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The use of a nonlinear equation for calculation of the retention indices of polar substances in gas chromatography with linear temperature programming

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New possibilities for using the equation that takes into account the nonlinear variation of parameters of the reference *n*-alkane scale for the calculation of retention indices of polar substances at different modes of temperature programming were considered. The advantages of this equation over the linear scale used traditionally were demonstrated in relation to C_3—C_{11} alkan-1-ols. The equation appears to have considerable promise regarding the search for the equivalent isothermal index.

Key words: capillary GC, linear temperature programming, alkan-1-ols, retention indices, nonlinear equation.

The problem of reproducibility of the retention indices of sorbates in gas chromatography with linear temperature programming (TPGC) and the relationship between these values and the isothermal retention indices is still of considerable interest. When analysis is carried out under isothermal conditions, the retention indices (I) are determined using the logarithmic scale of the retention parameters of *n*-alkanes as the reference series[1]

$$I = 100n + 100(\log V_x' - \log V_n')/(\log V'_{n+1} - \log V_n'), \quad (1)$$

where V_x', V_n', and V'_{n+1} are the corrected retention volumes of the substance x and two *n*-alkanes with the numbers of carbon atoms n and $n + 1$ between which the analyte is eluted. The corrected retention volumes in Eq. (1) can be replaced by the corresponding corrected retention times t' or retention factors k.[2]

In the case of analysis with linear temperature programming, the linear scale of the retention temperatures of *n*-alkanes is taken as the reference scale.[3] The retention indices for programming $I_{\rm pr}$ are calculated from the equation

$$I_{\rm pr} = 100n + 100(T_x - T_n)/(T_{n+1} - T_n), \quad (2)$$

where T_x, T_n, and T_{n+1} are the retention temperatures of the substance x under analysis and two *n*-alkanes between which it is eluted. The retention temperatures in Eq. (2) can be replaced by the corresponding retention times t_x, t_n, and t_{n+1} for the compound x and *n*-alkanes C_n and C_{n+1} because

$$T_x = T_0 + r \cdot t_x, \qquad T_x - T_n = r(t_x - t_n),$$
$$T_{n+1} - T_n = r(t_{n+1} - t_n),$$

where T_0 is the initial temperature of programming, r is the rate of programming of the analysis temperature.

One condition needed to calculate $I_{\rm pr}$ from Eq. (2) is the presence of two reference *n*-alkanes C_n and C_{n+1} for each substance x under analysis, between which this substance is eluted. However, the fulfillment of this condition does not ensure good reproducibility of the retention indices. The values of retention indices determined by TPGC are more poorly reproduced than those found under isothermal conditions; this hampers the use of these values for identification of components of complex mixtures. Previously,[4—7] attempts have been made to predict $I_{\rm pr}$ from the data of isothermal analysis. The empirical formulas proposed in these studies did not include characteristics of the TPGC experiment. On the basis of investigation of the dependence of $I_{\rm pr}$ on the TPGC parameters, a formula for predicting $I_{\rm pr}$ values for methyl ketones on polar and nonpolar columns in different modes of programming has been proposed.[8] A theoretical consideration concerning the transformation of $I_{\rm pr}$ into the equivalent isothermal index[9,10] resulted in elucidation of the dependence of the reproducibility of the indices obtained with temperature programming on the hold-up time of the nonsorbed gas t_0, which varies as a function of the temperatures of elution of the substance under analysis and the reference *n*-alkanes under TPGC conditions. Based on these studies, a method for the calculation of the $I_{\rm pr}$ values as well as the thermodynamic parameters, ΔH and ΔS, was proposed; however, it has not found practical application.

Analysis of the published data shows that the calculations according to Eq. (2) do not take into account a number of factors influencing the retention parameters, in particular, the nonlinear pattern of variation of the retention parameters under the TPGC conditions.[11,12] Study of the behavior of *n*-alkanes showed that the temperature increment of the retention parameters dt'/dT varies nonlinearly depending on the temperature range

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† Deceased.

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used in TPGC. It has been found experimentally[13] that the temperature increment for the homologous series of *n*-alkanes can vary by 60—80%. Variable temperature increments are also found for each homologue in the *n*-alkane series. The retention indices of substances for chromatography with temperature programming can be determined using the linear equation proposed previously for calculating the coefficients for the reference scale of *n*-alkanes[14]

$$I_{\mathrm{pr}} = A_n + B_n \cdot t_x' + C_n \ln t_x' + D_n/t_x', \qquad (3)$$

where A_n, B_n, C_n, and D_n are coefficients determined from the retention parameters of *n*-alkanes; t_x' is the corrected retention time of substance *x*. Instead of t_x', the retention factor k_x can be used.

