CHROM. 3999

THE GAS CHROMATOGRAPHY OF ALKYL IODIDES*

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(Received November 28th, 1968)

SUMMARY

Gas chromatographic separation and identification of several alkyl iodides has been accomplished using glass columns filled with tricresyl phosphate on DMCS treated Chromosorb W.

Detection by an electron capture detector (E.C.D.) permitted quantitative determination of about 10^{-12} grams of iodides in the presence of a large excess of hydrocarbons.

Absolute and relative retention times, retention indices and sensitivities to E.C.D. were determined.

The retention indices relative to n-alkanes and those relative to 1-iodoalkanes were calculated and correlated.

The homologous series of 1-iodoalkanes may be suitable as a reference for the calculation of retention indices of E.C.D. sensitive substances.

INTRODUCTION

In the course of research involving the radiolysis of hydrocarbons, the separation and analysis of minute amounts of branched chain alkyl iodides in the presence of a large excess of hydrocarbons was necessary.

Due to the extremely low concentration of the halogen containing compounds, the use of a specific and sensitive detector such as the electron capture detector (E.C.D.) was necessary. Unfortunately, lack of published retention, identification, and quantitative response data, made it necessary to carry out a systematic study to obtain the information necessary for the identification and quantitation of the detected substances.

After LOVELOCK's[1-3] early work where the responses for selected halogenated substances relative to chlorobenzene are reported, much work has been done on applying E.C.D. to analysis of halogenated organic compounds, such as pesticides, but few data are available on the separation and response values of the alkyl halides.

ADLOFF AND GUEGUENIAT[4], EGGLETON AND ATKINS[5] and HIPPE AND KRZYZA-NOWSKA[6] have separated some alkyl iodides, ranging from methyl iodide to butyl

iodides, by gas chromatography. BOETTNER AND DALLOS[7] and CLEMONS AND ALT-SHULLER[8] determined the response of the E.C.D. to various halogenated compounds, containing one to six carbon atoms and one to three fluorine, chlorine, bromine or iodine atoms. SMITH AND WEST[9] used gas chromatography to detect several organic iodides derived by the interaction between fission product iodine and organic solvents, tentatively identified three of them as iodoethane, 1-iodobutane and 2-iodobutane, and reported data on their relative sensitivity. DEVAUX AND GUIOCHON[10] determined the response factors of several chlorinated compounds relative to chlorobenzene, and examined the variation of such factors with various parameters, but few iodine compounds were examined.

Other authors have focussed their attention to the gas chromatographic separation of alkyl halides, but only data on isopropyl iodide[11] and 1-iodobutane[12,13] have been reported. Thus from the literature reported, it can be seen that little work has been done on the alkyl iodides. This may also be due to the relatively low stability of such compounds.

EXPERIMENTAL

Two Varian Aerograph Gas chromatographs were used: a Model 600-C and Hy-Fi III Mod. 1210-2, with isothermal proportional temperature control. Both instruments were equipped with Aerograph electron capture detectors, of the concentric type, containing 250 mC of titanium tritide. During our analysis a polarizing voltage of 90 V, d.c., was applied.

Ultrapure nitrogen was used as the carrier gas, and a molecular sieve trap was installed in the carrier gas line to remove moisture. A flow of 22 ml/min was used.

Some analyses were also made using a flame ionization detector (F.I.D.), which was simply placed on the base of the E.C.D., without disconnecting the column or changing the carrier gas flow. This technique allowed the analysis due to the two detectors to be comparable.

To avoid decomposition of the samples, glass columns were used. Two lengths of tubing were selected in order to allow: (a) a good separation of the light products on a 3 m column, or (b) a fast analysis of compounds up to eight carbon atoms on a 1.2 m column.

The pyrex glass tubing had an outside diameter of 1/8 in. and an inner bore of about 1.5 mm, and was coiled as a helix. The stationary phase was 15 % tricresyl phosphate on DMCS treated Chromosorb W 80–110 mesh. An on-column injection technique was used. The amount of injected sample was about 1 μl of a dilute solution of the various compounds (from 0.01 to 1 p.p.m.) in purified n-hexane.

The compounds examined are listed in Table I. As can be seen from the reported data, several products had to be synthesized in our laboratory, as they were not commercially available. The latter were prepared according to the methods reported in the literature quoted, with some minor modifications.

RESULTS

Separation

The columns described gave a satisfactory separation of all the products. Column

TABLE I

PHYSICAL CONSTANTS OF ANALYZED COMPOUNDS

Unless otherwise specified boiling points are at 760 torr, index of refraction and density at 20°C.

