A Convenient Method for Routine Estimation of Dead Time in Gas Chromatography

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Abstract

A set of retention times (t_R) of *n*-alkanes at different temperatures and the primary dead times (t_M) are used to determine the 4 numerical constants (*a*, *b*, c, and *d*) of an equation. This equation is rearranged into a second equation, used in turn for routine calculation of the secondary dead time (t_{MS}) of each chromatogram from any member of the *n*-alkane series. Equation 2 can be used to calculate the t_{MS} of both packed and capillary columns. The calculated t_{MS} values are in good agreement with those of the t_M values. The greatest difference is 3.38%, but it is speculated that the percent difference would be lower when more t_R data are collected for the determination of the 4 numerical constants of Equation 1. Error in measurement of retention time undoubtedly would affect the accuracy of the estimated dead time, but it is attenuated by a factor of $1 + e^{(a + bN + c/T + dN/T)}$.

Introduction

The importance of the adjusted retention time (t_R) for interlaboratory comparison of gas chromatographic (GC) data and for the determination of physico-chemical properties of the solute has been described by many authors (1–3). This implies that the determination of the hold-up time (dead time, t_M) and the raw retention time t_R must be accurate. Retention time can be read directly from the chromatogram, whereas the determination of dead time is still subjected to many controversial methods (2,4). Different gases have been suggested as indicators of the t_M value (3,5–9). Unfortunately, neon gas, which has the lowest retention time in many stationary phases, does not cause a response in flame ionization detection (FID) (4). Methane, the only gas that produces a signal in FID, has been reported to be retained in several stationary phases (10–15), and its use in measuring the t_M value should be done cautiously, especially at temperatures below 70°C (16). Therefore, several calculation methods for t_M values have been proposed (4,10,12,17–26). Nevertheless, one similar weakness of these methods is that when there is a change in chromatographic conditions (such as carrier gas flow rate or temperature), a series of *n*-alkane homologues have to be reinjected into the chromatographic column, and a new t_M value must be recalculated.

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Recently, Krisnangkura et al. (27) described an equation (Equation 1) for the calculation of equivalent chain lengths (ECL) of fatty acid methyl esters (FAMEs):

$$\ln[(t_R - t_M)/t_M] = a + bN + (c/T) + (dN/T) \quad \text{Eq. 1}$$

which is rewritten as Equation 2:

$$t_{MS} = t_R\{1 + e^{[a + bN + (c/T) + (dN/T)]}\}^{-1} \quad \text{Eq. 2}$$

where N is the carbon number, T is the absolute temperature, and a, b, c, and d are thermodynamic parameters.

$$a = -\Delta S^0/R + \ln \beta \quad \text{Eq. 3}$$

$$b = \delta S/R \quad \text{Eq. 4}$$

$$c = -\Delta H^0/R \quad \text{Eq. 5}$$

$$d = \delta H/R \quad \text{Eq. 6}$$

where β is the phase ratio of the column and ΔH^0 and ΔS^0 are the standard molar enthalpy and entropy, respectively. δH and δS are the increments in enthalpy and entropy, respectively, in relation to carbon number. Equation 1 serves as an alternative method for calculating the ECL without a reference standard. Furthermore, the ECL of a FAME can be converted to its retention index, and vice versa, using the same equation but different numeric constants (28). These four numeric constants are characteristic for the column and solute.

This paper demonstrates the possibility of using Equation 2 to calculate the t_M value from *n*-alkanes and at different temperatures by using data available in the literature (4,11).

Experimental

Theory

Rewriting Equation 1 in an exponential form results in the following:

$$(t_R - t_M)/t_M = e^{[a + bN + (c/T) + (dN/T)]} \quad \text{Eq. 7}$$

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and

$$t_M = t_R/\{1 + e^{[a + bN + (c/T) + (dN/T)]}\} \quad \text{Eq. 8}$$

Equation 8 is used to calculate the t_M value of any chromatogram from the retention time of an *n*-alkane at any temperature.

Analysis of data from Wainwright et al.

