important when the results are at variance with each other, as well as when attempts to use formamide-containing systems are unsuccessful.

The complete data will be published in Russian.

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Relative response of the flame ionization detector*

The relative response of the flame ionization detector for different organic substances has been the subject of considerable discussion[1–8]. For hydrocarbons, it is generally accepted that the responses per unit weight of the individual compounds (above about C_5) differ only slightly from each other[9–11] and that the relative molar responses seem to be directly proportional to the carbon number of the molecule[2–4]. However, it was demonstrated recently[13] that this rule is valid only in the first approximation; actually, the isomers with the same carbon number have different relative molar responses, but the relative molar responses of homologous series (*e.g.* normal paraffins, substituted cyclopentanes or substituted benzenes) follow a linear relationship with the carbon number.

* Based on papers presented at the Eastern Analytical Symposium, New York, N.Y., Nov. 15, 1961, and the combined Southwest-Southeast Regional Meeting of the American Chemical Society, New Orleans, La., Dec. 8, 1961.

It is also known that the relative molar response of organic substances containing other elements besides carbon and hydrogen in the molecule differs from that of the corresponding normal paraffin with the same carbon number[2,3]. However, only relatively few response data have been reported for such substituted organic compounds and even where such data are given, few conclusions have been offered

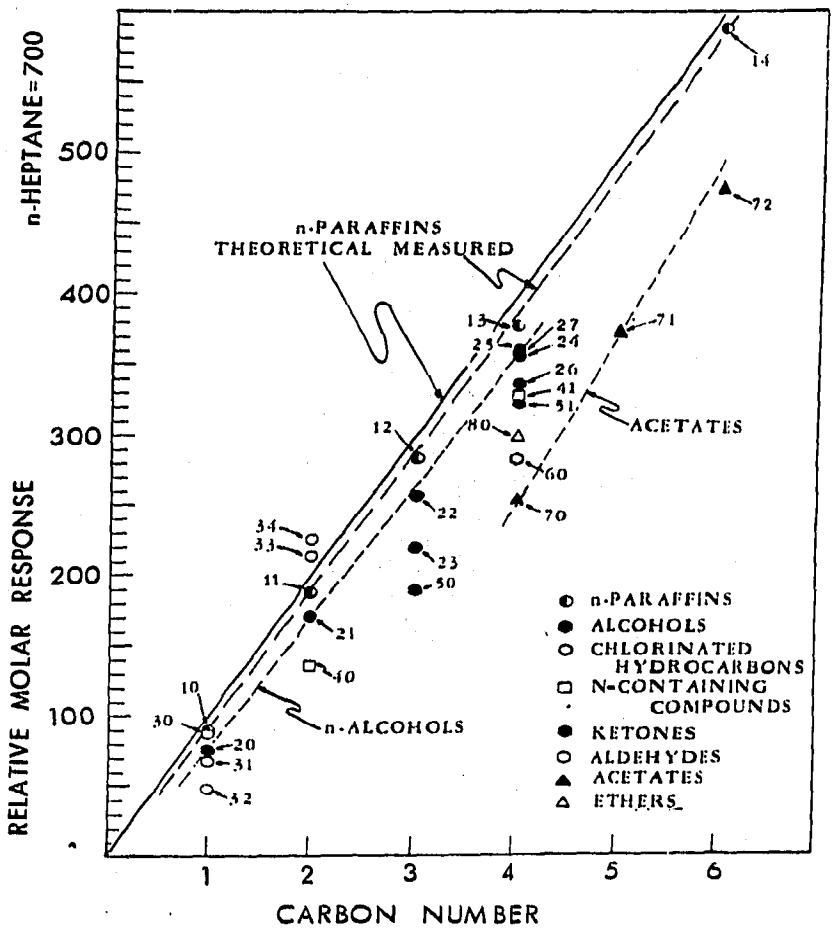

Fig. 1.

regarding their relationship within the homologous series. The purpose of this short communication is to suggest the possibility of such conclusions. For this purpose, literature data will be used but presented in a different form.

Fig. 1 plots the relative molar responses of some substituted organic compounds together with those of the normal paraffins. The respective numerical values are given in Table I; they are based on the data given by STERNBERG, *et al.*[7] except if otherwise given. The values are given uniformly relative to the response of one mole *n*-heptane which is taken equal to 700; if the reference substance originally was not *n*-heptane, the relative molar response given in the source was adjusted proportionally.