No.	Alkyl iodides	Boiling point (°C)	Index of refraction	Density (g/ml)	Source	
1	Iodomethane	42.3	1.5293	2.28	Fluka	(14)
2	Iodoethane	72	1.5133	1.93	Fluka	(14)
3	1-Iodopropane	102.5	1.5125 (15°)	1.74	Fluka	(14)
4	2-Iodopropane	102–103	1.5026	1.70	Fluka	(14)
5	1-Iodobutane	128–131	1.497	1.60	BDH	(14)
6	1-Iodopentane	154–155	1.4961	1.51	BDH	(14)
7	1-Iodohexane	63–65	1.493	1.44	Fluka	(14)
8	1-Iodoheptane	97 (26 torr)	1.4897	1.37	Fluka	(14)
9	1-Iodooctane	108 (18 torr)	1.4889	1.33 (15°)	Fluka	(14)
10	1-Iodononane	112.5 (12 torr)	1.49 (12°)	1.29 (12°)	Fluka	(15)
11	1-Iododecane	132 (15 torr)	1.4858	1.26	Fluka	(15)
12	1-Iodo-2-methylpropane	120	1.496	1.61	BDH	(16)
13	2-Iodo-2-methylpropane	40 (120 torr)	1.4918	1.55	BDH	(17)
14	2-Iodo-2-methylbutane	124.3–125.5	1.50	1.49	BDH	(18)
15	1-Iodo-3,3-dimethylbutane	162	1.4315	1.34	prepd.[a]	(19)
16	2-Iodo-2,3-dimethylbutane	145	1.4895	1.39	prepd.	(20)
17	2-Iodo-3,3-dimethylbutane	145	1.4973	1.42	prepd.	(20)
18	2-Iodo-2,4-dimethylpentane	140–142	1.4690	1.08	prepd.	(21)
19	1-Iodo-2,2,4-trimethylpentane		1.4770	1.22	prepd.[b]	(14)
20	Diiodomethane	72.5 (16 torr)		3.06	prepd.	(22)
21	1,2-Diiodoethane	melts 81–82°C		2.13	Fluka	(23)
22	1,3-Diiodopropane	79	1.64	2.58	Fluka	(14)
23	3-Iodopropene	100–101	1.5387	1.83	prepd.	(24)
24	5-Iodohexene-1	167		1.50	prepd.	(25)

[a] C_6H_{13} — % iodine: calculated 59.9, found 59.7.
[b] C_8H_{17} — % iodine: calculated 52.9, found 52.8.

efficiency was good and the medium HETP (height equivalent to a theoretical plate) ranged between 0.4 and 0.5 mm depending on the temperature and the compound.

An example of a separation is illustrated in Fig. 1; analysis conditions and peak identification are given.

Table II summarizes the results of runs at 60°, 100° and 120°C, expressed as adjusted retention times t_a (min) which are obtained by subtracting the hold-up time
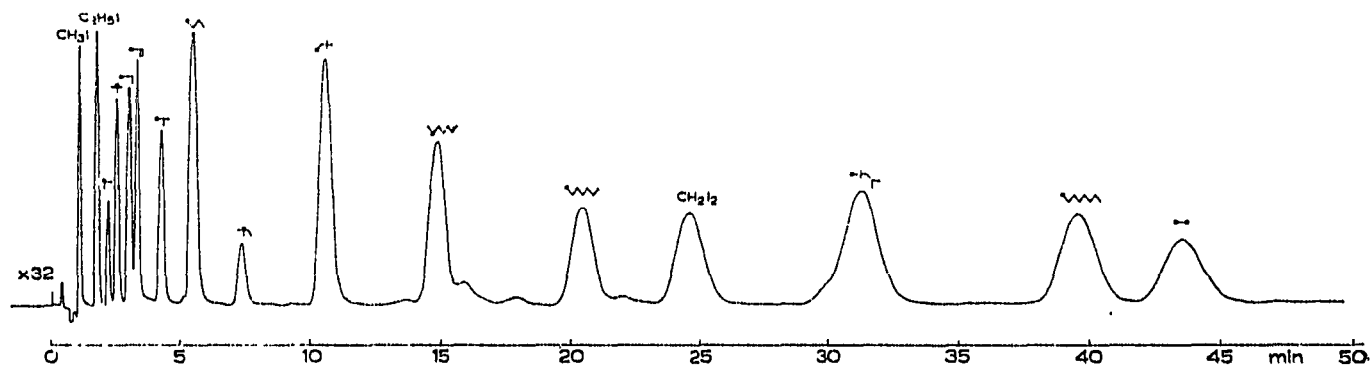

Fig. 1. Gas chromatographic separation of alkyl iodides. Column 3 m × 1/8 in. (glass) of 15% tricresyl phosphate on Chromosorb W 80–110 DMCS. Carrier N_2 22 ml/min. Temp. 100°C. E.C. detector.

TABLE II

ADJUSTED RETENTION TIME t_a (min) OF ALKYL IODIDES ON TRICRESYL PHOSPHATE COLUMNS
Carrier flow 25 ml/min.

