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Determination and evaluation of gas holdup time with the quadratic equation model and comparison with nonlinear equation models for isothermal gas chromatography

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Abstract

Gas holdup time (t_M) is a basic parameter in isothermal gas chromatography (GC). Determination and evaluation of t_M and retention behaviors of *n*-alkanes under isothermal GC conditions have been extensively studied since the 1950s, but still remains unresolved. The difference equation (DE) model [J. Chromatogr. A 1260:215–223] reveals retention behaviors of *n*-alkanes excluding t_M , while the quadratic equation (QE) model [J. Chromatogr. A 1260:224–231] including t_M is suitable for applications. In the present study, t_M values were calculated with the QE model, which is referred to as t_{MT} , evaluated and compared with other three typical nonlinear models. The QE model gives an accurate estimation of t_M in isothermal GC. The t_{MT} values are highly accurate, stable, and easy to calculate and use. There is only one t_{MT} value at each GC condition. The proper classification of t_M values can clarify their disagreement and facilitate GC retention data standardization for which t_{MT} values are promising reference t_M values.

Keywords

Gas chromatography; Gas holdup time; Retention model; QE model; n-Alkanes

1. Introduction

Gas holdup time (t_M) is a basic parameter in isothermal gas chromatography (GC). It is related to almost all gas chromatographic and some thermodynamic parameters. The chromatographic parameters include adjusted retention time (t_R'), retention factor (k), relative retention (r), partition coefficient (K), and retention index (I), while the thermodynamic parameters include Gibbs free-energy of solute (ΔG), molar enthalpy of solute (ΔH), molar entropy of solute (ΔS), activity coefficients (γ), and interaction parameter (χ). The t_M is the

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time the carrier gas travels from the point of injection to the point of detection in a GC system. It depends upon the volume of the column, injector, connecting pathways and the detector. It can be expressed as the retention time of an unretained solute. However, only the total retention time (t_R) is recorded, which consists of t'_R and t_M , that both are always mixed together [1,2].

$$t_R = t'_R + t_M \quad (1)$$

t'_R is an important retention parameter for GC theory and applications, reflecting interactions between the solutes and the stationary phase. How to separate t'_R and t_M accurately is an unresolved and extensively studied topic since the advent of GC. The controversy is an inevitable outcome with the advancement of GC technology. In their pioneering paper [3], James and Martin corrected the compressibility of the gas mobile phase, which is different from the incompressible liquid mobile phase in liquid-liquid chromatography. Littlewood et al. [4] first introduced the correction of gas holdup volume using air or hydrogen as unretained solute. Subsequently, inert gas [5] was commonly employed as a marker, because thermal conductivity detector (TCD) was then a modern GC detector. Discussions on whether gas holdup time would be needed or not lasted until the late 1960's [1]. Methane [6] and the front of solvent peak at a high column temperature have been used as a marker of an unretained solute, because the flame ionization detector (FID) does not respond to air and inert gas. However, further studies have shown that air, inert gases, methane and solvents (as the front of solvent peak) are clearly retained [7,8,9]. Neon is not always the least retained gas [10]. Actually, all real molecules permeate stationary phases [11], even helium can permeate the walls of fused silica column [12]. An unretained substance does not exist in GC [10,13]. Calculation methods were considered a good alternative approach [9,10,13–15].

Two calculation methods have been reported in the literature. One is the fluid dynamic approach. The equation is based on Poiseuille's law [9].

$$t_M = [16L^2 \mu(T) / (60jr^2)] (P_o / P_i^2 - P_o^{-2}) \quad (2)$$

where L is the column length (cm), r the column radius (cm), P_o the column outlet pressure (dyne cm^{-2}), P_i the column inlet pressure (dyne cm^{-2}), j the pressure gradient correction factor of James and Martin, and $\mu(T)$ the dynamic viscosity of the carrier gas (Poise). It is difficult to know the exact values of these parameters; and thus, the fluid dynamic approach has not been used widely.

Another approach is to estimate the t_M values using retention models. The linear relationship between t'_R and carbon number (z) of n -alkanes has been used commonly until now [1–6, 16–18].

$$\log t'_R = \log (t_R - t_M) = bz + c \quad (3)$$

$$\Delta \log t'_R = b = \text{constant} \quad (4)$$

where b and c are regression parameters that depend upon experimental conditions. Many calculation methods have been proposed based on the linear equation (LE) model. Peterson and Hirsch [19] proposed to use retention times of three members in a homologous series to

calculate the t_M value. Since then, a large number of papers and reviews have been published [8,20–23], among which the method proposed by Guardino et al. [24] has been well accepted to obtain a t_M value denoted with t_{MM} . The nonlinear relationship between t'_R and z of n -alkanes has been then pointed out in many papers and therefore, many nonlinear methods have been proposed [10,13,21,25–35]. Four representative nonlinear methods are listed below:

- a. a cubic equation proposed by Heeg et al. [25]:

$$\log t'_R = \log(t_R - t_M) = \alpha z^3 + pz^2 + qz + r \quad (5)$$

where α , p , q and r are four regression parameters; and t_M is obtained with two successive linear regressions [22].

- b. two nonlinear equations (hereafter called LQG) selected from 25 mathematical expressions [10, 28]:

$$t_R = A + \exp(B + Cz + Dz^2) \quad (6a)$$

$$t_R = A + \exp(B + Cz^D) \quad (6b)$$

Eq. (6b) was used later [29–30] and was recommended by IUPAC in 2001 [31].

