

## RELATIVE DETECTOR RESPONSE IN GAS CHROMATOGRAPHY

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In recent years a considerable amount of work has been carried out using gas chromatography for quantitative analysis of mixtures of organic compounds, and, in many cases, the technique has replaced infra-red and mass spectrometric determinations. A comparison of various types of differential detectors used in gas chromatography has been made by McWILLIAM<sup>1</sup>. He discusses the suitability of the different detectors for quantitative analysis and he also discusses the desirability of there being a direct relationship between the signal output of a detector and some molecular parameter; he concludes that a detector output equal for all compounds on a weight basis would be the most convenient.

Up to the present time the differential detector which has been most used has been the thermal conductivity cell and quantitative analysis with this type of detector has been discussed by KEULEMANS *et al.*<sup>2</sup> and for the most accurate analysis it is agreed that calibration of the detector is necessary. However, calibration is not always possible as the pure components of a mixture may not be readily available. Various corrections have been applied to the recorded peak area percentages to obtain better agreement with the actual weight percentages, *e.g.* BROWNING AND WATTS<sup>3</sup> employ a correction for the thermal conductivity of the component, and EASTMAN<sup>4</sup> employs a correction involving the square root of the molecular weight of the component. These workers apply the corrections to results obtained with helium as the carrier gas. The usefulness of these corrections when nitrogen is the carrier gas has been discussed by the author<sup>5</sup>.

With helium as the carrier gas, the detector responses for a large number of compounds of different types have been reported<sup>6,7</sup>, and it was found convenient to report these responses relative to the detector response given by a comparison compound, benzene. From the results obtained it was shown that there is a direct relationship between relative detector response and molecular weight in a given homologous series and the effect of chain branching within a series was also shown.

The purpose of the present investigation was to examine the relative response of thermal conductivity detectors to compounds of various types when nitrogen was the carrier gas. As the temperature range investigated was greater than that used by MESSNER *et al.*<sup>7</sup> it was not found possible to relate all the responses to that of one comparison compound. Three comparison compounds were used; benzene for temper-

atures up to  $95^{\circ}$ , *p*-cymene at a temperature of  $160^{\circ}$ , and methyl palmitate at a temperature of  $210^{\circ}$ .

The behaviour of thermal conductivity detectors when nitrogen is the carrier gas has been discussed by BOHEMEN AND PURNELL<sup>8</sup> with particular reference to partial and complete reversal of peaks. Such reversal of peaks has been found by many workers in this field<sup>2,9-11</sup> and various explanations for their occurrence have been advanced<sup>2,9,10</sup>. BOHEMEN AND PURNELL showed that peak reversal is both temperature and flow-rate dependent. Therefore, for satisfactory quantitative analyses based on peak areas, the operating conditions must be chosen such that peak reversal does not occur.

As more data on relative detector response becomes available and if the conditions of measuring the relative response become standardised, then relative response would be an important adjunct to retention volume for the identification of an unknown compound by the gas chromatographic method.

## EXPERIMENTAL

### *Apparatus*

Gas-liquid partition chromatography was carried out using a Griffin and George Mk IIA apparatus equipped with thermal conductivity detectors. Nitrogen was used as the carrier gas at a flow rate of approximately 33 ml/min.

The bridge current was 100 mA except for the determinations of the methyl esters of long-chain aliphatic acids when the bridge current was increased to 130 mA.

The liquid phases used were di-iso-octyl sebacate and silicone E301 supported on Celite 545 (60-80 mesh) and 6 ft. glass columns were used. For the determinations of the methyl esters of long-chain aliphatic acids, Apiezon L supported on Celite 545 (60-80 mesh) was used and good separations were obtained using a 3 ft. glass column.

### *Materials*

Liquids were dried using standard methods and finally purified by fractional distillation. Solids were recrystallised to constant melting point. Small amounts of the following compounds were purified by preparative scale gas chromatography:  $\alpha$ -pinene,  $\beta$ -pinene, camphene, limonene and myrcene.

### *Procedure*

Each compound to be investigated was mixed with a known amount of the comparison compound and the resulting blends were run a minimum of three times. A minimum of two blends was prepared for each compound. The volume of sample injected into the chromatographic column was not known accurately but was between 0.01 and 0.02 ml.

The areas under the peaks were found by multiplying the height of the peak by the width at half peak height. The comparison compound was arbitrarily assigned a signal response of 100 units per mole and the response of the other compounds were calculated relative to the comparison compound.



series being approximately 20 units per  $\text{CH}_2$  group. Also, for isomeric compounds, there is a decrease in relative response with increase in chain branching, and this decrease is more marked with alcohols than with either the alkyl acetates or methyl ketones.