The t_R and t_M (calculated) values on the 10-foot × 0.25-inch o.d. OV-25 (10%) were data reported by Wainwright et al. (11), and they were not repeated here. However, these data were converted into the natural logarithm of retention ratio (k') and listed in Table I. The four numeric constants (*a*, *b*, *c*, and *d*) were determined according to Krisnangkura et al. (27) and are listed in Table I. Thus, the working equation for this column is as follows:

$$t_M = t_R\{1 + e^{[-4.69 - 0.53N + (230.1/T) + (431.2N/T)]}\}^{-1} \quad \text{Eq. 9}$$

Analysis of Data from Quintanilla-López et al.

Only the t_R and t_M (t_R of neon gas) values on the 19.4% PS-255 (4 m × 2.2-mm i.d.), CPSIL-5CB (50 m × 0.32-mm i.d.), and HP-5 (60 m × 0.25-mm i.d.) columns from those reported by Quintanilla-López (4) were analyzed. Data on other columns were incomplete for the determination of the four numeric constants. The natural logarithm of retention ratios are summarized in Tables II–IV. The four constants (*a*, *b*, *c*, and *d*) are determined according to Krisnangkura et al. (27) and listed in the lower right-hand corner of the tables. The working equations for the PS-255 (packed), CPSIL-5CB (capillary), and HP-5 (capillary) columns are Equations 10, 11, and 12, respectively.

$$t_M = t_R\{1 + e^{[-3.32 - 0.606N + (159.39/T) + (477.12N/T)]}\}^{-1} \quad \text{Eq. 10}$$

$$t_M = t_R\{1 + e^{[-6.13 - 0.656N + (103.04/T) + (494.1N/T)]}\}^{-1} \quad \text{Eq. 11}$$

$$t_M = t_R\{1 + e^{[-6.678 - 0.646N + (119.56/T) + (493.38N/T)]}\}^{-1} \quad \text{Eq. 12}$$

Results and Discussion

To avoid confusion with the t_M in the literature, the t_M value calculated using Equation 2 is designated as the secondary t_M (t_{MS}). The t_{MS} in Table V are obtained by substituting the t_M and t_R of *n*-alkanes from Wainwright et al. (11) at different temperatures and carrier gas flow rates into Equation 9. The t_M values from Wainwright et al. (11) are also included in the *t*able for comparison. Numbers in parentheses are the percent difference between the t_{MS} and t_M. It can be seen that all t_{MS} values are in good agreement with the t_M values of those reported by Wainwright et al. (11). The greatest difference was 2.7 s, or

Table I. Natural Logarithms of Retention Factors of *n*-Alkanes at 120–140°C*

Carbon numbers	Temperature 120°C	130°C	140°C	Intercept	Slope
5	–1.275	–1.386	–1.567	–7.278	2364.90
6	–0.702	–0.847	–1.054	–7.950	2854.01
7	–0.129	–0.308	–0.527	–8.333	3228.59
8	0.440	0.229	–0.015	–8.950	3694.46
9	1.008	0.770	0.502	–9.416	4100.69
Intercept	–4.127	–4.081	–4.156	–4.69 (*a*)	230.10 (*c*)
Slope	0.571	0.539	0.518	–0.53 (*b*)	431.20 (*d*)

* Data were obtained from Wainwright et al. (11) for a 10% OV-25 column. The four numeric constants are included at the lower right.

Table II. Natural Logarithms of Retention Factors of *n*-Alkanes at 90–150°C*

Carbon numbers	Temperature 90°C	120°C	150°C	Intercept	Slope
5	0.659	0.097	–0.334	–6.364	2547.312
6	1.379	0.716	0.201	–6.946	3020.089
7	2.085	1.321	0.721	–7.552	3496.061
8	2.784	1.918	1.232	–8.182	3979.060
Intercept	–2.837	–2.860	–2.865	–3.32 (*a*)	159.339 (*c*)
Slope	0.703	0.597	0.512	–0.606 (*b*)	477.12 (*d*)

* Data were obtained from Quintanilla-López et al. (4) for a 19.4% PS-255 column. The four numeric constants are included at the lower right.

