIII). For each sample size, 5 injections of each gas were made, and the mean response values calculated. The gases used, together with relevant physical data, are listed in Table XV.

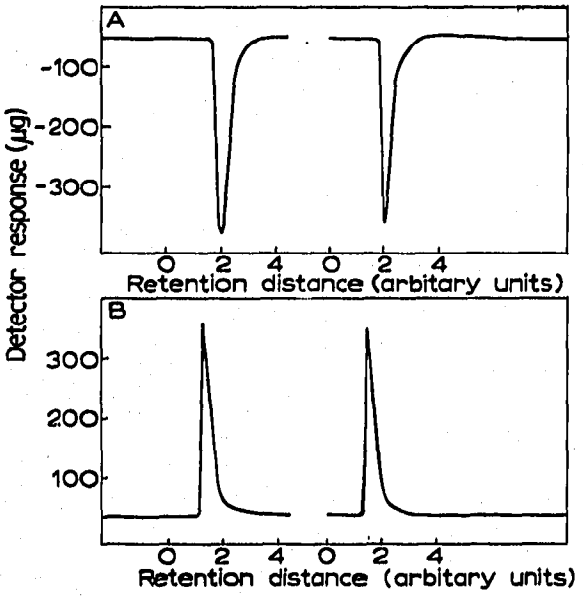
For each gas the weight injected was calculated from a knowledge of the sample loop volume, assuming ideal behaviour and injection at atmospheric pressure. This weight excludes any gas trapped in the sample valve itself which will add a constant amount to all sample injections. Care was taken to ensure that sample gases were supplied to the sample loop at the minimum pressure necessary to maintain a flow rate, to

TABLE XV

GASES ANALYSED

Gas	*b.p.* (°C)	*Molecular weight*
Hydrogen	−253	2
Methane	−162	16
Argon	−186	40
Carbon dioxide	− 79	44
Dichlorodifluoromethane	− 30	121

avoid errors due to compression. Using a detecting element containing adsorbent all samples gave peaks rather than steps (*i.e.* a differential rather than an integral response), indicating that if adsorption played any part, it was accompanied by very rapid desorption. The introduction of hydrogen into the detecting element resulted in a weight loss, indicating a predominance of buoyancy effects. The whole series of experiments was repeated using an unlined detecting element, and the same effects were observed. Examples of chromatograms are given in Fig. 6.



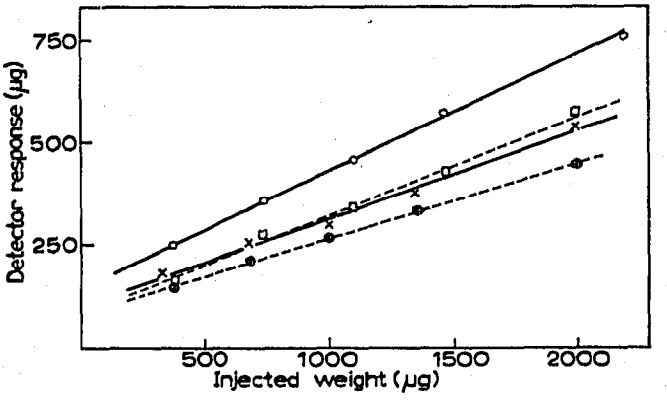


Fig. 6. Chromatograms of some permanent gases. A, hydrogen; B, argon.

Fig. 7. Response toward argon and carbon dioxide. × = argon (lined); ⊕ = argon (unlined); ○ = carbon dioxide (lined); □ = carbon dioxide (unlined).

For each series of runs, graphs were plotted of the weight of gas injected against the weight detected, obtained from the peak heights. The argon and carbon dioxide curves are shown in Fig. 7. Straight line plots were obtained both with a lined and an unlined detecting element, except for methane which gave curves, and distorted peaks for high sample sizes.

Response factors, defined as the ratio of the detected weight change and the injected weight are given in Table XVI.