A , B , C and D are four adjustable parameters. t_M value is obtained when $z = 0$. The t_M value here is called t_{ML} .

$$t_{ML} = A + \exp B \quad (7)$$

- c. equation (8) deduced from basic concepts of statistical thermodynamics to describe the relationship between t_R and z [13,27,32].

$$t_R = t_{MG} + \exp(A + B(z-2) + \ln(1 - Cz^2)) \quad (8)$$

where the t_M value here is called t_{MG} ; A , B and C are adjustable parameters.

- d. the difference equation (DE) and quadratic equation (QE) models recently proposed by Wu et al. [33,34]. The DE model [33] excludes the influence of t_M and expresses the accurate retention behavior of n -alkanes.

$$\log \Delta t_z = Az^2 + Bz + C \quad (9)$$

The slope of Eq. (9) is a LE; and the slope of LE is a constant:

$$\Delta \log \Delta t_z = \log(\Delta t_{z+1} / \Delta t_z) = \beta z + \gamma \quad (10)$$

$$\Delta^2 \log \Delta t_z = 2A = \text{constant} \quad (11)$$

where $\Delta t_z = t_{R(z+1)} - t_{R(z)}$ are the forward differences of retention times between two consecutive n -alkanes and A , B , C , β and γ are the regression coefficients that depend on experimental conditions.

The QE model [34] has been developed on the basis of the DE model.

$$\log t'_{\text{RT}} = \log(t_{\text{R}} - t_{\text{MT}}) = Uz^2 + Vz + W \quad (12)$$

the slope of Eq. (12) is a LE, and the slope of LE is a constant:

$$\Delta \log t'_{\text{RT}} = \beta z + \gamma \quad (13)$$

$$\Delta^2 \log t'_{\text{RT}} = 2U = \text{constant} \quad (14)$$

where U , V , W , β and γ are regression parameters that depend on the experimental conditions and t_{MT} is the retention time of an hypothetical unretained solute with $k=0$, which was calculated with the QE model. Eqs. (13) and (14) are the first and second order difference equations of Eq. (12), respectively. The QE model can quantitatively describe the retention behavior of solutes at three levels with Eqs. (12, 13 and 14).

Different t_{M} values were obtained from different methods [8, 10, 21, 28]; and no t_{M} value has been commonly accepted.

The present study focused on determination and evaluation of t_{MT} values with the QE model. The t_{MT} values were compared with t_{M} values experimentally obtained with methane (t_{MCH4}) and neon (t_{MNe}) as markers and those calculated using linear (t_{MM}) and two nonlinear (t_{ML} and t_{MG}) methods. To clarify the disagreement of t_{M} in the literature and facilitate the development of GC retention theories, classification of gas holdup times was proposed. The t_{MT} values are promising to serve as reference gas holdup time values.

2. Methods of t_{M} measurement and calculation

The t_{MCH4} and t_{MNe} values were obtained experimentally [10,33,34]. Published raw retention times were used to calculate t_{M} [10,25,30,33]. The t_{MT} and t_{MM} values were calculated using the Interactive Matrix Language (IML) procedure for multiple linear regression after the range of the iteration and step length were set in SAS software 9.2 (SAS Institute Inc., NC, USA). The t_{M} value was adjusted for curve fittings of Eq. (12). After iteration, the t_{M} value with the maximum coefficient of determination (R^2) was defined as t_{MT} value, because the R^2 is a statistic indicating the goodness of fit of a model. The t_{MM} value was calculated in the same way as t_{MT} , except using Eq. (3). The t_{ML} and t_{MG} values were also calculated with SAS software 9.2, using the NonLinear (NLIN) procedure for multi-parametric non-linear regressions. Four initial values were set for curve fittings of Eq. (6b) and Eq. (8). After iteration, four parameters of Eq. (6b) with the maximum R^2 were obtained, followed by the calculation of the t_{ML} values according to Eq. (7). The three parameters and t_{MG} of Eq. (8) with the maximum R^2 were also obtained by iteration processes.

3. Results and discussion

3.1. Characteristics concerning t_{MT} from the QE model and comparison with other nonlinear models

General characteristics of the QE model were discussed in our previous paper [34]. The present study focused on the characteristics related to t_{MT} and comparison with other nonlinear models.

3.1.1. Accuracy of curve fittings of Eq. (12)—The accuracy of a curve fitting for the t_{MCH4} and t_{MM} with the LE model was poor [34]. To compare the accuracy of curve fittings of Eq. (12) with the nonlinear equations Eq. (5) and (6b), the differences (ΔI) between calculated (I_{cal}) and defined (100z) reference points of retention indices were listed in Table 1. A comparison criterion is that each model and its correspondingly calculated t_M value should be treated as one system. Although Heeg et al. [25] proposed a cubic model, the t_M (129.9 s) value was calculated by two linear regressions [22], which actually is still equivalent to a linear method [8,23]. The t_M (129.9 s) value resulted in the mean difference (Δ) of absolute ΔI values as large as 0.28 index units (i.u.) [25]. Use of the QE model and t_{MT} (131.1 s) gave the Δ value (0.05 i.u.) more than 5 times smaller than that from Heeg's QE calculation (0.28 i.u.). It is commonly known that increasing the degree of or parameters in the equation will result in an improvement of fitting ability. The Δ values from both the CE and LOG models [25, 30] with four parameters were equivalent to that from the QE model [34] with three parameters only. The reason is that the less accurate t_M values counteracted the fitting power of the aforementioned 4-parameter equations. Therefore, we conclude that the best combination is the QE model and the t_{MT} values.

