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Journal of Chromatography A, 832 (1999) 165–172

JOURNAL OF
CHROMATOGRAPHY A

Consistency of gas hold-up determinations

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Received 15 September 1998; received in revised form 18 November 1998; accepted 18 November 1998

Abstract

The retention of methane on poly(dimethylsiloxane) capillary columns was studied focusing its relation with the gas hold-up time t_M , which was derived from the retention of n -alkanes. The [ideal gas/Van der Waals fluid] partition equation was applied in order to provide the mathematical expression for the retention factor of the n -alkanes as a function of the carbon number n . In this context the partial molar free energy of solution is a non-linear function of the chain length $\Delta G^s(n)$ ($n \geq 5$). The resultant retention factor k of methane, determined from its retention time and the calculated t_M , approaches an almost constant value when the temperature is increased beyond 100°C. This value of k has the order of the reciprocal column phase ratio $1/\beta$. Precisely, this is the theoretically expected limit of a non-interacting solute or inert marker. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hold-up time; Thermodynamic parameters; Alkanes

1. Introduction

The gas hold-up time t_M is a basic parameter in gas–liquid chromatography (GLC). It is indispensable for the determination of thermodynamic solution functions from the solute retention [1]. Conversely, it is necessary for the prediction of retention under different experimental conditions from known thermodynamic information [2–5]. Even for the calculation of a relative parameter, like the Kováts index, the knowledge of t_M remains indispensable. Currently, the determination of t_M has been derived from a relationship for the retention of n -alkanes and other homologous series [6–16]. These procedures were extensively reviewed and evaluated by Haken

and Wainwright [15,16]. All methods rely on the application of the basic equation:

$$t_R(n) = t_M[1 + k(n)] \quad (p \text{ and } T = \text{constant}) \quad (1)$$

This implicitly neglects extra-column effects and interfacial phenomena. The retention time $t_R(n)$, for the different n -alkanes, is measured under the same conditions (p and T), or preferably on the same chromatogram. Thus, the unique variable is the carbon number n .

Some assumption must be made on the mathematical form of retention factor $k(n)$, so t_M can be determined by multiparametric regression of experimental data $t_R(n)$ to a given curve or expression. Since $k = (1/\beta) \exp(-\Delta G^s/RT)$, implies that some assumption must be made on the dependence of the partial molar free energy of solution ΔG^s with the

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chain length of the n -alkanes. The phase ratio of the column is $\beta = V_G/V_L$, where V_G and V_L are the volumes of the gas and liquid phases. Most of the proposed procedures of t_M calculation implicitly adopt the empirical linear expression: $\Delta G^s(n) = \Delta G^+ + \Delta G^m n$, first settled by Martin [17]. ΔG^+ is a contribution independent of n and ΔG^m is an average contribution per methylene monomer.

A potential controversy is installed in the literature on whether can be assured if $\Delta G^s(n)$ is linear or not. Wainwright et al. [18] and Touabet et al. [19] reviewed the early literature concerning this issue. From their detailed statistical analysis on capillary column data, the authors in Ref. [19] concluded that non-linear empirical models, involving only the least number of parameters possible, are generally adequate for describing the experimental information. More recently, Le Vent analyzed retention data of n -alkanes in the form of specific retention volumes V_g [20]. He 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. He also corroborated the previous observation that the linearly calculated t_M is significantly lower than the retention of an “insoluble gas” like neon, suggesting that this direct measurement of the gas hold-up t_M should be preferred to the calculation through the retention of n -alkanes. Conversely, Lebron-Aguilar and co-workers, using raw $t_R(n)$ data from capillary and packed columns, detected statistically meaningful deviations from linearity [21–24]. By the application of mass spectrometry, they observed that neon is not invariably the least retained gas. In packed columns sometimes it is eluted after methane [22]. The retention times of gases like He, Ne, Ar, N₂, H₂ or CH₄ are always mutually close, but significantly greater than the t_M calculated from $t_R(n)$ data applying empirical non-linear expressions [21,22].