Table III. Natural Logarithms of Retention Factors of *n*-Alkanes at 60–150°C*

Carbon numbers	Temperature 60°C	90°C	120°C	150°C	Intercept	Slope
5	–1.686	–2.356	–2.887	–3.334	–9.44	2580.63
6	–0.833	–1.633	–2.268	–2.788	–10.05	3064.74
7	0.005	–0.924	–1.663	–2.264	–10.69	3556.22
8	0.832	–0.225	–1.069	–1.751	–11.35	4051.25
9	1.654	0.467	–0.480	–1.249	–12.03	4550.89
10	2.470	1.155	0.103	–0.749	–12.71	5048.56
Intercept	–5.821	–5.847	–5.858	–5.892	–6.13 (*a*)	103.04 (*c*)
Slope	0.830	0.701	0.597	0.516	–0.656 (*b*)	494.09 (*d*)

* Data were obtained from Quintanilla-López et al. (4) for a CPSIL-5CB capillary column. The four numeric constants are included at the lower right.

Table IV. Natural Logarithms of Retention Factors of *n*-Alkanes at 60–150°C*

Carbon numbers	Temperature 60°C	90°C	120°C	150°C	Intercept	Slope
6	–1.298	–2.097	–2.738	–3.265	–10.57	3082.69
7	–0.451	–1.378	–2.120	–2.730	–11.19	3570.39
8	0.386	–0.671	–1.516	–2.207	–11.83	4063.81
9	1.216	0.031	–0.919	–1.694	–12.50	4562.82
Intercept	–6.323	–6.347	–6.368	–6.401	–6.678 (*a*)	119.56 (*c*)
Slope	0.838	0.709	0.606	0.524	–0.646 (*b*)	493.38 (*d*)

* Data were obtained from Quintanilla-López et al. (4) for an HP-5 capillary column. The four numeric constants are included at the lower right.

2.84%, for *n*-heptane at 120°C with a carrier gas flow rate of 40 mL/min. The next highest value was 2.8 s, or 2.78%, for *n*-nonane at 140°C with a carrier gas flow rate of 40 mL/min. Thus, it might be concluded that Equation 1, which has been used for the calculation of the ECL of FAMEs (27) or Kováts retention index (28), could be extended to calculate the t_{MS} value from the t_R of an *n*-alkane in the chromatogram. Furthermore, the equation, which has been set up for use with the capillary column, can be extended to the packed column as well. However, the percent difference (2.84%) between t_M and t_{MS} in this analysis seemed to be slightly high. It is speculated that the difference would be lower when more t_R data are collected for the determination of the numerical constants in Equation 9.

Similar results were obtained when data from Quintanilla-López et al. (4) were analyzed. Substituting the t_M and t_R of *n*-alkanes for the PS-255 (packed column) into Equation 10, the t_{MS} values were obtained and are summarized in Table VI. Most of the t_{MS} values are similar to the retention times of neon gas. The greatest difference between the t_M and t_{MS} was 3.6 s, or 2.35%, for *n*-octane at 120°C. Results in this analysis confirm that Equation 1 can be extended to the packed column as well. Substituting the t_M and t_R of *n*-alkanes for the CPSIL-5CB (capillary) and HP-5 (capillary) columns into Equation 11 and 12, the calculated t_{MS} were obtained and are summarized in Table VII and Table VIII, respectively. Again, t_{MS} values are in good agreement with the retention times of neon gas, which was used for determination of the t_M values. The greatest difference between the t_M and t_{MS} for the CPSIL-5CB column is 7.3 s, or 3.38%, for *n*-decane at 90°C, and the greatest difference for the HP-5 column is 5.2 s, or 1.63%, for *n*-nonane at 60°C. Therefore, it is a very optimistic conclusion that Equation 1, with the specific numeric constants, can be used to estimate the t_{MS} value of each chromatogram from *n*-alkanes of any carbon number between 5 and 10. However, it should be pointed out that using *n*-alkanes of lower or higher carbon numbers usually leads to a greater error in the estimation of t_{MS}. The lower accuracy probably arises from the determination of the numeric constants. If the experimental data are increased, it is generally believed that the uncertainty in the results is smaller.

The major burden for this method, from a practical standpoint, is the process in obtaining the four numeric constants for each column. However, it is expected that the manufacturer would take care of this burden in the future by predetermining these four numeric constants for the customer. This would be very possible, because these four numeric constants would be specific for the column during the entire lifetime of the column, unless the chemistry of the liquid phases is changed (e.g., by oxidation or hydrolysis to a smaller molecule) or it is heavily contaminated with nonvolatile samples.