No.	Column length (m)	1,2			3		
	Temperature (°C)	60	100	120	60	100	120
1	Iodomethane	0.77	0.38	0.23	1.15	0.64	0.56
2	Iodoethane	1.74	0.71	0.39	2.04	1.32	1.02
3	1-Iodopropane	3.67	1.33	0.76	5.82	2.64	1.81
4	2-Iodopropane	2.36	1.00	0.59		1.84	
5	1-Iodobutane	7.95	2.52	1.42	14.64	5.16	3.31
6	1-Iodopentane	18.35	4.84	2.65	34.63	10.32	5.98
7	1-Iodohexane	41.25	9.54	4.90	78.23	20.32	10.79
8	1-Iodoheptane	89.88	18.43	8.96	170.12	39.76	19.29
9	1-Iodooctane	204.00	35.57	16.23		79.81	34.40
10	1-Iodononane		68.32	29.27		155.00	60.87
11	1-Iododecane		134.90	53.01			106.92
12	1-Iodo-2-methylpropane	5.89	2.12	1.10		3.96	
13	2-Iodo-2-methylpropane	2.87	1.09	0.64		2.16	
14	2-Iodo-2-methylbutane	8.27	2.73	1.88		7.04	
15	1-Iodo-3,3-dimethylbutane	18.07	5.20	2.74		10.02	
16	2-Iodo-2,3-dimethylbutane	18.40	5.88	2.88		10.36	
17	2-Iodo-3,3-dimethylbutane	18.15	5.64	2.80		10.15	
18	2-Iodo-2,4-dimethylpentane	41.60	9.60	5.31		20.96	
19	1-Iodo-2,2,4-trimethylpentane	65.30	15.75	7.49		31.36	
20	Diiodomethane	47.00	12.23	6.04		24.52	
21	1,2-Diiodoethane	91.25	21.95	10.14		43.84	
22	1,3-Diiodopropane	126.40	44.83	26.40		80.10	
23	3-Iodopropene	4.00	1.47	0.89		2.96	
24	5-Iodohexene-1	23.60	6.56	3.66		14.68	

t_a (or the time the carrier gas needs to pass through the column) from the total time that a given substance needs to pass through the column (t_r)[26].

From reported data, it can be seen that branched chain or 2-iodo compounds have a lower retention time than the 1-iodo, and the 1-iodoalkenes have a higher rentention time than the corresponding saturated compound.

In Fig. 2 this behavior is demonstrated for a 1.2 m column at 100°C, and linearity may be observed. With a different column length and/or different temperature conditions, similar behavior was observed.

Identification

The data reported in Table II may be used for qualitative identification of the compounds, but, as is well known, absolute retention values greatly depend on the analysis parameters and therefore cannot be universally applied.

A better way to identify any given substance X is to use its relative retention value, or its retention $r = t_{aX}/t_{aS}$ where t_{aS} is the adjusted retention time of a substance S taken as standard, when adjusted retention times are used.

In our calculations we have used 1-iodopropane as standard reference substance, and the retentions relative to it are reported in Table III.

These values are less affected by operating conditions but, as some compounds have very close retention times, the observed fluctuations are too large to allow unambiguous identification. The use of retention indices I, first proposed by KOVATS[27]
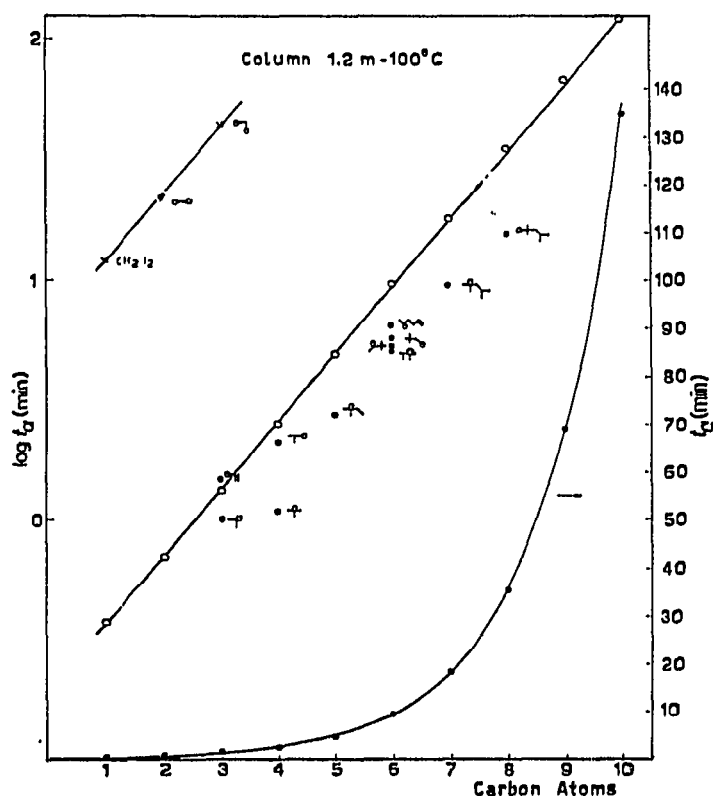
Fig. 2. Adjusted retention times t_a of 1-iodoalkanes (values on the right). Log t_a of: 1-iodo-alkanes (white circles); branched iodoalkanes (black dots with symbols); diiodoalkanes (x) (values on the left).

seems to be the best way to solve the problem, but a difficulty arises due to the very low sensitivity of the E.C.D. to the n-paraffins.

For this reason, the E.C.D. had to be replaced by a F.I.D., without varying the column conditions, and the chromatograms resulting from injection of paraffins from n-pentane to n-hexadecane, plus a reference amount of 1-iodopropane, correlated with those obtained by the injection of alkyl iodides.

The resulting retention indices I are reported in Table IV, and their independence of experimental conditions, especially column length and carrier gas flow rate, seems to be quite satisfactory (cf. values at 100° C on two columns).

