CHROM. 16,320

CONTRIBUTION TO THE CALCULATION OF THE CONSTANTS OF THE n-ALKANE RETENTION TIME CURVE AND GAS HOLD-UP TIME IN GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

There is a lack of methods in which the parameters of the function of logarithm of adjusted retention time *versus* carbon number can be calculated by a numerical technique from the uncorrected retention times of neither successive nor evenly spaced homologues. In this paper some simple expressions for the calculation of the constants of the n-alkane retention time curve and gas hold-up time in gas–liquid chromatography are introduced in order to eliminate the above problem. The numerical results obtained by using the new method are compared with those obtained by an iterative method.

INTRODUCTION

The determination of Kováts[1] retention indices is connected directly or indirectly with the calculation of the parameters of the equation

$$\log [t_{R(Z)} - t_M] = bZ + c \qquad (1)$$

where $t_{R(Z)}$ is the uncorrected retention time of an n-alkane of carbon number Z, b and c are the slope and intercept, respectively, and t_M is the gas hold-up time.

Of the classical algorithms, the methods of Peterson and Hirsch[2], Hafferkamp[3], Hansen and Andresen[4], Al-Thamir *et al.*[5], Ševčík[6] and Ševčík and Löwentap[7] all require the use of evenly spaced homologues. However, there are some classical methods that do not require the above restriction. For example, the method of Gold[8] contains a successive approximation step and that of Garcia-Dominguez *et al.*[9] is a combination of numerical and iterative methods.

Wainwright and Haken[10] presented a detailed evaluation of procedures for the determination of gas hold-up time and discussed the classical and statistical or iterative procedures for determining t_M.

Among the statistical and iterative methods, the method of Gröbler and Bá-lizs[11] has been commonly used, but it also requires successive homologues. The differences between the theoretical and calculated retention indices were minimized in the iterative method of Guardino et al.[12], which contains an iteration on t_M and a least-squares fitting to b and c. The iteration step requires an initial value of t_M calculated according to Hafferkamp[3].

After a critical evaluation of the reported methods, we developed a mathematical method that allows the calculation of the constants b, c and t_M for non-successive n-alkanes[13].

THEORETICAL

Computer method for calculation of the constants of the n-alkane retention time curve formed by either successive or non-successive series

The later derived equations for calculating b, c and t_M were validated by comparison of their results with those of an iterative technique prepared by one of the authors (E.Z.). The computer program used is applicable to either successive or non-successive series.

First, the program computes the estimates of the parameters t_M, A and B of the model represented by eqn. 2 (this model is identical with the objective function used by Guardino et al.[12]),

$$\log (t_R - t_M) = AI + B \tag{2}$$

on the basis of t_{R_i} and I_i ($i = 1, 2, ..., n$) data for the n-alkane series, where t_{R_i} and I_i are the uncorrected retention times and the theoretical retention indices of the ith n-alkane of the investigated series with n members, respectively, by means of minimizing the deviation

$$\sum (I_i - \hat{I}_i)^2 \tag{3}$$

where $\hat{I}_i$ is the estimated retention index of the ith homologous member.

To estimate the parameters of eqn. 2 the estimate of t_M must be computed first. On the basis of data pairs (t_{R_i}, I_i) obtained by measurements on the n-alkanes, the coefficient of determination (R^2) between the quantities I_i and $\log(t_{R_i} - t_M)$ as a function of t_M is

$$R^2 = R^2(t_M) = \frac{\left[\sum \log (t_{R_i} - t_M)\left(I_i - \frac{\sum I_i}{n}\right)\right]^2}{\left[\sum I_i^2 - \frac{(\sum I_i)^2}{n}\right]\left\{\sum [\log(t_{R_i} - t_M)]^2 - \frac{[\sum \log(t_{R_i} - t_M)]^2}{n}\right\}} \tag{4}$$

For calculating the gas hold-up time we can use the value at which $R^2(t_M)$ is a maximum. This value of t_M can be obtained by solving the non-linear equation

$$\frac{dR^2}{dt_M} = 0 \tag{5}$$

by an iterative technique.

