

A Comparative Study of Methods for Determining Gas Hold-Up Time

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Abstract

It has been proved mathematically that there exists an identity between the various published methods for determining the hold-up times in gas chromatography. All of these methods are based on the equation: $\ln t'_{R,Z} = \ln(t_R - t_M) = a + bZ$, where t_R , $t'_{R,Z}$, and t_M are retention times, adjusted retention times, and hold-up times, respectively; a and b are coefficients that depend on the experimental conditions, and Z is the numbers of carbon atom of a homologue. So long as there are no errors in the values of the retention times, the hold-up times obtained by different methods based on this equation will be the same. The calculated results of experimental data reported in the literature support the viewpoints presented here.

Introduction

Traditionally, equation 1 has been used to calculate hold-up times in isothermal chromatography:

$$\ln t'_{R,Z} = \ln(t_{R,Z} - t_M) = a + bZ \quad \text{Eq. 1}$$

where $t_{R,Z}$ and $t'_{R,Z}$ are the retention time and the adjusted retention time of an n -alkane containing Z carbon atom, respectively; t_M is the hold-up time; Z is the carbon number of members of a homologue, and a and b are coefficients that depend on the experimental conditions. Quinatanilla-Lopez et al. (1) proposed to calculate hold-up times using equation 2:

$$t_{R,Z} = A + \exp(B + CZ^D) \quad \text{Eq. 2}$$

where A , B , C , and D are adjustable parameters that depend on the chromatographic variables. Le Vent (2) concluded that there is no statistical evidence for the linear approach being less satisfactory than more complicated expressions, such as quadratic or non-linear ones. The methods of Ambrus (3), Peterson and Hirsch (4), Grobler and Bálizs (5), and Guardino et al. (6) are all based on equation 1.

This study reports on recent results dealing with the identity of these methods.

Experimental

Ambrus (3) showed that the plot of $t_{R,(Z+1)}$ versus $t_{R,Z}$ should fit a straight line, expressed as equation 3, where q and $-t_M(q-1)$ are the slope and intercept of the line, respectively.

$$t_{R,(Z+1)} = qt_{R,Z} - t_M(q-1) \quad \text{Eq. 3}$$

$$\frac{t'_{R,(Z+1)}}{t'_{R,Z}} = q \quad \text{Eq. 4}$$

where $q = e^b$. From the slope and intercept of equation 3, the hold-up time was obtained. $t_M = \text{intercept} / (1 - \text{slope})$. Generally speaking, the plot of $t_{R,(Z+1)}$ versus $t_{R,Z}$ ($i = 1$ or 2) would fit a straight line, and the slope of the line was expressed as:

$$\frac{t_{R,(Z+i)} - t_M}{t_{R,Z} - t_M} = \prod_{n=1}^i \left(\frac{t'_{R,(Z+n)}}{t'_{R,Z}} \right) = q^i \quad \text{Eq. 5}$$

where ($i = 1$ or 2)

Rearranging equation 5, equation 6 is obtained.

$$t_{R,(Z+i)} = q^i t_{R,Z} - t_M(q^i - 1) \quad \text{Eq. 6}$$

q^i and $-t_M(q^i - 1)$ were the slope and intercept of equation 6, respectively. When only three retention times of evenly spaced n -alkanes were used, the slope of the line AB was (see Figure 1):

$$q^i = \frac{t_{R,(Z+i)} - t_{R,Z}}{t_{R,Z} - t_{R,(Z-i)}} \quad \text{Eq. 7}$$

From equations 6 and 7, equation 8 was obtained:

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$$t_M = \frac{t_{R,Z}^2 - t_{R,(Z+i)} t_{R,(Z+i)}}{2 t_{R,Z} - t_{R,(Z+i)} - t_{R,(Z+i)}} \quad \text{Eq. 8}$$

Where $i = 1$ or 2 . Equation 8 was just the expression of the method of Peterson and Hirsch (4). Therefore, the method of Peterson and Hirsch (4) was considered as a special case of the method of Ambrus (3).

