

Note

Precalculation of gas chromatographic retention indices of linear 1-halogenoalkanes

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The precalculation of retention indices of alkyl halides in gas chromatography (GC) was performed by Kováts¹ and continues to be of interest^{2–15}. Some authors used the experimentally found contributions of halogen atoms to the index values^{1–3}. Morishita *et al.*⁴ proposed an additive approach for precalculation of the retention index, *I*, of 1-halogenoalkanes. The maximum discrepancy between the experimental and calculated *I* value is 2 index units (i.u.).

Linear correlations with solute properties, such as the number of carbon atoms, $n^{5–7}$, boiling point^{7–11}, Van der Waals volume⁹, etc., have been proposed. Sabljic¹², using the experimental data of Morishita *et al.*⁴, proposed a topological approach. The correlation coefficient obtained is high (0.999), but the discrepancies between $I_{\text{exp.}}$ and $I_{\text{calc.}}$ are from 1 to 8 i.u.

When applied to a particular series of alkyl halides, *e.g.*, chlorides, bromides or iodides, some of the approaches proposed are sufficiently exact. However, none is able to predict the retention when different 1-halogenoalkanes are present in the sample.

The present paper proposes an equation for exact precalculation of the retention indices of various linear 1-halogenoalkanes. Isomers are not included, in order to obtain precise results. Once correctly identified, the 1-halogenoalkanes may serve for an easier identification of the isomers. The identification currently necessitates only a limited set of standards. This saves expense and time, especially if a GC–mass spectrometric (MS) system is involved in the investigation. Besides, the calculative identification is sufficient in many cases.

To assess the accuracy of the calculative identification approach, data on the reproducibility of the experimental results are necessary. Unfortunately there are few data in the literature to allow a reliable statistical calculation of the reproducibility. On the basis of the experimentally established repeatability of ± 2 i.u., we accepted for the reproducibility the value of 4 i.u.

EXPERIMENTAL

The retention indices of 21 (C₂–C₉ straight chain) 1-halogenoalkanes were

obtained on a gas chromatograph Sigma 3B (Perkin-Elmer) equipped with flame ionization detection (FID). The column was a fused-silica capillary 50 m \times 0.32 mm I.D. coated with silicon oil OV-101. Samples were injected in split mode. The carrier gas was hydrogen with a flow-rate of 20 cm s⁻¹ and splitting ratio was 1:100. The temperature of the column oven was programmed linearly from 40 to 280°C at 2° min⁻¹.

Data handling

The calculations were based on the recently proposed model for deriving predictive equations in chromatography¹⁶

$$I_{\text{calc.}} = b_0 + \Sigma b_i \cdot B_i + \Sigma b_j \cdot T_j \quad (1)$$

where B and T are respectively basic and tuning contributors to the retention index value and b_0 , b_i and b_j are constants. The term B includes such solute properties, which correlate very highly with the retention index and after calculation of $I_{\text{calc.}}$ its value covers 100 ± 10 –15% of the experimental index value, $I_{\text{exp.}}$. This term may be used also in any relationship, linear or non-linear, connecting the retention with any solute physicochemical properties. The second part of the model also includes solute properties, which however have insignificant correlation with the retention, but which possess an high discrimination power and are able to approximate the roughly calculated value of $I_{\text{calc.}}$ to the value of $I_{\text{exp.}}$.

The selection of suitable solute properties is performed in two steps. First, the best parameters B are chosen, by studying the linear regression between a series of solute features and $I_{\text{exp.}}$.

$$I_{\text{exp.}} = b_0 + b_1 \cdot B \quad (2)$$

The non-linear regression between I and n proposed recently by Golovnya^{17,18} and which has been confirmed by others^{19,20} was also examined for the term B . The second step requires a study of the discrepancies between $I_{\text{calc.}}$ and $I_{\text{exp.}}$ in connection with specific solute features and definition of the term T .

RESULTS AND DISCUSSION

The correlation coefficients, r , of eqn. 2, the variances, s^2 , as well as the values of the intercorrelation coefficients, R , are summarized in Table I. The best correlation is obtained with the molecular refraction, R_m , but the maximum deviation, Δ_{max} , of 21 i.u. is too high. The investigation of the quadratic regressions did not give better results. For the boiling point, B_p , the correlation coefficient was 0.9991, but Δ_{max} remains high, 23 i.u.