Non-linear equation (3) allows one to carry out interpolation and extrapolation calculations of I_{pr} with high accuracy. The experimental verification of Eq. (3) performed in relation to analysis of complex mixtures of fatty acid esters in twelve different TPGC modes[14] confirmed good reproducibility of the I_{pr} values. The assay was performed for low-polarity compounds. Meanwhile, it still remains unclear whether Eq. (3) is valid for the description of the chromatographic behavior of polar substances in different temperature-programming modes.

In this work an attempt is made to use Eq. (3) to calculate the retention parameters of polar compounds in TPGC, taking the series of *n*-alkanols as an example, and to study the interpolation and extrapolation potential of this equation.

Experimental

GC analysis was carried on a Micromat 412 chromatograph (Finland) using two fused silica capillary columns, one with the nonpolar stationary phase, SE-30 (25 m × 0.32 mm), layer thickness d_f = 1.0 μm (Nordion Instr., Finland), and one with the polar phase PEG-40M/Na_3PO_4 (25 m × 0.32 mm), d_f = 0.20 μm prepared by a known procedure.[15] The compounds analyzed were C_5—C_{15} *n*-alkanes and C_3—C_9, C_{11} alkan-1-ols. The linear temperature programming with the initial temperature T_0 = 60 °C and the heating rates r = 2, 4, 6, and 8 deg $\min^{-1}$ was used. The injector temperature was 225 °C, the temperature of the flame ionization detector was 250 °C. The excess pressure of the carrier gas (helium) at the inlet of the column was 0.7 atm, and the split ratio at the inlet of the column was 1 : 100. The sample volume was 0.2—0.3 μL of the vapor of a mixture of *n*-alkanes or alkan-1-ols.

The retention factors were calculated from the equation

$$k_x = t_x'/\delta_0, \qquad (4)$$

where t_x' is the corrected retention time of the compound *x*;

$$t_x' = t_x - \delta_0, \qquad (5)$$

δ_0 is the hold-up time of the nonsorbed gas in the column, which is found from the relation

$$\delta_0 = [t_0(T_0) + t_0(T_x)]/2, \qquad (6)$$

where $t_0(T_0)$ and $t_0(T_x)$ are the times of elution of methane at the initial temperature of analysis T_0 and at the temperature of elution of the analyte T_x. The I_{pr} values were determined on the basis of five to seven parallel runs; the error did not exceed 1 i.u. The corrected retention times and retention factors of *n*-alkanes and alkan-1-ols are listed in Tables 1 and 2.

Table 1. Corrected retention times (t'/s) of *n*-alkanes and alkan-1-ols in different temperature programming modes (r = 2—8) on polar and nonpolar capillary columns at T_0 = 60 °C

Compound	r/deg $\min^{-1}$						
	2	4	6	8	4	6	8
	SE-30				PEG-40M/Na_3PO_4		
n-Alkane							
C_5	20.3	19.6	19.5	18.5	—	—	—
C_6	46.3	44.2	43.2	40.4	—	—	—
C_7	102.3	95.0	89.5	82.7	—	—	—
C_8	214.9	188.7	170.9	153.4	41.0	37.9	35.5
C_9	412.0	336.0	290.6	252.6	80.2	72.7	66.5
C_{10}	711.3	535.1	439.0	371.2	146.5	129.5	115.6
C_{11}	1091.8	759.3	603.2	497.1	245.5	212.0	184.4
C_{12}	1515.1	995.2	765.3	623.5	388.1	317.1	269.5
C_{13}	—	1229.4	925.1	745.8	553.9	437.2	363.9
C_{14}	—	1455.8	1079.6	862.8	741.1	571.6	467.6
C_{15}	—	—	—	—	923.0	692.8	562.7
Alkan-1-ol							
C_3	30.8	29.5	29.3	27.3	50.5	46.3	43.2
C_4	72.7	68.2	65.1	60.3	100.1	90.2	82.3
C_5	161.3	143.5	132.7	120.1	185.4	161.0	141.2
C_6	326.0	272.3	239.5	210.2	306.9	255.9	218.4
C_7	591.4	454.4	379.9	323.7	460.9	369.9	312.3
C_8	948.8	673.6	539.6	449.0	635.3	494.0	410.1
C_9	1362.7	908.7	705.0	576.8	816.4	619.6	507.5
C_{11}	—	1375.7	1025.6	821.7	—	—	—