Another interesting point in using Equation 2 for the calculation of the t_{MS} should be mentioned here: the comment of Sharples and Vernon (29) on the method of Peterson and Hirsch (17). A small error in measurement of retention time would greatly amplify the deviation in the determination of t_M. In con-

Table V. Secondary Dead Times (s) Calculated from Raw Retention Times of *n*-Alkanes (11) Eluted from a 10% OV-25 Packed Column Using Equation 9*

	120°C		130°C			140°C		
***n*-Alkanes**	**Exp. 1**	**Exp. 2**	**Exp. 1**	**Exp. 2**	**Exp. 3**	**Exp. 1**	**Exp. 2**	**Exp. 3**
Carrier gas flow rate: 45 mL/min								
5	80.6 (0.37)	80.6 (0.25)	78.8 (–0.51)	80.0 (0.25)	80.8 (0.12)	78.4 (0.25)	78.8 (0.63)	78.8 (0.38)
6	80.6 (0.37)	80.6 (0.25)	78.9 (–0.64)	80.0 (0.25)	80.7 (0.25)	78.3 (0.38)	78.7 (0.76)	78.7 (0.51)
7	80.6 (0.37)	80.4 (0.50)	79.0 (–0.77)	79.6 (0.75)	80.5 (0.49)	78.5 (0.13)	78.5 (1.01)	78.8 (0.38)
8	80.6 (0.37)	80.6 (0.25)	79.0 (–0.77)	79.9 (0.37)	80.4 (0.62)	78.2 (0.51)	78.5 (1.01)	78.8 (0.38)
9	80.4 (0.62)	80.4 (0.50)	79.1 (–0.89)	79.7 (0.62)	80.0 (1.11)	78.2 (0.51)	78.2 (1.39)	78.4 (0.88)
t_M	80.9	80.8	78.4	80.2	80.9	78.6	79.3	79.1
Carrier gas flow rate: 40 mL/min								
5	95.5 (1.04)	95.1 (–0.11)	91.7 (0.54)	92.1 (0.86)	92.1 (0.86)	100.3 (–0.20)	99.9 (–0.20)	100.3 (0.59)
6	95.0 (1.55)	95.0 (0.00)	91.3 (0.98)	91.6 (1.40)	91.6 (1.40)	100.1 (0.00)	99.7 (0.00)	99.9 (0.99)
7	95.2 (1.35)	92.3 (2.84)	91.2 (1.08)	91.5 (1.51)	91.5 (1.51)	99.6 (0.50)	99.5 (0.20)	99.5 (1.39)
8	94.8 (1.76)	94.7 (0.32)	90.7 (1.63)	91.1 (1.94)	91.1 (1.94)	99.1 (1.00)	98.8 (0.90)	99.1 (1.78)
9	94.8 (1.76)	94.4 (0.63)	90.1 (2.28)	90.7 (2.37)	90.6 (2.48)	97.9 (2.20)	97.8 (1.91)	98.1 (2.78)
t_M	96.5	95.0	92.2	92.9	92.9	100.1	99.7	100.9
Carrier gas flow rate: 30 mL/min								
5	112.6 (0.35)	112.6 (0.79)	109.3 (0.18)	108.5 (–0.93)	108.9 (0.09)	109.4 (–0.09)	109.4 (0.00)	109.4 (0.09)
6	112.3 (0.62)	112.3 (1.06)	109.2 (0.27)	108.9 (–1.30)	108.9 (0.09)	109.3 (0.00)	109.3 (0.09)	109.3 (0.18)
7	112.5 (0.44)	112.3 (1.06)	109.5 (0.00)	109.1 (–1.49)	109.3 (–0.28)	109.4 (–0.09)	109.2 (0.18)	109.2 (0.27)
8	112.4 (0.53)	112.4 (0.97)	109.6 (–0.09)	109.4 (–1.77)	109.4 (–0.37)	109.1 (0.18)	109.2 (0.18)	109.1 (0.37)
9	112.0 (0.88)	112.4 (0.97)	109.6 (–0.09)	109.2 (–1.58)	109.4 (–0.37)	108.8 (0.46)	108.8 (0.55)	108.9 (0.55)
t_M	113.0	113.5	109.5	107.5	109.0	109.3	109.4	109.5

* Numbers in parentheses are the percent differences between the t_{MS} and t_M values.

