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CALCULATION OF CONSTANTS OF LOGARITHMIC ADJUSTED RETENTION TIME *VERSUS* CARBON NUMBER FUNCTION USED IN GAS-LIQUID CHROMATOGRAPHY

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SUMMARY

New equations are given for the calculation of constants of the logarithmic adjusted retention time *versus* carbon number function for consecutive homologous series. These equations take into consideration all of the retention times of any number of investigated homologues. The numerical results agree well with those of Gröbner's statistical method and those of an iterative algorithm.

INTRODUCTION

Many publications during the last 25 years have dealt with problems concerning the logarithmic adjusted retention time *versus* carbon number function. The main problems relate to the linearity of this function and/or to the methods of calculation of constants of the function

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

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

The mathematical methods for determining the constants b , c and t_M can be divided into two basic groups: (i) classical and statistical and (ii) iterative methods. The statistical and iterative methods have the advantage that they take into consideration the scatter of the measured data and the whole plot of the curve. Most classical methods use the retention times of two, three or four consecutive homologues for the determination of t_M and two or three retention times for the calculation of b and c .

Many workers have evaluated and compared the different methods for calculating or computing the constants in eqn. 1, especially the gas hold-up time. We cite here only to some review papers without claiming to be complete¹⁻¹⁰.

In this paper, an equation is derived for expressing the value of b , considering all possible ratios of the differences in retention times of neighbouring members of a consecutive homologous series. Our method can be considered as a classical one, but it gives an equation for the value of b that takes into consideration the retention times of all homologues investigated.

We have worked out expressions for calculating the values of c and t_M by using the value of b , which also take into consideration the retention values of all homologues of a consecutive series.

Numerical results obtained by the use of our expressions are compared with those obtained by the statistical method of Gröbler and Bálizs¹¹ and our recently published iterative method¹².

EXPERIMENTAL

A Carlo Erba D-type gas chromatograph equipped with a flame-ionization detector was used for measuring the retention times. The column dimensions were 100 cm × 5 mm I.D. The stationary phase was OV-17 (5%, w/w) on silanized Chromosorb W (60–80 mesh) (both from Carlo Erba). The column and the injector temperatures were 100 and 150°C, respectively. The carrier gas was nitrogen. The injected n -alkane mixture was prepared by mixing Merck reference substances. The amount injected was 0.05 μ l. The retention times were measured with a stop-watch.

The carbon numbers of the n -alkanes (Z), their average retention times $[\bar{t}_{R(Z)}]$ calculated using the results from six repeated measurements and the standard deviation of in the measurements (s) calculated with the usual equation

$$s = \sqrt{[t_{R(i)} - \bar{t}_R]^2 (n - 1)^{-1}}$$

where s is the standard deviation, $t_{R(i)}$ is the i th retention time ($1 \leq i \leq n$), n is the number of repetitions and \bar{t}_R is the average value of retention times, are given in Table I.

TABLE I
PROPERTIES OF C₉-C₁₃ n -ALKANES

Z	$t_{R(Z)}$ (sec)	s
9	115.7	0.21
10	200.7	0.32
11	370.0	0.66
12	706	3.20
13	1371	6.90

CALCULATIONS

According to Al-Thamir *et al.*¹³, we can express the ratios between two neighbouring retention time differences in the following way:

$$b = \log \frac{\Delta_i}{\Delta_{i-1}} \quad (2)$$

where Δ_i and Δ_{i-1} are consecutive retention differences ($i \geq 2$). If we express the value of b more generally by using not necessarily consecutive retention differences, we obtain

$$b \frac{i}{i-j} = \frac{1}{j} \log \left(\frac{\Delta_i}{\Delta_{i-j}} \right) \quad (1 \leq j \leq i-1) \quad (3)$$

where $b \frac{i}{i-j}$ is the value of b expressed by the ratio of the i th and $(i-j)$ th retention differences.

We obtain $N-1$ Δ values using the retention times of a homologous series with N members. By combining the of these differences by twos we can express altogether $\binom{N-1}{2}$ Δ pairs on the basis of eqn. 3, where $\binom{N-1}{2}$ is the binominal coefficient $\frac{(N-1)!}{2[(N-1)-2]!}$.

