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CORRELATIONS BETWEEN PHYSICAL PROPERTIES OF HALOGENATED ALKANES AND THEIR GAS CHROMATOGRAPHIC BEHAVIOUR ON POLAR AND NON-POLAR STATIONARY PHASES

LINEAR CHLORO-, BROMO- AND IODOALKANES*

GIANRICO CASTELLO AND GIUSEPPINA D'AMATO

Istituto di Chimica Industriale, Università, Via Pastore 3, 16132 Genoa (Italy)

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SUMMARY

Normal alkanes and linear chloro-, bromo- and iodoalkanes with the halogen atom in the 1-, 2- and 3-positions have been analyzed on Apiezon L, tricresyl phosphate and Carbowax 20M columns at 75°, 100° and 125°C, using a flame ionization detector.

The retention times and retention indices relative to normal iodoalkanes were determined for every compound, and their relationships with the stationary phase and the analysis temperature were investigated.

The relationships between the retention data and the following physical properties were also studied: molecular weight, boiling point and molecular volume.

INTRODUCTION

In previous papers¹⁻⁴, the gas chromatographic behaviour of alkyl iodides was investigated, using a tricresyl phosphate column and an electron capture detector.

Some relationships were found between the structure of the compounds, their retention indices and their physical properties. The position of the iodine atom in the molecule and the number and the positions of methyl groups were shown to have a strong effect on the retention time. If the iodine is substituted on a carbon atom within the chain, a decrease in the retention time with respect to the 1-iodoalkane was observed. This decrease in retention index was found to be roughly proportional to the difference between the boiling points of the 1-iodoalkane and the isomeric compound.

In this work, in order to obtain better correlations of the retention time with

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TABLE I

PHYSICAL CONSTANTS OF SYNTHESIZED AND ANALYZED ALKYL CHLORIDES

Unless otherwise specified, densities and refractive indices are at 20°C.

<i>Alkyl chloride</i>	<i>T_b (°C) at 760 torr</i>	<i>Refractive index</i>	<i>Density (g/ml)</i>	<i>Molecular volume (cm³)</i>	<i>Source</i>
Chloromethane	-23.76	1.366 (-10°)	0.92	54.89	—
Chloroethane	13.1	1.3742 (10°)	0.9028 (15°)	71.44	Fluka
1-Chloropropane	46.60	1.3886	0.8923	87.97	BDH
2-Chloropropane	34.8	1.3781	0.8590	91.38	BDH
1-Chlorobutane	78.4	1.4021	0.8865	104.34	Fluka
2-Chlorobutane	68.2 ^a	1.3971	0.8732	105.93	Fluka
1-Chloropentane	108.2	1.4128	0.8828	120.64	Chemical Samples Co.
2-Chloropentane	96.5	1.4079	0.8732	121.96	Chemical Samples Co.
3-Chloropentane	98	1.4082	0.8723	122.09	Chemical Samples Co.
1-Chlorohexane	134	1.4199	0.8784	137.18	Chemical Samples Co.
2-Chlorohexane	122.5	1.4142 (22°)	0.8694	138.60	Prepared ^b
3-Chlorohexane	123	1.4163	0.870	138.50	Prepared ^b
1-Chloroheptane	159.5 ^a	—	0.881 (16°)	152.68	Chemical Samples Co.
2-Chloroheptane	146	1.4221	0.8725 (15°)	154.15	Prepared ^b
3-Chloroheptane	144.3 ^b	1.4237	0.8960 ^c	150.11	Prepared ^b
4-Chloroheptane	144	1.4237	0.8710	154.42	Prepared ^b
1-Chlorooctane	181 ^a	1.4306	0.8748	169.75	Chemical Samples Co.

^a Values extrapolated from low-pressure data^{4,5}.^b See refs. 3 and 6.^c Taken from ref. 5.

TABLE II

PHYSICAL CONSTANTS OF ANALYSED BROMIDES

<i>Alkyl bromides</i>	<i>T_b (°C) at 760 torr</i>	<i>Refractive index</i>	<i>Density (g/ml)</i>	<i>Molecular volume (cm³)</i>	<i>Source</i>
Bromomethane	3.59	1.4234 (10°)	1.732 (0°)	54.85	Fluka
Bromoethane	38.4	1.4239	1.4604	74.64	Fluka
1-Bromopropane	70.82	1.4341	1.3559	90.71	BDH
2-Bromopropane	59.41	1.4251	1.3097	93.91	BDH
1-Bromobutane	101.3	1.4398	1.2764	107.33	Fluka
2-Bromobutane	91.2	1.4366	1.2556	109.11	Fluka
1-Bromopentane	129.6	1.4444	1.2177	124.00	Fluka
2-Bromopentane	117.5	1.4413	1.2039	125.43	Fluka
3-Bromopentane	118.2	1.4443	1.2170	124.07	Fluka
1-Bromohexane	156	1.4478	1.1763	140.27	Fluka
2-Bromohexane	144	1.4432 (25°)	1.1658	141.54	Fluka
3-Bromohexane	144.6 ^a	1.4486	1.1799	139.84	Fluka
1-Bromoheptane	180	1.4505	1.1384	157.24	Fluka
2-Bromoheptane	168.3 ^a	—	1.1277	158.73	Fluka
3-Bromoheptane	169 ^a	1.4507	1.1362	157.54	Fluka
4-Bromoheptane	165.5 ^a	1.4506	1.1351	157.70	Fluka
1-Bromooctane	202.3	1.4527	1.118	172.63	Fluka

^a See footnote to Table I.

structure and physical properties, the alkyl iodides were analysed on columns of different polarity at three temperatures.