The plot of Fig. 1 shows that the relative molar response of homologous series (*e.g.* the normal primary alcohols and acetates) follows a linear relationship as indicated by the dotted lines; this is similar to the rule already demonstrated for hydrocarbons. Another interesting correlation can be found in investigating the relative

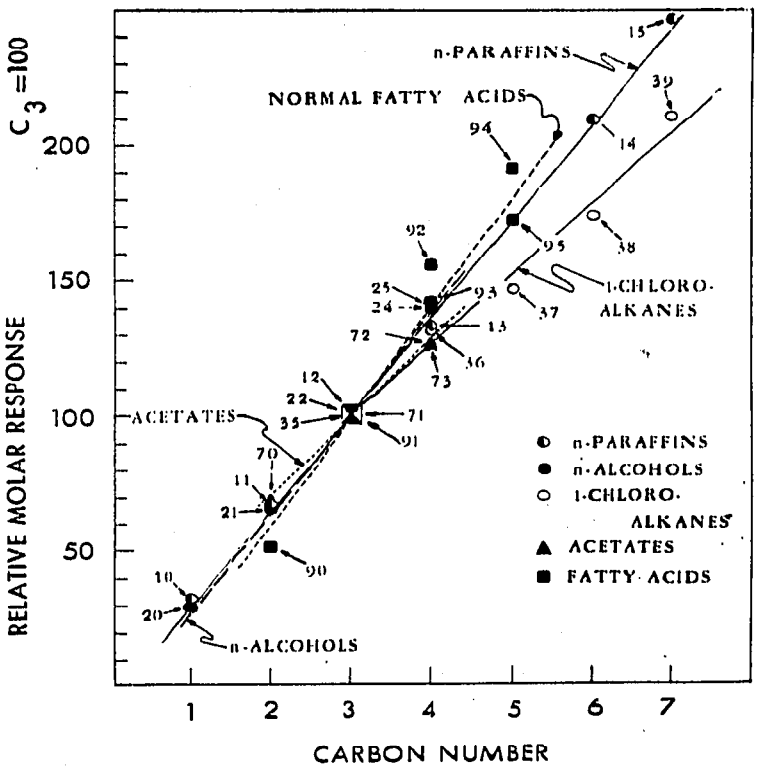
RELATIVE MOLAR RESPONSE
C_3=100
200
150
100
50
1
2
3
4
5
6
7
CARBON NUMBER
n-PARAFFINS
NORMAL FATTY ACIDS
1-CHLORO-ALKANES
ACETATES
n-ALCOHOLS
n-PARAFFINS
n-ALCOHOLS
1-CHLORO-ALKANES
ACETATES
FATTY ACIDS

Fig. 2.

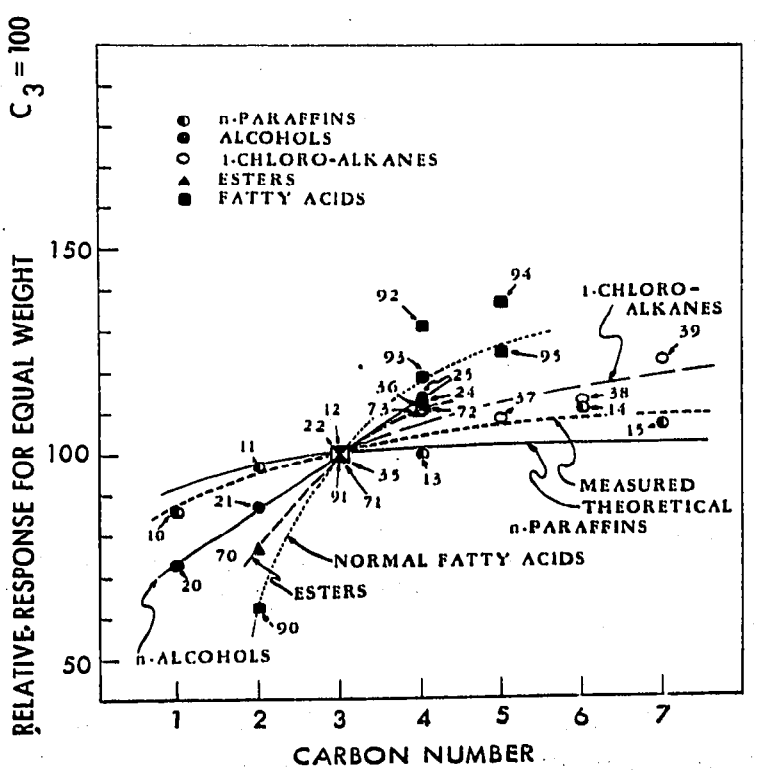
RELATIVE RESPONSE FOR EQUAL WEIGHT
C_3 = 100
150
100
50
1
2
3
4
5
6
7
CARBON NUMBER
n-PARAFFINS
ALCOHOLS
1-CHLORO-ALKANES
ESTERS
FATTY ACIDS
1-CHLORO-ALKANES
MEASURED
THEORETICAL
n-PARAFFINS
NORMAL FATTY ACIDS
ESTERS
n-ALCOHOLS

Fig. 3.

molar responses of the C_3–C_4 alcohols. The comparison of the two primary and secondary alcohol pairs (Nos. 22 and 23; 24 and 27) shows that the response of the secondary alcohol is lower in both cases; on the other hand, among the two primary butyl alcohols (Nos. 24 and 25), the normal has the lower response.