These deviations mean that the correlations are without practical significance. Obviously it is necessary to search for suitable solute features for the tuning of the $I_{\text{calc.}}$ values. A careful study of the discrepancies between $I_{\text{exp.}}$ and $I_{\text{calc.}}$ revealed that they depend on the type of halogen when the correlation is made with n , R_m or the molecular volume, V_{mol} . The discrepancies for chlorides are -80 i.u., for bromides ± 10 i.u. and for iodides $+90$ i.u. (see Table II). The intergroup (one type of halogen) discrepancies

TABLE I
CORRELATION COEFFICIENT, r , VARIANCE, s^2 , MAXIMUM DEVIATION, Δ_{max} , IN i.u. AND THE INTERCORRELATION COEFFICIENT, R

No. Parameter	r	s^2	Δ_{max}	R				
				R_m	B_p	V_{mol}	n	M_m
1 Molecular refraction, R_m	0.9989	11	21	1	0.99	0.98	0.95	0.81
2 Boiling point, B_p	0.9967	381	35		1	0.97	0.94	0.82
3 Molecular volume, V_{mol}	0.9779	2524	74			1	0.99	0.66
4 Number of carbon atoms, n	0.9537	5244	102				1	0.58
5 Molecular mass, M_m	0.8064	$2 \cdot 10^4$	264					1

change systematically when the molecular mass, M_m , is the parameter. Hence, it is reasonable to examine the combination of M_m and any of the other solute features studied.

The combination of n with M_m gives the best results

$$I_{calc.} = 155.0217 + 76.9862n + 1.8828M_m \quad (3)$$

TABLE II
COMPARISON OF $I_{exp.}$ WITH $I_{calc.}$ CALCULATED ACCORDING TO DIFFERENT EQUATIONS

No.	Compound	$I_{exp.}$	I_n	$I_{calc.}$		
				Eqn. 3	Eqn. 6	Eqn. 7
1	C ₂ H ₅ Cl	432 ± 1	517	430.5	431.2	431.4
2	C ₃ H ₇ Cl	534 ± 1	617	533.9	534.4	533.9
3	C ₄ H ₉ Cl	638 ± 1	718	637.2	637.8	637.5
4	C ₅ H ₁₁ Cl	742 ± 1	818	740.6	741.2	741.6
5	C ₆ H ₁₃ Cl	845 ± 1	919	844.0	844.6	845.4
6	C ₇ H ₁₅ Cl	949 ± 1	1019	947.4	947.9	948.6
7	C ₈ H ₁₇ Cl	1051 ± 2	1119	1050.8	1051.3	1051.1
8	C ₉ H ₁₉ Cl	1152 ± 2	1219	1154.2	1154.7	1153.1
9	C ₂ H ₅ Br	514 ± 1	517	514.1	513.0	513.2
10	C ₃ H ₇ Br	618 ± 1	617	617.6	616.4	615.9
11	C ₄ H ₉ Br	719 ± 1	718	720.9	719.8	719.3
12	C ₅ H ₁₁ Br	822 ± 1	818	824.3	823.1	823.9
13	C ₆ H ₁₃ Br	926 ± 1	919	927.7	926.5	927.3
14	C ₇ H ₁₅ Br	1030 ± 2	1019	1031.1	1029.9	1030.4
15	C ₈ H ₁₇ Br	1133 ± 2	1119	1134.5	1133.3	1133.0
16	C ₂ H ₅ I	602 ± 1	517	602.6	603.4	603.5
17	C ₃ H ₇ I	705 ± 1	617	706.1	706.8	706.1
18	C ₄ H ₉ I	809 ± 1	718	809.5	810.1	809.6
19	C ₆ H ₁₃ I	1018 ± 1	919	1016.2	1016.9	1017.5
20	C ₇ H ₁₅ I	1122 ± 2	1019	1119.6	1120.2	1120.7
21	C ₈ H ₁₇ I	1225 ± 2	1119	1223.0	1223.6	1223.3

with $r = 0.999980$, $s^2 = 2.4$, standard deviation (S.D.) = 1.56 and $\Delta_{\max} = 2.4$ i.u. We consider that the rôle of M_m accounts for the type of halogen at equal number of carbon atoms, *i.e.*, it belongs to the term T of the model. This was confirmed when M_m was exchanged for the contribution of the halogen atoms, calculated according to

$$I_{\text{calc.}} = b_0 + b_1n + b_2(\text{Cl}^-) + b_3(\text{Br}^-) + b_4(\text{I}^-) \quad (4)$$

where (X^-) has values of 1 or 0 depending on the presence or absence of the corresponding halogen atom. To decrease the number of parameters a relative contributor, $\text{Halo}(\text{X}^-)$, is calculated.

$$\text{Halo}(\text{Cl}^-) = b_2/b_3 \text{ and } \text{Halo}(\text{I}^-) = b_4/b_3 \quad (5)$$

assuming $\text{Halo}(\text{Br}^-) = 1.00$.

Using the calculated $\text{Halo}(\text{X}^-)$ values as the term T in eqn. 1, the following equation is obtained

$$I_{\text{calc.}} = 12.6327 + 103.3724n + 293.645\text{Halo}(\text{X}^-) \quad (6)$$

where $\text{Halo}(\text{Cl}^-) = 0.7209$ and $\text{Halo}(\text{I}^-) = 1.3077$. The correlation coefficient is 0.999986, $s^2 = 1.5$, S.D. = 1.26 and $\Delta_{\max} = 2.4$ i.u.

The index values calculated by eqns. 3 and 6 are very similar (Table II) which confirms the hypothesis about the rôle of M_m .