In addition, normal hydrocarbons and linear chloro- and bromoalkanes were analysed on the same columns at the same temperatures, in order to investigate the effect of the presence of different halogen atoms at various positions in the molecule.

EXPERIMENTAL

The analysed alkyl chlorides and bromides are listed in Tables I and II with their main physical constants. Some boiling points (T_b) were extrapolated from low-pressure data^{4,5}. The corresponding data for the alkyl iodides have been previously reported^{3,4}.

The products were obtained from BDH Chemicals Ltd., Poole, Great Britain, Fluka A.G., CH-9470 Buchs, Switzerland, and Chemical Samples Co., Columbus, Ohio 43221, U.S.A. Some compounds were synthesized⁶.

The analyses were carried out with a Varian Aerograph Model 1520 gas chromatograph with proportional temperature control. An all-glass arrangement was used so as to prevent the decomposition of the samples, and the injection was made directly into the column.

Three different columns, each 3 m \times 1/8 in., filled with 15% of Apiezon L, tricresyl phosphate (TCP) or Carbowax 20M on DMCS-treated Chromorb W, acid-washed, 80-100 mesh, were used. Great care was taken to ensure that the same weight of stationary phase was used in each column.

The analyses were carried out at three temperatures, 75°, 100° and 125°C, with a maximum fluctuation of $\pm 1^\circ\text{C}$ between different series of analyses at the same nominal temperature.

Pure nitrogen was used as the carrier gas, and the inlet pressure was adjusted to give a constant flow of 30 ± 1 ml/min at different temperatures and at various degrees of ageing of the columns.

While in the previous work^{1,3} an electron capture detector (ECD) was used, in this case a flame ionization detector (FID) was preferred, owing to the difference in the electron affinities of chlorides and iodides⁷ and to the necessity for detecting the hydrocarbons also, to which the ECD is almost insensitive.

Volumes of samples of about 0.1 μl , pure or dissolved in *n*-hexane, were injected. About 1 μl of methane was injected with each sample so as to indicate the gas hold-up time of the column. As previously seen⁸, the use of methane as a "retention zero marker" is not completely correct. Nevertheless, at the temperatures and flows used, the error in the calculation of the adjusted retention times (t_a), due to this cause, is less than 2% for the lightest compounds, and decreases to 0.1% for heavier members of the homologous series.

RESULTS AND DISCUSSION

Effect of column temperature

For all of the homologous series analysed, the plots of the logarithm of the adjusted retention times *versus* the number of carbon atoms in the chain are linear and parallel for each column at constant temperature (Fig. 1). With increase in the

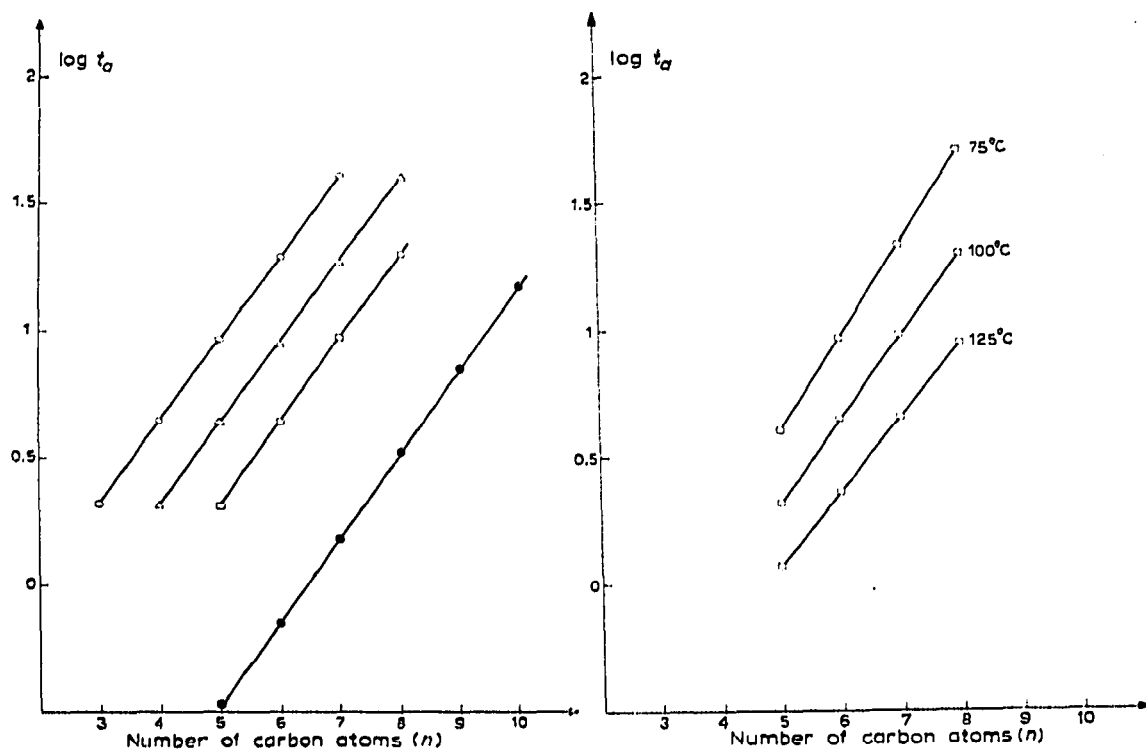


Fig. 1. Logarithms of the adjusted retention times, t_a , as functions of the number of carbon atoms, n , on 15% Apiezon L at 100°C: ○, 1-iodoalkanes; △, 1-bromoalkanes; □, 1-chloroalkanes; ●, n -alkanes.