3.1.2. Effects of regression range of n-alkanes on t_M values—Varying regression range of *n*-alkanes should not affect t_M values [10,28]. Standard deviations (SDs) were used as an indicator to compare the effect of the regression range of *n*-alkanes on t_M values calculated by different methods (Tables 2 and 3). Although the sources of raw data were different [10,33], the results agreed well.

The SDs of the LE model [Eq. (3)] were the largest, indicating least satisfactory precision. The SDs by LQG were the smallest, which is due to the inclusion of methane in the regression [10,28]. Such treatment is unsuitable, because methane notably deviates from the regular property of *n*-alkanes starting from propane [33,35]. The SDs of the QE [Eq. (12)] were smaller than those of Eq. (8). The data show the insensitivity of the regression range of *n*-alkanes on t_M values in LQG [Eq. (6b)], González [Eq. (8)] and QE [Eq. (12)] models.

3.1.3. One t_{MT} value at one GC condition—Fig. 1a shows a linear relationship between $\Delta \log t'_{RT}$ and *z* on the ZB-1 column at 70 °C (t_{MT} line), which $\Delta \log t'_{RT}$ decreased with increasing *z*, following Eq. (13). The excellent correlation (R^2 , 0.9995) between the experimental points and the theoretical line indicates one t_{MT} value at one GC condition and the closeness of the t_{MT} to the true t_M value. Only the true t_M value would give a perfect straight line between $\Delta \log t'_{RT}$ and *z*. Based on the dispersion of the t_M values (Fig. 1c), an assumption was made by adding and subtracting a value of 0.03 and 0.06 from the t_{MT} to further illustrate the concept of one t_{MT} value at one GC condition. Two curves of $\Delta \log (t'_{RT} \pm 0.03 \text{ and } 0.06)$ versus *z* occur on each side of the $\Delta \log t'_{RT}$ versus *z* line (t_{MT} line). The four curves deviate from Eq. (13), of which the magnitude of the deviations depends upon the degree of the t_M deviations from the t_{MT} . Effects of t_M errors on the $\Delta \log t'_{RT}$ values of different carbon numbers of *n*-alkanes are described in the section 3.3 below.

3.1.4. Comparison of the calculation method for t_{MT} with that for the t_{ML} and t_{MG} —The t_{ML} and t_{MG} values were calculated by the multi-parameters nonlinear regressions according to Eqs. (6b) and (8). The procedures require an initial input of arbitrary values as the four adjustable parameters to obtain four estimated parameters. It is necessary to take into account the maximum number of iterations and the convergence criteria in order to obtain a good estimation. After arbitrary initial parameter values were carefully selected, the F statistic reached 10^7 – 10^9 in the present study. Almost all t_{ML} and t_{MG} values we calculated with SAS at different GC conditions agreed very well with those

published (Table S1). Therefore, the t_{ML} and t_{MG} values were meaningful for comparisons among different models in the present study. The t_{MT} values from the nonlinear Eq. (12) were calculated by multiple linear regression equation. The procedures were to give an initial t_M and thus, the three parameters U , V and W can be determined for the QE model. It is a basic mathematic calculation. Therefore, the method is simple and reliable, and there is only one t_{MT} value obtained at each GC condition. The t_{MT} values can be calculated easily with commercial software such as SAS and Statgraphics as well as public-assessable software such as R (see supporting information for details).

3.2. Current disagreement of holdup times and standardization requirements

3.2.1. The current disagreement of holdup time—Table 4 shows the different t_M values at each GC condition obtained by different methods. The t_M values decreased in the order of t_{MCH4} , t_{MNe} , t_{ML} , t_{MT} , t_{MG} and t_{MM} . The disagreement [$\Delta(t_{MCH4} - t_{MM})$] can be expressed by the differences between maximum (t_{MCH4}) and minimum (t_{MM}). The $\Delta(t_{MCH4} - t_{MM})$ values ranged from 0.030 to 0.103 and from 0.137 to 0.325 min for three capillary and two packed columns, respectively. The latter was larger than the former because the phase ratios (β) of the packed columns [10] were smaller than those of the capillary columns [10,33].

Disagreement of gas holdup time [$\Delta(t_{MCH4} - t_{MM})$] causes variations of subsequent retention data, such as retention index (I) values. For example, on the ZB-1 column at 70 °C, the mean differences (Δ) (C_7 - C_{14}) between calculated (I_{cal}) and defined (100 z) reference points of retention indices were 1.52 and 0.37 index unit (i.u.) (data not shown) when t_{MCH4} and t_{MM} of 3.705 and 3.602 min, respectively, were used. It is difficult to compare the results from different methods. Standardization of t_M is a powerful way to solve the problem. Therefore, it is necessary to have an accepted reference t_M value. The reference t_M value should meet three requirements: good accuracy and precision, good stability and easy applications.