TABLE XVI

RESPONSE FACTORS FOR GASES

Gas	*Mean response factor*	
	Lined detector	*Unlined detector*
Hydrogen	−4.5	−3.5
Methane	(−0.22)	(−0.15)
Argon	2.19	1.68
Carbon dioxide	2.87	2.45
Dichlorodifluoromethane	0.47	0.29

In all cases the slopes of the graphs for each material converged and gave finite responses for zero injected weight, indicating that the sample valve volume was significant. For simple adsorption, a response factor cannot exceed unity and certainly cannot be negative. Response factors, both for lined and unlined detectors were of the same order so that buoyancy must contribute predominantly to the detector response (but least for dichlorodifluoromethane). Although detector response in terms of peak

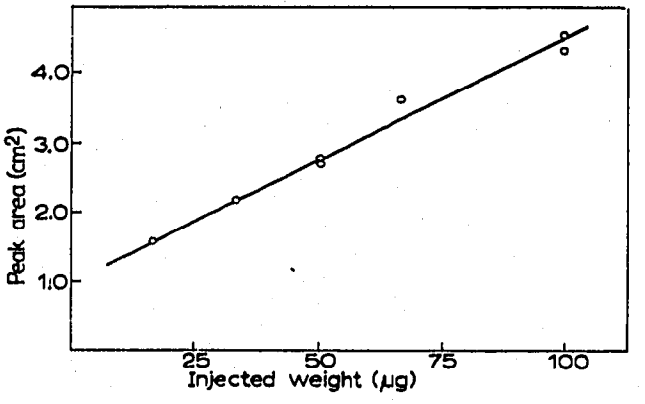
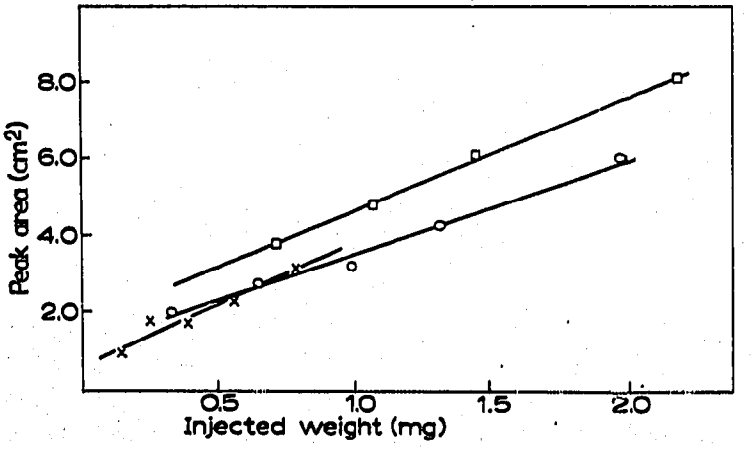


Fig. 8. Response toward hydrogen.



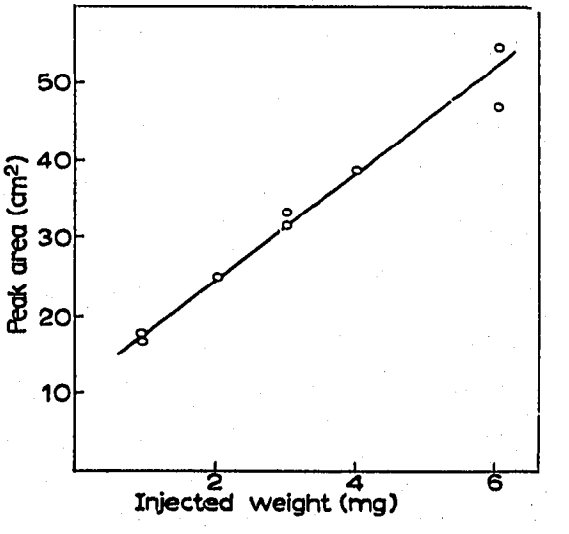


Fig. 9. Response toward methane, argon, and carbon dioxide. × = methane, ○ = argon, □ = carbon dioxide.