Table 2. Retention factors (k) of n-alkanes and alkan-1-ols at in different temperature programming modes (r = 2—8) on polar and nonpolar capillary columns at T_0 = 60 °C

Compound	r/deg min^{-1}						
	2	4	6	8	4	6	8
	SE-30				PEG-40M/Na_3PO_4		
n-Alkane							
C_5	0.38	0.36	0.36	0.34	—	—	—
C_6	0.86	0.82	0.80	0.75	—	—	—
C_7	1.90	1.76	1.65	1.52	—	—	—
C_8	3.97	3.47	3.12	2.79	0.55	0.51	0.47
C_9	7.57	6.12	5.26	4.54	1.08	0.97	0.88
C_{10}	12.96	9.64	7.84	6.58	1.96	1.72	1.53
C_{11}	19.67	13.51	10.62	8.69	3.31	2.80	2.42
C_{12}	29.96	17.46	13.29	10.75	5.11	4.14	3.50
C_{13}	—	21.27	15.84	12.68	7.22	5.66	4.68
C_{14}	—	24.89	18.27	14.48	9.56	7.31	5.94
C_{15}	—	—	—	—	11.79	8.24	7.07
Alkan-1-ol							
C_3	0.57	0.55	0.54	0.50	0.68	0.62	0.58
C_4	1.35	1.26	1.20	1.11	1.34	1.20	1.09
C_5	2.99	2.64	2.44	2.19	2.47	2.14	1.82
C_6	6.02	4.98	4.35	3.80	4.06	3.36	2.76
C_7	10.81	8.22	6.82	5.77	6.05	4.82	4.04
C_8	17.19	12.03	9.55	7.89	8.25	6.36	5.24
C_9	24.38	16.03	12.30	10.00	10.49	7.89	6.42
C_{11}	—	23.64	17.44	13.86	—	—	—

Results and Discussion

The nonlinear equation proposed previously for the calculation of the retention indices I_{pr} of compounds analyzed by TPGC[14] makes it possible to calculate the I_{pr} values for alkan-1-ols for a wide range of heating rates (Tables 3 and 4). Both the corrected retention times t' (see Eq. (3) and Table 1) and the retention factors k (see Eq. (7) and Table 2) were used as the parameters for the equation

$$I_{pr} = A_n' + B_n' \cdot k_x + C_n' \ln k_x + D_n'/k_x. \qquad (7)$$

The coefficients of Eqs. (3) and (7) were calculated by the least-squares method using the t' and k values found experimentally for a number of n-alkanes assuming that for alkanes, $I_{pr} = 100n$. Then, by substituting the t' and k values found for alkan-1-ols into Eqs. (3) or (7), respectively, their I_{pr} values were calculated.

As an example, we will consider the calculation of I_{pr} on a column with SE-30 for heptan-1-ol using Eq. (3) at T_0 = 60 °C and r = 6 deg min^{-1} and a mixture of C_5, C_7, C_{10}, and C_{13} n-alkanes as the reference series. The experimental t' values for n-alkanes and heptan-1-ol were taken from Table 1. The coefficients of Eq. (3) were found from t' for n-alkanes

$$500 = A + B \cdot 19.5 + C \cdot \ln 19.5 + D/19.5,$$

$$700 = A + B \cdot 89.5 + C \cdot \ln 89.5 + D/89.5,$$

$$1000 = A + B \cdot 439.0 + C \cdot \ln 439.0 + D/439.0,$$

$$1300 = A + B \cdot 925.1 + C \cdot \ln 925.1 + D/925.1.$$

This gave A = 363.0; B = 0.51; C = 68.6; and D = −1494.0. By substituting these values into Eq. (3), we found the I_{pr} value for heptan-1-ol, for which t' = 373.9

$$I_{pr} = 363.0 + 0.51 \cdot 379.9 + 68.6 \cdot \ln 379.9 - 1494.0/373.9.$$

The calculation gives I_{pr} = 960 (see Table 3). Similarly, the I_{pr} values for the compounds under investigation were found using the retention factors k and Eq. (7).

