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TEMPERATURE-PROGRAMMED RETENTION INDICES OF 221 HALOGENATED ORGANIC COMPOUNDS WITH 1-BROMOALKANES AS REFERENCES

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SUMMARY

Retention indices (I') of 221 halogenated aliphatic and alicyclic compounds were measured on the 1-bromoalkane scale by temperature-programmed gas chromatography using a fused-silica capillary column coated with methyl silicone. A linear relationship was observed between the retention indices of the solutes and their boiling points. There is a correlation between boiling point and carbon number in a homologous series. Consequently, there is also a correlation between I' and boiling point and molecular refraction. Regularities were obtained between retention index and molecular structure.

INTRODUCTION

Surface and underground water pollution by halogenated organic compounds is an important problem[1]. It is therefore important to screen halogenated organic compounds as potential pollutants, and they can be characterized by their retention indices. Retention index is better than retention time with respect to reliability. Temperature-programmed gas chromatography (GC) is the best method for screening various kinds of compounds, and in this study, retention indices of 221 halogenated aliphatic and alicyclic compounds were measured by this technique using a fused-silica capillary column coated with methyl silicone. 1-Bromoalkanes were used as reference compounds because they were convenient standards for the electron-capture detector. Several empirical regularities between retention index and physicochemical properties or molecular structure were investigated.

EXPERIMENTAL

The instruments used were a Hewlett-Packard Model 5890 A gas chromatograph equipped with a flame-ionization detector and a System Instruments (Tokyo, Japan) Model 7000B microcomputer. The column was a fused-silica capillary column (50 m × 0.2 mm I.D.) coated with methyl silicone. Samples were injected in the split

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mode. The carrier gas (nitrogen) flow velocity was *ca.* 10 cm/sec. The injection port and detector were heated at 270°C. A typical temperature programme was an initial period of 5 min at 20°C, followed by a linear increase at 2°C/min to 250°C and then an isothermal period at this temperature.

Most chemicals were purchased from Wako, Tokyo Kasei and Kanto Chemical Industries; a few compounds were synthesized. Mixtures of (*Z*)- and (*E*)-isomers were separated by preparative GC if possible and the configuration of the isomer was confirmed by NMR spectroscopy.

RESULTS AND DISCUSSION

Various expressions for retention data have been proposed in the literature. The retention ratio is the simplest, but it fluctuates significantly with slight changes in the operating conditions. Retention index (I_R) was proposed by Kováts[2] and is used very often, with high reliability. However, isothermal GC, which is needed for the calculation of I_R, is not suitable for screening various kinds of compounds. Temperature-programmed GC is more useful. In this study, the retention index (I') defined by Van den Dool and Kratz[3] as follows was used:

$$I' = 100\,(t_x - t_z)/(t_{z+1} - t_z) + 100z$$

where t is retention time. The subscripts x, z and $z + 1$ represent a sample with x carbon atoms, a standard compound with z carbon atoms and standard compound with $z + 1$ carbon atoms, respectively. In this investigation, homologues of 1-bromoalkane were used as standards, because 1-bromoalkanes show a moderate response to an electron-capture detector, which is widely used for screening purposes. A high reproducibility of I' was obtained with a non-polar capillary column[4]. Methyl silicone was chosen as the stationary phase in this study. Retention times measured with a typical temperature programme are shown in Fig. 1. A good relationship between retention time and carbon number of the 1-bromoalkane was observed, except for bromomethane and bromoethane. If the retention time of any compound was smaller than that of bromomethane, I' for the compound was calculated by considering methane as standard substance with $z = 0$.

The reliability of I' was investigated by checking the reproducibility and temperature–gas flow-rate dependence. Twenty replicate measurements each were made over 4 days for 1-chlorobutane, 1-chloropentane, 1-chlorohexane and 1-chloroheptane. The results are shown in Table I. The relative ratio of deviation (*RD*) was calculated as follows:

$$RD = 100 \cdot \text{standard deviation/average } (I' - 100z)$$

where z is the carbon atom number of the corresponding standard substance. As *RD* is very small, the reproducibility of I' is considered to be high. Variation of I' was investigated with different rates of oven temperature increase. The results are shown in Table II. The degree of deviation was very small. Next, changes of I' were measured when several different initial temperatures were applied in the temperature programme. Table III shows the results. It was confirmed that I' is affected slightly by

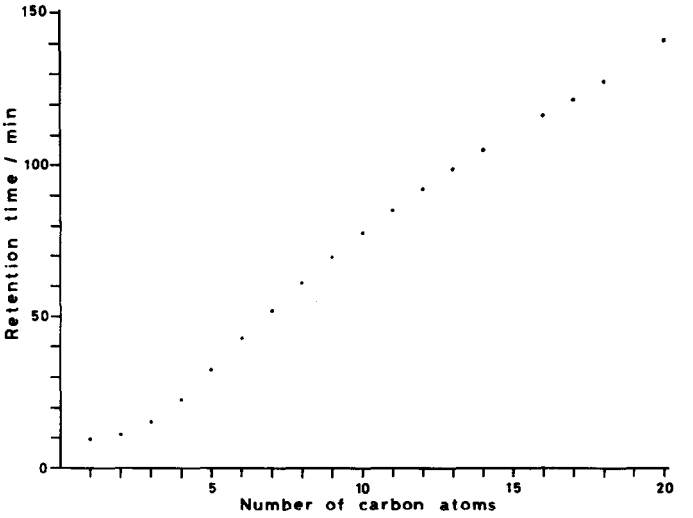


Fig. 1. Retention times of 1-bromoalkanes.

differences in the initial temperature of the temperature programme. Finally, we investigated whether I' depends on the flow velocity of the carrier gas. The results are shown in Table IV. I' did not change. From these results, I' is considered to be very reliable, although attention must be paid to the initial temperature of the temperature programme.