Fig. 2. Logarithms of the adjusted retention times, t_a , as functions of the number of carbon atoms, n , on 15% Apiezon L at various temperatures for 1-chloroalkanes.

temperature of analysis, the slope decreases, as shown in Fig. 2. This behaviour was observed on all of the stationary phases tested, and it is probable that a common point of convergence of all the plots will be found at low n and t_a values⁸.

To study the effect of temperature, the specific retention volume, V_g , should be used^{9,10}. However, as only the variations of the retention values are considered, the behaviour of $d \log t_a/dn$ is very similar to that of $d \log V_g/dn$.

In Fig. 3 the $d \log t_a/dn$ values are reported as a function of the reciprocal of the absolute temperature. The higher values for Apiezon L confirm that the separation on this phase depends mainly on the molecular weight of the analysed compounds⁶ and therefore is very dependent on the chain length. For alkanes and 1-haloalkanes, the dependence is linear for the three stationary phases. For 2- and 3-haloalkanes, the plot on Carbowax 20M is still linear, while the curvature of the plots on Apiezon L and TCP shows that these liquid phases give better separations at low temperature, and therefore are more suitable for the analysis of the lower members of the homologous series.

Effect of the polarity of the stationary phase

To compare the behaviour of the three phases, it is convenient to use the

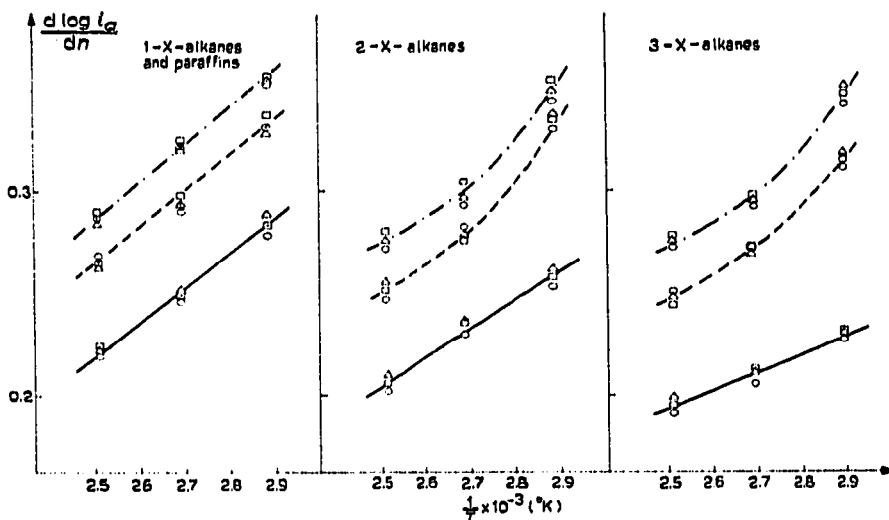


Fig. 3. Dependence of $d \log t_R/dn$ on column temperature. - · -, Apiezon L; - - -, tricresyl phosphate; —, Carbowax 20M. For symbols, see Fig. 1.

retention indices, which do not depend on small variations in the experimental conditions.

Retention indices relative to both normal alkanes, I (ref. 11), and to linear α -iodoalkanes, I_{ni} (ref. 1), were determined. These two parameters are linearly related⁴ and it is therefore possible to use each of them to identify a compound, but in the following tables and discussion, preference is given to the I_{ni} values, because the peaks of normal alkanes are asymmetric on the Carbowax column, which causes an error in the determination of their retention times and, consequently, of the I values of other compounds. The precision of the I_{ni} values is generally about 1 index unit, though in some instances a reproducibility of better than 0.2 units was observed.

The dependence of I_{ni} on the number of carbon atoms of the chain (n) is linear

TABLE III

SLOPE A_1 OF THE EQUATION $I_{ni} = A_0 + A_1n$, FOR n -ALKANES (H) AND CHLORO-, BROMO- AND IODO-ALKANES, ON DIFFERENT STATIONARY PHASES AT VARIOUS TEMPERATURES