Unlike the classical van der Dool and Kratz equation,[3] the equations that we propose take into account the nonlinear variation of the retention parameters of n-alkanes with the analysis temperature and permit the calculation of I_{pr} without the full set of reference n-alkanes. The interpolation and extrapolation techniques used for this purpose extend the scale of n-alkanes, while maintaining the accuracy of determination of the retention indices. To verify the interpolation and extrapolation properties of Eqs. (3) and (7), we used different sets of n-alkanes. The results of calculation of the I_{pr} values for a column with SE-30 are presented in Table 3. It can be seen from the data obtained that the I_{pr} values for alkan-1-ols remain constant to within the experimental error irrespective of the ten- or four-member set of n-alkanes chosen.

The coefficients of Eqs. (3) and (7) depend slightly on the set of reference n-alkanes used but change as functions of the heating rate. The data of Table 3 also demonstrate that the use of the k parameters in the calculation of I_{pr} is preferred because they ensure a higher accuracy of calculations than t'. This is apparently due to the fact that the retention factors k are relative values. When the k scale of n-alkanes is employed to calculate I_{pr} from Eq. (7), the standard deviation exceeds the experimental error only for the last homolog, undecan-1-ol (see Table 3).

In order to extend the scope of applicability of Eq. (7), we analyzed the homologous series of alkan-1-ols on a column with a polar stationary phase, PEG-40M/Na_3PO_4, using the same temperature-programming modes. The results of calculations using Eqs. (3) and (7) of the retention indices I_{pr} of alkan-1-ols on this column for temperature programming with r = 4 and 8 deg min^{-1} are presented in Table 4. Since the retention indices of alkan-1-ols on a polar column with PEG-40M/Na_3PO_4 are higher than those on the nonpolar SE-30 phase, mixtures of n-alkanes with higher molecular masses, C_8—C_{15}, were chosen in this case for the calculation of I_{pr}; however, the results were the same as those found for the nonpolar column with SE-30. Thus, the proposed Eqs. (3) and (7) are convenient for the calculation of retention indices for gas chromatography with temperature programming on columns with both polar and nonpolar phases and are promising for the search for the equivalent isothermal index. The I_{pr} values are well reproducible and can be used for identification of polar compounds in complex mixtures. The results of the investigation allow the

Table 3. Retention indices I_{pr} for alkan-1-ols for temperature programming on a nonpolar column with SE-30 calculated from Eqs. (3) and (7) using various sets (*1—3*) of *n*-alkanes (T_0 = 60 °C, r = 2, 4, 6, 8 deg min^{-1})

Equation, sets of *n*-alkanes*	Alkan-1-ol								Coefficient			
	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{11}	A (A')	B (B')	C (C')	D (D')
						r = 2						
(3)												
1	551	660	759	860	963	1065	1163		179.9	0.14	109.8	−280.9
2	552	660	759	860	962	1063	1160		187.6	0.14	109.4	−342.5
3	553	658	759	860	964	1068	1168		196.4	0.15	106.4	−399.7
(7)												
1	552	658	759	860	964	1068	1165		(618.5)	(8.38)	(107.4)	(−6.6)
2	553	657	759	860	964	1067	1166		(621.1)	(8.54)	(105.4)	(−8.1)
3	553	658	759	869	962	1067	1166		(622.2)	(8.87)	(102.9)	(−9.5)
						r = 4						
(3)												
1	555	659	754	854	958	1064	1166	1355	303.7	0.33	82.8	−1149.4
2	556	660	756	856	961	1066	1167	1353	286.2	0.32	86.8	−996.1
3	556	659	755	855	959	1066	1169	1359	294.4	0.33	84.6	−1029.0
(7)												
1	556	660	754	853	959	1067	1172	1360	(639.0)	(20.97)	(71.7)	(−28.0)
2	557	661	756	855	960	1067	1170	1353	(637.4)	(20.10)	(76.4)	(−24.6)
3	557	660	753	852	958	1066	1170	1357	(636.9)	(20.68)	(73.4)	(−25.6)
						r = 6						
(3)												
1	557	659	754	854	959	1065	1169	1358	364.7	0.51	68.1	−1547.4
2	559	661	754	855	959	1064	1166	1353	365.1	0.50	68.7	−1540.1
3	559	660	755	855	960	1067	1170	1360	363.0	0.51	68.6	−1494.0
(7)												
1	559	659	752	852	959	1068	1172	1360	(641.4)	(32.74)	(52.2)	(−37.2)
2	561	662	755	854	960	1067	1169	1354	(645.1)	(32.07)	(52.9)	(−37.2)
3	561	661	753	852	959	1067	1171	1357	(643.0)	(32.69)	(51.2)	(−37.1)
						r = 8						
(3)												
1	556	658	753	854	960	1067	1171	1361	405.5	0.69	58.2	−1669.8
2	557	660	754	854	959	1064	1165	1351	400.1	0.67	60.0	−1624.9
3	558	659	754	854	960	1066	1169	1359	411.9	0.69	57.0	−1680.0
(7)												
1	558	659	751	852	960	1068	1173	1359	(641.9)	(44.8)	(37.8)	(−40.8)
2	560	661	754	854	960	1067	1170	1352	(645.1)	(43.7)	(39.8)	(−40.2)
3	560	660	752	851	958	1066	1170	1356	(645.1)	(44.9)	(34.9)	(−42.1)