Table V shows the I values of 221 halogenated aliphatic and alicyclic compounds, arranged according to empirical formula. Boiling points and molecular refraction values, taken or calculated from reference data, are also given in Table V. Table VI shows the I' values of normal aliphatic hydrocarbons for reference. When retention indices using normal aliphatic hydrocarbons as references are necessary, they can easily be calculated by using the data in Table VI.

The relationship between I' and boiling point at 760 mmHg was investigated

TABLE I

REPRODUCIBILITY OF RETENTION INDICES (I') FOR TWENTY REPLICATE MEASUREMENTS FOR FOUR CHLOROALKANES

I' is the retention index defined by Van den Dool and Kratz[3], using 1-bromoalkanes as references. GC conditions were as follows: fused-silica capillary column (50 m × 0.2 mm I.D.) coated wih methyl silicone (fluid); oven temperature, an initial period of 5 min at 40°C, followed by a linear temperature increase of 2°C/min to 200°C and then an isothermal period at this temperature; injection port and detector temperatures, 270°C; carrier gas (nitrogen) flow velocity, 10 cm/sec.

Compound	*Average I'*	*Standard deviation*	*Relative standard deviation (%)*
1-Chlorobutane	319.5	0.17	0.9
1-Chloropentane	423.1	0.29	1.3
1-Chlorohexane	524.1	0.33	1.4
1-Chloroheptane	625.5	0.34	1.3

TABLE II

VARIATION OF RETENTION INDEX (I') ON USING DIFFERENT RATES OF TEMPERATURE INCREASE IN THE TEMPERATURE PROGRAMME

Conditions as in Table I, except for rate of temperature increase.

Compound	*Rate of temperature increase (°C/min)*		
	2	*3*	*4*
1-Chlorobutane	320	320	320
1-Chloropentane	423	424	424
1-Chlorohexane	524	525	524
1-Chloroheptane	626	626	624

TABLE III

VARIATION OF RETENTION INDEX (I') ON USING DIFFERENT INITIAL TEMPERATURES IN THE TEMPERATURE PROGRAMME

Conditions as in Table I, except initial temperature and rate of temperature increase (4°C/min).

Compound	*Initial temperature (°C)*					
	40	*50*	*60*	*70*	*80*	*90*
1-Chlorobutane	320	319	318	317	317	315
1-Chloropentane	424	423	421	420	419	417
1-Chlorohexane	525	523	522	521	520	518
1-Chloroheptane	626	625	624	623	622	620

TABLE IV

VARIATION OF RETENTION INDEX (I') ON USING DIFFERENT FLOW VELOCITIES OF THE CARRIER GAS (NITROGEN)

Conditions as in Table I except for flow velocity and rate of temperature increase (4°C/min).

Compound	*Velocity (cm/sec)*					
	9.36	*10.6*	*11.8*	*12.9*	*15.1*	*17.4*
1-Chlorobutane	320	320	320	320	319	319
1-Chloropentane	424	425	424	424	424	424
1-Chlorohexane	525	525	525	525	525	525
1-Chloroheptane	626	626	626	627	627	628

TABLE V

RETENTION INDICES (I'), BOILING POINTS (B.P.) AND MOLECULAR REFRACTIONS (R_M) OF 221 HALOGENATED COMPOUNDS

Compounds are listed according to their empirical formulae. I' is the retention index defined by Van den Dool and Kratz[3], using 1-bromoalkanes as references. GC conditions were as follows: fused-silica capillary column (50 m × 0.2 mm I.D.) coated with methyl silicone (fluid); oven temperature, an initial period for 5 min at 20°C, followed by a linear temperature increase at 2°C/min to 250°C and then an isothermal period of this temperature; injection port and detector temperatures, 270°C; carrier gas (N_2) flow velocity, 10 cm/sec.