The contradiction confronting the conclusions by Le Vent, in one hand, and those by Touabet or Lebron-Aguilar and coworkers on the other, seems not to proceed from the expansion of the standard error resulting from the conversion of raw $t_R(n)$ data into specific retention volumes $V_g(n)$. Although there are huge intrinsic standard errors in the factors needed for the conversion, such as in the estimation of the flow rate at the column temperature or the gas

compressibility correction, these factors are constant for all the $t_R(n)$ data. This is the consequence of the fact that all $t_R(n)$ are measured under the same conditions, or straightforwardly belong to the same chromatogram.

It has been shown, through statistical thermodynamic considerations, that there exists theoretical expectancy for the non linear behavior of $\Delta G^s(n)$ [25].² Other theoretical arguments, of a different nature, also have been exposed [26–28]. Assuming that the excluded volume effects in the liquid solution are the molecular origins for the deviation from linearity of $\Delta G^s(n)$, in Ref. [25] it was found that the theoretical orders of magnitude and expected trends for the non linear term are consistent with the experimental observations from Ref. [22]. Following this line, the objective of the present work is to study the consistency of the non-linearly calculated parameter t_M . For performing this task, we firstly have to derive the theoretical relationship between t_M and a related physical observable. We, then, will be enabled to carry out an experimental corroboration of the expected behavior for t_M in relation to this observable. The study of the relationship between t_M and the retention of an inert solute or marker is our present aim.

2. General

The foundations of the gas chromatographic theory are the hypotheses inherent to the differential equation of peak motion. This is the starting point of GC:

$$\frac{dz}{dt} = \frac{u(z)}{(1+k)} \quad (2)$$

Eq. (2) assumes that the position of the peak migrates at a local velocity dz/dt , which is slowed down with respect to the local velocity of the carrier gas $u(z)$ by the retardation factor $R = n_G/(n_G + n_L) = 1/(1+k)$; where n_G and n_L are, respectively, the

²There is an error in Ref. [25] arising from the application of the statistically derived chemical potentials to the standard states, leading into an erroneous dependence of ΔG on $\ln \beta$. Nevertheless, this error has no consequences for the dependence of ΔG on n .

number of solute molecules in the gas and in the liquid stationary phase.³ The factor R is the probability for finding the solute molecule in the gas stream, a condition necessary for moving along the axial coordinate z . The probability is that correspondent to the thermodynamic equilibrium. Hence the probability measured by the macroscopic quantity $1/(1+k)$ is directly related, at a molecular level, to the average energy difference for the solute molecule being placed in the liquid and gas phases.

Since the chromatographic observables are not local values, but the global quantities of the process, Eq. (2) must be integrated, yielding Eq. (1). The definition of the gas hold-up t_M arises from this integration as an average: $t_M \equiv \int_0^L (dz/u(z))$, so $t_M \equiv Lu^{-1} = L/\bar{u}$, where \bar{u} is the usual time-average velocity of the gas in the column of length L , while u^{-1} is the space-averaged reciprocal local velocity, $1/u(z)$. Therefore, the integrated equation of peak motion, the equation of retention, Eq. (1), settles the physical meaning of t_M as the residence time t_R of a solute marker with $k=0$. From a thermodynamic point of view, the partial molar free energy of solution of the marker should tend to infinite, $\Delta G^s/RT \rightarrow +\infty$. Thus, the probability for finding the marker molecule in the gas stream is equal to unity, or n_L should be null; physically meaning that the liquid phase is impermeable to the solute. This is consistent with the fluid dynamic significance of t_M . In a capillary column the convective transport of the marker molecule would occur in a cross section determined by the inner diameter of the column d_c , considering the liquid coating as part of an impermeable wall. Of course, this is a completely hypothetical condition. There always will be some probability for a gas molecule to permeate the liquid phase. Molecular repulsive forces are of very short range, with a dependence on r^{-12} , r being the intermolecular distance. The current statistical mechanics repre-

sentation of this fact is the assimilation to a hard core or sphere. When the molecular dimensions of the liquid are greater, with respect to the solute marker, the liquid lattice becomes more permeable to the marker molecule. Polymeric phases are most permeable to permanent gases [29].

