

# Determination and Application in GLC of Semilog Function of Retention Time and Chain Length: Effect of Temperature Variation on Function

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## Abstract

The equation relating the log of the reaction time to chain length is extended to include equivalent chain lengths, relative retention times and separation factors. The temperature dependence of the slope and the dependence of the constant on the slope is shown.

## Introduction

The practical basis of identifying compounds using GLC is that, for a homologous series, a plot of the log of the retention time ( $t$ ) against carbon number is linear. Mathematically this is represented by:

$$\log t = Bn - A \quad [1]$$

This equation, where  $A$  and  $B$  are constants and  $n$  is an integral carbon number, holds for a given column and operating conditions. Relative retention time ( $t'$ ), obtained by equating the retention time of one member of the series to unity and making the remaining times proportional, can be used in the same type of equation. In the case of the methyl esters of the fatty acids the retention time of methyl stearate is generally used as unity.

This idea brought some order into the area by simplifying the numbers involved and by showing that, for similar columns operating under similar conditions, the relative retention times ( $t'$ ) for the same compounds are constant. For dissimilar columns and temperatures this is not the case. Since each operating column can be characterized by Eq. [1], there is no difficulty here in comparing values.

In this laboratory the best fit for the curve is determined by the method of least squares. This method also measures goodness of fit by the correlation coefficient and all other statistical values can be calculated.

This method can be demonstrated using data from three authors quoted by Haken (1) (in his Table I) for three different columns operating at three dif-

TABLE II  
Column Constants for Equation,<sup>a</sup>  
 $\log t' = Bn - A$

Stationary phase	Temperature C	Type acid <sup>b</sup>	B	-A
DEGS	200	Normal	0.1252	2.2495
EGA	197	Normal	0.1305	2.3505
APL	207	Normal	0.1702	3.0732
DEGS	200	Iso	0.1232	2.1499
EGA	197	Iso	0.1322	2.4468
APL	207	Iso	0.1782	3.2666

<sup>a</sup>  $r^2 \geq 0.999$  for each equation.  
<sup>b</sup> All saturated acids.

ferent temperatures. All the relative retention times are made proportional to methyl stearate taken as unity. Using iso acids data the best fitting curve is determined for each column. Carbon numbers are then calculated from the equation  $t'$ 's determined for the ethyleneglycol adipate (EGA) column; these calculated carbon numbers are integers. Inserting these carbon numbers into the other two equations yields their relative retention times which can be compared with the observed retention times. (Table I)

Table I shows that in general the data are consistent and the correlations high. By specifying the retention time of methyl stearate, in addition to the usual description of the operating conditions, all the original data could be calculated.

The data for the esters of the normal saturated acids can be treated in the same manner. Data for all six systems are summarized in Table II.

The case for unsaturated series is more complicated, but an idea suggested by Miwa et al. (2) proved practical. This was the idea of equivalent chain length (ECL) which related the unsaturated compounds to the line established for the saturated compounds and produced fractions of carbon numbers. These, too, are fairly constant for similar operating conditions, but lack predictability and, not being integers, are not easily identifiable by visual inspection. The equations for the various homologous series of esters determine points which form a family of nearly parallel lines. There are two ways to use the

TABLE I  
Relative Retention Data of Methyl Esters of Saturated Iso Acids

Chain length	DEGS <sup>a</sup> at 200 C log t'		EGA <sup>a</sup> at 197 C log t'		APL <sup>a</sup> at 207 C log t'	
	From data	Calculated from Eq. (d) <sup>b</sup>	From data	Calculated from Eq. (e) <sup>b</sup>	From data	Calculated from Eq. (f) <sup>b</sup>
12	-0.6704	-0.6709	.....	-0.8593	.....	-1.1282
13	-0.5454	-0.5476	.....	-0.7270	.....	-0.9500
14	-0.4330	-0.4244	-0.5986	-0.5947	-0.7851	-0.7718
15	-0.2967	-0.3011	.....	-0.4624	.....	-0.5936
16	-0.1719	-0.1779	-0.3260	-0.3302	-0.4089	-0.4153
17	-0.0590	-0.0546	.....	-0.1979	.....	-0.2371
18	.....	0.0686	-0.0665	-0.0656	-0.0655	-0.0589
19	.....	0.1918	.....	0.0666	.....	0.1192
20	.....	0.3151	0.2014	0.1989	.....	0.2974
21	.....	0.4383	.....	0.3312	.....	0.4756
22	.....	0.5616	0.4638	0.4635	.....	0.6538
23	.....	0.6848	.....	0.5958	.....	0.8320
24	.....	0.8081	0.7259	0.7281	.....	1.0102

<sup>a</sup> DEGS is diethyleneglycol succinate; EGA is ethyleneglycol adipate; APL is Apiezon L grease.  
<sup>b</sup> Constants for these equations are given in Table II;  $r^2$  (coefficient of determination)  $\geq 0.999$  for each equation.