With a knowledge of t_M, the estimates of A and B can be computed by the linear regression of I *versus* $\log(t_R - t_M)$.

The constants b and c in eqn. 1 can be given as follows, from the parameters A and B of eqn. 2:

$$b = \frac{1}{A}; \quad c = -\frac{B}{A} \tag{6}$$

EXPERIMENTAL

A Carlo Erba Model D gas chromatograph equipped with a flame-ionization detector was used for measuring the retention times. The carrier gas was nitrogen. All measurements were repeated three times and the average retention times were used in the calculations.

n-Alkanes were selected as members of a referencia kit (Reanal, Budapest, Hungary). The amounts injected were 0.05–0.1 μl.

The chromatographic parameters are shown in Table I.

TABLE I

CHROMATOGRAPHIC PARAMETERS USED FOR MEASURING THE RETENTION TIMES OF *n*-AL-KANES

Column	Support material	Stationary phase	Column temperature (°C)	Injection port temperature (°C)	Carrier gas flow-rate (cm³/min)*
Stainless steel (350 × 0.5 cm)	Kieselguhr silanized (0.1–0.2 mm)	SE-30 (10%, w/w)	130	250	50
Glass (220 × 0.27 cm)	Gas-Chrom Q silanized (80–120 mesh)	Carbowax 20M (12%, w/w)	125	200	42
Stainless steel (150 × 0.2 cm)	Chromosorb W AW (60–80 mesh)	Hallcomid M-18** (9%, w/w)	75	200	13

  * The carrier gas flow-rate was calculated for an outlet pressure of 100 kPa and for the column temperature.
  ** N,N-Dimethylstearicamide.

Expression of the constant of b from uncorrected retention data of three non-successive n-alkanes

Assume that there is one homologous member with unknown retention and three that are known. If the known retention times are $t_{R(Z)}$, $t_{R(Z+1)}$ and $t_{R(Z+3)}$ and $t_{R(Z+2)}$ is the unknown, the value of b will be expressed by

$$b = \log \left[\frac{\sqrt{\dfrac{4t_{R(Z+3)} - 3t_{R(Z+1)} - t_{R(Z)}}{t_{R(Z+1)} - t_{R(Z)}}} - 1}{2} \right] \tag{7}$$

As an illustration, we present a calculation with some data from Table II [$t_{R(12)}$ = 104.4, $t_{R(13)}$ = 153.9 and $t_{R(15)}$ = 365.8]. Inserting these values into eqn. 7 we obtain

$$b = \log \left(\frac{\sqrt{\dfrac{4 \cdot 365.8 - 3 \cdot 153.9 - 104.4}{153.9 - 104.4}} - 1}{2} \right) = 0.2118$$

If the known retention times are $t_{R(Z)}$, $t_{R(Z+2)}$ and $t_{R(Z+3)}$ and $t_{R(Z+1)}$ is the unknown, the value of b will be expressed by

$$b = \log \left\{ \frac{t_{R(Z+3)} - t_{R(Z+2)} + \sqrt{[t_{R(Z+2)} - t_{R(Z+3)}][4t_{R(Z)} - 3t_{R(Z+2)} - t_{R(Z+3)}]}}{2[t_{R(Z+2)} - t_{R(Z)}]} \right\} \tag{8}$$

Inserting values from Table III (Z = 12, $t_{R(12)}$ = 104.4, $t_{R(14)}$ = 234.5, $t_{R(15)}$ = 365.8) into eqn. 8, we obtain

$$b = \log \frac{365.8 - 234.5 + \sqrt{(234.5 - 365.8)(4 \cdot 104.4 - 3 \cdot 234.5 - 365.8)}}{2(234.5 - 104.4)}$$
$$= 0.2119$$