Compound	*I'*	*B.p.** (°C/Torr)*	*R_M (cm^3)*	*Empirical formula*
Bromotrichloromethane	434	105	29.2	$CBrCl_3$
Tetrabromomethane	726	190		CBr_4
Dichlorodifluoromethane	0	−30		CCl_2F_2
Trichlorofluoromethane	158	23.7	21.4	CCl_3F
Chloropicrin	443	112		CCl_3NO_2
Tetrachloromethane	338	77	26.4	CCl_4
Tetraiodomethane	1497			CI_4
Bromodichloromethane	374	87	24.1	$CHBrCl_2$
Chlorodibromomethane	458	119–120/748	26.9	$CHBr_2Cl$
Bromoform	546	150–151	29.7	$CHBr_3$
Chloroform	292	60.5–61.5	21.3	$CHCl_3$
Iodoform	905			CHI_3
Bromochloromethane	284	68	18.6	CH_2BrCl
Dibromomethane	363	96–98	22.1	CH_2Br_2
Dichloromethane	206	39.8–40.0	16.4	CH_2Cl_2
Diiodomethane	582	181		CH_2I_2
Bromomethane	100	4.5		CH_3Br
Iodomethane	200	41–43	19.2	CH_3I
1,1,1-Trichloro-2,2,2-trifluoroethane	210	46	26.2	$C_2Cl_3F_3$
1,1,2-Trichloro-1,2,2-trifluoroethane	211	47–48	26.1	$C_2Cl_3F_3$
Trichloroacetonitrile	351	83–84	26.4	C_2Cl_3N
Tetrachloroethylene	481	121	30.3	C_2Cl_4
1,2-Difluoro-1,1,2,2-tetrachloroethane	387			$C_2Cl_4F_2$
Hexachloroethane	744	185.5/777		C_2Cl_6
Tribromoethylene	637	163–164		C_2HBr_3
Pentabromoethane	1172	210/300		C_2HBr_5
Trichloroethylene	372	87	25.4	C_2HCl_3
Trichloroacetaldehyde	382	98	35.6	C_2HCl_3O
Pentachloroethane	641	161–162	25.7	C_2HCl_5
(*Z*)-1,2-Dibromoethylene	410	112.5	25.9	$C_2H_2Br_2$
(*E*)-1,2-Dibromoethylene	438	108		$C_2H_2Br_2$
1,2-Dibromo-1,1-dichloroethane	689	176–178		$C_2H_2Br_2Cl_2$
rac-1,2-Dibromo-1,2-dichloroethane*	744	195		$C_2H_2Br_2Cl_2$
meso-1,2-Dibromo-1,2-dichloroethane*	747			$C_2H_2Br_2Cl_2$
1,1,2,2-Tetrabromoethane	929	243	41.8	$C_2H_2Br_4$
Chloroacetonitrile	345	124–126	16.1	C_2H_2ClN
1,1-Dichloroethylene	202	30–32	20.5	$C_2H_2Cl_2$
(*E*)-1,2-Dichloroethylene	234	48	20.6	$C_2H_2Cl_2$
1,1,1,2-Tetrachloroethane	513	135	29.9	$C_2H_2Cl_4$
1,1,2,2-Tetrachloroethane	565	147	30.8	$C_2H_2Cl_4$
Bromoethylene	131	16/750	18.4	C_2H_3Br

(*Continued on p. 40*)

TABLE V *(continued)*

Compound	*I'*	*B.p.*** *(°C/Torr)*	R_M *(cm³)*	*Empirical formula*
1,1,2-Tribromoethane	687	189		$C_2H_3Br_3$
Chloroethylene	50	−14		C_2H_3Cl
Methyl chloroformate	252	70–72	18.2	$C_2H_3ClO_2$
1,1,1-Trichloroethane	318	74–76	26.1	$C_2H_3Cl_3$
1,1,2-Trichloroethane	433	110–115	25.9	$C_2H_3Cl_3$
1-Bromo-2-chloroethane	390	106–107	24.0	C_2H_4BrCl
1,1-Dibromoethane	406	112.5		$C_2H_4Br_2$
1,2-Dibromoethane	465	131–132	27.0	$C_2H_4Br_2$
1,2-Dichloroethane	315	83	20.9	$C_2H_4Cl_2$
Dichloromethyl methyl ether	340	82–84	23.4	$C_2H_4Cl_2O$
1,1-Difluoroethane	0	−24.7		$C_2H_4F_2$
1,2-Diiodoethane	682			$C_2H_4I_2$
Bromoethane	200	37–40	19.0	C_2H_5Br
Chloroethane	110	13		C_2H_5Cl
Chloromethyl methyl ether	226	59.5	18.3	C_2H_5ClO
Iodoethane	284	69–73	24.0	C_2H_5I
Octachloropropane	1225	268–269/734		C_3Cl_8
1,1,1,2,3,3,3-Heptachloropropane	1034	249		C_3HCl_7
3-Bromo-1-propyne	314	88–90	25.8	C_3H_3Br
3-Chloro-1-propyne	227	65	18.9	C_3H_3Cl
(*Z*)-1,2,3-Trichloropropene*	532	140–145		$C_3H_3Cl_3$
(*E*)-1,2,3-Trichloropropene*	573			$C_3H_3Cl_3$
Methyl trichloroacetate	585	152–153		$C_3H_3Cl_3O_2$
1,1,2,3,3-Pentachloropropane	787	198–200		$C_3H_3Cl_5$
1,1,3-Trichloroacetone	613	172	30.9	$C_3H_3Cl_3O$
2,3-Dibromopropene	532	42–44/17	32.8	$C_3H_4Br_2$
1,1-Dichloropropene	327	76–77	25.3	$C_3H_4Cl_2$
(*Z*)-1,3-Dichloropropene	406	104.3	26.2	$C_3H_4Cl_2$
(*E*)-1,3-Dichloropropene	425	112	26.2	$C_3H_4Cl_2$
2,3-Dichloropropene	367	94	25.3	$C_3H_4Cl_2$
Methyl dichloroacetate	513	143	27.4	$C_3H_4Cl_2O_2$
1,1,1,2-Tetrachloropropane	596	150		$C_3H_4Cl_4$
1,1,2,3-Tetrachloropropane	682	179		$C_3H_4Cl_4$
1,2,2,3-Tetrachloropropane	639	164		$C_3H_4Cl_4$
3-Bromo-1-propene	284	70–71	24.1	C_3H_5Br
(*Z*)-1-Bromo-1-propene*	265	58.7	23.2	C_3H_5Br
(*E*)-1-Bromo-1-propene*	275	64.4	23.2	C_3H_5Br
Bromoacetone	433	137		C_3H_5BrO
Methyl bromoacetate	490	144	25.9	$C_3H_5BrO_2$
3-Chloro-1,2-dibromopropane	734	196		$C_3H_5Br_2Cl$
1,2,3-Tribromopropane	815	220		$C_3H_5Br_3$
3-Chloro-1-propene	208	44–46	20.3	C_3H_5Cl
(*Z*)-1-Chloro-1-propene*	194	32.8		C_3H_5Cl
(*E*)-1-Chloro-1-propene*	203	37.4		C_3H_5Cl
Chloroacetone	310	120	20.8	C_3H_5ClO
Methyl chloroacetate	431	130/740	22.3	$C_3H_5ClO_2$
1,1,2-Trichloropropane	507	133		$C_3H_5Cl_3$
1,2,3-Trichloropropane	572	156	30.3	$C_3H_5Cl_3$
1-Bromo-3-chloropropane	521	144–145	28.4	C_3H_6BrCl
1,2-Dibromopropane	515	140–142	31.6	$C_3H_6Br_2$
1,3-Dibromopropane	597	167	31.0	$C_3H_6Br_2$
2,2-Dibromopropane	436	114/740	33.2	$C_3H_6Br_2$

