Relative detector response in gas chromatography
II. Benzene hydrocarbons, phenols and phenol ethers

In a previous communication[1] it was shown that, in a homologous series there is a relationship between relative detector response and molecular weight. The object of the present work was to investigate the relative detector response to isomeric benzene derivatives to find if the relative detector responses altered

(a) with the relative positions of substituents attached to the benzene ring, and

(b) when the substituent was attached to the benzene ring or when it was attached to a side chain.

MESSNER *et al.*[2], using helium as the carrier gas, found that ethylbenzene, *o*-, *m*- and *p*-xylene had similar responses. GRANT[3], using nitrogen as the carrier gas, found that *o*-xylene had a lower response than either *m*- or *p*-xylene which had similar responses.

Experimental. Gas–liquid partition chromatography was carried out using the apparatus and liquid phases described previously[1]. Nitrogen was used as the carrier gas at a flow-rate of approximately 33 ml/min, and the bridge current was 100 mA.

It was convenient to use two comparison compounds, benzene for a column temperature of 95°, and *p*-cymene for column temperatures between 125° and 145°.

TABLE I

RELATIVE DETECTOR RESPONSE TO BENZENE HYDROCARBONS AND HALOGEN DERIVATIVES

Compound	*Mol. wt.*	*Response per mole relative to benzene (= 100)*
Benzene	78	100
Toluene	92	121
Ethylbenzene	106	144
o-Xylene		128
m-Xylene		143
p-Xylene		145
n-Propylbenzene	120	162
Isopropylbenzene		147
1,3,5-Trimethylbenzene		165
1,2,4-Trimethylbenzene		155
n-Butylbenzene	134	193
sec.-Butylbenzene		183
tert.-Butylbenzene		174
p-Cymene		180
1,2,4,5-Tetramethylbenzene		181
1,2,3,5-Tetramethylbenzene		180
		Response per mole relative to p-cymene (= 100)
Chlorobenzene	112.6	85
o-Chlorotoluene	126.6	95
m-Chlorotoluene		106
p-Chlorotoluene		106
Benzyl chloride		105
Bromobenzene	157	108
o-Bromobenzene	171	113
m-Bromobenzene		126
p-Bromobenzene		128

Under these conditions no reversal of peaks was observed for any of the compounds studied.

Results and discussion. The relative detector responses to a number of monocyclic aromatic hydrocarbons and halogen derivatives are shown in Table I, and the relative detector responses to a number of phenols and phenol ethers are shown in Table II.

TABLE II

RELATIVE DETECTOR RESPONSE TO PHENOLS AND PHENOL ETHERS

Compound	*Mol. wt.*	*Response per mole relative to p-cymene (= 100)*
Phenol	94	48
o-Cresol	108	59
m-Cresol		65
p-Cresol		64
Benzyl alcohol		68
2-Ethylphenol	122	76
4-Ethylphenol		84
2,3-Dimethylphenol		77
2,4-Dimethylphenol		82
2,5-Dimethylphenol		80
2,6-Dimethylphenol		76
3,4-Dimethylphenol		81
3,5-Dimethylphenol		86
3-Methyl-5-ethylphenol	136	104
2,3,5-Trimethylphenol		93
2,4,5-Trimethylphenol		92
2,4,6-Trimethylphenol		93
o-Chlorophenol	128.6	83
m-Chlorophenol		93
p-Chlorophenol		93
4-Chloro-2-methylphenol	142.6	100
4-Chloro-3-methylphenol		101
Anisole	108	66
Phenetole	122	85
o-Cresyl methyl ether		74
m-Cresyl methyl ether		83
p-Cresyl methyl ether		82
o-Cresyl ethyl ether	136	90
m-Cresyl ethyl ether		102
p-Cresyl ethyl ether		103
o-Chloroanisole	142.6	101
m-Chloroanisole		113
p-Chloroanisole		113

An examination of these results shows that, within a homologous series, there is an increase in relative detector response with an increase in molecular weight. Also, for isomeric compounds, there is a decrease in relative detector response with an increase in chain branching, *e.g.* for the butylbenzenes, the relative detector responses decrease in the order normal, secondary, tertiary.

In all the types of compounds studied it is found that the *ortho*-isomer has a lower relative detector response than either the *meta*- or *para*-isomer, these last two having similar relative detector responses. It is also found that, *ortho*-effects being absent, a

compound with a group forming part of a side-chain has a similar relative detector response to the isomeric compound which has the group attached to the benzene ring, *e.g.* *n*-propylbenzene has a relative detector response similar to 1,3,5-trimethylbenzene, but 1,2,4-trimethylbenzene, which has a pair of *ortho*-methyl groups, has a lower relative detector response; also, phenol ethers have similar relative detector responses to the isomeric phenols.

The introduction of a hydroxyl or an alkoxyl group into a benzene ring lowers the relative detector response, since phenols and phenol ethers have much lower relative detector responses than would be expected from benzene hydrocarbons of similar molecular weights.

The introduction of a chlorine atom into the ring of a phenol or a phenol ether has little effect on the relative detector response since the chlorophenols and chlorophenol ethers have relative detector responses similar to those expected from the phenols or phenol ethers with similar molecular weights. Chlorobenzene has a relative detector response similar to that expected from a benzene hydrocarbon of similar molecular weight; *m*- and *p*-chlorotoluenes have relative detector responses slightly higher than the expected values.

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An apparatus for elution from paper chromatograms

There is a long-standing need for an easily-constructed and easily-operated apparatus for eluting substances from paper strips with small volumes of solvents, particularly for those solvents which are so volatile that the whole eluting system must be enclosed. Serial equilibration of the whole or dissected paper with aliquots of the solvent in small vessels does not always meet the need, for the resulting solution is dilute and bulky and must often be reduced in volume before the eluted substances can be further treated. Also, for large pieces of paper it is difficult to get complete contact between paper and solvent in a small vessel. The following simple apparatus is offered for eluting with small volumes of the most volatile solvents from large pieces of paper.

Fig. 1 shows the unmounted assembly. A glass tube of suitable length and diameter