In consequence, we have to admit that t_M is only an hypothetical limit arising from a mathematical necessity, a contour condition. In current gas chromatography, the parameter t_M will not correspond to the retention of any real substance or marker. Thus, no direct accurate experimental measure of t_M is feasible in GLC. It can only be determined indirectly through the application of Eq. (1).

Some confusion arises from the literature when the gas hold up t_M calculated by the application of Eq. (1) (i.e. the residence time of an hypothetical unretained solute with $k=0$ or $\Delta G^s/RT \rightarrow +\infty$) is directly compared to the retention of an inert gas. The unretained solute and the inert gas are actually different theoretical concepts.

3. The relationship between the retention of an inert marker and t_M

By definition, an inert or non-interacting molecule, in a given environment, is one that behaves as a free or independent particle. In the vapor phase solution, this condition corresponds to the behavior of the ideal gas, a condition met by mixtures of real gases at low densities and relatively high temperatures. In a polymeric liquid stationary phase it corresponds to two possible situations. One case is the Θ condition of the solution [30,31]. The other is manifested at sufficiently high temperatures. While the first condition is attained at a defined temperature Θ , the second is reached asymptotically.

If the solute is not submitted to net forces in both phases, the average energy change involved in transferring the molecule from one phase to the other will be zero, so $\Delta G^s/RT=0$. This implies that the solute distributes uniformly over the total volume of the system, comprising the sum of the liquid and gas volumes: $V=V_L+V_G$, as it does not perceive any energetic difference between phases. This condition renders a uniform concentration in the whole volume of the system V or a unitary distribution coefficient

³In non-ideal chromatography, or by influence of extra-column effects, the peaks become skewed. The position z of an asymmetric peak is defined by its center of mass, viz. the first moment temporal average of concentration (see e.g. Ref. [1]). In the conditions of our study the difference between the peak maximum and its center of gravity is in the order of the standard error of t_R . Here, we shall not make any distinction or correction concerning this problem. This important issue is discussed in Appendix A.

$K=1$. Namely, $k=1/\beta$. So the inert gas is defined by specifying $k=1/\beta$ or $\Delta G^s/RT=0$, a condition well differentiated from that of the hypothetical unretained solute with $k=0$ or $\Delta G^s/RT \rightarrow +\infty$.

From the point of view of statistical thermodynamics, the simplest approach to the gas–liquid partition would be the consideration of a binary ideal gas phase solution in contact with an infinitely diluted binary liquid solution. Under this approximation we have [25,32,33]:⁴

$$-\frac{\Delta G^s}{RT} = -\frac{E_t}{2kT} + \ln \frac{q_{r,v}^L}{q_{r,v}^G} + \ln(1 - u_e) \quad (3)$$

where $-E_t/2kT$ is the factor representing the solute molecule behaving as a rigid particle interacting with the liquid phase. This term only accounts for the three translational degrees of freedom of a hypothetical rigid sphere interacting with a mean force field. The ratio of the molecular partition functions $q_{r,v}^L/q_{r,v}^G$, of the solute in the liquid and in the gas solutions, accounts for the internal degrees of freedom of the molecule, rotational and vibrational. The excluded volume per unit liquid solution volume is u_e . Thus, the free volume fraction of the solution is $(1-u_e)$, a factor placed in the third term of Eq. (3). As shown in Ref. [25], this term would be responsible for the deviations from linearity of $\Delta G^s(n)$ of *n*-alkanes, and most linear solutes. The excluded volume fraction u_e asymptotically tends to zero when T is incremented sufficiently. Therefore, the third term of Eq. (3) will vanish at high temperatures.