Temp. (°C)	Position of halogen	Apiezon L				Tricresyl phosphate				Carbowax 20M			
		H	Cl	Br	I	H	Cl	Br	I	H	Cl	Br	I
75	1	100.6	100.8	101.0	100.0	99.4	103.9	101.0	100.0	104.3	106.9	108.4	100.0
	2		98.9	96.2	94.3		100.0	99.1	98.4		107.2	100.1	92.4
	3		95.5	95.0	94.4		95.6	96.5	94.9		100.8	90.7	92.0
100	1	100.2	100.9	99.7	100.0	98.6	102.3	100.9	100.0	103.2	106.0	102.8	100.0
	2		96.1	95.4	93.8		100.5	96.9	98.4		100.5	98.4	94.0
	3		95.8	93.4	95.8		97.0	96.2	93.7		98.3	98.3	96.0
125	1	100.3	100.9	101.0	100.0	97.8	100.9	101.9	100.0	101.8	103.0	106.1	100.0
	2		95.1	95.4	93.1		98.7	94.2	91.4		107.6	99.9	92.5
	3		96.1	98.1	95.3		91.0	94.4	92.9		101.7	91.2	91.8

at every temperature and for the three stationary phases. In Table III are reported the slopes, A_1 , of the equation

$$I_{nt} = A_0 + A_1 n \quad (1)$$

A_1 tends to decrease from 1- to 2- and 3-haloalkanes and to increase with increasing polarity of the stationary phases.

A_0 , which can be calculated by the least-squares method by extrapolation of the experimental data (see Table IV), may be affected by some errors because small

TABLE IV

INTERCEPT A_0 (FOR $n = 0$) OF THE EQUATION $I_{nt} = A_0 + A_1 n$, FOR AN APIEZON L COLUMN AT 125°C

Temperature (°C)	Position of halogen	Halogen		
		Cl	Br	I
125	1	-209.2	-125.0	0
	2	-218.8	-132.2	-14.9
	3	-223.9	-149.9	-25.3

variations of experimental parameters produce large differences in the extrapolated intercepts. It appears to be more convenient to calculate the I_{nt} values of the various compounds by using the following equation:

$$I_{nt}(C_n) = I_{nt}(C_6) + (n - 6) A_1 \quad (2)$$

where C_n is the substance with n carbon atoms for which the I_{nt} value is to be calculated; A_1 is the slope in eqn. 1 for the homologous series (taken from Table III); and $I_{nt}(C_6)$ is the retention index of the homologous compound with $n = 6$, experimentally measured, as reported in Table V.

In Table VI are reported the I_{nt} values of several members of some homologous series, experimentally measured and calculated by means of eqns. 1 and 2. The

TABLE V

I_{nt} OF THE SIXTH TERM OF EVERY HOMOLOGOUS SERIES $I_{nt}(C_6)$, ON DIFFERENT STATIONARY PHASES AT VARIOUS TEMPERATURES

Temp. (°C)	Position of halogen	Apiezon L				Tricresyl phosphate				Carbowax 20M			
		H	Cl	Br	I	H	Cl	Br	I	H	Cl	Br	I
75	1	159.8	407.4	499.7	600	25.1	406.5	500.1	600	-91.1	382.8	497.0	600
	2		361.8	448.0	546.3		347.0	443.8	542.0		300.7	414.1	527.5
	3		363.5	449.4	545.7		350.3	440.9	541.5		299.6	415.1	523.2
100	1	152.4	400.9	494.7	600	22.5	403.4	500.1	600	-104.6	361.1	500.4	600
	2		358.5	443.2	548.6		341.3	441.4	540.0		278.2	407.3	526.9
	3		359.4	445.6	545.5		342.5	437.8	540.5		286.9	404.2	524.0
125	1	147.2	396.1	481.0	600	20.5	398.9	494.4	600	-102.2	356.3	479.1	600
	2		352.1	440.4	543.9		338.6	435.2	540.9		275.3	405.3	527.1
	3		352.7	439.7	546.8		342.4	444.0	541.2		290.5	410.6	525.0

TABLE VI

COMPARISON BETWEEN THE I_{nt} VALUES EXPERIMENTALLY MEASURED ON APIEZON L AT 125°C CALCULATED BY EQN. 1 (FROM THE DATA OF TABLES III AND IV), AND BY EQN. 2 (FROM THE DATA OF TABLES III AND V)

Compound	I_{nt}		
	Experimental	Calc. by eqn. 1	Calc. by eqn. 2
1-Chloropentane	295.23	295.3	295.2
1-Chlorohexane	396.11	396.2	396.1
1-Chloroheptane	496.99	497.1	497.0
1-Chlorooctane	597.87	598.0	597.9
2-Bromobutane	249.52	249.4	249.6
2-Bromopentane	344.94	344.8	345.0
2-Bromohexane	440.36	440.2	440.4
2-Bromoheptane	535.78	535.6	535.8
2-Iodobutane	357.64	375.5	357.7
2-Iodopentane	450.78	450.6	450.8
2-Iodohexane	543.92	543.7	543.9
2-Iodoheptane	637.06	636.8	637.0
3-Chloropentane	256.60	256.6	256.6
3-Chlorohexane	352.70	352.7	352.7
3-Chloroheptane	448.80	448.8	448.8

agreement is satisfactory, but the better correspondence between columns 1 and 3 demonstrates that the use of eqn. 2 is convenient in terms of both speed and precision.

The higher slope for the 1-haloalkanes (Table III) shows that the effect of increasing the length of the molecule is greater when the halogen is substituted on the first carbon atom of the chain. As the difference increases with the polarity of the column, this effect is probably due to the greater interaction, with the polar stationary phase, of the linear molecule that has the halogen atom at the end of the chain, *i.e.*, in a more reactive position. This effect decreases from iodine to bromine and chlorine.