The use of Golovnya's equation as for the term B of eqn. 1 leads to

$$I_{\text{calc.}} = 112.1545 + 98.3908n - 229.3558(\log n/n) - \\ 0.9564 [(n-2)^2 + 0.1]^{-1} + 293.3475\text{Halo}(\text{X}^-) \quad (7)$$

with the highest $r = 0.99999$ and the lowest $s^2 = 1.3$. The maximum error, $\Delta_{\max} = 2.1$ i.u. (see Table II).

Comparison of the variances of eqns. 3 and 7 according to the Fisher criterion

$$F_{\text{exp}} = 1.84 \quad F_{21,21} = 2.08 \text{ at } \alpha = 0.95$$

shows that both equations are statistically equal, but eqn. 7 with its Δ_{\max} about 2 i.u. is adequate considering the experimental repeatability.

In terms of the number of parameters, eqn. 3 is considered more suitable because less pure compounds are necessary for the calculation of the equation constants. We shall show this with an example. Considering only four alkyl halides, namely ethyl iodide, butyl chloride, butyl bromide and hexyl iodide, and a sample the chromatogram of which consists of 21 peaks. After chromatographing the standards under the same conditions as those for the sample, we obtain the retention indices. Using these values, the following regression equation is obtained:

$$I_{\text{calc.}} = 152.26 + 77.54346n + 1.88638M_m \quad (8)$$

Applying this equation to the experimental I values of the sample, it is possible to

TABLE III

COMPARISON OF $I_{\text{exp.}}$ WITH $I_{\text{calc.}}$ ACCORDING TO EQN. 8 AND VERIFICATION OF THE TENTATIVE IDENTIFICATION BY $I_{\text{calc.}}$ ACCORDING TO THE NEWLY OBTAINED CONSTANTS FOR EQN. 7

No.	Peak $I_{\text{exp.}}$	$I_{\text{calc.}}$, eqn. 8	Expected compound	$I_{\text{calc.}}$, new eqn. 7	Identified compound
1	432	429	—	431.1	C ₂ H ₅ Cl
2	514	512.9	C ₂ H ₅ Br	513.7	C ₂ H ₅ Br
3	534	533	C ₃ H ₇ Cl	535.8	C ₃ H ₇ Cl
4	602 (standard)	601.6	C ₂ H ₅ I	602.2	C ₂ H ₅ I
5	618	616.9	C ₃ H ₇ Br	616.5	C ₃ H ₇ Br
6	638 (standard)	637.0	C ₄ H ₉ Cl	638.8	C ₄ H ₉ Cl
7	705	705.6	C ₃ H ₇ I	705.8	C ₃ H ₇ I
8	719 (standard)	720.9	C ₄ H ₉ Br	719.5	C ₄ H ₉ Br
9	742	741.0	C ₅ H ₁₁ Cl	741.6	C ₅ H ₁₁ Cl
10	809	809.6	C ₄ H ₉ I	809.3	C ₄ H ₉ I
11	822	824.9	—	822.7	C ₅ H ₁₁ Br
12	845	845.0	C ₆ H ₁₃ Cl	844.3	C ₆ H ₁₃ Cl
13	926	928.9	—	926.1	C ₆ H ₁₃ Br
14	949	949.0	C ₇ H ₁₅ Cl	947.3	C ₇ H ₁₅ Cl
15	1018 (standard)	1017.5	C ₆ H ₁₃ I	1017.1	C ₆ H ₁₃ I
16	1030	1032.9	—	1029.7	C ₇ H ₁₃ Br
17	1051	1053.0	C ₈ H ₁₇ Cl	1050.5	C ₈ H ₁₇ Cl
18	1122	1121.6	C ₇ H ₁₅ I	1121.2	C ₇ H ₁₅ I
19	1133	1136.9	—	1133.5	C ₈ H ₁₇ Br
20	1152	1157.0	—	1153.9	C ₉ H ₁₉ Cl
21	1225	1225.5	C ₈ H ₁₇ I	1225.4	C ₈ H ₁₇ I

identify 14 compounds (about 66% of the peaks) with the same reliability as if standard substances had been used. The discrepancies are in the limits of repeatability of ± 2 i.u. (see Table III). Now using all 14 data (instead of only the 4), new constants of eqn. 7 are recalculated. The new $I_{\text{calc.}}$ values are given in Table III too. It is noteworthy that the tentative identification of the 14 peaks is confirmed and that all the remaining peaks are identified within the same limit of ± 2 i.u.

To check eqn. 3, we transferred the experimental data published for alkyl chlorides⁴ and those published for alkyl bromides²¹ into one regression matrix. The following equation is obtained

$$I_{\text{calc.}} = 151.23 + 57.6037n + 3.60467M_m \quad (9)$$

with $r = 0.999932$, S.D. = 1.97 and $A_{\text{max}} = 2.7$ i.u. Evidently, when the experimental results are reliable, even though from different sources, they can be handled together.

Eqn. 3 allows one to overcome the lack of all necessary pure standard compounds. Only a limited number of halides, irrespective of the halogen, satisfies the calculation demand. The reliability of the calculative identification is comparable with those obtained with standard substances.

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