The method of Grobler and Bálizs (5) relied on the use of two successive linear regressions. After obtaining the value of b in equation 1 from the previous linear regression, the further regression of $t_{R,Z}$ versus q^Z , according to equation 9, gave t_M as the intercept.

$$t_{R,Z} = t_M + e^{ae^{bZ}} = t_M + e^{aq^Z} \quad \text{Eq. 9}$$

The methods of Ambrus (3) and of Grobler and Bálizs (5) gave hold-up times by use of equations 3 and 9, respectively. Multiplying equation 9 by q , equation 3 was obtained:

$$qt_{R,Z} = qt_M + qe^{ae^{bZ}} = qt_M + (t_{R,(Z-1)} - t_M) \quad \text{Eq. 3}$$

Obviously, the hold-up times obtained by both methods were the same, although the ways of obtaining and using equations 3 and 9 were different.

The method of Guardino et al. (6) started with the following equation:

$$\ln t'_{R,Z} = \ln(t_{R,Z} - t_M) = a + cI_Z \quad \text{Eq. 10}$$

where a and c were coefficients ($c = b/100$). I_Z was the retention index of an n -alkane containing Z carbon atoms ($I_Z = 100 \times Z$). In this method, an iteration was carried on t_M , with a and c calculated using a least-squares fit. The optimum value of t_M , a , and c were determined by minimizing the sum of squares of the difference between the known and calculated retention index values.

The hold-up times obtained from the method of Guardino et al. (6) would satisfy equation 1 and, consequently, satisfy equation 3. They would also be the same as those obtained by other methods based on equation 1 as well because equation 3 is derived from equation 1.

Calculation

All calculations were carried out using basic programs. Furr's Basic program (7) was used for calculating hold-up times of the method of Guardino et al. (6). Retention times of n -alkanes were all taken from the literature (1). The retention times were obtained on various chromatographic columns, columns 1–9 [for more details see the literature (1)]. The retention times of methane were not used because there are no data for ethane, propane, and n -butane in the literature (1).

Results

Tables I and II list the hold-up times obtained by different

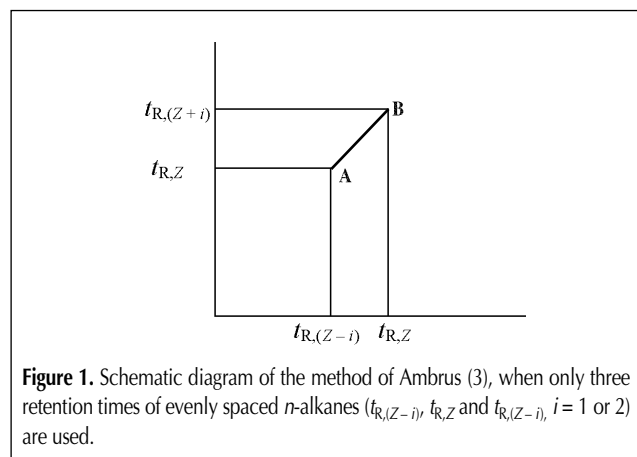


Figure 1. Schematic diagram of the method of Ambrus (3), when only three retention times of evenly spaced n -alkanes ($t_{R,(Z-i)}$, $t_{R,Z}$ and $t_{R,(Z+i)}$, $i = 1$ or 2) are used.

Table I. Comparison of the Hold-Up Times Obtained by Different Methods

Hold-up times obtained by the methods of	Hold-up times (s) on column*								
	1	2	3	4	5	6	7	8	9
Ambrus [†]	220.4	113.2	– [‡]	113.4	121.5	190.8	215.4	319.5	319.0
Grobler and Bálizs [†]	219.6	113.2	–	113.3	121.9	189.3	221.2	320.4	319.1
Guardino et al. [†]	219.8	113.2	–	113.3	121.8	190.0	156.4	320.1	318.9
Ambrus [§]	–	128.0	131.7	128.2	135.4	204.6	209.3	340.6	339.8
Grobler and Bálizs [§]	–	128.9	133.1	129.4	136.2	203.1	210.7	342.0	340.0
Guardino et al. [§]	–	128.8	132.7	129.2	135.9	203.5	209.0	341.5	340.0
Ambrus ^{**}	–	137.3	141.7	135.7	–	–	221.5	358.3	357.7
Grobler and Bálizs ^{**}	–	139.7	142.6	137.6	–	–	223.7	360.1	357.9
Guardino et al. ^{**}	–	139.1	142.5	137.2	–	–	222.8	359.5	357.9
Ambrus ^{††}	–	144.8	–	–	–	–	233.1	373.9	–
Grobler and Bálizs ^{††}	–	148.8	–	–	–	–	235.1	376.2	–
Guardino et al. ^{††}	–	147.9	–	–	–	–	234.2	375.3	–

* Columns refer to the chromatographic columns on which the retention times were obtained [for details see (1)].