The comparison of the I_{nt} values of chloro-, bromo- and iodoalkanes on the three stationary phases shows that, by changing the halogen atom, the difference is about 100 at every temperature.

On the other hand, the difference between the I_{nt} values of the halogenated alkanes and those of the corresponding *n*-alkanes (*i.e.*, the "retarding effect" due to substitution of a hydrogen atom by a halogen atom), increases greatly with the polarity of the phases, as can be seen in Table VII.

The values reported in the two last columns of Table VII are equivalent to the ΔI values (differences between the retention indices on polar and non-polar stationary phases) of Kováts¹¹. These differences are lower for TCP, in agreement with the intermediate "polarity" attributed to this phase by Rohrschneider¹².

The retarding effect and the ΔI value may be due either to the dipole moment or to the polarizability of the molecules with various substituents, and to different interactions with stationary phases of various polarities.

The dipole moments of the chloro-, bromo- and iodoalkanes are practically the same¹³ and therefore cannot cause the observed differences. The polarizability can be deduced from the molar refraction, R , of the compound, which is, to a first approxima-

TABLE VII

DIFFERENCES BETWEEN THE I_{nt} (C_6) VALUES OF 1-HALOALKANES, 2-HALOALKANES AND 3-HALOALKANES, AND THE I_{nt} VALUE OF *n*-HEXANE ON VARIOUS STATIONARY PHASES

Difference in I_{nt} values	Temp. ($^{\circ}C$)	Apiezon L			Tricresyl phosphate			Carbowax 20M			Tricresyl phosphate - Apiezon L			Carbowax 20M - Apiezon L		
		Cl	Br	I	Cl	Br	I	Cl	Br	I	Cl	Br	I	Cl	Br	I
I_{nt} (1-halohexane) -	75	247.6	339.9	400.2	381.4	475.0	574.9	473.9	588.1	691.7	133.8	137.5	134.7	286.3	248.2	291.5
I_{nt} (<i>n</i> -hexane)	100	248.5	342.3	447.6	380.9	477.6	577.5	465.7	605.0	704.6	132.4	135.3	129.9	217.2	262.7	257.0
	125	248.9	333.8	452.8	378.4	473.9	579.5	458.5	581.3	702.2	129.5	140.1	126.7	209.6	247.5	249.4
I_{nt} (2-halohexane) -	75	202.0	288.2	386.5	321.9	418.7	516.9	391.8	505.2	618.6	119.9	130.5	130.4	189.8	217.0	232.1
I_{nt} (<i>n</i> -hexane)	100	206.1	296.8	396.2	318.9	418.9	517.5	382.2	511.9	631.5	112.8	128.1	121.3	176.1	221.1	235.3
	125	204.9	293.2	386.7	318.1	414.7	520.4	377.5	507.5	629.3	113.2	121.5	133.7	172.6	214.3	242.6
I_{nt} (3-halohexane) -	75	203.7	289.6	385.9	325.2	415.8	516.4	390.7	506.2	614.3	121.5	126.2	130.5	187.0	216.6	228.4
I_{nt} (<i>n</i> -hexane)	100	207.0	293.2	393.1	320.0	415.3	518.0	391.5	508.8	628.6	113.0	122.1	124.9	184.5	215.6	235.5
	125	205.5	292.5	399.6	321.9	423.5	520.7	392.7	512.8	627.2	116.4	141.0	121.1	187.2	220.3	227.6

tion, independent of temperature. For a very large number of compounds, R is approximately additive for the atoms and bonds present in the molecule.

The influence of the paraffinic chain is therefore the same for compounds with the same value of n , and the difference in polarizability is correlated with the different molar refractions of hydrogen ($R = 1.028$), chlorine ($R = 5.84$) bromine ($R = 8.74$), and iodine ($R = 13.95$).

The variation of ΔI due to different stationary phases, as with the retarding effect due to different substituents, should therefore depend on the polarizability of the molecules, but the observed maxima when the halogen atom is at the end of the chain cannot be explained on the basis of the very small differences in the molar refractions of linear compounds, which differ only in the position of the halogen atoms⁵.

Other reasons (physical properties, steric hindrance, cross-section of the molecule, etc.) should therefore be invoked to explain the different behaviour of the 1-, 2- and 3-haloalkanes.

Dependence of retention time on various physical properties

When a hydrogen atom is replaced by a halogen atom, all of the properties of the compound change, thus influencing the gas chromatographic behaviour. The retention time and index change, therefore, and their correlation with physical properties is sometimes linear and in other instances is more complex.

Relationship between I_{nt} and molecular weight. By changing the halogen atom, the difference in I_{nt} between the corresponding compounds with the same value of n is not completely proportional to the variation in molecular weight, M_w , also on the Apiezon L column⁹. In fact, by dividing I_{nt} by M_w , decreasing values are observed for chloro-, bromo- and iodoalkanes.

As two members of any homologous series differ by the molecular weight of a methylene group, the dependence of I_{nt} on M_w is always linear and the slopes are proportional to the values of A_1 in eqn. 1.

The relationship between n and M_w is:

$$M_w = 14.026 n + 1.008 + A_w(\text{halo}) \quad (3)$$

where

14.026 = molecular weight of a methylene group;

1.008 = atomic weight of hydrogen;

$A_w(\text{halo})$ = atomic weight of the halogen.