TABLE V *(continued)*

Compound	*I'*	*B.p.** (°C/Torr)*	*R_M (cm^3)*	*Empirical formula*
1,2-Dichloropropane	362	95–96	25.7	$C_3H_6Cl_2$
1,3-Dichloropropane	441	120–122	25.4	$C_3H_6Cl_2$
2,2-Dichloropropane	287	68–69	26.1	$C_3H_6Cl_2$
1-Bromopropane	300	71	23.6	C_3H_7Br
2-Bromopropane	248	59	24.0	C_3H_7Br
1-Chloropropane	218	46–47	20.8	C_3H_7Cl
2-Chloropropane	177	34–36	21.1	C_3H_7Cl
Chloromethyl ethyl ether	315	82	22.7	C_3H_7ClO
1-Iodopropane	385	101–102	28.9	C_3H_7I
2-Iodopropane	337	88–90	29.3	C_3H_7I
Hexachloro-1,3-butadiene	885	210–220	50.3	C_4Cl_6
Ethyl trifluoroacetate	209	60–62	22.7	$C_4H_5F_3O_2$
meso-1,2,3,4-Tetrabromobutane	1195	180–181/60		$C_4H_6Br_4$
(*Z*)-1,3-Dichloro-2-butene	493	127.9/745	30.0	$C_4H_6Cl_2$
(*E*)-1,3-Dichloro-2-butene	509	129.9/745	30.0	$C_4H_6Cl_2$
(*Z*)-1,4-Dichloro-2-butene	553	152/758	30.3	$C_4H_6Cl_2$
(*E*)-1,4-Dichloro-2-butene	573	74–76/40	30.6	$C_4H_6Cl_2$
3,4-Dichloro-1-butene	451	123	30.1	$C_4H_6Cl_2$
3-Bromo-1-butene	338	98–102		C_4H_7Br
4-Bromo-1-butene	378	98.5	27.8	C_4H_7Br
(*E*)-1-Bromo-2-butene	416	103–106	29.1	C_4H_7Br
(*Z*)-2-Chloro-2-butene*	278	63	24.8	C_4H_7Cl
(*E*)-2-Chloro-2-butene*	305	70.6	24.8	C_4H_7Cl
3-Chloro-1-butene	259	62–65	25.2	C_4H_7Cl
1-Chloro-2-methyl-1-propene	297	68		C_4H_7Cl
3-Chloro-2-methyl-1-propene	303	71–72		C_4H_7Cl
1,2-Dibromobutane	622	166	36.3	$C_4H_8Br_2$
1,3-Dibromobutane	648	175	35.8	$C_4H_8Br_2$
1,4-Dibromobutane	725	198	36.2	$C_4H_8Br_2$
rac-2,3-Dibromobutane*	581	157		$C_4H_8Br_2$
meso-2,3-Dibromobutane*	593	157		$C_4H_8Br_2$
1,2-Dichlorobutane	466	124		$C_4H_8Cl_2$
1,3-Dichlorobutane	490	134	30.2	$C_4H_8Cl_2$
1,4-Dichlorobutane	558	161–163	29.6	$C_4H_8Cl_2$
2,2-Dichlorobutane	404	104		$C_4H_8Cl_2$
2,3-Dichlorobutane	428	117–119	30.4	$C_4H_8Cl_2$
1,2-Dichloroethyl ethyl ether	526	145.5		$C_4H_8Cl_2O$
2,2'-Dichlorodiethyl ether	632	177–178		$C_4H_8Cl_2O$
1-Bromobutane	400	100–104	28.3	C_4H_9Br
2-Bromobutane	356	91	28.6	C_4H_9Br
2-Bromo-2-methylpropane	301	75	29.6	C_4H_9Br
2-Bromoethyl ethyl ether	479	149–150/750	30.0	C_4H_9BrO
1-Chlorobutane	320	77–78	25.4	C_4H_9Cl
2-Chlorobutane	284	68–70	25.4	C_4H_9Cl
1-Chloro-2-methylpropane	291	68–69	25.0	C_4H_9Cl
2-Chloro-2-methylpropane	220	51–52	25.5	C_4H_9Cl
1-Iodobutane	483	130–131	33.4	C_4H_9I
2-Iodo-2-methylpropane	381	99	34.4	C_4H_9I
Hexachlorocyclopentadiene	999	239/753	52.2	C_5Cl_6
1,1,1,5,5,5-Hexafluoropentan-2,4-dione	208	70–71	29.0	$C_5H_2F_6O_2$

(Continued on p. 42)