3.2.2. Accuracy of t_{MT} values and comparison with others—The accuracy of a t_M value is the closeness of agreement between a test t_M value to the accepted reference value [36]. Because there is still no accepted reference t_M value, the accuracy of t_M values can only be assessed based on relative terms such as comparison with a preferred method or assuming the smallest value as a correct value [18]. We considered that the t_{MT} value is equal or close to true gas holdup time based on theoretical interpretation, experimental data and comparison with the other t_M values [Tables 2–4]. According to the definition of t_{MT} values, only when $t_{MT} = t_M$, then $k = (t_{MT} - t_M)/t_M = 0$, the t_{MT} values in Eq. (12) are indeed theoretically equal or close to true gas holdup time. If the t_{MT} values were not accurate or not close to the true t_M , i.e., $k \neq 0$, the retention behavior of n -alkanes could not be quantitatively described by the QE [Eqs. (12, 13, 14), including t_M] and DE [Eqs. (9, 10, 11), excluding t_M] models at three levels, which has never happened experimentally. The QE model is always better than the DE model for applications [34]. Finally, the t_{MT} values are reasonable, being the middle values between the experimental t_M and calculated t_{MM} values at all GC conditions and agreed with the t_{MG} values at most GC conditions (Tables 2–4).

A strong point of Eq. (8) is that it is deduced from basic concepts of statistical thermodynamics based on $k = 0$. Unfortunately, the parameter A in Eq. (8) consists of two terms, $A = \ln(t_M/\beta) - \Delta G^+/RT$ [32,37]. There are apparently two t_M values (t_{MG} and the t_M value included in parameter A) in Eq. (8). Only t_{MG} value in Eq. (8) is calculated, whereas the t_M in the A term is lost. It is noteworthy that when the A term is small, the loss of t_M in

the A term is negligible under most GC conditions. However, when A term is large, the loss of t_M in the A term becomes apparent, which consequentially decreases the t_{MG} values.

The LQG model is based on retention time of an hypothetical n -alkane with $z = 0$ and use of neon as a reference to check the validity [10,28]. In theory, the molecular formula of a hypothetical n -alkane with $z = 0$ should be methane (CH_4) subtracted with CH_2 , i.e., hydrogen (H_2). As mentioned above, all real molecules permeate the stationary phases [11], including hydrogen. Therefore, the t_{ML} values actually are retention times of a slightly retained substance, which can be confirmed by rewriting Eq. (12) to Eq. (15) and then comparison with Eqs. (6a) and (7).

$$t_R = t_{MT} + \exp(Uz^2 + Vz + W) \quad (15)$$

The t_{ML} values ($t_{ML} = A + \exp B$) in Eq. (6a) contain an extra term “exp B”. It was verified [10,28] that the t_{ML} values from Eq. (6a) agreed well with those from Eq. (6b). Therefore, the t_{ML} values deviated relatively large (Fig. 2, Tables 2–4).

The precision of t_{MT} is satisfactory. The confidence intervals of 95% of five t_{MT} measurements ranged from ± 0.001 to ± 0.007 min (Table S2), which were much smaller than the disagreement $\Delta(t_{MCH_4} - t_{MM})$ values (0.077 to 0.103 min) (Table 4).

3.2.3. Stability of t_{MT} values and user-friendly applications—The t_{MT} value is derived from multi-point corrections (at least 6 points) rather than a single-point correction according to the retention of a specific solute such as air, neon, or a hypothetical n -alkane with $z = 0$. The systematic errors from improper selection of a special solute are avoided and random errors from single point data are minimized. The t_{MT} values are consistently stable. The mean SDs values were 0.003 min and 0.10 s (0.002 min) in Tables 2 and 3, respectively, which were at least 26 times smaller than the disagreement $\Delta(t_{MCH_4} - t_{MM})$ values (0.077 to 0.103 min). Therefore, the effect of the regression range of n -alkanes on calculated t_{MT} values is negligible.

The t_{MT} values can be easily calculated with multiple linear regressions. The t_{MT} can be determined from a wide range of n -alkanes starting from propane which can be adjusted by column temperature (T_c), as long it consists of six or more n -alkane members. The method is applicable to commonly used GC detectors such as TCD, FID and mass spectrometric detector.

3.3. Classification of holdup time

The methods used for t_M estimation have been classified [8–10,18,21,38,39]. To our knowledge, t_M values have not been classified in the literature. In order to clarify the disagreement of the t_M values and facilitate GC retention data standardization, we propose that t_M values can be grouped into three classes: under-, accurate- and over-correction, when a t_{MT} value is used as reference value (Fig. 1).

The difference method [33, 34] is very helpful for studies of retention model and classification of t_M values. Fig. 1b shows five relationship curves of log

t'_R (t'_{RCH_4} , t'_{RL} , t'_{RT} , t'_{RG}) and t'_{RMM} corresponding to corrections with t_{MCH_4} , t_{ML} , t_{MT} , t_{MG} and t_{MM} versus z on the ZB-1 column at 70 °C. The five curves are apparently overlapped and linear, although they actually are slightly convex. It is practically impossible to distinguish the differences of the five t_M values at this level. However, the five curves of $\Delta \log t'_R$ versus z at the first order difference level [Eq. (13)] have revealed very distinct differences (Fig. 1c).