However, the detector change may be difficult or impossible with some types of instruments, and injections of very large amounts of n-paraffins, in order to obtain a signal from the E.C.D., must be avoided for the following reasons:

(1) Large amounts of high boiling hydrocarbons will contaminate the tritium detector, as it cannot be operated at a temperature above 220°C;

(2) Large amounts of injected sample will saturate the column, resulting in peak broadening and uncertainty in retention time measurements.

From the qualitative point of view, the "dual channel" technique, i.e. splitting the flow at the end of the column and analysis on the E.C.D. and F.I.D. mounted in parallel, will solve this problem, but fluctuations in the splitting ratio will affect the accuracy.

TABLE III

RETENTION r RELATIVE TO 1-IODOPROPANE

No.	Column length (m)	1,2			3		
	Temperature (°C)	60	100	120	60	100	120
1	Iodomethane	0.21	0.28	0.30	0.20	0.24	0.31
2	Iodoethane	0.47	0.53	0.51	0.35	0.50	0.56
3	1-Iodopropane	1.00	1.00	1.00	1.00	1.00	1.00
4	2-Iodopropane	0.64	0.75	0.78		0.70	
5	1-Iodobutane	2.16	1.89	1.87	2.52	1.95	1.83
6	1-Iodopentane	4.99	3.64	3.48	5.95	3.91	3.30
7	1-Iodohexane	11.22	7.17	6.45	13.44	7.70	5.96
8	1-Iodoheptane	24.45	13.86	11.79	29.23	15.06	10.66
9	1-Iodooctane	55.49	26.71	21.36		30.23	19.01
10	1-Iodononane		51.37	38.52		58.71	33.63
11	1-Iododecane		101.43	69.76			59.07
12	1-Iodo-2-methylpropane	1.60	1.59	1.45		1.50	
13	2-Iodo-2-methylpropane	0.78	0.82	0.84		0.82	
14	2-Iodo-2-methylbutane	2.25	2.05	2.47		2.67	
15	1-Iodo-3,3-dimethylbutane	4.91	3.91	3.60		3.79	
16	2-Iodo-2,3-dimethylbutane	5.00	4.42	3.79		3.92	
17	2-Iodo-3,3-dimethylbutane	4.94	4.24	3.68		3.84	
18	2-Iodo-2,4-dimethylpentane	11.31	7.22	6.99		7.94	
19	1-Iodo-2,2,4-trimethylpentane	17.76	11.84	9.86		11.88	
20	Diiodomethane	12.78	9.19	7.95		9.29	
21	1,2-Diiodoethane	24.82	16.50	13.34		16.61	
22	1,3-Diiodopropane	34.38	33.70	34.74		30.34	
23	3-Iodopropene	1.09	1.10	1.17		1.12	
24	5-Iodohexene-1	6.42	4.93	4.82		5.56	

TABLE IV

RETENTION INDICES I (RELATIVE TO n-ALKANES) ON TRICRESYLPHOSPHATE COLUMNS
Flow 25 ml/min.

No.	Column length (m)	1,2			3
	Temperature (°C)	60	100	120	100
1	Iodomethane	675	676	676	677
2	Iodoethane	781	782	761	784
3	1-Iodopropane	868	872	871	877
4	2-Iodopropane	811	836	832	840
5	1-Iodobutane	985	984	982	989
6	1-Iodopentane	1068	1082	1089	1084
7	1-Iodohexane	1168	1185	1193	1186
8	1-Iodoheptane	1264	1286	1295	1286
9	1-Iodooctane	1366	1388	1395	1390
10	1-Iodononane		1501	1494	1498
11	1-Iododecane			1593	
12	1-Iodo-2-methylpropane	928	947	933	948
13	2-Iodo-2-methylpropane	837	855	844	857
14	2-Iodo-2-methylbutane	969	996	1031	996
15	1-Iodo-3,3-dimethylbutane		1106		
16	2-Iodo-2,3-dimethylbutane	1068	1094	1104	1094
17	2-Iodo-3,3-dimethylbutane	1066	1098	1099	1094
18	2-Iodo-2,4-dimethylpentane	1168	1186	1266	1188
19	1-Iodo-2,2,4-trimethylpentane	1255	1262	1276	1260
20	Diiodomethane	1184	1222	1229	1224
21	1,2-Diiodoethane	1266	1313	1316	1310
22	1,3-Diiodopropane		1427	1477	1420
23	3-Iodopropene	879	900	895	905
24	5-Iodohexene-1	1098	1128	1144	1136
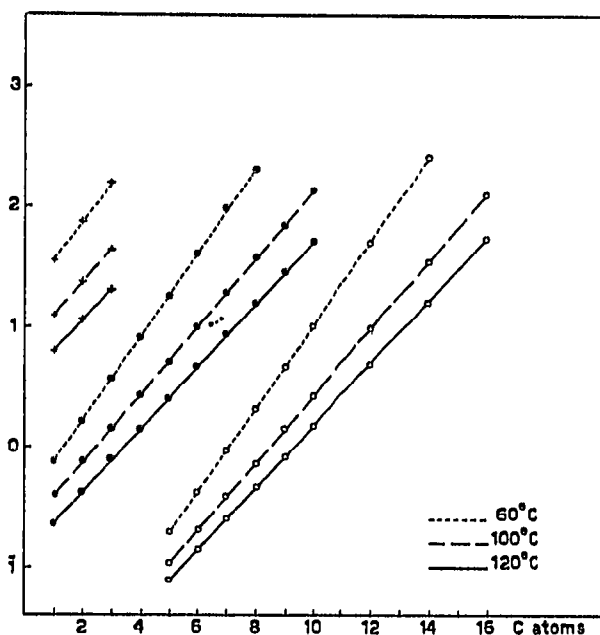
Fig. 3. Log t_a of diiodoalkanes ($+$), 1-iodoalkanes ($\bullet$), and n-paraffins ($\bigcirc$) on a 1.2 m column at various temperatures.
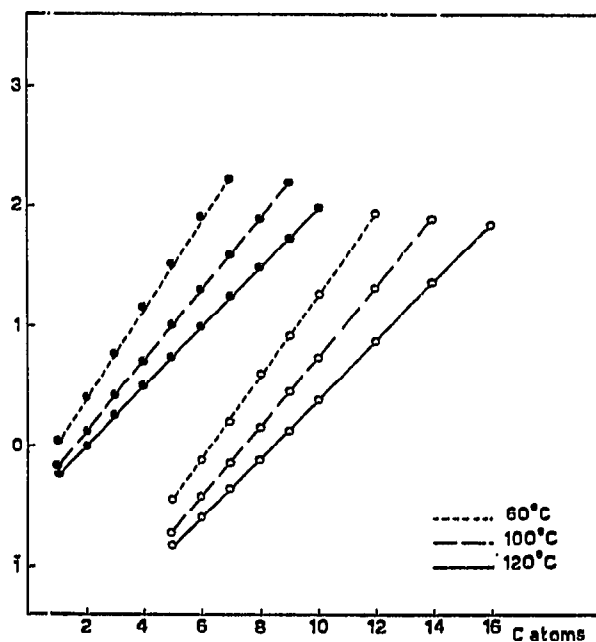
Fig. 4. Log t_a of 1-iodoalkanes ($\bullet$) and n-paraffins ($\bigcirc$) on a 3 m column at various temperatures.