We shall now consider a spherical solute molecule, like a noble gas or methane. In this case the potential function U of the molecular interaction with a segment of the solvent would be the simplest possible. It can be assimilated to a simple Lennard-Jones potential. When the temperature of the system is incremented sufficiently, the average energy of the solute molecules $\ln \langle e^{-U/kT} \rangle$ will reach a state such

that the interaction term will tend to zero ($-E_t/2kT \rightarrow 0$). Unlike a noble gas, methane presents the vibrational degrees of freedom of the C–H bonds. The energetic difference between the liquid and gas phases $\ln(q_{r,v}^L/q_{r,v}^G)$ will be in relation to the ratio of frequencies of the vibration modes $\ln \nu^G/\nu^L$, assuming independent oscillators. At a sufficiently high temperature, this difference will become negligible also. All three terms, on the right-hand side of Eq. (3), gradually vanish when the temperature is raised. As there is no perceptible net interaction in both phases, the energetic boundary between V_G and V_L disappears. Considering the trifling contributions to ΔG^s of methane's molecular degrees of freedom, we should expect that, at not too elevated temperatures, it would approximate the condition of a non-interacting or inert solute ($k=1/\beta$ or $\Delta G^s/RT=0$).

When Eq. (3) in conjunction with Eq. (1) are applied to the retention of *n*-alkanes, the resultant expression for $t_R(n)$ has the form:

$$t_R(n) = t_M + \exp[A + B(n-2) + \ln(1 - Cn^2)] \quad (4)$$

This expression is valid for those *n*-alkanes which admit intramolecular interactions ($n \geq 5$). The significance of t_M corresponds to the unretained solute ($k=0$ or $\Delta G^s/RT \rightarrow +\infty$), derived from Eq. (1). Eq. (4) allows the performance of multiparametric regressions of $t_R(n)$ data. These are usually carried out using available commercial software applying the methods of Marquardt or Gauss [34].

Four parameters ought to be determined: t_M , A , B and C . Thus, a sufficient number of *n*-alkanes must be included in each chromatogram in order to ensure the convergence to the correct values. Lebron-Aguilar et al. [21,22] found that the non-linear term has a relative order 10^{-3} with respect to the other terms. This fact suggests a great difficulty at the moment of determining the parameters of Eq. (4) with sufficient precision to meet the requirements of our present purpose. We should bear in mind that the comparison of the calculated t_M with the retention of a gas whose k is in the order of $1/\beta$ would have to be carried out. Consequently, a difference ($t_R - t_M$) of only a few thousandths of a minute would generate huge percentage errors. Additionally, the absence of extra-column effects and a negligible influence of the interfaces on the retention must be ensured in order

⁴Here, the presentation of Eq. (3) differs, from what was stated in Ref. [25], in the fact that we are attributing it a more general character, and that the erroneous $\ln\beta$ contribution is lacking. The form of Eq. (3) is not limited to the van der Waals fluid treatment for the liquid phase. This can be deduced from more general formulations, as that given by Ben Naim (see Refs. [32,33]). These issues will be discussed in a forthcoming paper.

to meet the hypotheses of Eq. (4). These conditions should be better achieved in capillary columns with non-polar stationary phases. The incidence of the gas–liquid interface extension in the retention of *n*-alkanes on polar stationary phases is well known [35–38]. This fact prevents the accurate application of Eq. (4) to those systems.

4. Results

In view of the experimental difficulties to which our evaluation is submitted, great care has to be taken for the selection of adequate information. This was restricted to retention data of *n*-alkanes that had been obtained and processed under the following specifications: (a) non-polar capillary columns, (b) longer than 30 m, (c) only including raw retention

times $t_R(n)$ with at least four significant digits, (d) obtained with high split ratios, generally greater than 50:1. (e) Convergent regressions, yielding a perfect curve fit (with a square regression coefficient $r^2 = 1$), were uniquely considered.