The curve of $\Delta \log t'_{\text{RMM}}$ is under-corrected. The two curves ($\Delta \log t'_{\text{MT}}$ and $\Delta \log t'_{\text{RG}}$) are close to each other. The two curves of $\Delta \log t'_{\text{RCH}_4}$ and $\Delta \log t'_{\text{RL}}$ are over-corrected. When the t_{MT} value is used as an accepted reference value, the under, accurately- and over-corrected t'_R values can be expressed by Eqs. (15), (16) and (17):

$$t'_{\text{R(under)}} = t_R - t_{\text{M(under)}} = t_R - (t_{\text{MT}} - \Delta t) \quad (15)$$

$$t'_{\text{RT}} = t_R - t_{\text{MT}} \quad (16)$$

$$t'_{\text{R(over)}} = t_R - t_{\text{M(over)}} = t_R - (t_{\text{MT}} + \Delta t) \quad (17)$$

where Δt is the under- or over-corrected retention time. For example, the t_{MCH_4} , t_{MT} and t_{MM} values were 3.705, 3.660 and 3.602 min, respectively (Table 4). The t'_{RMM} values can be obtained by subtracting the t_{MM} (i.e., $t_{\text{MT}} - 0.058$) from t_R for each n -alkane member. The value of 0.058 min (Δt) was the amount of under subtracted from t_R ; the lower the carbon number of n -alkanes, the more relative values added to t'_{RMM} [Eq. (15)]. The t'_{RCH_4} values can be obtained by subtracting the t_{MCH_4} (i.e., $t_{\text{MT}} + 0.045$) from t_R for each n -alkane member. The value of 0.045 min is the over-corrected portion which was subtracted from t_R ; and the lower the carbon number of n -alkanes, the more relative loss for t'_{RCH_4} values [Eq. (17)]. The two curves of t_{MM} and t_{ML} in Fig. 1c are about the same as the two hypothetical curves of -0.06 and $+0.03$ in Fig. 1a. The curves from [10] also show the same phenomena of under- and over-corrections (Fig. 1e). At the second order difference level [Eq. (14)], Fig. 1d also shows that the $\Delta^2 \log t'_R$ values can be grouped as three classes. Therefore, the QE model not only can determine t_{M} values, but also can evaluate and classify t_{M} values.

Relationships between t_{M} and T_c also show the same classification characteristics of t_{M} . The t_{M} values increase with T_c due to the increased dynamic viscosity of the carrier gas [9,39,40]. Fig. 2 shows that the experimental t_{MCH_4} values and calculated t_{ML} , t_{MT} , t_{MG} and t_{MM} values linearly increased when T_c increased from 70 °C to 170 °C on ZB-1 column. The R^2 values were larger than 0.998. The t_{MT} and t_{MG} lines are close together and located between the under-corrected line (t_{MM}) and the over-corrected lines (t_{ML} and t_{MCH_4}). The t_{M} values on the four columns [10] in Table 4 also show similar trends - t_{MM} stays alone, t_{MCH_4} , t_{MNe} and t_{ML} in a cluster, and t_{MT} and t_{MG} in another cluster.

3.4. Comparison of different models to determine t_{M} values

Table 5 compares different retention models and their corresponding characteristics of the t_{M} values. The LE model is simple, but the other characteristics listed in Table 5 are unsatisfactory. Although the accuracy of curve fittings of the three 4-parameter models is good, the QE model using 3 parameters is better when all characteristics are considered.

4. Conclusion

Retention behaviors of n -alkanes and determination of gas holdup time under isothermal GC are unresolved even though being extensively studied since the 1950s. There are two major challenges. One is that t_{M} is always hidden in t_{R} and an estimation of t_{M} and retention models are intertwined. Most reported t_{M} values were approximate values and the different t_{M} values obtained by different methods were considered to be similar [18]. The QE model allows clear separation of the t_{MT} values from t_{R} , easy evaluation and convenient

classification of t_M values. The other challenge is no accepted reference t_M value. Most authors used neon or a preferred method as a reference to confirm the validity of method, which resulted in a system error for the estimation of t_M . The fitting accuracy of the QE model with three parameters is equivalent to those of 4-parameter models published in the literature. Based on the relationship between DE and QE models and the definition of t_{MT} values, the t_{MT} values obtained from the QE model are highly accurate, stable and easy to use. The QE model is a promising method for retention data standardization in isothermal GC. When the t_{MT} value is used as a reference, the gas holdup time obtained from different methods can be classified as under-, accurate- and over-correction. The t_{MG} [13,27] and t_{MT} values obtained in the present work are accurate-correction; the t_{MM} values belong to under-correction and experimentally measured (t_{MCH_4} , t_{MNe}) and t_{ML} values [10,28] are over-correction.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chroma>.

Highlight

1. The quadratic equation (QE) model gives highly accurate retention curve fittings for isothermal GC.
2. Gas holdup times (t_M) calculated with the QE model are termed as t_{MT} , and are accurate, stable and easy to use.
3. There is only one t_{MT} value at each GC condition.
4. t_M corrections can be classified as under-, accurate- and over-correction.
5. t_{MT} can serve as t_M reference values for GC retention data standardization.

Fig. 1.

One accurate t_{MT} value at one GC condition (a) and comparison of t_M values obtained from different methods according to Eqs. (12–14) (b–e). Raw retention times on the ZB-1 column at 70 °C in Fig. 1a–1d were cited from Table 1 in [33]. Raw retention times on the HP-5 column (60 m × 0.25 mm × 0.25 μm) at 120 °C in Fig. 1e were cited from [10].