An examination of data reported in Table II and in Fig. 2 may lead to a satisfactory solution of these problems at least for the stationary phases used. It can be seen that 1-iodoalkanes behave regularly and similarly to the n-paraffins. In Figs. 3 and 4, the logarithms of the adjusted retention times of the iodoalkanes (t_a) and the n-paraffins (t_{aP}) are plotted against the number of carbon atoms, for different column lengths and temperatures. The plots are linear and the values obtained, at the same temperature, for the three kinds of compounds lie on parallel lines. From the parallel behavior of the plots, it can be assumed that the values of log (t_a/t_{aP}) for the iodoalkanes and paraffins having the same number of carbon atoms depends only on the column temperature. With the above limitations, an empirical relationship can be derived, by plotting log (t_a/t_{aP}) against the reciprocal of absolute temperature (Fig. 5).
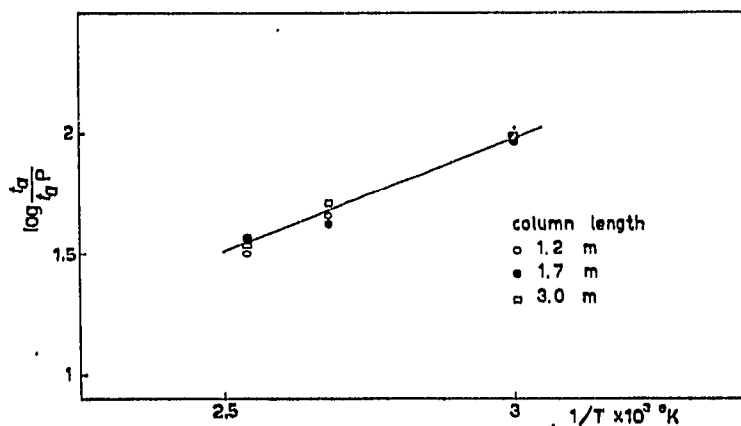

Fig. 5. The logarithm of adjusted retention time of 1-iodoalkanes (t_a) divided by that of n-paraffins (t_{aP}) is a linear function of the reciprocal of absolute temperature, independent of column length.

The mean values at 60, 100 and 120°C (respectively 1.967; 1.677 and 1.549) are strictly linear, following the relation:

$$\log \frac{t_a}{t_{aP}} = \frac{\alpha}{T} - \beta$$

where $\alpha = 909$ and $\beta = 0.760$.

This regular behavior of the 1-iodoalkanes with respect to the n-paraffins allows us to use the series of n-iodoalkanes as a reference for the identification of unknown compounds sensitive to E.C.D.

The inherent difficulties of the use of n-paraffins as standards are thus overcome, as the E.C.D. responds very well to minute amounts of iodoalkane, and retention indices relative to 1-iodoalkanes can therefore be determined.