TABLE III  
Relative Retention Time Ratios of Similarly Unsaturated Derivatives and Some Related Values

Ester shorthand designation <sup>a</sup>	Relative retention time $t'$	Separation factor $\frac{t'_{n+2}}{t'_n}$	Log $t'$	$\frac{d \log t'}{dn = 2}$	$\frac{\text{Log } t'_{n+2}}{t'_n}$
18:0	1.00	.....	.....	.....	.....
18:1 <sup>9</sup>	1.12	.....	0.0492	.....	.....
20:1 <sup>11</sup>	2.04	1.82	0.3096	0.2604	0.2601
22:1 <sup>13</sup>	3.66	1.79	0.5635	0.2539	0.2529
24:1 <sup>15</sup>	6.70	1.83	0.8261	0.2626	0.2625
18:2 <sup>9,12</sup>	1.32	.....	0.1206	.....	.....
20:2 <sup>11,14</sup>	2.42	1.83	0.3838	0.2632	0.2625
18:3 <sup>9,12</sup>	1.43	.....	0.1553	.....	.....
20:3 <sup>9,11,14</sup>	2.63	1.84	0.4200	0.2647	0.2648
18:4 <sup>9,12,15</sup>	1.84	.....	0.2648	.....	.....
20:4 <sup>8,11,14,17</sup>	3.31	1.80	0.5198	0.2550	0.2553
20:4 <sup>8,11,14</sup>	2.94	.....	0.4683	.....	.....
22:4 <sup>7,10,13,16</sup>	5.30	1.80	0.7243	0.2560	0.2553
20:5 <sup>8,11,14,17</sup>	3.61	.....	0.5575	.....	.....
22:5 <sup>7,10,13,16,19</sup>	6.61	1.83	0.8202	0.2627	0.2625

<sup>a</sup> The first figure is the carbon chain length (n). The figure after the colon is the number of unsaturations in the carbon chain. The superscript indicates the position of the unsaturation(s) counted from the carboxyl end of the chain.

equations. If they are used independently of each other and if the retention time of a member of each series is used to establish the relative retention time, then each ECL will be a whole number. If the retention time of a member of one series, say methyl stearate, is used as unity in all the equations for all the different series, then the ECLs of the esters of the one series, in this case the saturated, will be integers while ECLs of the members of other series will be fractions. These are ECLs as generally used. Ackman and Burgher (3) and Jamieson and Reid (4) have shown that separation factors ( $t'_{n+2}/t'_n$ ) may be used to predict  $t'$  values for unsaturated compounds. The position of the double bonds, especially the distance (in carbon number) from the terminal carbon, is the key factor. If compounds can be found whose separation factors are similar, then this may be a homologous series.

From data of Jamieson and Reid Table III was constructed. Here  $d \log t'/dn$  is the slope of the line and  $dn = 2$ . The  $\log t'_{n+2}/t'_n$  which is the log of the separation factor and  $d \log t'/dn$  are practically identical as they should be, since they are the same measure. From this an equation could be determined to fit all points on each line of these homologous series. Of course, the fewer points available the less accurate the equation for the line. The crux of the matter is that the familiar ambiguity results in assigning carbon numbers to similar relative retention times, a problem which is not solved by using ECL. Some, but not all of these ambiguities can be resolved by using another column with another liquid phase.

Since the interaction of each unique solute-solvent system determines the equation, the rate of change of the slope with the temperature ( $dB/dC$ ) should be unique for each homologous series in each solvent. Or, conversely, at a given temperature, other operating conditions being constant, B is determined for each system. Thus, retention times which could refer to more than one carbon number at a given temperature would not do so at other temperatures, since different homologous series have different rates of change of slope with temperature.

### Experimental Procedures

Operational temperature: 160 C–200 C; Flow rate: 20 ml/min; Carrier gas: H<sub>2</sub>; Column length: 6 ft; Column O.D.: 1/8 in.; Support: 80/100 GAS-CHROM P; Liquid phases: 18% HI-EFF-IB (DEGS), 18% S. F. 96 (silicone grease), and 18% Apiezon N (hydrocarbon grease); F. & M. Model 810 Gas Chromatograph with a Flame Ionization detector on

line with an Infotronics CRS-11AB/HS/42 integrator with a printout of retention time.

By varying temperature, the variable most easily controlled, the equations shown in Table IV were obtained. To repeat, the basis of practical GLC is Eq. [1] which can be written in the form of Clairaut's equation:

$$\log t = Bn - f(B) \quad [2]$$

By means of this equation, a relation was established for both retention times and relative retention times. (Retention times were measured from the solvent point, hexane, which was practically identical with the air peak.) Since the data fit the function defined in Eq. [2] so precisely, the dependence of the constant on the slope can be shown.