Fig. 2. Comparison of t_M values obtained by different methods using raw retention times [33] on the ZB-1 column at 70–170 °C. [41]

Table 1

Comparison of different nonlinear methods for the accuracy of curve fittings

No. of carbon in <i>n</i> -alkanes	QE calculation [25] (<i>t</i> _M , 129.9 s) ^a		CE [25] (<i>t</i> _M , 129.9 s) ^b		QE model [34] (<i>t</i> _M , 131.1 s) ^c		No. of carbon in <i>n</i> -alkanes	LQG [30] (<i>t</i> _M , 151.38 s) ^d		QE model [34] (<i>t</i> _M , 150.8 s) ^c	
	<i>I</i> _{cal} (i.u.)	Δ <i>I</i> (i.u.)	<i>I</i> _{cal} (i.u.)	Δ <i>I</i> (i.u.)	<i>I</i> _{cal} (i.u.)	Δ <i>I</i> (i.u.)		<i>I</i> _{cal} (i.u.)	Δ <i>I</i> (i.u.)	<i>I</i> _{cal} (i.u.)	Δ <i>I</i> (i.u.)
13	1300.46	0.46	1300.02	0.02	1299.95	0.05	6	599.96	0.04	600.07	0.07
14	1399.84	0.16	1399.99	0.01	1400.10	0.10	7	699.89	0.11	699.85	0.15
15	1499.60	0.40	1499.97	0.03	1500.03	0.03	8	800.08	0.08	800.05	0.05
16	1599.64	0.36	1599.97	0.03	1599.93	0.07	9	900.05	0.05	900.05	0.05
17	1699.92	0.08	1700.05	0.05	1699.96	0.04	10	999.96	0.04	999.98	0.02
18	1800.15	0.15	1800.02	0.02	1799.96	0.04	11	1100.00	0.00	1100.01	0.01
19	1900.35	0.35	1900.02	0.02	1900.03	0.03	12	1200.01	0.01	1200.00	0.00
20	2000.34	0.34	1999.96	0.04	2000.05	0.05	13	1300.00	0.00	1299.98	0.02
21	2100.11	0.11	2099.96	0.04	2100.05	0.05	14	1400.00	0.00	1400.01	0.01
22	2199.58	0.42	2200.03	0.03	2199.94	0.06					
Mean Δ <i>I</i> (Δ)									0.04		0.04

^a, ^b The I_{cal} values in index unit (i.u.) were calculated by a quadratic equation and a cubic equation, respectively, and t_M = 129.9 s, which data were cited from [25].

^c The I_{cal} and t_M = 131.1 s and t_M = 150.8 s were calculated by the QE model [34] in the present work, and raw retention times were cited from [25] and [30], respectively.

^d The I_{cal} values were calculated by LQG model and t_M = 151.38 s was calculated according to Eq. (7) using A and B values in [30].

Table 2
Effects of regression ranges of *n*-alkanes on t_M values calculated by different methods^a

T_c (°C) ^b	Range of <i>n</i> -alkanes	Eq. (12)	Eq. (3)	Eq. (8)	Range of <i>n</i> -alkanes		Eq. (6b,7)
		t_{MT} (min)	t_{MM} (min)	t_{MG} (min)			t_{ML} (min) t_{MCH4} (min)
100	C ₇ -C ₁₆	3.831	3.794	3.811	C ₁ , C ₇ -C ₁₆		3.866
	C ₇ -C ₁₅	3.830	3.799	3.812	C ₁ , C ₇ -C ₁₅		3.865
	C ₇ -C ₁₄	3.830	3.804	3.807	C ₁ , C ₇ -C ₁₄		3.864
	C ₈ -C ₁₆	3.833	3.773	3.810	C ₁ , C ₈ -C ₁₆		3.870
	C ₈ -C ₁₅	3.832	3.783	3.811	C ₁ , C ₈ -C ₁₅		3.868
	C ₈ -C ₁₄	3.832	3.791	3.803	C ₁ , C ₈ -C ₁₄		3.868
	C ₉ -C ₁₆	3.831	3.740	3.810	C ₁ , C ₉ -C ₁₆		3.872
	C ₉ -C ₁₅	3.829	3.755	3.812	C ₁ , C ₉ -C ₁₅		3.871
	C ₉ -C ₁₄	3.825	3.770	3.794	C ₁ , C ₉ -C ₁₄		3.870
	C ₁₀ -C ₁₆	3.838	3.692	3.813	C ₁ , C ₁₀ -C ₁₆		3.873
150	C ₁₀ -C ₁₅	3.837	3.719	3.821	C ₁ , C ₁₀ -C ₁₅		3.872
	C ₁₀ -C ₁₄	3.829	3.742	3.785	C ₁ , C ₁₀ -C ₁₄		3.871
	Mean	3.831	3.764	3.807			3.869 3.878
	SD	0.004	0.035	0.010			0.003
	$\Delta(t_M - t_{MT})$	0.000	-0.067	-0.024			0.038 0.047
	C ₈ -C ₂₀	4.105	4.070	4.097	C ₁ , C ₈ -C ₂₀		4.140
	C ₈ -C ₁₈	4.104	4.078	4.099	C ₁ , C ₈ -C ₁₈		4.135
	C ₈ -C ₁₆	4.104	4.084	4.089	C ₁ , C ₈ -C ₁₆		4.138
	C ₉ -C ₂₀	4.105	4.056	4.096	C ₁ , C ₉ -C ₂₀		4.143
	C ₉ -C ₁₈	4.104	4.068	4.098	C ₁ , C ₉ -C ₁₈		4.138
	C ₉ -C ₁₆	4.102	4.077	4.101	C ₁ , C ₉ -C ₁₆		4.140