TABLE V *(continued)*

Compound	*I'*	*B.p.*** *(°C/Torr)*	R_M *(cm³)*	*Empirical formula*
Bromocyclopentane	525	137–139	30.9	C_5H_9Br
1-Bromo-3-methyl-2-butene	517	59–60/60		C_5H_9Br
Chlorocyclopentane	449	114	28.0	C_5H_9Cl
1,4-Dibromopentane	772	98–99/25	40.7	$C_5H_{10}Br_2$
1,5-Dibromopentane	836	223/758	40.9	$C_5H_{10}Br_2$
2,4-Dibromopentane	677	40/4		$C_5H_{10}Br_2$
1,5-Dichloropentane	676	182	34.6	$C_5H_{10}Cl_2$
2,2-Dimethyl-1,3-dichloropropane	554			$C_5H_{10}Cl_2$
1-Bromopentane	500	130	32.9	$C_5H_{11}Br$
2-Bromopentane	451	116–117	32.6	$C_5H_{11}Br$
2-Bromo-2-methylbutane	416	107		$C_5H_{11}Br$
1-Chloropentane	423	107–108	30.0	$C_5H_{11}Cl$
1-Chloro-3-methylbutane	389	100		$C_5H_{11}Cl$
2-Chloro-2-methylbutane	338	86		$C_5H_{11}Cl$
1-Iodopentane	590	62/20	38.1	$C_5H_{11}I$
1-Iodo-3-methylbutane	547	149–150		$C_5H_{11}I$
2-Iodo-2-methylbutane	509	128/737		$C_5H_{11}I$
Tetradecafluoro-2-methylpentane	0			C_6F_{14}
Tetradecafluorohexane	0	60		C_6F_{14}
α-BHC***	1356			$C_6H_6Cl_6$
β-BHC***	1388			$C_6H_6Cl_6$
γ-BHC***	1434			$C_6H_6Cl_6$
δ-BHC***	1454			$C_6H_6Cl_6$
3-Bromocyclohexene	663	56–57/11		C_6H_9Br
cis-1,4-Dichlorocyclohexane	775	193		$C_6H_{10}Cl_2$
trans-1,4-Dichlorocyclohexane	741	193–194	38.1	$C_6H_{10}Cl_2$
Bromocyclohexane	645	166–167	35.9	$C_6H_{11}Br$
Chlorocyclohexane	559	142	22.3	$C_6H_{11}Cl$
Iodocyclohexane	738	80–81/20	40.8	$C_6H_{11}I$
2,3-Dibromo-2,3-dimethylbutane	726	78/10		$C_6H_{12}Br_2$
1,6-Dibromohexane	965	243	45.8	$C_6H_{12}Br_2$
1-Bromohexane	600	154–158	37.5	$C_6H_{13}Br$
1-Bromo-4-methylpentane	564	146–147		$C_6H_{13}Br$
1-Chlorohexane	524	133–134	34.7	$C_6H_{13}Cl$
2-Chlorohexane	476	122		$C_6H_{13}Cl$
3-Chlorohexane	476	123		$C_6H_{13}Cl$
1-Iodohexane	692	179–180	42.8	$C_6H_{13}I$
Tetradecafluoromethylcyclohexane	68	76		C_7F_{14}
Hexadecafluoroheptane	30	82		C_7F_{16}
Bromocycloheptane	779	71–72/10	40.8	$C_7H_{13}Br$
Chlorocycloheptane	699	175		$C_7H_{13}Cl$
1-Bromoheptane	700	180	42.2	$C_7H_{15}Br$
2-Bromo-2-methylhexane	604	59/25		$C_7H_{15}Br$
2-Bromo-2,4-dimethylpentane	565	83–84/100		$C_7H_{15}Br$
1-Chloroheptane	626	159–161	39.1	$C_7H_{15}Cl$
2-Chloroheptane	572	46/19.5		$C_7H_{15}Cl$
1-Iodoheptane	791	204	47.4	$C_7H_{15}I$
1,8-Dibromooctane	1170	270–272	54.0	$C_8H_{16}Br_2$
1,8-Dichlorooctane	987	240–242		$C_8H_{16}Cl_2$
1-Bromooctane	800	201	46.6	$C_8H_{17}Br$
1-Bromo-2-ethylhexane	753	75–77/16	48.1	$C_8H_{17}Br$
1-Chlorooctane	720	183	43.9	$C_8H_{17}Cl$

TABLE V *(continued)*

Compound	*I'*	*B.p.*** *(°C/Torr)*	R_M *(cm³)*	*Empirical formula*
1-Iodooctane	892	225–226	52.0	$C_8H_{17}I$
1-Bromononane	900	201	51.8	$C_9H_{19}Br$
1-Chlorononane	820	202–204	48.9	$C_9H_{19}Cl$
1-Chloroadamantane	945			$C_{10}H_{15}Cl$
2-Chloroadamantane	989			$C_{10}H_{15}Cl$
1,10-Dibromodecane	1374	160/15		$C_{10}H_{20}Br_2$
1,10-Dichlorodecane	1192	167–168/28	58.0	$C_{10}H_{20}Cl_2$
1-Bromodecane	1000	238	56.4	$C_{10}H_{21}Br$
1-Chlorodecane	919	223	53.3	$C_{10}H_{21}Cl$
1-Bromoundecane	1100	137–138/18	60.7	$C_{11}H_{23}Br$
1-Chloroundecane	1019	240–241/772		$C_{11}H_{23}Cl$
Aldrin	1657			$C_{12}H_8Cl_6$
Dieldrin	1836			$C_{12}H_8Cl_6O$
1,12-Dibromododecane	1579	215/15		$C_{12}H_{24}Br_2$
1-Bromododecane	1200	134–135/6	65.5	$C_{12}H_{25}Br$
1-Bromotridecane	1300	148–150/10	69.9	$C_{13}H_{27}Br$
1-Bromotetradecane	1400	175–178/20	81.5	$C_{14}H_{29}Br$
1-Chlorotetradecane	1315	139–142/4	72.3	$C_{14}H_{29}Cl$
1-Bromohexadecane	1600	190/11	83.9	$C_{16}H_{33}Br$
1-Chlorohexadecane	1506	149/1	80.9	$C_{16}H_{33}Cl$
1-Bromoheptadecane	1700	193–200/10		$C_{17}H_{35}Br$
1-Bromooctadecane	1800	214–216/12		$C_{18}H_{37}Br$
1-Chlorooctadecane	1711	157–158/1.5	91.7	$C_{18}H_{37}Cl$
1-Iodooctadecane	1900	194–197/2		$C_{18}H_{37}I$
1-Bromoeicosane	2000			$C_{20}H_{41}Br$
1-Chloroeicosane	1902	193–196/2		$C_{20}H_{41}Cl$