Note. Set *1* is C_5—C_{14}; set *2* is C_5, C_7, C_9, C_{11}, C_{12}; set *3* is C_5, C_7, C_{10}, C_{12}.

Table 4. Retention indices I_{pr} for alkan-1-ols for temperature programming on a polar column with PEG-40M/Na_3PO_4 calculated from Eqs. (3) and (7) using various sets (*1—3*) of *n*-alkanes (T_0 = 60 °C, r = 4 and 8 deg min^{-1})

Equation, sets of *n*-alkanes*	Alkan-1-ol							Coefficient			
	C_3	C_4	C_5	C_6	C_7	C_8	C_9	A (A')	B (B')	C (C')	D (D')
						r = 4					
(3)											
1	831	936	1039	1141	1243	1343	1439	439.1	0.38	103.1	−1580.2
2	831	935	1039	1142	1244	1346	1442	420.9	0.38	106.2	−1288.4
3	831	934	1039	1143	1247	1349	1446	397.7	0.38	110.3	−933.5
(7)											
1	832	937	1040	1142	1246	1348	1443	(886.6)	(32.4)	(93.3)	(−27.4)
2	832	936	1039	1142	1247	1349	1445	(881.1)	(32.3)	(96.8)	(−23.0)
3	831	934	1038	1142	1248	1350	1447	(874.6)	(32.0)	(101.3)	(−17.6)

(*to be continued*)

Table 4 (*continue*)

Equation, набор алканов*	Alkan-1-ol							Coefficient			
	C_3	C_4	C_5	C_6	C_7	C_8	C_9	A (A')	B (B')	C (C')	D (D')
						$r = 8$					
(3)											
1	832	938	1038	1140	1246	1347	1442	556.6	0.8	77.7	−2238.9
2	831	936	1038	1140	1247	1349	1445	532.4	0.8	82.0	−1921.3
3	831	936	1037	1140	1248	1350	1447	515.0	0.8	85.0	−1664.6
(7)											
1	832	938	1033	1131	1247	1348	1443	(893.2)	(70.1)	(57.4)	(−40.1)
2	830	937	1032	1131	1248	1351	1446	(884.6)	(69.5)	(65.1)	(−32.5)
3	832	935	1031	1130	1248	1351	1448	(880.8)	(69.9)	(66.2)	(−30.7)

* Set *1* is C_8—C_{15}; set *2* is C_8, C_9, C_{11}, C_{13}, C_{15}; set *3* is C_8, C_9, C_{12}, C_{15}.

conclusion that, without allowance made for the nonlinear behavior of the scale of *н*-alkanes under the TPGC conditions, it is difficult to derive correlations that would relate the isothermal retention index to the retenion indices found with temperature programming.

The rates used in the temperature programming in this study, r = 2—8 deg min^{-1}, cover almost the whole range of heating rates used conventionally in analyses.

The data obtained here indicate that the nonlinear equations we propose, whose coefficients are found from the retention parameters of *n*-alkanes, are applicable to the calculation of retention indices of polar compounds on polar and nonpolar columns in capillary gas chromatography with linear temperature programming. The equations permit the calculation of the retention indices for a mixture of compounds in the absence of a full set of reference *n*-alkanes.

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