T_c (°C) ^b	Range of <i>n</i> -alkanes	Eq. (12)	Eq. (3)	Eq. (8)	Range of <i>n</i> -alkanes		Eqs. (6b,7)	
		t_{MT} (min)	t_{MM} (min)	t_{MG} (min)			t_{ML} (min)	t_{MCH4} (min)
		t_{MT} (min)						
	C ₁₀ -C ₂₀	4.109	4.038	4.101	C ₁ , C ₁₀ -C ₂₀		4.145	
	C ₁₀ -C ₁₈	4.108	4.055	4.089	C ₁ , C ₁₀ -C ₁₈		4.140	
	C ₁₀ -C ₁₆	4.108	4.070	4.091	C ₁ , C ₁₀ -C ₁₆		4.141	
	C ₁₁ -C ₂₀	4.109	4.010	4.106	C ₁ , C ₁₁ -C ₂₀		4.146	
	C ₁₁ -C ₁₉	4.108	4.024	4.088	C ₁ , C ₁₁ -C ₁₉		4.141	
	C ₁₁ -C ₁₈	4.107	4.035	4.088	C ₁ , C ₁₁ -C ₁₈		4.141	
	Mean	4.106	4.055	4.095			4.141	4.147
	SD	0.002	0.024	0.006			0.003	
	$\Delta(t_M - t_{MT})$	0.000	-0.051	-0.011			0.035	0.041

^aRaw retention times on the ZB-1 column at 100 and 150 °C were cited from Table 1 in [33].

^b T_c , column temperature

Table 3

Effects of regression ranges of *n*-alkanes on k_M values calculated by different methods^a

T_c (°C) ^b	Range of <i>n</i> -alkanes		Eq. (12)	Eq. (3)	Eq. (8)	Range of <i>n</i> -alkanes		Eq. (6b) and (7)
			k_{MT} (s)	k_{MM} (s)	k_{MG} (s)			k_{ML} (s) k_{MCH4} (s)
90	C ₅ -C ₁₂		209.98	209.04	209.6	C ₁ , C ₅ -C ₁₂		210.69
	C ₅ -C ₁₁		210.03	209.35	209.7	C ₁ , C ₅ -C ₁₁		210.79
	C ₅ -C ₁₀		210.10	209.19	209.9	C ₁ , C ₅ -C ₁₀		210.78
	C ₆ -C ₁₂		209.76	208.37	209.4	C ₁ , C ₆ -C ₁₂		210.79
	C ₆ -C ₁₁		209.80	208.63	209.6	C ₁ , C ₆ -C ₁₁		210.79
	Mean k_M		209.93	208.92	209.64			210.77 211.4
	SD		0.15	0.41	0.18			0.04
	$\Delta(k_M - k_{MT})$		0.00	-1.02	-0.29			0.83 1.47
120	C ₅ -C ₁₃		223.45	222.78	223.3	C ₁ , C ₅ -C ₁₃		224.14
	C ₅ -C ₁₂		223.46	222.88	223.2	C ₁ , C ₅ -C ₁₂		224.07
	C ₅ -C ₁₁		223.51	222.97	223.4	C ₁ , C ₅ -C ₁₁		224.06
	C ₆ -C ₁₃		223.31	222.39	223.3	C ₁ , C ₆ -C ₁₃		224.14
	C ₆ -C ₁₂		223.29	222.56	223.1	C ₁ , C ₆ -C ₁₂		224.07
	C ₆ -C ₁₁		223.31	222.69	223.3	C ₁ , C ₆ -C ₁₁		224.06
	C ₇ -C ₁₃		223.42	221.94	223.3	C ₁ , C ₇ -C ₁₃		224.14
	C ₇ -C ₁₂		223.41	222.21	223.0	C ₁ , C ₇ -C ₁₂		224.07
	Mean k_M		223.40	222.55	223.24			224.09
	SD		0.08	0.35	0.13			0.04
150	$\Delta(k_M - k_{MT})$		0.00	-0.84	-0.16			0.70 1.20
	C ₅ -C ₁₅		234.72	234.25	234.6	C ₁ , C ₅ -C ₁₅		235.60 236.0

T_c ($^{\circ}\text{C}$) ^b	Range of <i>n</i> -alkanes	Eq. (12)	Eq. (3)	Eq. (8)	Range of <i>n</i> -alkanes	Eqs. (6b) and (7)	
						t_{MT} (s)	t_{ML} (s)
		t_{MT} (s)	t_{MM} (s)	t_{MG} (s)		t_{ML} (s)	t_{MCH4} (s)
	C ₅ -C ₁₄	234.71	234.31	234.8	C ₁ , C ₅ -C ₁₄	235.60	
	C ₅ -C ₁₃	234.68	234.38	234.7	C ₁ , C ₅ -C ₁₃	235.53	
	C ₆ -C ₁₅	234.77	234.05	234.6	C ₁ , C ₆ -C ₁₅	235.60	
	C ₆ -C ₁₄	234.76	234.16	234.8	C ₁ , C ₆ -C ₁₄	235.60	
	C ₆ -C ₁₃	234.71	234.25	234.8	C ₁ , C ₆ -C ₁₃	235.53	
	C ₇ -C ₁₅	234.86	233.76	234.6	C ₁ , C ₇ -C ₁₅	235.60	
	C ₇ -C ₁₄	234.86	233.92	234.9	C ₁ , C ₇ -C ₁₄	235.60	
	C ₇ -C ₁₃	234.79	234.07	234.8	C ₁ , C ₇ -C ₁₃	235.53	
	Mean t_{M}	234.76	234.13	234.73		235.58	
	SD	0.07	0.20	0.11		0.03	
	$\Delta(t_{\text{M}} - t_{\text{MT}})$	0.00	-0.63	-0.03		0.81	1.24

^aRaw retention times on the CPSIL-5CB column at 90, 120 and 150 $^{\circ}\text{C}$ were cited from [10].