* Configuration is tentatively assigned.
** Boiling points given without a pressure are at 1 atm (760 Torr).
*** BHC = 1,2,3,4,5,6-hexachlorocyclohexane.

on 170 halogenated compounds. Estimated boiling points were employed for substances whose boiling points were reported at 700–760 or 760–780 mmHg. The results are shown in Fig. 2. The following linear regression equation was obtained for these data, except for five polyfluorinated hydrocarbons and diiodomethane, which deviate considerably from a straight line:

$$I' = 3.789\ T + 14.73$$

where T is boiling point (°C). The correlation coefficient was 0.996. Fig. 3 shows the linear relationship between retention index and the number of carbon atoms for several series of homologues. It is interesting that the slopes of the straight lines are almost the same for two series, one for α,ω-dibromoalkanes and α,ω-dichloroalkanes and the other for 1-chloroalkanes, 1-iodoalkanes and normal alkanes. It is obvious that a linear correlation exists for 1-bromoalkanes, because series of 1-bromoalkanes are used as references. Fig. 4 shows the linear relationships for other halogenated compounds, where the slopes are not the same.

TABLE VI

RETENTION INDICES (I') OF NORMAL HYDROCARBONS

Conditions as in Table V.

Compound	I'	*Compound*	I'
Butane	78	Tetradecane	1053
Pentane	186	Pentadecane	1149
Hexane	282	Hexadecane	1245
Heptane	382	Heptadecane	1339
Octane	480	Octadecane	1434
Nonane	578	Nonadecane	1536
Decane	674	Eicosane	1629
Undecane	769	Heneicosane	1730
Dodecane	865	Docosane	1816
Tridecane	959		

Some investigators have reported that there is an appropriate relationship between retention index and molecular refraction (R_M) for homologues[5–7]. Molecular refraction, related to electron polarizability, is a measure of the dispersive interaction of sample molecules with the stationary phase. The relationship between R_M and I' was studied and the results are shown in Figs. 5 and 6. The I' values of 1-bromoalkanes, 2-bromoalkanes, bromocycloalkanes and α,ω-dibromoalkanes were linearly related to R_M. The I' values of dibromoalkanes, except for the α,ω-isomers, fitted a straight line for bromocycloalkanes. In Fig. 6, the I' values of 1-chloroalkanes, 2-chloroalkanes and α,ω-dichloroalkanes also vary linearly with R_M. Plots for other chlorinated compounds were mostly situated in the region surrounded by the straight lines for 1-chloroalkanes and α,ω-dichloroalkanes. In general, a simple linear relationship between R_M and I' for all kinds of halogenated compounds does not

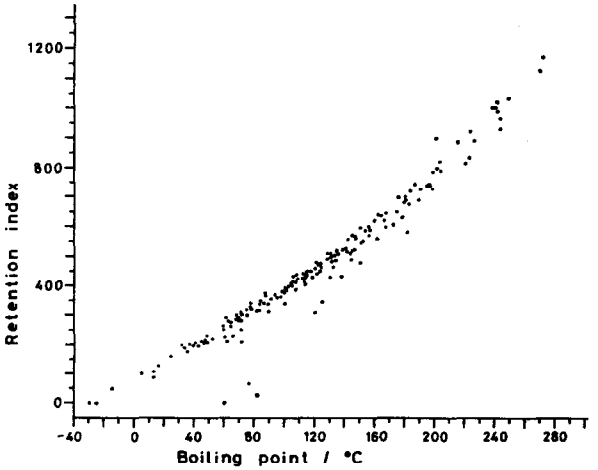
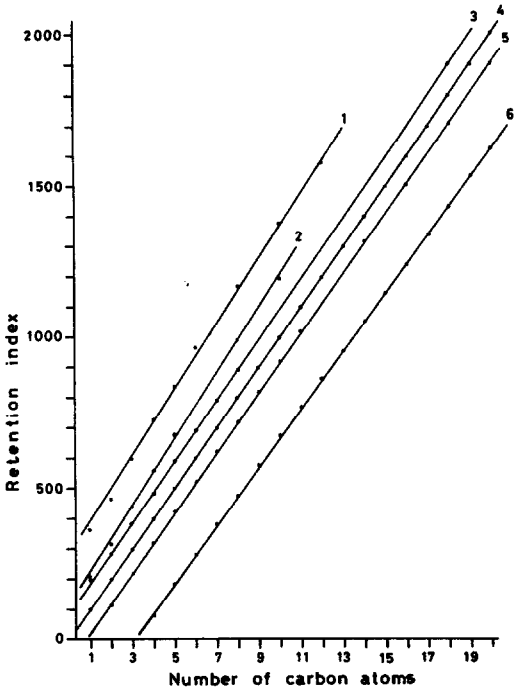


Fig. 2. Correlation between boiling point and retention index (I') of 170 halogenated compounds.