From eqn. 1, the dependence of I_{nt} on M_w is given by:

$$I_{nt} = B_0 + B_1 M_w = (A_0 - A_1 R) + \frac{A_1}{14.026} M_w \quad (4)$$

where

$$R = 0.072 - \frac{A_w(\text{halo})}{14.026}$$

R is equal to 2.599, 5.77 and 9.12 for chloro-, bromo- and iodoalkanes, respectively, and to 0.144 for the unsubstituted linear alkanes.

The nature of the halogen atom therefore influences both the slope and the intercept of the plots.

Relationship between I_{nt} and boiling point. The difference between the boiling points of two consecutive members of any homologous series (ΔT_b) decreases as n increases. The various series are regularly convergent and all tend to a common limit at which the addition of the $(n + 1)$ th methylene group does not increase the boiling point, because its influence on a very long chain may be neglected. At this limit the substitution of a hydrogen atom by a halogen atom also has practically no effect on the vapour pressure of the compound, and no variation can be expected by changing the position of this halogen atom.

For the lower members of the homologous series, however, the change of the halogen atom from the terminal position to within the carbon chain alters the boiling point. As can be seen from Table VIII, the δT_b values (*i.e.*, the differences between the boiling points of the 1-haloalkanes and those of the corresponding isomers) are nearly constant, while the values of δI_{nt} (I_{nt} of the 1-haloalkane minus I_{nt} of the isomer), greatly differ.

Consequently, the ratio $\delta I_{nt}/\delta T_b$ is not constant and is about equal to 5, as previously found¹¹, but differs from one series to another⁴.

TABLE VIII

RELATIONSHIP BETWEEN THE δT_b AND THE δI_{nt} VALUES OF LINEAR HALOGENATED ALKANES
Values of δI_{nt} and of $\delta I_{nt}/\delta T_b$ at 100°C.

Compound	δT_b	δI_{nt}			$\delta I_{nt}/\delta T_b$		
		Apiezon L	Tricresyl phosphate	Carbowax 20M	Apiezon L	Tricresyl phosphate	Carbowax 20M
2-Chloropentane	11.7	37.7	59.5	67.8	3.22	5.08	5.79
2-Chlorohexane	11.5	42.4	60.8	80.0	3.69	5.29	6.96
2-Chloroheptane	13.1	47.1	61.6	92.2	3.59	4.70	7.04
3-Chloropentane	10.2	34.8	55.5	56.9	3.41	5.44	4.57
3-Chlorohexane	11.0	35.8	60.9	71.3	3.25	5.53	6.48
3-Chloroheptane	15.2	54.8	66.2	85.6	3.60	4.35	5.63
4-Chloroheptane	15.5	52.0	65.7	101.5	3.35	4.24	6.55
2-Bromobutane	10.1	45.5	40.8	84.4	4.50	4.04	8.36
2-Bromopentane	12.1	53.0	49.3	88.8	4.38	4.07	7.34
2-Bromohexane	12.0	52.7	57.8	93.1	4.39	4.81	7.76
2-Bromoheptane	11.7	53.9	66.4	97.5	4.61	5.67	8.33
3-Bromopentane	11.4	45.8	48.8	91.8	4.02	4.28	8.05
3-Bromohexane	11.4	49.7	58.7	96.2	4.36	5.15	8.44
3-Bromoheptane	11.0	54.8	68.9	100.7	4.98	6.26	9.15
4-Bromoheptane	14.5	53.5	67.9	139.6	3.69	4.68	9.63
2-Iodobutane	10.0	39.0	40.5	64.2	3.90	4.05	6.42
2-Iodopentane	11.2	45.2	66.0	67.1	4.03	5.89	5.99
2-Iodohexane	11.4	51.4	60.0	69.9	4.51	5.26	6.13
2-Iodoheptane	13.8	57.7	64.0	72.8	4.18	5.42	5.27
3-Iodopentane	10.2	50.3	42.0	72.1	4.93	4.12	7.10
3-Iodohexane	10.0	54.5	59.5	76.0	5.45	5.95	7.60
3-Iodoheptane	10.6	58.7	66.5	80.0	5.54	6.27	7.55
4-Iodoheptane	13.0	60.5	81.5	84.3	4.65	6.27	6.48

On Apiezon and TCP, a nearly constant value of $\delta I_{nl}/\delta T_b$ was observed for each series, but this was not true for Carbowax.

A useful approach to the study of the dependence of retention on physical properties can be made by using the concept of "equivalent methylenes", *i.e.*, by calculating the number of methylene groups that must be added to a paraffinic chain to have the same effect on its properties as the addition of a polar group or of a halogen atom.

This calculation, for example, in the case of the boiling points, can be made by using the following equation:

$$Me(T_b) = \frac{T_b(x\text{-halo-C}_n) - T_b(P_n)}{T_b(P_{n+1}) - T_b(P_n)} = \frac{T_b(\text{halo}) - T_b(P)}{\Delta T_b(P)} \quad (5)$$

where

Me = equivalent methylenes;

T_b = boiling point at 760 torr;

x = substitution point of the halogen in the linear saturated chain with n carbon atoms;

P_n = normal alkane with n carbon atoms in the paraffinic chain.