The relationship between relative response and the square root of the molecular weight shown by EASTMAN<sup>4</sup> cannot be generally applied when nitrogen is the carrier

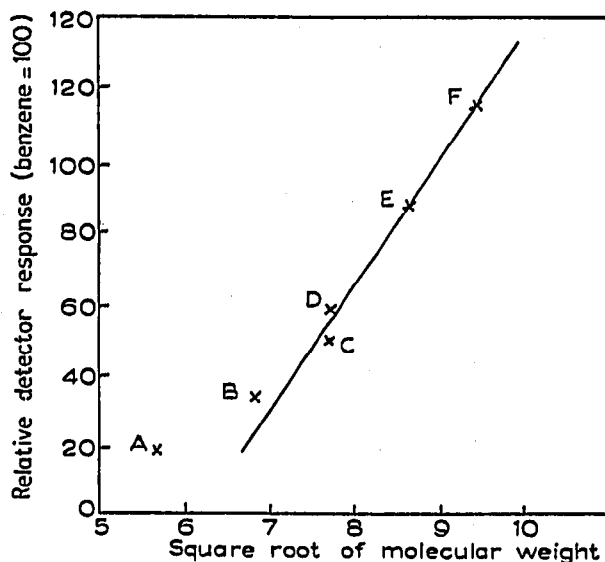


Fig. 1. Relation between relative detector response to aliphatic alcohols and square root of molecular weight. A: methanol; B: ethanol; C: allyl alcohol; D: propan-1-ol; E: butan-1-ol; F: pentan-1-ol.

gas. The graph of relative response *vs.* square root of molecular weight is shown in Fig. 1 for aliphatic straight-chain alcohols and even in this series the first members do not fall on the straight line.

An examination of the response data relative to *p*-cymene shows that compounds of similar type have similar responses and this data has been used for a semi-quantitative analysis of essential oils when the pure components were not available for calibration purposes.

The relative responses of the methyl esters of the long-chain aliphatic acids increase regularly with molecular weight. It has been reported previously<sup>12, 13</sup> that

TABLE II

QUANTITATIVE DATA ON METHYL ESTERS OF LONG-CHAIN ALIPHATIC ACIDS  
Column: 3 ft. Apiezon L on Celite; Temperature: 210°; Flow rate: 33 ml/min, nitrogen

Ester	Weight %	Area %
Methyl decoate	30.6	30.4
Methyl laurate	10.7	10.5
Methyl myristate	25.1	25.5
Methyl palmitate	33.6	33.6
Methyl stearate	—	24.1
Methyl arachidate	—	32.9

these compounds can be analysed quantitatively without calibrating the detector and this is confirmed in the present work (Table II).

#### *Relative response and flow rate*

BOHEMEN AND PURNELL<sup>8</sup> have discussed the flow-rate dependence of the temperature at which peak inversion occurs when nitrogen is the carrier gas and so it would be wrong to assume that relative response to a particular substance is independent of flow rate of nitrogen. It may be, however, that the relative response to a particular compound does not change appreciably when the flow rate of carrier gas is varied between comparatively narrow limits. The results shown in Table III indicate that there is little change in the relative response to *tert.*-butyl acetate when the flow rate of nitrogen is varied by a factor of 2.5.

TABLE III  
RELATIVE RESPONSE TO *tert.*-BUTYL ACETATE AT DIFFERENT FLOW RATES

Flow rate ml/min, nitrogen	Response per mole relative to benzene = 100
17	140
23	142
35	139
42	139

#### *Relative response and temperature*

MESSNER *et al.*<sup>7</sup> report that, when helium is the carrier gas, relative response values are independent of temperature over a range from 30° to 160°. Using nitrogen as the carrier gas it is unlikely that such a temperature independence would be found since it has been found<sup>8</sup> that the phenomenon of peak inversion is temperature dependent.

TABLE IV  
RELATIVE RESPONSE AT DIFFERENT DETECTOR TEMPERATURES

Temperature °C	Response per mole relative to benzene = 100	
	Cyclopentanone	Cyclohexanone
81	109	114
98	108	105
116	106	99
130	105	92
Response per mole relative to <i>p</i> -cymene = 100 <i>n</i> -Butyl acetate		
105	86	
120	87	
138	86	
152	86	

In the present work no indication of peak inversion was observed with any of the compounds used at the operation temperatures of the detector. Even under these circumstances, however, a variation in relative response with detector temperature was observed with cyclopentanone and cyclohexanone but not with *n*-butyl acetate (Table IV).