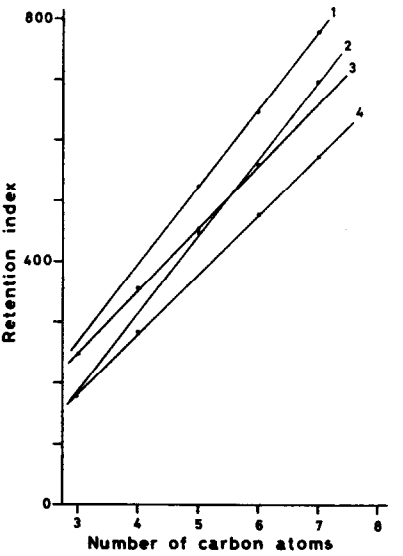


Fig. 3. Linear relationship between the number of carbon atoms and retention index (I'). 1 = α,ω-Dibromoalkanes; 2 = α,ω-dichloroalkanes; 3 = 1-iodoalkanes; 4 = 1-bromoalkanes; 5 = 1-chloroalkanes; 6 = *n*-alkanes.

Fig. 4. Linear relationship between the number of carbon atoms and retention index (I'). 1 = Bromocycloalkanes; 2 = chlorocycloalkanes; 3 = 2-bromoalkanes; 4 = 2-chloroalkanes.

seem to exist. Further, these results suggest that I' is not concerned directly with molecular volume, as molecular refraction, having the dimensions of cm^3, is related to molar volume. Other relationships between I' and physico-chemical properties have been reviewed in the literature[8], but useful results were not obtained in this study.

Several investigators have studied the relationship between I' and molecular structure[7–9]. Fig. 7 shows several relationships between I' and the number of chlorine atoms. A few linear relationships were clearly observed. It is noteworthy that a linear correlation exists for compounds only containing both chlorine and bromine atoms except for methyl esters of chlorinated acetic acid. For homologues containing only chlorine, bromine or iodine atoms, another type of linearity was observed, as shown in Fig. 8. Linear correlations were observed between log I' and the ratio of the number of hydrogen atoms to the total number of halogen atoms in all instances except for iodinated compounds. The deviation from a linear relationship for iodides might be due to steric effects of the iodine atom, with a large atomic radius. There seems to be another linear relationship between log I' and the logarithm of the number of halogen atoms in halogenated ethanes. The results are shown in Fig. 9. As all these relationships were obtained empirically, the theoretical basis needs to be exam-

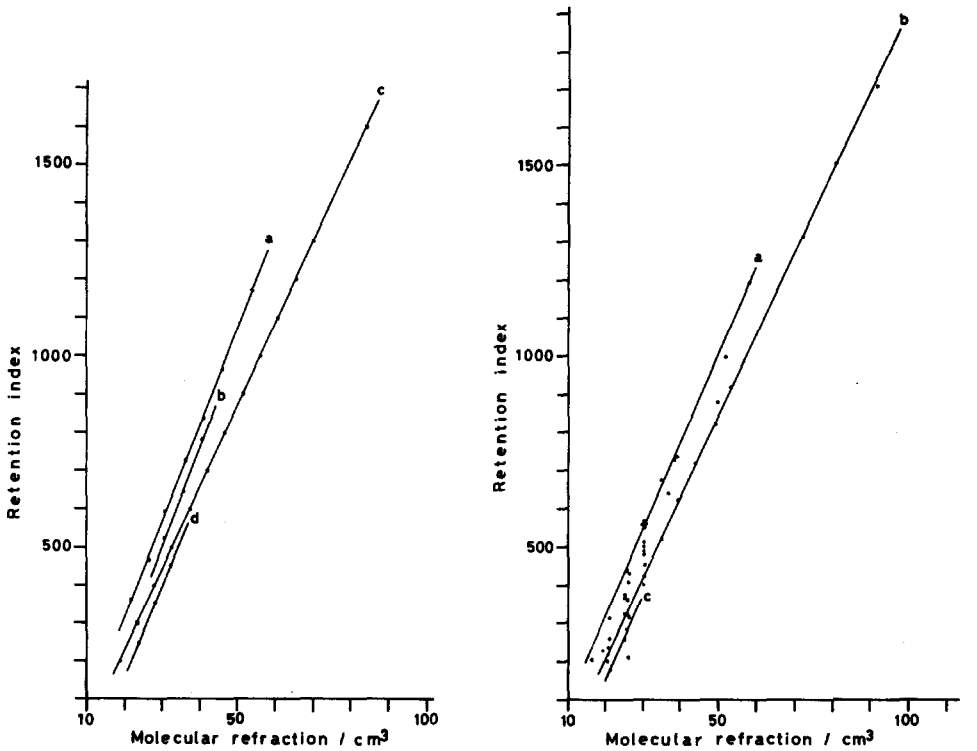


Fig. 5. Linear relationship between molecular refraction (R_M) and retention index (I') of (a) α,ω-dibromoalkanes, (b) bromocycloalkanes, (c) 1-bromoalkanes and (d) 2-bromoalkanes.

Fig. 6. Relationship between molecular refraction (R_M) and retention index (I') of chlorinated compounds: (a) α,ω-dichloroalkanes; (b) 1-chloroalkanes; (c) 2-chloroalkanes.