[†] Table 3 in the literature (1).

[‡] – denotes that there is no data in the literature (1).

[§] Table 4 in the literature (1).

^{**} Table 5 in the literature (1).

^{††} Table 6 in the literature (1).

Table II. Comparison of Hold-Up Times Obtained by Different Methods When Three Equally Spaced Retention Times Are Used

Hold-up times (s) obtained by the methods of				Retention times (s) taken from column 9 in the literature (1)
Ambrus (3)	Peterson and Hirsch (4)	Grobler and Bálizs (5)	Guardino et al. (6)	
319.1	319.1	319.1	319.1	C ₆ -C ₈
318.8	318.8	318.8	318.8	C ₇ -C ₉
318.9	318.9	318.9	318.9	C ₈ -C ₁₀
318.8	318.8	318.8	318.8	C ₉ -C ₁₁
318.8	318.8	318.8	318.8	C ₁₀ -C ₁₂
319.6	319.6	319.6	319.6	C ₁₁ -C ₁₃

Table III. Comparison of the Given Hold-Up Times and the Hold-up Times Obtained by a Different Method*

Given hold-up times (s)	Hold-up times(s) obtained by the methods of				
	Peterson and Hirsch (4)	Ambrus (3)	Grobler and Bálizs (5)	Guardino et al. (6)	
156.4	–	156.4	156.4	156.4	C ₅ -C ₁₀
	156.4	156.4	156.4	156.4	C ₅ -C ₇
	156.4	156.4	156.4	156.4	C ₆ -C ₈
	156.4	156.4	156.4	156.4	C ₇ -C ₉
	156.4	156.4	156.4	156.4	C ₈ -C ₁₀
	156.4	156.4	156.4	156.4	C ₅ , C ₇ , C ₉
	156.4	156.4	156.4	156.4	C ₆ , C ₈ , C ₁₀
270.0	–	270.0	270.0	270.0	C ₅ -C ₁₀
	270.0	270.0	270.0	270.0	C ₅ -C ₇
	270.0	270.0	270.0	270.0	C ₆ -C ₈
	270.0	270.0	270.0	270.0	C ₇ -C ₉
	270.0	270.0	270.0	270.0	C ₈ -C ₁₀
	270.0	270.0	270.0	270.0	C ₅ , C ₇ , C ₉
	270.0	270.0	270.0	270.0	C ₆ , C ₈ , C ₁₀

* For the method of obtaining retention times, see the Discussion section in the text.

methods. It can be seen that the hold-up times obtained by different methods were the same, except for the results of column 7 in the literature (1), (hold-up times are 215.4, 221.2, and 156.4s, respectively, see Table I). Most likely an error occurred in the retention times (described later). These results show that the methods of Ambrus (3), Peterson and Hirsch (4), Grobler and Bálizs (5), and Guardino et al. (6) are identical. Therefore, this research leads to the conclusion that there exists an identity between the methods based on equation 1 for determining the hold-up time.

Discussion

Rewriting the regression equation of the retention times

obtained on column 7 in the literature (1), given by Furr's program, into the form of equation 1, equation 11 is obtained:

$$\ln t'_R = 1.1633 + 0.64672Z \quad \text{Eq. 11}$$

where $Z = 5 - 10$. Letting the hold-up time be a certain value (for example 156.4 or 270.0 s) and adding either of the given hold-up times to the adjusted retention times calculated from equation 11, the retention times, which do not contain any errors, were obtained. From these data, hold-up times obtained by different methods were all equal to the given values. As expected, Table III shows that this inference holds true.

Obviously, as long as there were no errors in the retention times, the values of the hold-up times obtained by different methods were the same. If there were errors in the retention times, this is not the case because error propagation is different from method to method. The higher the accuracy of the retention times, the less the differences between the hold-up times obtained by different methods. This fact was very useful. From this fact, it was asserted whether the data of retention times were accurate enough by comparing the hold-up times obtained by different methods. However, the hold-up times obtained from the method of Peterson and Hirsch (4) cannot be compared with those from the method of Ambrus (3). The results obtained from these two methods were all the same, even if there were greater errors in the retention times. This was because the method of Ambrus was identical with the method of Peterson and Hirsch when three equally spaced retention times were used.

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