We can then calculate $N-2$ values of b from a homologous series having N members (here we have $N-1$ Δ values), using only the neighbouring Δ values for the calculation of b (in this case $j=1$). The sum of these values of b is as follows:

$$\sum_{i=2}^{N-1} b \frac{i}{i-1} = \log \left(\frac{\Delta_2 \Delta_3 \dots \Delta_{N-2} \Delta_{N-1}}{\Delta_1 \Delta_2 \dots \Delta_{N-3} \Delta_{N-2}} \right) \quad (4)$$

where Δ_{N-1} is the retention difference between the N th and the $(N-1)$ th homologues, and so on.

We can obtain $N-3$ values of b using the ratios of those Δ values which follow each other by omission of one Δ (in this case $j=2$). The sum of the values of b is as follows:

$$\sum_{i=3}^{N-1} b \frac{i}{i-2} = \frac{1}{2} \log \left(\frac{\Delta_3 \Delta_4 \dots \Delta_{N-2} \Delta_{N-1}}{\Delta_1 \Delta_2 \dots \Delta_{N-4} \Delta_{N-3}} \right) \quad (5)$$

By increasing the value of j we obtain the ratio of the first and the last of the Δ values (here $j=N-2$):

$$b \frac{i}{i-(N-2)} = \frac{1}{N-2} \log \left(\frac{\Delta_{N-1}}{\Delta_1} \right) \quad (6)$$

The sum of all values of b expressed by all possible values of j (that is, by all possible pairs of Δ values) is given by:

$$\sum_{i-j} b \frac{i}{i-j} = \log \left(\frac{\Delta_2 \Delta_3 \dots \Delta_{N-2} \Delta_{N-1}}{\Delta_1 \Delta_2 \dots \Delta_{N-3} \Delta_{N-2}} \right) +$$

$$+ \frac{1}{2} \log \left(\frac{\Delta_3 \Delta_4 \dots \Delta_{N-2} \Delta_{N-1}}{\Delta_1 \Delta_2 \dots \Delta_{N-4} \Delta_{N-3}} \right) + \dots + \frac{\Delta_1}{N-2} \log \left(\frac{\Delta_{N-1}}{\Delta_1} \right) \quad (7)$$

The transformation of eqn. 7 gives:

$$\sum b \frac{i}{i-j} = \log \prod_{i=1}^L \left(\frac{\Delta_{N-i}}{\Delta_i} \right)^{\frac{1}{i} + \frac{1}{i+1} + \dots + \frac{1}{N-i-1}} \quad (8)$$

where $L = (N-1)/2$ if N is odd and $L = (N/2)-1$ if N is even.

Taking into consideration that we have $\binom{N-1}{2}$ pairs of Δ values, we have the sum of $\binom{N-1}{2}$ values of b , so the average value of b is given by

$$\bar{b} = \frac{1}{\binom{N-1}{2}} \log \prod_{i=1}^L \left(\frac{\Delta_{N-i}}{\Delta_i} \right)^{\frac{1}{i} + \frac{1}{i+1} + \dots + \frac{1}{N-i-1}} \quad (9)$$

A calculation using the data given in the Experimental section is presented next.

The differences between the retention times of consecutive homologues are $\Delta_1 = t_{R(10)} - t_{R(9)} = 85.0$, $\Delta_2 = t_{R(11)} - t_{R(10)} = 169.3$, $\Delta_3 = t_{R(12)} - t_{R(11)} = 336.0$ and $\Delta_4 = t_{R(13)} - t_{R(12)} = 665.0$.

The values of the above-defined symbols are $N = 5$, $\binom{N-1}{2} = \binom{5-1}{2} = 6$ and $L = \frac{5-1}{2} = 2$.

Substituting the above values in eqn. 9, we obtain

$$\bar{b} = \frac{1}{6} \log \left(\frac{665.0}{85.0} \right)^{\frac{1}{1} + \frac{1}{2} + \frac{1}{3}} \cdot \left(\frac{396.0}{169.3} \right)^{\frac{1}{2}} = 0.2978$$

After calculating the average value of b , the values of c and t_M can be obtained by using the expressions published earlier^{5,13,14}. The following equations can be considered to be suitable¹²:

$$c = \log \left[\frac{t_{R(Z_l)} - t_{R(Z_k)}}{\exp(bZ_l) - \exp(bZ_k)} \right] \quad (l > k) \quad (10)$$

and

$$t_M = t_{R(Z)} - \exp(bZ + c) \quad (11)$$

where $t_{R(Z_l)}$ and $t_{R(Z_k)}$ are the retention times of homologues having carbon numbers Z_l and Z_k , respectively.