If the known retention times are $t_{R(Z)}$, $t_{R(Z+3)}$ and $t_{R(Z+4)}$ and $t_{R(Z+1)}$ and $t_{R(Z+2)}$ are unknowns, but let

$$q = -0.12963 + \frac{t_{R(Z)} - t_{R(Z+3)}}{2[t_{R(Z+4)} - t_{R(Z+3)}]} \tag{9}$$

$$U = \sqrt[3]{-q + \sqrt{0.01097 + q^2}} \tag{10}$$

and

$$V = \sqrt[3]{-q - \sqrt{0.01097 + q^2}} \tag{11}$$

then b can be expressed as

$$b = \log \left(\frac{1}{U + V - 1/3} \right) \tag{12}$$

Inserting values from Table IV [$t_{R(12)}$ = 104.4, $t_{R(15)}$ = 365.8 and $t_{R(16)}$ = 579.0] into eqns. 9–12, we obtain

$$q = -0.12963 + \frac{104.4 - 365.8}{2(579.0 - 365.8)} = -0.7427$$

$$U = \sqrt[3]{0.7427 + \sqrt{0.01097 + 0.7427^2}} = 1.1429$$

$$V = \sqrt[3]{0.7427 - \sqrt{0.01097 + 0.7427^2}} = -0.1944$$

and

$$b = \log \left(\frac{1}{1.1429 - 0.1944 - 1/3} \right) = 0.2111$$

If the known retention times are $t_{R(Z)}$, $t_{R(Z+1)}$ and $t_{R(Z+4)}$ and $t_{R(Z+2)}$ and $t_{R(Z+3)}$ are unknowns, then

$$b = \log (U + V - 1/3) \tag{13}$$

where

$$q = -0.12963 + \frac{t_{R(Z+1)} - t_{R(Z+4)}}{2[t_{R(Z+1)} - t_{R(Z)}]} \tag{14}$$

As an example, inserting values from Table V [$t_{R(12)} = 104.4$, $t_{R(13)} = 153.9$ and $t_{R(16)} = 579.0$] into eqns. 14, 10, 11 and 13, we obtain

$$q = -0.12963 + \frac{153.9 - 579.0}{2(153.9 - 104.4)} = -4.4236$$

$$U = \sqrt[3]{4.4236 + \sqrt{0.01097 + 4.4236^2}} = 2.0683$$

$$V = \sqrt[3]{4.4236 - \sqrt{0.01097 + 4.4236^2}} = -0.1074$$

and

$$b = \log (2.0683 - 0.1074 - 1/3) = 0.2115$$

After obtaining the value of b, the value of c can be calculated from every two retention time combinations. After calculating c, the value of t_M can be obtained from every known retention time using the earlier expressions[5,9]. The following equations can be considered suitable, among others:

$$c = \log \left[\frac{t_{R(Z_j)} - t_{R(Z_i)}}{\exp(bZ_j) - \exp(bZ_i)} \right] (j > i) \tag{15}$$

where $t_{R(Z_i)}$ and $t_{R(Z_j)}$ are the uncorrected retention times of the homologous members with carbon numbers Z_i and Z_j.

and

$$t_M = t_{R(Z)} - \exp(bZ + c) \tag{16}$$

TABLE II

COMPARISON OF THE VALUES OF b, c AND t_M CALCULATED BY THE ITERATIVE METHOD AND BY THE NUMERICAL METHOD WITH EQNS. 7, 15 AND 16

Stationary phase	Carbon numbers (above) and uncorrected retention times (sec) (below)				b		c		t_M	
					Iterative	Eqn. 7	Iterative	Eqn. 15	Iterative	Eqn. 16
Carbowax 20M	12 / 104.4	13 / 153.9	14 / –	15 / 365.8	0.2118	0.2118	−0.6454	−0.6454	25.6	25.6
	13 / 153.9	14 / 234.5	15 / –	16 / 579.0	0.2114	0.2114	−0.6390	−0.6390	25.4	25.4
SE-30	5 / 138.5	6 / 173.0	7 / –	8 / 343.5	0.2501	0.2501	0.3961	0.3962	94.2	94.2
	6 / 173.0	7 / 284.5	8 / –	9 / 537.0	0.2493	0.2492	0.4038	0.4039	93.7	93.7
Hallcomid M-18	7 / 81.4	8 / 132.7	– / –	10 / 532.7	0.3686	0.3686	−0.9961	−0.9963	43.0	43.0
	8 / 132.7	9 / 252.6	10 / –	11 / 1187	0.3685	0.3685	−0.9948	−0.9948	43.0	43.0