Table 1 shows the comparison of the retention factor of methane $k(\text{CH}_4)$ at increasing temperatures with the reciprocal phase ratio of the column $1/\beta$. The retention factor of methane was determined from its experimental retention time $t_R(\text{CH}_4)$ and the calculated t_M as $k(\text{CH}_4) = [t_R(\text{CH}_4) - t_M]/t_M$. In the calculation of t_M , Eq. (4) was applied with the above-mentioned specifications. The values of $t_R(\text{CH}_4)$ and t_M are also tabulated. The phase ratio of each column is that reported by the manufacturer. Fig. 1 shows the data from Table 1, altogether, represented as distribution coefficients $K = k(\text{CH}_4)\beta$.

As can be observed, $k(\text{CH}_4)$ reaches the order of

Table 1
Comparison of the reciprocal column phase ratio $1/\beta$ and the retention factor of methane $k(\text{CH}_4)$ at different temperatures

Column specifications	T °C	$1/\beta$	$k(\text{CH}_4)$	$t_R(\text{CH}_4)$	t_M Regr. Eq. (4)
HP-1 50 m × 0.20 mm, 0.33 μm	50	0.0067	0.0134	4.209 min	4.1535 min
	60		0.0112	4.295	4.2472
	70		0.0101	4.385	4.3410
	90		0.0086	4.573	4.5340
	100		0.0075	4.657	4.6225
	120		0.0063	4.835	4.8046
	140		0.0065	5.019	4.9865
	160		0.0065	5.183	5.1496
	180		0.0070	5.352	5.3148
	200		0.0072	5.515	5.4758
AT-1 30 m × 0.25 mm, 0.25 μm	60	0.0040	0.0089	2.215 min	2.1955 min
	70		0.0086	2.265	2.2457
	80		0.0035	2.308	2.300
	100		0.0038	2.409	2.400
CPSil 5CB 50 m × 0.32 mm, 0.43 μm from Ref. [22]	60	0.0054	0.0111	195.3 s	193.15 s
	90		0.0079	211.4	209.75
	120		0.0059	224.6	223.29
	150		0.0052	236.0	234.77
HP-5 60 m × 0.25 mm, 0.25 μm from Ref. [22] from Ref. [23]	60	0.0040	0.0056	322.8 s	321.01 s
	90		0.0052	344.0	342.23
	120		0.0041	361.8	360.31
	150		0.0041	377.4	375.87
	150		0.0040	14.58 min	14.522 min
	160		0.0050	14.97	14.895
CPSil 5CB from Ref. [21]	90	0.0054	0.0086 CH ₄	211.38 s	209.57 s
	90		0.0066 Ne	210.96	209.57