TABLE I

Number[a]	*Substance*	*Carbon number*	*Relative molar response*[b]
10	Methane	1	90[c]
20	Methanol	1	75
30	Dichloromethane	1	87
31	Chloroform	1	68
32	Carbon tetrachloride	1	48
11	Ethane	2	189[c]
21	Ethanol	2	170
33	Trichloroethylene	2	213
34	Tetrachloroethylene	2	225
40	Acetonitrile	2	135
12	Propane	3	284[c]
22	Propanol-1	3	256
23	Propanol-2	3	219
50	Acetone	3	189
13	*n*-Butane	4	378[c]
24	Butanol-1	4	356
25	2-Methylpropanol-1	4	359
26	Butanol-2	4	336
27	2-Methylpropanol-2	4	357
41	*n*-Butylamine	4	328
51	Butanone-2	4	322
60	Isobutyraldehyde	4	283
70	Ethyl acetate	4	253
80	Diethyl ether	4	300
71	*n*-Propyl acetate	5	375
14	*n*-Hexane	6	596[c]
72	Isobutyl acetate	6	476

[a] The first number of the two-digit-numbers refers to the type of the compound: *10 etc*; normal paraffins; *20 etc.*: alcohols; *30 etc.*: chlorinated hydrocarbons; *40 etc.*: nitrogen-containing compounds; *50 etc.*: ketones; *60 etc.*: aldehydes; *70 etc.*: acetates; *80 etc.*: ethers.

[b] Relative to *n*-heptane (= 700).

[c] From ref.[4].

Only in a limited number of cases are response values available relative to the normal paraffins; in most cases, they are given relative to one member of the same homologous series. For example, in the case of Fig. 2 (Table II), the relative molar

response of the three-carbon atom containing member of each homologous series is always taken as 100; the values for the other substances were adjusted accordingly. When investigating the values of fatty acids, one finds that the relative molar responses of the isomers with side groups are higher than the responses of the respective

TABLE II

Number[a]	Substance	Carbon number	Relative[b] response for equal mole	Relative[b] response for equal weight	Reference
10	Methane	1	32	86	4
11	Ethane	2	67	97	4
12	Propane	3	100	100	4
13	*n*-Butane	4	133	100	4
14	*n*-Hexane	6	210	111	4
15	*n*-Heptane	7	247	107	4
20	Methanol	1	29	73	7
21	Ethanol	2	66	87	7
22	Propanol-1	3	100	100	7
24	Butanol-1	4	139	113	7
25	2-Methylpropanol-1	4	140	114	7
35	1-Chloropropane	3	100	100	12, 14
36	1-Chlorobutane	4	131	111	12, 14
37	1-Chloropentane	5	147	108	12, 14
38	1-Chlorohexane	6	174	113	12, 14
39	1-Chloroheptane	7	211	123	12, 14
70	Ethyl acetate	2[c]	67	77	7, 12, 14
71	*n*-Propyl acetate	3[c]	100	100	7, 12, 14
72	Isobutyl acetate	4[c]	127	112	7
73	*n*-Butyl acetate	4[c]	126	111	12, 14
90	Acetic acid	2	51	62	15
91	Propionic acid	3	100	100	15
92	Isobutyric acid	4	156	131	15
93	*n*-Butyric acid	4	142	119	15
94	Isovaleric acid	5	190	137	15
95	*n*-Valeric acid	5	172	125	15

[a] The first number of the two-digit-numbers refers to the type of compound: *10 etc.*: *n*-paraffins; *20 etc.*: alcohols; *30 etc.*: chlorinated hydrocarbons; *70 etc.*: acetates; *90 etc.*: fatty acids.
[b] Relative to the three-carbon atom containing member of the individual homologous series (= 100).
[c] Carbon number of the alcohol.

straight chain fatty acids (Nos. 92 and 93, 94 and 95); the same is true for the acetates (Nos. 72 and 73). This observation—together with that mentioned previously—seems to prove a general rule already mentioned in connection with the paraffins[13]; among

isomers with the same general structure (*i.e.* with the same functional group), that substance has a higher molar response, the molecule of which consists of side groups connected to a shorter main chain.

Another interesting observation is related to the slope of the plots of the relative molar response values against carbon atoms for the different homologous series: it seems that each plot has a different slope. This observation is contradictory to the data given by ROUAYHEB *et al.*[8]; Figs. 1 and 2, however, seem to prove its validity.

The investigation of the relative responses for equal weight shows again a trend previously described for hydrocarbons. When taking the response of the three-carbon atom containing member of each homologous series as 100 and plotting the responses for equal weight against the carbon number (Fig. 3, Table II), one can see that each plot has a tendency to level off, which is the result of a diminished effect of the functional group relative to the long alkyl groups. The plot of *n*-alcohols up to C_4 still gives a straight line; a leveling-off can, however, be expected at higher carbon numbers.

The practical meaning of this trend is that about above C_6–C_7, the response for unit weight may be taken in good approximation as equal or in other words, for a mixture of substances with a carbon number above C_6–C_7, the area percent can be taken in good approximation as the concentration by weight regardless of the structure of the individual sample components.

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