trast to the method of Peterson and Hirsch (17), error in calculation of the t_{MS} by Equation 2 tends to be attenuated. If an error of Δt seconds (may be negative or positive) is introduced to the t_R, the new t_{MS} (t_{MSt}) will be as follows:

$$t_{MSt} = (t_R + \Delta t)\,(1 + e^{x})^{-1} \qquad \text{Eq. 13}$$

where

$$x = a + bN + (c/T) + (dN/T) \qquad \text{Eq. 14}$$

and

$$t_{MSt} = t_{MS} + \Delta t/(1 + e^{x}) \qquad \text{Eq. 15}$$

Table VI. Secondary Dead Times (t_{MS}) Calculated from Raw Retention Times (4) of *n*-Alkanes Eluted from a 19.4% PS-255 Column Using Equation 10*

	Temperature		
***n*-Alkane**	**90°C**	**120°C**	**150°C**
5	142.6 (1.79)	150.71 (1.30)	161.48 (–0.11)
6	143.99 (0.83)	151.33 (0.90)	162.73 (–0.89)
7	143.91 (0.89)	150.76 (1.27)	162.89 (–0.99)
8	142.89 (1.59)	149.11 (2.35)	161.82 (–0.32)
t_M	145.2	152.7	161.3

* Numbers in parentheses are the percent difference between the t_{MS} and t_M values.

Table VII. Secondary Dead Times (t_{MS}) Calculated from Raw Retention Times (4) of *n*-Alkanes Eluted from a CPSIL-5CB Capillary Column Using Equation 11*

	Temperature			
***n*-Alkane**	**60°C**	**90°C**	**120°C**	**150°C**
5	194.8 (0.00)	210.3 (0.28)	223.9 (0.12)	235.6 (0.02)
6	196.2 (–0.76)	210.4 (0.23)	224.1 (0.01)	236.1 (416)
7	198.2 (–1.78)	210.2 (0.29)	224.1 (0.01)	236.6 (–0.38)
8	199.6 (–2.52)	209.3 (0.69)	223.7 (0.18)	237.1 (–0.61)
9	199.6 (–2.56)	207.2 (1.71)	222.5 (0.74)	237.3 (–0.72)
10	198.2 (–1.84)	203.6 (3.38)	219.7 (1.94)	237.2 (–0.65)
t_M	194.8	210.9	224.2	235.7

* Numbers in parentheses are the percent difference between the t_{MS} and t_M values.

Table VIII. Secondary Dead Times (t_{MS}) Calculated from Raw Retention Times (4) of *n*-Alkanes Eluted from an HP-5 Capillary Column Using Equation 12*

	Temperature			
***n*-Alkane**	**60°C**	**90°C**	**120°C**	**150°C**
6	323.1 (–0.24)	342.7 (0.26)	361.1 (0.11)	377.2 (–0.04)
7	325.2 (–0.89)	342.4 (0.09)	361.2 (0.09)	377.7 (–0.16)
8	327.1 (–1.50)	340.9 (0.24)	360.6 (0.24)	378.2 (–0.28)
9	327.5 (–1.63)	337.7 (0.74)	358.8 (0.74)	378.4 (–0.33)
t_M	322.3	343.6	361.5	377.1

* Numbers in parentheses are the percent difference between the t_{MS} and t_M values.

That is, an error of $\Delta t/(1 + e^{x})$ will be added. Since e^{x} is always positive, the error will be less than Δt. This may also be illustrated by the experimental data of Wainwright et al. (11) or Quintanilla-López et al. (4). According to the third table of Quintanilla-López et al. (4), *n*-pentane at 60°C was eluted out at 232.9 s. The t_{MS} would be 194.8 s, as reported in Table VII. If an error in measurement of retention time of +2 s is introduced, the new t_{MS} will be 196.5 s. That is a change of 1.7 s, which is less than 2 s as originally presumed.

Conclusion

The GC retention times of *n*-alkanes at different temperatures and dead times are used to set up the numeric values of the four constants of Equation 1. Either the calculated dead time or the retention time of neon gas can be used as the t_{MS} reference. The equation, in turn, can be used to estimate the dead time (secondary, t_{MS}) of the subsequent chromatogram. The highest difference between t_M and t_{MS} for two packed and two capillary columns is 3.38%. Furthermore, error in the measurement of retention time, which tends to amplify the estimated t_M in the method of Peterson and Hirsch (17), is slightly attenuated in this calculation.

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