The retention indices relative to 1-iodoalkanes (I_{nt}) are reported in Table V;

TABLE V

RETENTION INDICES RELATIVE TO 1-IODOALKANES (I_{nt}) ON TRICRESYLPHOSPHATE COLUMNS

Column length (m)	1.2			3
Temperature (°C)	60	100	120	100
Iodomethane	100	100	100	100
Iodoethane	200	200	200	200
...	...	...	...	...
1-Iododecane	1000	1000	1000	1000
2-Iodopropane	241	255	262	245
1-Iodo-2-methylpropane	375	373	359	360
2-Iodo-2-methylpropane	267	268	274	271
2-Iodo-2-methylbutane	405	412	444	445
1-Iodo-3,3-dimethylbutane	498	510	506	496
2-Iodo-2,3-dimethylbutane	501	507	514	501
3-Iodo-2,2-dimethylbutane	499	522	509	498
2-Iodo-2,4-dimethylpentane	601	601	613	604
1-Iodo-2,2,4-trimethylpentane	659	679	670	665
Diiodomethane	621	638	629	628
1,2-Diiodoethane	703	726	749	721
1,3-Diiodopropane		833	834	835
3-Iodopropene	308	321	325	317
5-Iodohexene-1	526	545	552	552

these values have fluctuations of the same order of those given in Table IV and can therefore be used with the same reliability as a means of identification.

Retention index $vs.$ temperature plots (Fig. 6) similar to those suggested by ETTRE AND BILLEB[28] may be used as a further aid in identification, as they permit the interpolation to any desired temperature.

Quantitative response

In order to determine the quantitative response to E.C.D., injections of known amounts of dilute solutions of alkyl iodides were made, and the peak areas were plotted against the moles of pure compound injected*.

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* Due to electrometer characteristics, with a Leeds and Northrup W strip chart recorder (1 mV full scale, scale width 21 cm, chart speed 30 in./h) every mm² of area corresponds to $8.17 \cdot 10^{-12}$ A sec.
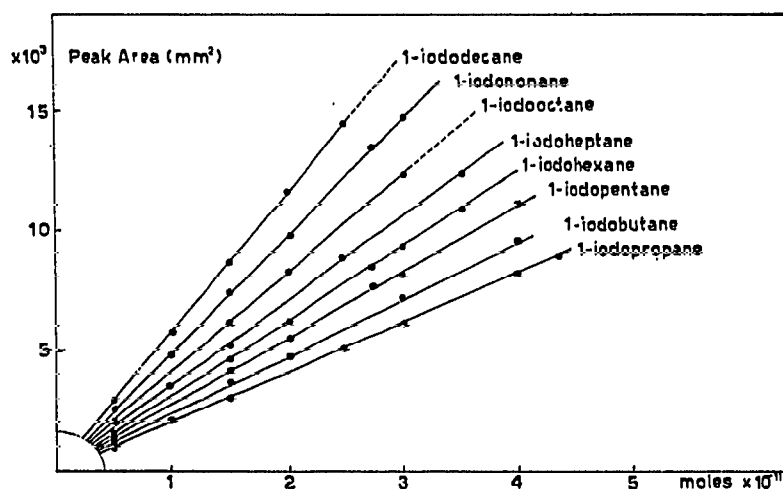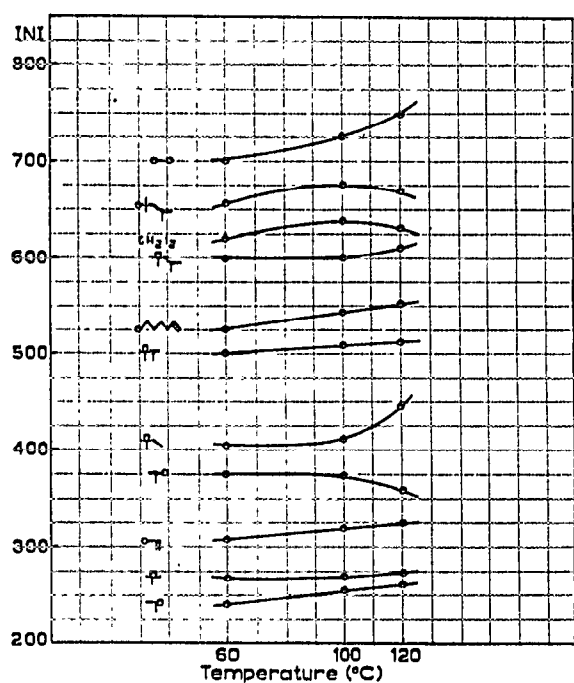
Fig. 6. Retention indices relative to 1-iodoalkanes I_{nt} (see text) as a function of column temperature for various compounds.