Fig. 10. Response toward dichlorodifluoromethane.

height cannot be predicted, the response is linear at least over the range investigated for all the gases except methane, and could therefore be used as a basis for quantitative measurement with calibration.

The response of the unlined detector, based on peak area measurements is shown in Figs. 8–10. A straight line was obtained in all cases. Scatter of points was greater than for the step height plots, but this is to be expected, in view of the inherent difficulties in measuring peak areas. The sensitivities of the detector, *i.e.* the slopes of the graphs, have been measured, and assuming a response based solely on buoyancy have been corrected for the density differences of the different gases. The results are given in Table XVII.

TABLE XVII

SENSITIVITY OF DETECTOR TOWARDS GASES

Gas	*Figure*	*Sensitivity* $cm^2\ mg^{-1}$	*Correction factor*	*Corrected response* $(cm^2\ mg^{-1})$
Hydrogen	8	−34.7	−0.077	2.67
Methane	9	− 3.15	−1.33	4.21
Argon	9	2.50	3.33	8.35
Carbon dioxide	9	3.18	2.75	8.74
Dichlorodifluoromethane	10	7.12	1.30	9.27

The corrected response values are not identical for all gases, but increase with increasing molecular weight. For those materials of molecular weight greater than the carrier gas, the values are very similar, and much greater than those for materials of lower molecular weight than the carrier gas. This is to be expected, since the detecting element was closed at the base, rather than the top, thus ensuring more efficient trapping of the heavier materials. Materials lighter than the carrier gas (and lighter than air) are not effectively trapped and therefore the detector cannot give a calculable response. An estimate of the sample valve dead volume was obtained from Figs. 8, 9 and 10. The weight of material detected at zero sample loop volume was calculated from the intercept of the curves with the ordinates and assuming ideal behaviour, the corresponding gas volumes found. The results are given in Table XVIII.

TABLE XVIII

ESTIMATE OF SAMPLE VALVE DEAD VOLUME

Gas	*Intercept* (cm^2)	*Amount of gas*	
		mg	*ml*
Hydrogen	−1.04	0.030	0.36
Methane	−0.58	1.85	0.28
Argon	0.98	0.393	0.23
Carbon dioxide	1.22	0.384	0.21
Dichlorodifluoromethane	10.4	1.46	0.29

The dead volume of the sample valve is about 0.3 ml, which is larger than the smallest sample loop used. An estimate of the sample valve volume, calculated from the dimensions of the valve, the associated tubing and unions, was 0.22 ml.

TABLE XIX

KEY TO COLUMN REFERENCES

Reference	*Stationary Phase*		*Inert Support*		*Length (m)*	*I.D. (mm)*	*Material*
	Type	%	*Type*	*BS mesh*			
A	ApL	7.5	Chromosorb G	80–100	1.1	3	S/steel
D	Porapak Q	—	—	100–120	0.56	3	S/steel
E	PEGA	20	Chromosorb G	72–85	4	4	S/steel
G	ApL	7.5	Chromosorb G	80–100	1.5	4	Copper
H	ApL	20	Chromosorb G	72–85	2	4	Copper
K	ApL	10	Chromosorb G	80–100	6	1.5	S/steel

CONCLUSIONS

The mass detector responds to all materials in the carrier gas. It responds on a weight basis to materials boiling up to at least 350°, and gives quantitative analyses without calibration. The limited number of experiments carried out on low boiling materials indicated that the mass detector can give satisfactory results. However, considerable improvement in detector chamber design is necessary for the operation of the detector significantly below ambient temperature.

The same apparatus has been used at room temperature for the analysis of gases, including the permanent gases. The response in this case is predominantly a function of molecular weight, and adsorption effects are negligible.

ACKNOWLEDGEMENT

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REFERENCE

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