Similar equations are used for other properties.

In Table IX are reported the values of $T_b(\text{halo}) - T_b(P)$ and the ratio $Me(T_b)$ for chloro-, bromo- and iodoalkanes with 3-8 carbon atoms.

For every series of compounds, the values of $Me(T_b)$ are nearly constant and the differences between 2- and 3-haloalkanes are very small. This correlation is useful when the boiling point of any compound is not well known, and cannot be easily measured because of decomposition, the small amount available, or the presence of impurities in the sample. The knowledge of the equivalent methylenes enables the missing value to be calculated.

TABLE IX

DIFFERENCES BETWEEN THE BOILING POINTS OF HALOGENATED COMPOUNDS, $T_b(\text{halo})$, AND OF THE CORRESPONDING LINEAR PARAFFINS $T_b(P)$, AND EQUIVALENT METHYLENES $Me(T_b)$.

Compounds	$T_b(\text{Cl}) - T_b(P)$	$T_b(\text{Br}) - T_b(P)$	$T_b(\text{I}) - T_b(P)$	$Me(T_b)$		
				Cl	Br	I
1-Halopropane	88.7	112.9	144.5	2.13	2.71	3.47
1-Halobutane	78.9	101.8	130.5	2.15	2.78	3.56
1-Halopentane	72.1	93.5	119.6	2.21	2.87	3.67
1-Halohexane	65.3	87.3	108.3	2.20	2.94	3.65
1-Haloheptane	61.1	81.6	99.6	2.24	2.99	3.65
1-Halooctane	55.3	76.6	92.4	2.19	3.04	3.66
2-Halopropane	76.9	101.5	131.5	1.85	2.44	3.16
2-Halobutane	68.3	91.7	120.5	1.87	2.50	3.29
2-Halopentane	60.4	81.4	108.4	1.85	2.50	3.32
2-Halohexane	53.8	75.3	96.9	1.81	2.53	3.26
2-Haloheptane	47.6	69.9	87.8	1.74	2.56	3.22
2-Halooctane	46.0	65.0	84.0	1.82	2.58	3.33
3-Halopentane	61.9	82.1	109.4	1.90	2.52	3.36
3-Halohexane	54.3	75.9	98.3	1.83	2.56	3.31
3-Haloheptane	45.9	70.6	89.0	1.68	2.59	3.26

TABLE X

EQUIVALENT METHYLENES FOR THE I_{nt} OF C_n , $Me(I_{nt})$, ON DIFFERENT COLUMNS AT 100°C, AND THE RATIO $Me(I_{nt})/Me(T_b)$ FOR THE SAME CONDITIONS

	Position of halogen	Apiezon L			Tricresyl phosphate			Carbowax 20M		
		Cl	Br	I	Cl	Br	I	Cl	Br	I
$Me(I_{nt})$	1	2.48	3.42	4.47	3.86	4.84	5.85	4.51	5.86	6.83
	2	2.06	2.90	3.95	3.23	4.25	5.25	3.71	4.96	6.12
	3	2.06	2.93	3.92	3.24	4.21	5.25	3.79	4.93	6.09
$Me(I_{nt})$ $\Delta Me(T_b)$	1	1.13	1.16	1.22	1.75	1.65	1.60	2.05	1.99	1.87
	2	1.14	1.15	1.21	1.78	1.68	1.61	2.05	1.96	1.88
	3	1.13	1.14	1.18	1.77	1.64	1.59	2.07	1.93	1.84

The equivalent methylenes for the $I_{nt}(C_n)$ on different columns, calculated by using the data in Tables III and V, are reported in Table X.

In the lower part of Table X, it can be seen that the ratio $Me(I_{nt})/Me(T_b)$ is constant. The same values of $Me(I_{nt})/Me(T_b)$ are found for all the other components with different n . This means that the variation of I_{nt} between different isomers with the halogen atom in the 1-, 2- or 3-position is mainly connected with the change in T_b .

As the polarity of the column increases, the ratio $Me(I_{nt})/Me(T_b)$ increases, showing clearly that I_{nt} depends on some polar effects in addition to the boiling point.

Relationship between I_{nt} and molecular volume, V_m . The study of the correlations between I_{nt} and V_m can be also made by using the "equivalent methylenes", $Me(V_m)$.

In Table XI are reported the values of the differences $V_m(\text{halo}) - V_m(\text{P})$ and their ratios $Me(V_m)$ to the increment of molecular volume between two consecutive members of the n -alkane series ($\Delta V_m(\text{P})$). These ratios tend to increase because in

TABLE XI

DIFFERENCE BETWEEN THE MOLECULAR VOLUME OF HALOGENATED COMPOUNDS, $V_m(\text{halo})$, AND OF THE CORRESPONDING LINEAR PARAFFINS $V_m(\text{P})$, AND EQUIVALENT METHYLENES $Me(V_m)$.