Fig. 7. Response of 1-iodoalkanes. E.C. detector, 90 V applied potential, 22 ml/min N_2 as carrier gas.
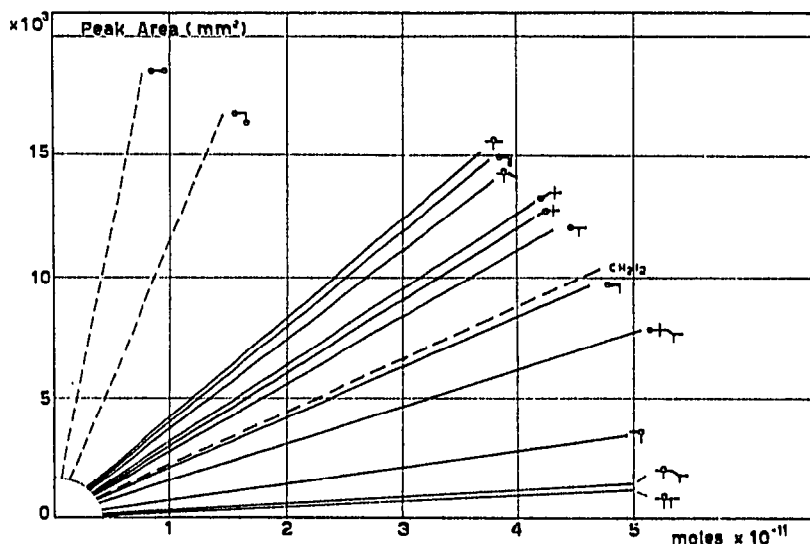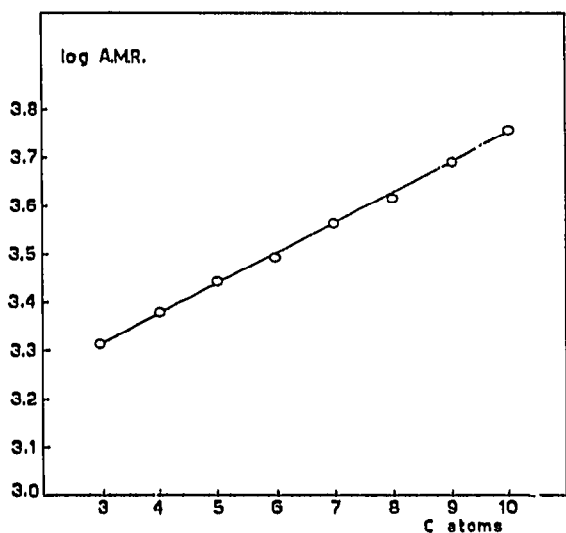

Fig. 8. The logarithm of a absolute molar response (AMR) for 1-iodoalkanes is a linear function of the number of carbon atoms in the chain.

Fig. 9. Response for various alkyl iodides. E.C. detector, 90 V applied potential, 22 ml/min N_2 as carrier gas.

The molar responses (MR) of 1-iodoalkanes from 3 to 10 carbon atoms are plotted in Fig. 7. In the range considered, the plots are strictly linear, and the absolute molar responses (AMR) can be calculated by dividing the area by the number of moles. In Fig. 8, log (AMR) is plotted against the number of carbon atoms, and the linearity shows that the AMR depends logarithmically on the chain length.

The plots for the MR of the other alkyl iodides examined are shown in Fig. 9. No valuable correlation can be made between the AMR values of these compounds.

The AMR and the RMR (molar response relative to 1-iodopropane) are reported for all the compounds analyzed in Table VI.

TABLE VI

ABSOLUTE MOLAR RESPONSE (AMR) AND MOLAR RESPONSE RELATIVE TO 1-IODOPROPANE (RMR)

Compound	AMR $mm^2/moles \cdot 10^{-12}$	RMR
1-Iodopropane	207	1.00
2-Iodopropane	68	0.33
1-Iodobutane	238	1.15
1-Iodopentane	275	1.33
1-Iodohexane	314	1.52
1-Iodoheptane	352	1.70
1-Iodooctane	409	1.98
1-Iodononane	486	2.35
1-Iododecane	574	2.78
1-Iodo-2-methylpropane	275	1.33
2-Iodo-2-methylpropane	407	1.97
2-Iodo-2-methylbutane	324	1.57
1-Iodo-3,3-dimethylbutane	306	1.48
2-Iodo-2,3-dimethylbutane	23	0.11
2-Iodo-3,3-dimethylbutane	312	1.51
2-Iodo-2,4-dimethylpentane	25	0.12
1-Iodo-2,2,4-trimethylpentane	153	0.74
Diiodomethane	215	1.04
1,2-Diiodoethane	2330	11.30
1,3-Diiodopropane	1110	5.40
3-Iodopropene	389	1.88

The behavior of the data shows that the sensitivity of the E.C.D. to various compounds greatly depends on molecular structure, as was well established by ZIELINSKY et al.[20]. Furthermore, some analytical parameters (especially carrier gas flow and detector temperature) also affect the quantitative response[10,30].