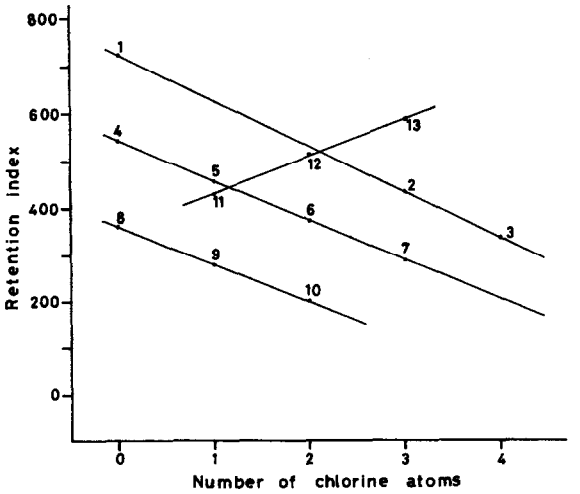


Fig. 7. Linear relationship between the total number of chlorine atoms and retention index (I') of halogenated methanes and halogenated acetates. 1 = CBr_4; 2 = $CBrCl_3$; 3 = CCl_4; 4 = $CHBr_3$; 5 = $CHBr_2Cl$; 6 = $CHBrCl_2$; 7 = $CHCl_3$; 8 = CH_2Br_2; 9 = CH_2BrCl; 10 = CH_2Cl_2; 11 = methyl chloroacetate; 12 = methyldichloroacetate; 13 = methyl trichloroacetate.

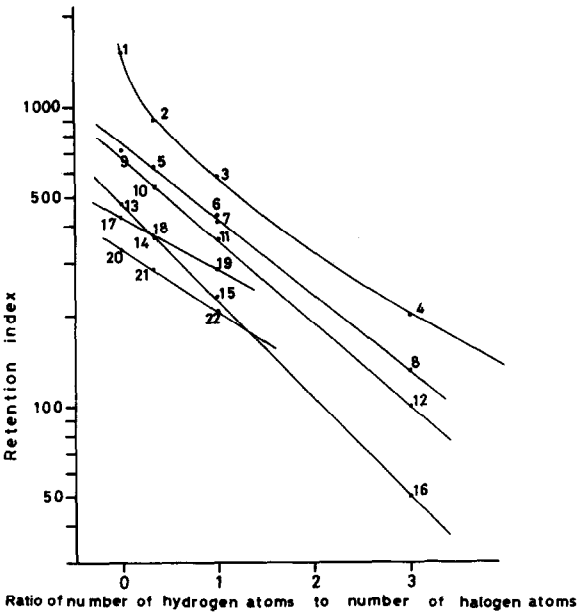


Fig. 8. Correlation between the ratio of number of hydrogen atoms to number of halogen atoms and retention index (I') of halogenated methanes and halogenated ethylenes. 1 = CI_4; 2 = CHI_3; 3 = CH_2I_2; 4 = CH_3I; 5 = tribromoethylene; 6 = (*E*)-1,2-dibromoethylene; 7 = (*Z*)-1,2-dibromoethylene; 8 = bromoethylene; 9 = CBr_4; 10 = $CHBr_3$; 11 = CH_2Br_2; 12 = CH_3Br; 13 = tetrachloroethylene; 14 = trichloroethylene; 15 = (*E*)-1,2-dichloroethylene; 16 = chloroethylene; 17 = $CBrCl_3$; 18 = $CHBrCl_2$; 19 = CH_2BrCl; 20 = CCl_4; 21 = $CHCl_3$; 22 = CH_2Cl_2.

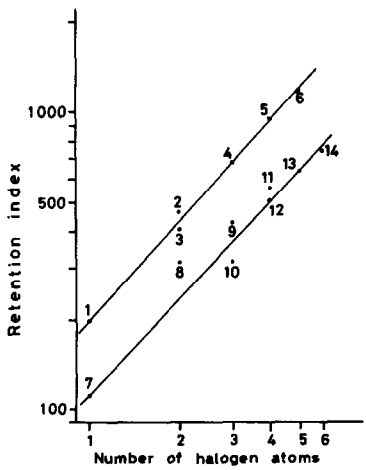


Fig. 9. Correlation between the number of halogen atoms and retention index (I') of halogenated ethanes. 1 = Bromoethane; 2 = 1,2-dibromoethane; 3 = 1,1-dibromoethane; 4 = 1,1,2-tribromoethane; 5 = 1,1,2,2,-tetrabromoethane; 6 = pentabromoethane; 7 = chloroethane; 8 = 1,2-dichloroethane; 9 = 1,1,2-trichloroethane; 10 = 1,1,1-trichloroethane; 11 = 1,1,2,2-tetrachloroethane; 12 = 1,1,1,2-tetrachloroethane; 13 = pentachloroethane; 14 = hexachloroethane.

ined. Roughly, I' seems to be related to the length of the molecule, with a few exceptions. For saturated linear hydrocarbons bearing a halogen atom in an inner position, I' is 40–50 units smaller than those bearing the same halogen atom at a terminal position, irrespective of the type of halogen. For saturated aliphatic hydrocarbons bearing a halogen atom at a terminal position, an isomer bearing a branched methyl group at the other terminal position has I' about 30 units smaller than that of the unbranched isomer. I' of $RCX(CH_3)CH_3$ is about 90 units smaller than that of $RCH_2CH_2CH_2X$, where X is a halogen. I' of a (*Z*)-isomer is smaller than that of the corresponding (*E*)-isomer for halogenated olefins. I' of an inner linear olefin is greater than that of a terminal olefin. For example, the I' values of 1-bromo-3-butene and (*E*)-1-bromo-2-butene are 378 and 416, respectively.

Identification of halogenated compounds, mainly hydrocarbons, will be easier by using these retention indices and regularities and, further, screening for potent pollutants should be more convenient in the future.

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