We can now express $N-1$ values of Δ and same values of c by using eqn. 10 from the retention data for a consecutive series having N members:

$$(N-1)c = \log \left\{ \frac{\Delta_1}{\exp[(Z_1 + 1)\bar{b}] - \exp(Z_1\bar{b})} \right\} +$$

$$\log \left\{ \frac{\Delta_2}{\exp [(Z_1 + 2)\bar{b}] - \exp [(Z_1 + 1)\bar{b}]} \right\} + \dots +$$

$$\log \left\{ \frac{\Delta_{N-1}}{\exp [(Z_1 + N-1)\bar{b}] - \exp [(Z_1 + N-2)\bar{b}]} \right\} \quad (12)$$

where Z_1 is the carbon number of the lowest homologous member.

We can derive eqn. 13 from eqn. 12 by elementary calculations, but the details are omitted:

$$\bar{c} = \log \left[\frac{(\Delta_1 \Delta_2 \dots \Delta_{N-1})^{\frac{1}{N-1}}}{(\exp \bar{b}) - 1} \right] - \frac{\bar{b} (2Z_1 + N - 2)}{2} \quad (13)$$

where \bar{c} is the average value of c taking into consideration all retention times of a consecutive homologous series.

A calculation using the data given in the Experimental section is now presented ($N=5$, $Z_1=9$):

$$\bar{c} = \log \left[\frac{(85.0 \cdot 169.3 \cdot 336.0 \cdot 665.0)^{\frac{1}{4}}}{10^{0.2978} - 1} - \frac{0.2978 (2 \cdot 9 + 5 - 2)}{2} \right] = -0.7436$$

We can also express the average value of t_M for a consecutive homologous series on the basis of eqn. 11, having the values of \bar{b} and \bar{c} . Easy calculations show that

$$\bar{t}_M = \frac{\sum t_{R(Z)}}{N} - \frac{\exp (Z_1 \bar{b} + \bar{c}) [\exp (\bar{b} N) - 1]}{N [(\exp \bar{b}) - 1]} \quad (14)$$

where \bar{t}_M is the average value of the gas hold-up time. The value of \bar{t}_M is not really effected by the carbon number of the lowest member but we have used it in eqn. 14 in order to have a simple form of the expression.

For example, a calculation with the data given in the Experimental section is now presented:

$$\bar{t}_M = \frac{115.7 + 200.7 + 370 + 706 + 1371}{5} -$$

$$\frac{10^{(9 \cdot 0.2978 - 0.7436)} (10^{5 \cdot 0.2978} - 1)}{5(10^{0.2978} - 1)}$$

$$= 29.3 \text{ sec}$$

CONCLUSIONS

Table II shows the values of b , c and t_M calculated by three different methods: by the Gröbler's statistical method¹¹, by our earlier iterative method¹² and by the method proposed here. Table II contains the calculated retention indices of the chromatographed n -alkanes, obtained by using the measured retention times and the numerical values of b , c and t_M obtained by using the above methods.

TABLE II

COMPARISON THE VALUES OF b , c AND t_M OBTAINED BY DIFFERENT METHODS AND THE RETENTION INDICES CALCULATED FROM THEM, AND THE SCATTERS OF RETENTION INDICES

Method	b	c	t_M	I_{C_9}	$I_{C_{10}}$	$I_{C_{11}}$	$I_{C_{12}}$	$I_{C_{13}}$	s
Gröbler's method	0.2978	-0.7437	29.4	899.8	999.8	1100.0	1200.2	1300.0	0.1343
Iterative method	0.2978	-0.7433	29.2	900.0	999.8	1100.0	1200.0	1299.9	0.0838
Present method	0.2978	-0.7436	29.3	899.9	999.8	1100.0	1200.1	1300.0	0.1062

The scatters of the retention indices are also tabulated. The scatters were calculated by using the equation

$$s^* = \sqrt{\frac{\sum(I_t - I_c)^2}{N}} \quad (15)$$

where s^* is the scatter, I_t and I_c are the theoretical and calculated retention indices, respectively and N is the number of homologues. The data in Table II show that the values of b obtained by the proposed method are the same as those calculated by either the iterative or the statistical method. The values of c show differences in the third decimal figures, and the values of t_M show differences in the first decimal figures. The retention indices calculated through the different methods agree well, and their scatters are of the same magnitude.

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