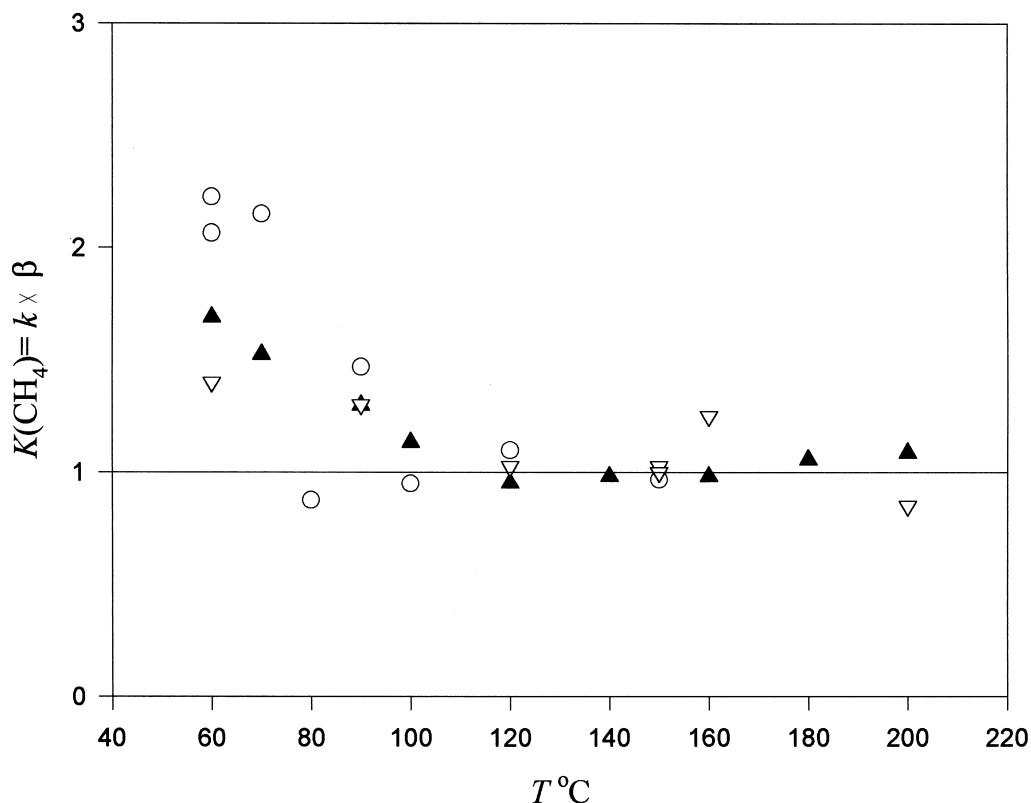


Fig. 1. Distribution coefficient of methane $K(\text{CH}_4)$ on poly(dimethylsiloxane) capillary columns as a function of temperature. All data from Table 1 are represented. These involve columns with different phase ratios and from different manufacturers. Symbols: ∇ =column HP5 (5% phenyl substitution), \triangle =column HP1, \circ =other columns.

$1/\beta$, or $K=1$, over 100°C . This means that at this temperature the vibrational degrees of freedom from the C–H bonds would negligibly contribute to the energetic difference of the solute in both phases.

In one aspect these results are in agreement with those recently obtained by Vezzani et al. [39]. At constant pressure, these authors found that, over 100°C , the curve of methane $t_{\text{R}}(T)$ practically joins the curve $t_{\text{M}}(T)$ calculated through its theoretical fluid dynamic expression [40], $t_{\text{M}}(T) = (128\eta(T)/3)(L/d_c)^2(p_i^3 - p_o^3/[p_i^2 - p_o^2]^2)$. Obviously, the errors associated with the determination of the gas viscosity η , the inner column diameter d_c , and the inlet and outlet pressures (p_i , p_o), would not allow $t_{\text{R}}(\text{CH}_4)$ to be differentiated from t_{M} when $T > 100^\circ\text{C}$. But at lower temperatures, the difference $[t_{\text{R}}(\text{CH}_4) - t_{\text{M}}]$ overcomes the standard error of the fluid dynamically calculated t_{M} . Therefore, in consideration of the

results by Vezzani et al., the fluid dynamic consistency of the non-linearly calculated t_{M} over 100°C , can be indirectly assured.

5. Conclusions

It is clear that the condition of the hypothetical unretained solute ($k=0$ or $\Delta G^s/RT \rightarrow +\infty$) is not experimentally attainable. When T is increased sufficiently, it is reasonable to expect that all solutes should asymptotically converge to $k=1/\beta$ or $\Delta G^s/RT=0$, behaving as inert compounds. The t_{M} calculated through Eq. (4) consistently resembles the behavior expected a priori when it is compared to the retention of methane. In poly(dimethylsiloxane) stationary phases this gas would converge to the non-interacting behavior in the range of T over

100°C. However, the errors are too great to permit a detailed study at significantly higher temperatures. What takes place beyond will probably remain in the grounds of conjecture, considering the experimental difficulties. However, there are precedents in this direction [41].

No consistent behavior of the calculated t_M is found when the linear $\Delta G^s(n)$ hypothesis is applied to $n \geq 5$. In the settled controversy, this fact adds more evidence that is favorable to the non-linear hypothesis.