### Reproducibility

It is necessary to examine the relative responses given by similar detectors since MESSNER *et al.*<sup>7</sup> conclude that their data should be applicable to all gas chromatographs using thermal conductivity detectors and helium as the carrier gas. A comparison of

TABLE V

COMPARISON OF RELATIVE RESPONSE TO DIFFERENT DETECTORS WITH HELIUM AS THE CARRIER GAS

Compound	Response per mole relative to benzene = 100		
	Detector		
	1*	2**	3***
Benzene	100	100	100
Toluene	116	116	—
<i>o</i> -Xylene	130	130	—
<i>p</i> -Xylene	131	133	—
<i>n</i> -Heptane	143	135	—
<i>n</i> -Octane	160	156	—
Cyclopentane	97	91	—
Cyclohexane	114	116	—
Methylcyclopentane	115	105	—
Methylcyclohexane	120	120	—
Water	21	—	21
Butan-1-ol	95	—	95
<i>n</i> -Butyl acetate	135	—	127
Di- <i>n</i> -butyl ether	160	—	155

\* Results of MESSNER *et al.*<sup>7</sup>\*\* Results of NUNEZ *et al.*<sup>14</sup> recalculated on a mole basis.\*\*\* Results of HASKIN *et al.*<sup>15</sup> recalculated on a mole basis.

TABLE VI

COMPARISON OF RELATIVE RESPONSE TO DIFFERENT DETECTORS WITH NITROGEN AS THE CARRIER GAS

Compound	Response per mole relative to benzene = 100		
	Detector		
	1*	2*	3**
Benzene	100	100	100
Toluene	120	121	120
Chloroform	179	—	182
Carbon tetrachloride	253	—	255
Acetone	65	65	—
Ethanol	34	35	—
Propan-1-ol	57	56	—
Propan-2-ol	49	49	—

\* Present work.

\*\* Results of GRANT<sup>10</sup> recalculated on a mole basis.

their results and those of other investigators using similar instruments is shown in Table V. The results shown in Table VI indicate that ~~there is an agreement between~~ the detectors used in the present investigation and a similar detector. However there is, as yet, not enough published work on relative responses to show to what extent the reproducibility exists.

#### CONCLUSION

A correlation is shown to exist between relative detector response and molecular weight for a given homologous series. With nitrogen as the carrier gas it is important that the detector temperature and the flow rate of nitrogen should be chosen such that no peak inversion takes place. Further investigation is required on a wider range of compounds and also on the relative detector response using various types of thermal conductivity detector. As this data becomes available then relative detector response could be used in conjunction with retention volume data for identification purposes.

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#### SUMMARY

The response of thermal conductivity detectors in gas chromatography to compounds of different types is shown relative to comparison compounds and the effect of detector temperature and carrier gas flow rate is discussed. Results are compared when helium and when nitrogen is the carrier gas.

#### REFERENCES

- <sup>1</sup> I. G. MCWILLIAM, *J. Appl. Chem. (London)*, 9 (1959) 379.
- <sup>2</sup> A. I. M. KEULEMANS, A. KWANTES AND G. W. A. RIJNDERS, *Anal. Chim. Acta*, 16 (1957) 29.
- <sup>3</sup> L. C. BROWNING AND J. O. WATTS, *Anal. Chem.*, 29 (1957) 24.
- <sup>4</sup> R. H. EASTMAN, *J. Am. Chem. Soc.*, 79 (1957) 4243.
- <sup>5</sup> G. R. JAMIESON, *Analyst*, 84 (1959) 74.
- <sup>6</sup> D. M. ROSIE AND R. L. GROB, *Anal. Chem.*, 29 (1957) 1263.
- <sup>7</sup> A. E. MESSNER, D. M. ROSIE AND P. A. ARGABRIGHT, *Anal. Chem.*, 31 (1959) 230.
- <sup>8</sup> J. BOHEMEN AND J. H. PURNELL, *J. Appl. Chem. (London)*, 8 (1958) 433.
- <sup>9</sup> J. G. KEPPLER, G. DIJKSTRA AND J. A. SCHOLS, *Vapour Phase Chromatography*, Butterworths, London, 1957, p. 222.
- <sup>10</sup> D. HARVEY AND D. O. MORGAN, *Vapour Phase Chromatography*, Butterworths, London, 1957, p. 74.
- <sup>11</sup> J. BOHEMEN AND J. H. PURNELL, *Chem. & Ind. (London)*, (1957) 815.
- <sup>12</sup> G. DIJKSTRA, J. G. KEPPLER AND J. A. SCHOLS, *Rec. trav. chim.*, 74 (1955) 805.
- <sup>13</sup> E. R. ADLARD AND B. T. WHITHAM, *Gas Chromatography*, (Preprint), Butterworths, London, 1958, p. 177.
- <sup>14</sup> L. J. NUNEZ, W. H. ARMSTRONG AND H. W. COGSWELL, *Anal. Chem.*, 29 (1957) 1164.
- <sup>15</sup> J. F. HASKIN, G. W. WARREN, L. J. PRIESTLY AND V. A. YARBOROUGH, *Anal. Chem.*, 30 (1958) 217.
- <sup>16</sup> D. W. GRANT, *Gas Chromatography*, (Preprint), Butterworths, London, 1958, p. 25.