In addition, Fig. 10 shows that the response has a linear interval which differs from one compound to another. For some compounds (e.g. diiodoethane or 1-iodo-2-propene) this may be due to detector saturation when the signal approaches the value of the standing current, for others (e.g. 1-iodopropane) lack of linearity may be connected with an increase of the amount of injected sample. Relatively large amounts of compound may in fact cause absorption on the solid support or partial decomposition. The latter seems to occur especially for 2-iodoalkanes (e.g. 2-iodo-2,3-dimethylbutane), which show a large scatter of the data above 5×10^{-11} moles of injected
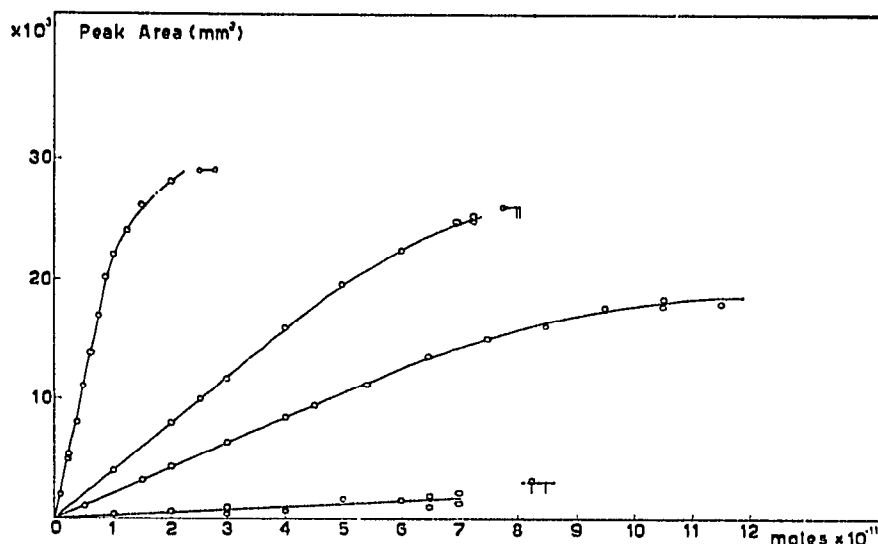
Fig. 10. Linear dynamic range for some typical compounds. Deviation from linearity due to detector saturation, absorption or partial decomposition of the injected samples.

sample. Obviously many other factors can greatly influence the linearity of the detector response and these problems are also under investigation.

The determination of response factors provides a valuable analytical tool for quantitative evaluation of results obtained under similar and well controlled conditions, but loses its reliability when the parameters are drastically changed. If changes are necessary to perform special separations, a new series of factors must be determined experimentally.

However, the use of the tabulated data can save a lot of time, and if a check of few relative response factors may be done with standard compounds, a good agreement of the experimental results with the corresponding tabulated data assures the reliability of a whole series of response values.

ACKNOWLEDGEMENT

REFERENCES

1 J. E. LOVELOCK, Nature, 189 (1961) 721.
2 J. E. LOVELOCK AND N. L. GREGORY, Gas Chromatography, Academic Press, New York, 1962, p. 219.
3 J. E. LOVELOCK, Anal. Chem., 35 (1963) 474.
4 J. P. ADLOFF AND P. GUEGUENIAT, J. Chromatog., 12 (1963) 96.
5 A.E.J. EGGLETON AND D. H. F. ATKINS, Radiochim. Acta, 3 (1967) 151.
6 Z. HIPPE AND T. KRZYZANOWSKA, Chem. Anal. (Warsaw), 11 (1966) 937.
7 E. D. BOETTNER AND F. C. J. DALLOS, J. Gas Chromatog., 3 (1965) 190.
8 G. A. CLEMONS AND A. P. ALTSHULLER, Anal. Chem., 38 (1966) 133.
9 S. R. SMITH AND D. L. WEST, Nuclear Appl., 3 (1967) 43.
10 P. DEVAUX AND G. GUIOCHON, J. Gas Chromatog., 5 (1967) 341.
11 H. R. COOPER AND J. G. ROBERTS, J. Soc. Dyers Colourists, 80 (1964) 428.
12 A. R. LEPLEY AND W. A. KHAN, J. Org. Chem., 31 (1966) 2061.
13 A. R. LEPLEY AND W. A. KHAN, J. Org. Chem., 31 (1966) 2064.

14 A. J. VOGEL, *A Textbook of Practical Organic Chemistry*, Longmans, Green, London, New York, Toronto, 1948.
15 F. KRAFFT, *Ber.*, 19 (1886) 2219.
16 A. WURTZ, *Ann. Chem.*, 93 (1855) 116.
17 D. G. COE, S. R. LANDAUER AND H. N. RYDON, *J. Chem. Soc.*, (1954) 2281.
18 A. MICHAEL AND F. ZEIDLER, *Ann. Chem.*, 385 (1911) 273.
19 H. FINKELSTEIN, *Ber.*, 43 (1909) 1528.
20 H. COHN, E. D. HUGHES, M. H. JONES AND M. G. PEELSING, *Nature*, 169 (1952) 291.
21 G. CHONIN, *Chem. Zentr.*, (1905) II, 813; (1909) II, 587.
22 R. ADAMS AND C. S. MARVEL, *Org. Syn. Coll.*, I (1932) 358.
23 A. SEMENOW, *Jahresberichte über die Fortschritte der Chemie*, (1864) 483.
24 R. B. BETSINGER AND J. G. TRAYNHAM, *J. Am. Chem. Soc.*, 70 (1948) 2818.
25 A. WURTZ, *Ann. de Chemie et de Physique*, 3 (1864) 168.
26 R. KAISER, *Gas Phase Chromatography*, Vol. III, Butterworths, London, 1963.
27 E. KOVATS, *Helv. Chim. Acta*, 41 (1958) 1915.
28 L. S. ETTRE AND K. BILLEB, *J. Chromatog.*, 30 (1967) I.
29 W. L. ZIELINSKY, Jr., L. FISHBEIN AND L. MARTIN, Jr., *J. Gas Chromatog.*, 5 (1967) 552.
30 W. E. WENTWORTH AND E. CHEN, *J. Gas Chromatog.*, 5 (1967) 170.