The retention of methane is a quite good approximate measure of t_M in silicone capillary columns at $T > 100^\circ\text{C}$. However, in this temperature range, for low phase ratios the following correction should be applied:

$$t_M = t_R(\text{CH}_4) \frac{\beta}{(\beta + 1)} \quad (5)$$

Appendix 1

Discussion on the consideration of peak asymmetry

Due to the greater impact of extra column effects, the first detected peak belonging to an inert solute will be more markedly skewed than those peaks from the later part of the chromatogram. In cases in which asymmetric peaks are involved, the position z indicated in Eq. (2) refers to the position of their center of mass. The final residence time t_1 , of the peak center of gravity, will be provided by the first moment of the detected distribution function $h(t)$ (see e.g. Ref. [1]):

$$t_1 = \frac{\int_0^{\infty} th(t)dt}{\int_0^{\infty} h(t)dt} \quad (\text{A.1})$$

The experimentally measured quantity is the residence time t_R corresponding to the peak maximum, and the difference $(t_1 - t_R)$ is not constant for all the peaks along the chromatogram. In view of this

situation, it may be argued that peak asymmetry should be taken into consideration in the present study. The objective of this section is to discuss this important issue.

Le Vent recently showed that, either for fronting or tailing peaks eluting from capillary columns, the experimental $h(t)$ can be well represented by some simple empirical distribution functions [42]. He compared the experimental peak profiles with the exponentially modified gaussian, bigaussian and gaussian–lorentzian distributions, finding a reasonable agreement. If we are interested in obtaining an expression for the correct position of the peak center of gravity, namely an expression for $(t_1 - t_R)$, we have to choose those $h(t)$ allowing an analytical solution of the integrals in Eq. (A.1). Fixing the origin of the coordinate system for $h(t)$ in $0 = t_R$ results in the first moment directly providing the difference $(t_1 - t_R)$.

In the present discussion we shall adopt the bigaussian $h(t)$. This is defined by:

$$h(t) = h_o \exp\left(-\frac{t^2}{2\sigma^2}\right) \text{ if } t < 0;$$

$$h(t) = h_o \exp\left(-\frac{t^2}{2x^2\sigma^2}\right) \text{ if } t > 0 \quad (\text{A.2})$$

The maximum height of the peak occurs at $[t = t_R = 0, h(t) = h_o]$. The standard deviation for the first part of the peak ($t < t_R$) is σ , and for the second part ($t > t_R$) is $x\sigma$. The skew factor x is only defined for positive values. For $0 < x < 1$ there is peak fronting, and peak tailing when $x > 1$. By applying this distribution function, the following solution is obtained:

$$t_1 - t_R = \frac{2}{\sqrt{2\pi}} \frac{(x^2 - 1)}{(x + 1)} \sigma \quad (\text{A.3})$$

The value of σ is related to the peak width at half the height, w_h , by the relationship:

$$\sigma = \frac{w_h}{(x + 1)\sqrt{2 \ln 2}} \quad (\text{A.4})$$

The skew factor x can be determined from the ratio of two distances at half the peak height: $x = \overline{oa}/\overline{ob}$. The segment \overline{oa} is the horizontal distance, taken from the vertical line passing through the maximum,

to the right curve $h(t)$, and \overline{ob} is that taken to the left $h(t)$.

The early eluting peaks, from the experimental results of our laboratory, invariably presented values of $w_h < 0.020$ min. The skew factor for these peaks was always $x < 1.3$ (30% greater standard deviation for the trailing part of the peaks). Replacing this limiting values in Eqs. (A.3) and (A.4) results in a difference $(t_1 - t_R) < 0.0018$ min. In this work we also analyze t_R 's reported by another laboratory. Unfortunately the information concerning peak dispersion was not available for these data. Considering that $(t_1 - t_R)$ is in the order of the standard error of measurement, it was concluded that it is not convenient to realize any correction concerning peak asymmetry in the present study. In this way, all the experimental information from Table 1 is analyzed on the same basis.

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