^b T_c , column temperature

Table 4

Comparison of t_M values that were experimentally determined (t_{MCH4} and t_{MNe}) or calculated (t_{ML} , t_{MT} , t_{MG} and t_{MM}) by different methods

Columns	Range of carbon	Column temp.(°C)	t_{MCH4} (min)	t_{MNe} (min)	t_{ML} (min)	t_{MT} (min)	t_{MG} (min)	t_{MM} (min)	$\Delta(t_{MCH4} - t_{MM})$ (min)
Capillary	C ₇ -C ₁₄	70	3.705	-	3.693	3.660	3.647	3.602	0.103
ZB-1 ^a	C ₇ -C ₁₆	100	3.878	-	3.866	3.831	3.811	3.794	0.084
	C ₈ -C ₁₉	130	4.062	-	4.057	4.015	4.005	3.968	0.094
	C ₈ -C ₂₀	140	4.101	-	4.096	4.056	4.043	4.016	0.085
	C ₈ -C ₂₀	150	4.147	-	4.140	4.105	4.097	4.07	0.077
	C ₉ -C ₂₀	160	4.209	-	4.200	4.166	4.158	4.126	0.083
	C ₉ -C ₂₂	170	4.262	-	4.260	4.220	4.212	4.179	0.083
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Capillary	C ₃ -C ₁₀	60	195.3	194.8	194.3	193.5	193.3	193.2	2.1 (0.035) ^c
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CPSIL-5CB ^b	C ₃ -C ₁₂	90	211.4	210.9	210.7	209.8	209.7	209.6	1.8 (0.030) ^c
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	C ₅ -C ₁₀	60	195.3	194.8	194.5	193.4	193.1	192.3	3.0 (0.050) ^c
	C ₅ -C ₁₂	90	211.4	210.9	210.7	210.0	209.6	209.0	2.4 (0.040) ^c
	C ₅ -C ₁₃	120	224.6	224.2	224.1	223.5	223.3	222.8	1.8 (0.030) ^c
	C ₅ -C ₁₅	150	236.0	235.7	235.6	234.7	234.6	234.3	1.8 (0.030) ^c
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Capillary	C ₅ -C ₉	60	322.8	322.3	322.1	321.2	321.0	320.1	2.7 (0.045) ^c
HP-5 ^b	C ₅ -C ₁₁	90	344.0	343.6	343.4	342.1	342.2	341.5	2.5 (0.042) ^c
	C ₆ -C ₁₃	120	361.8	361.5	361.3	360.3	360.3	359.5	2.3 (0.038) ^c
	C ₆ -C ₁₅	150	377.4	377.1	376.9	376.1	375.9	375.3	2.1 (0.035) ^c
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Packed	C ₅ -C ₉	60	130.0	128.0	127.4	122.7	120.0	121.8	8.2 (0.137) ^c
QF-1 ^b	C ₆ -C ₁₁	90	145.5	143.4	143.1	137.6	137.0	136.0	9.5 (0.158) ^c
<hr/>									
Packed	C ₅ -C ₉	120	158.6	152.7	151.3	144.6	145.2	139.1	19.5 (0.325) ^c

Columns	Range of carbon	Column temp. ^a (°C)	<i>t</i> _{MCH4} (min)	<i>t</i> _{MNe} (min)	<i>t</i> _{ML} (min)	<i>t</i> _{MT} (min)	<i>t</i> _{MG} (min)	<i>t</i> _{MM} (min)	$\Delta(t_{\text{MCH4}} - t_{\text{MM}})$ (min)
PS-255 ^b	C ₅ -C ₁₁	150	166.6	161.3	160.2	153.5	152.6	147.9	18.7 (0.312) ^c

^a Experimental holdup times (*t*_{MCH4}) and the raw retention times were cited from Table 1 in [33].

^b Experimental holdup times (*t*_{MCH4} and *t*_{MNe}) and raw retention times in seconds were cited from [10].

^c For direct comparison, values in the parenthesis are in minutes.

Table 5
Comparison of different retention models and their corresponding characteristics of k_M values

Models	LE [24]	QE [34]	CE, [25]	LQG [10,28]	Gonzalez et al. [13,27]
No. of model parameters	2	3	4	4	4
Methods to get k_M and model parameters	experimentally determine k_M or calculate k_{MM} by linear regression, and then to get model parameters in 2 steps	calculate k_{MT} and model parameters by multiple linear regression in 1 step	calculate k_{MM} by 2 linear regressions and then model parameters in 2 steps	calculate 4 model parameters by multi-parameters regression and then k_{ML} using 2 of the 4 parameters in 2 steps	calculate k_{MG} and model parameters by multi-parameters regression in 1 step
Significance of k_M values	k_M is obtained with solutes such as air, neon and methane as an unretained solute. k_{MM} has no real meaning, is not related to retention of a true unretained solute.	k_{MT} is a retention time of an hypothetical unretained solute with $k = 0$. It is calculated by the QE model that is based on the DE model.	k_{MM} has no real meaning, is not related to and does not match with the cubic equation.	k_{ML} is a retention time of an hypothetical <i>n</i> -alkane with $z = 0$. Neon was used as a reference to confirm the validity	k_{MG} is a retention time of an hypothetical unretained solute with $k = 0$ or $\Delta G^S/RT \rightarrow +\infty$.
Effect of regression range on k_M	Large	Small	Large	Smallest	Small or moderate, depending on GC conditions
Accuracy of curve fittings	Not good	Good	Good	Good	Good
Classification of k_M corrections	over and under	accurate	under	over	accurate