TABLE III

COMPARISON OF THE VALUES OF b, c AND t_M CALCULATED BY THE ITERATIVE METHOD AND BY THE NUMERICAL METHOD WITH EQNS. 8, 15 AND 16

Stationary phase	Carbon numbers (above) and uncorrected retention times (sec) (below)								b		c		t_M	
									Iterative	Eqn. 10	Iterative	Eqn. 15	Iterative	Eqn. 16
Carbowax 20M	12	13	—	14		15			0.2119	0.2119	−0.6465	−0.6465	25.7	25.7
	104.4			234.5		365.8								
	13	14	—	15		16			0.2109	0.2109	−0.6309	−0.6309	24.8	24.8
	153.9			365.8		579.0								
SE-30	5	6	—	7		8			0.2492	0.2492	0.4035	0.4036	93.9	93.9
	138.5			234.5		343.5								
	6	7	—	8		9			0.2499	0.2499	0.3977	0.3978	94.1	94.1
	173.0			343.5		537.5								
Hallcomid M-18	7	8	—	9		10			0.3685	0.3685	−0.9955	−0.9954	43.0	43.0
	81.4			252.6		532.7								
	8	9	—	10		11			0.3685	0.3685	−0.9947	−0.9948	43.0	43.0
	132.7			532.7		1187								

TABLE IV

COMPARISON OF THE VALUES OF b, c AND t_M CALCULATED BY THE ITERATIVE METHOD AND BY THE NUMERICAL METHOD WITH EQNS. 9–12, 15 AND 16

Stationary phase	Carbon numbers (above) and uncorrected retention times (sec) (below)					b		c		t_M	
						Iterative	Eqns. 9–12	Iterative	Eqn. 15	Iterative	Eqn. 16
Carbowax 20M	12 104.4	13 –	14 –	15 365.8	16 579.0	0.2111	0.2111	−0.6338	−0.6335	25.1	25.1
SE-30	5 138.5	6 –	7 –	8 343.5	9 537.5	0.2499	0.2499	0.3975	0.3976	94.1	94.1
Hallcomid M-18	7 81.4	8 –	9 –	10 532.7	11 1187	0.3685	0.3684	−0.9950	−0.9947	43.0	43.0

TABLE V

COMPARISON OF THE VALUES OF b, c AND t_M CALCULATED BY THE ITERATIVE METHOD AND BY THE NUMERICAL METHOD WITH EQNS. 10–11, 13–14, 15 AND 16

Stationary phase	Carbon numbers (above) and uncorrected retention times (sec) (below)					b		c		t_M	
						Iterative	Eqns. 10–11, 13–14	Iterative	Eqn. 15	Iterative	Eqn. 16
SE-30	5 138.5	6 173.0	7 –	8 –	9 537.5	0.2500	0.2500	0.3965	0.3965	94.2	94.2
Carbowax 20M	12 104.4	13 153.9	14 –	15 –	16 579.0	0.2115	0.2115	−0.6416	−0.6415	25.5	25.5
Hallcomid M-18	7 81.4	8 132.7	9 –	10 –	11 1187	0.3686	0.3686	−0.9959	−0.9959	43.0	43.0

RESULTS AND DISCUSSION

Values of b, c and t_M calculated from retention data for three non-successive n-alkanes (one of which has an unknown retention time) by the proposed numerical method are presented in Table II and III and compared with corresponding values obtained by the iterative technique. The differences in the fourth decimal figure can be regarded as a consequence of rounding off.

Tables IV and V show the values of b, c and t_M calculated from the retention times of three non-successive n-alkanes. There are two successive members with unknown retention times in the interval determined by the lowest and the highest carbon numbers. The values of b obtained by the proposed numerical method agree with those calculated by the iterative method. The values of c calculated by the numerical and iterative methods show slight differences in the third decimal figures, but the corresponding values of t_M are the same.

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