Compounds	$V_m(\text{Cl}) - V_m(\text{P})$	$V_m(\text{Br}) - V_m(\text{P})$	$V_m(\text{I}) - V_m(\text{P})$	$Me(V_m)$		
				Cl	Br	I
1-Halopropane	-0.21	2.53	9.51	—	0.21	0.79
1-Halobutane	4.13	7.12	14.18	0.27	0.47	0.94
1-Halopentane	5.39	8.75	15.91	0.35	0.56	1.02
1-Halohexane	6.41	9.49	16.50	0.41	0.60	1.05
1-Haloheptane	6.18	10.74	18.54	0.38	0.66	1.14
1-Halooctane	7.03	9.91	17.34	0.43	0.61	1.08
2-Halopropane	3.20	5.73	11.81	0.25	0.48	0.98
2-Halobutane	5.72	8.90	14.33	0.36	0.59	0.95
2-Halopentane	6.71	10.18	14.19	0.43	0.65	0.91
2-Halohexane	7.83	10.77	17.84	0.50	0.68	1.13
2-Haloheptane	7.65	12.23	17.35	0.47	0.75	1.07
3-Halopentane	6.84	8.82	15.05	0.44	0.57	0.97
3-Halohexane	7.73	9.07	15.48	0.49	0.58	0.98
3-Haloheptane	3.61	11.04	17.35	0.22	0.68	1.07

every homologous series the variation of molecular weight is constant, while the density changes greatly for alkanes and less for the halogenated compounds.

The $Mc(V_m)$ values for iodoalkanes increase slowly and are very close to unity. The iodine atom, independently of its position and of the chain length, therefore gives a nearly constant contribution, and is practically equivalent to a methylene group. This may be due to the fact that the atomic radius of iodine is very similar to the radius of a methyl group and therefore the steric hindrance of the molecule with n carbon atoms and one iodine atom is about the same as that of the corresponding molecule with $n + 1$ carbon atoms.

As in the case of T_b , the regular behaviour of $Mc(V_m)$ permits the calculation of the density of some compounds when experimental determination is not possible. The observation of irregularities in the behaviour of $Mc(T_b)$ or $Mc(V_m)$ showed clearly when incorrect values of T_b or density were used for calculations. By experimental measurement of the missing values or by using more recent literature values, such irregularities have disappeared.

Some uncertainty still remains for 1- and 2-halopropanes. Different values have, in fact, been reported by various workers for the densities of propane and butane at 20°. The values used for calculation, taken from refs. 14 and 13, respectively, probably give low values of $Mc(V_m)$.

The low value for 3-chloroheptane depends, in our opinion, on the high value of the density (0.8960 g/ml) taken from ref. 5, which we unfortunately could not check owing to the small amount of sample available.

If one accepts, for this compound, a value of 0.5 for $Mc(V_m)$ on the basis of the other values, a density of 0.8717 g/ml can eventually be calculated, which seems to be more similar to the densities of the isomeric compounds reported in Table I.

In previous work⁴ it was noted that by empirically multiplying the boiling point by the molecular volume, values roughly proportional to I_{nt} were obtained for linear and branched iodoalkanes, because the fluctuation in T_b tends to be balanced by an opposite variation in V_m .

A similar observation may be made for linear chloro- and bromoalkanes, but a true linear dependence of I_{nt} on $(T_b - V_m)$ cannot be found. For every series, both V_m and I_{nt} are linear functions of n , and therefore I_{nt} depends linearly on V_m .

As previously seen, the dependence of I_{nt} on T_b is expressed by a plot which is concave towards the T_b axis, as ΔT_b decreases when n increases. Consequently, the plot of I_{nt} against $(T_b - V_m)$ will show a similar curve. The deviation from linearity is small, and, especially for high-boiling compounds, interpolation or extrapolation of the plot is possible and will give the value of any required variable (I_{nt} , T_b or V_m) to a good approximation.

REFERENCES

- 1 G. CASTELLO, G. D'AMATO AND E. BIAGINI, *J. Chromatogr.*, 41 (1969) 313.
- 2 G. CASTELLO AND G. D'AMATO, *Rass. Chim.*, (Dec. 1970) 215.
- 3 G. CASTELLO AND G. D'AMATO, *J. Chromatogr.*, 54 (1971) 157.
- 4 G. CASTELLO AND G. D'AMATO, *J. Chromatogr.*, 58 (1971) 127.
- 5 H. B. HASS AND R. F. NEWTON, in R. C. WEAST (Editor), *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., Cleveland, Ohio, 51st ed., 1970, Section IV, D 139.
- 6 A. I. VOGEL, *A Textbook of Practical Organic Chemistry*, Longmans Green, London, New York and Toronto, 1948.

- 7 G. CASTELLO, *J. Chromatogr.*, **58** (1971) 117.
- 8 G. CASTELLO, *J. Chromatogr.*, **66** (1972) 213.
- 9 D. AMBROSE, A. I. M. KEULEMANS AND J. H. PURNELL, *Anal. Chem.*, **30** (1958) 1582.
- 10 J. H. PURNELL, *Gas Chromatography*, John Wiley, New York and London, 1962, Ch. 10.
- 11 E. KOVÁTS, *Helv. Chim. Acta*, **41** (1958) 1915.
- 12 L. ROHRSCHEIDER, *J. Chromatogr.*, **22** (1966) 6.
- 13 J. TIMMERMANS, *Physico-Chemical Constants of Pure Organic Compounds*, Vol. II, Elsevier Amsterdam, London, and New York, 1965.
- 14 *Fluka Katalog 6*, Fluka A.G., Buchs, Switzerland, 1966.