Using data from  $\log t$  (Table IV) the following equations were determined by the method of least squares:

$$B = -0.687 \times 10^{-3} C + 0.2536 \quad [3]$$

$$A = -1.791 \log B - 1.8107 \quad [4]$$

For Eq. [3] and Eq. [4]  $r^2$  was 0.988 and 0.839 respectively. Here C is the temperature in degrees centigrade. A and B can be substituted in the equation for  $\log t'$ . From the data for  $\log t'$  (Table IV) the following equations were derived:

$$B = -0.691 \times 10^{-3} C + 0.2543 \quad [5]$$

$$A = -5.546 \log B - 7.2633 \quad [6]$$

For Eq. [5] and Eq. [6]  $r^2$  is respectively 0.984 and 0.998. A and B can be substituted in equation for  $\log t'$ .

$$\log t' = Bn - A$$

Then if n is equated to 18 (1 is  $t'$  for methyl stearate), all temperatures should give  $\log 1 = 0$ . This, for all practical purposes, was true. The data in Table IV were derived from two series of runs. Com-

TABLE IV  
Constants for the Equation,  $\log t = Bn - A$  With DEGS Liquid Phase and Methyl Esters of the Even Members of the Normal, Aliphatic, Fatty Acids (C<sub>14</sub>-C<sub>24</sub>) as Samples

Temperature <sup>b</sup> C	t of methyl stearate in seconds	Retention time $t$		Relative retention time $t'$	
		B	-A	B	-A
160	763	0.1460	0.2537	0.1460	2.6285
165	547	0.1385	0.2438	0.1380	2.4858
175	411	0.1333	0.2132	0.1340	2.4123
185	282	0.1250	0.2000	0.1257	2.2629
190	.....	0.1230	0.1153	0.1212	2.1822
200	162	0.1176	0.0929	0.1179	2.1223

<sup>a</sup>  $r^2 \geq 0.999$  for each equation.

<sup>b</sup> This covers the usual operating range for a DEGS column.

TABLE V  
 Constants for the Equation,<sup>a</sup>  $\log t' = B_n - A$  Using Two Different  
 Liquid Phases With the Even Members of the Normal, Aliphatic,  
 Hydro-Carbon Series ( $C_{12}$ - $C_{20}$ ) as Samples

Liquid phase	Temperature C	$C_{18}$ Hydro-carbon t	B	-A
Apiezon N	155	3857	0.2288	4.1355
Apiezon N	179	1294	0.2072	3.7314
Apiezon N	187	891	0.1991	3.5846
Apiezon N	200	558	0.1868	3.3640
SF 96	177	772	0.1814	3.2664
SF 96	185	576	0.1743	3.1398
SF 96	192	421	0.1664	2.9951
SF 96	205	266	0.1504	2.7047

<sup>a</sup>  $r^2 \cong 0.999$  for each equation.

parison of the slopes for each series shows very good repeatability, as do the values for A.

Table V gives the parameters for the same sample (normal, aliphatic, hydrocarbon series) on two different stationary phases. As might be expected the equations for the two liquid phases are not the same.

From the data in Table V we can derive the following equations for the Apiezon column:

$$A = -8.794 \log B - 9.7583 \quad [7]$$

$$B = 0.933 \times 10^{-3} C + 0.3737 \quad [8]$$

For these equations  $r^2$  is respectively 0.998 and 0.999.

For the S. F. 96 column we can derive the following equations:

$$A = -6.881 \log B - 8.3627 \quad [9]$$

$$B = -1.118 \times 10^{-3} C + 0.3803 \quad [10]$$

For these equations  $r^2$  is respectively 0.999 and 0.994.

Guerin and Banks (5) show a linear relation between  $\log b$  (our  $\log B$ ) and C. For our sample and temperature range linearity was better between B and C. Guerin and Banks mention the importance of b and the desirability of adjusting conditions to yield some desired value of b. Values of b can be determined by means of the equations derived above.

### Discussion

If the effect of variation in temperature on the basic equation could be determined more accurately, a better equation would result. The reliability of the equations is established by the overall consistency of the individual equations and verified by the high correlation coefficients.

The use of Eq. [2] does not preclude the use of equivalent chain lengths which can be obtained by substituting  $\log t'$  in the equation for the saturated series and solving for n which is the chain length. By first statistically fitting the appropriate data to a curve and verifying that the equation delivers integers for the data  $t'$  the validity of all chain lengths is checked. The same  $t'$  data can then be substituted in the equation for the saturated series producing fractional ECL.

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