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Homologous series methods for determining hold-up parameters in isothermal gas chromatography

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Abstract

In isothermal gas chromatography, analysis of retention parameters for successive members of homologous series forms the basis of several established, related methods for determining corresponding hold-up parameters. These parameters may be times, volumes or volumes per mass of stationary phase, with or without volume correction for gas compression. With full statistical considerations, the present paper compares some of these methods and their extensions. The procedures are applied, through a set of microcomputer programmes, to selected experimental data.

Keywords: Retention time; Retention volume; Hold-up time; Hold-up volume

1. Introduction

Key parameters in isothermal gas chromatography are hold-up time and hold-up volume [1]. These are essentially (a) the time, and (b) the volume of mobile (carrier gas) phase, required to elute an unretained compound; since the volume is the product of carrier gas average volume flow-rate and the time, the volume will be proportional to the time for the usual condition of constant flow-rate. Equivalently, hold-up time is the time spent in the mobile phase by any compound between injection and detection. For some purposes, a correction is applied to hold-up volume for gas compressibility within the column [1] to yield a value for a hypothetically incompressible gas. Hold-up time is a function of column characteristics (physical dimensions including packing information where relevant, stationary phase nature, temperature), extracolumn characteristics (time intervals— injection block to column, column to detector, detector response) and mobile phase flow-rate; hold-up volume

excludes dependence upon the last of these. Very many papers have described procedures for determining hold-up time or volume and several reviews (e.g., [2,3]) summarise and classify these procedures. A popular direct method simply measures the time or volume for elution of a supposedly unretained compound. Methane is the favourite here, but doubt is often cast over the assumption of complete non-retention [3]. Hydrogen, air and neon have also been used, but then there is the added complication of impossible/difficult flame ionisation detection and, in the case of air, oxidation of the stationary phase in elevated temperature columns. Because of these problems, many chromatographers resort to the use of indirect methods based upon the hypothesis of a linear relationship between the logarithm of retention factor (formerly capacity factor) and carbon number in a homologous series (excluding lower members); the hypothesis has substantial experimental support when hold-up times or volumes are determined by unretained solute methods. The present paper analy-

ses variants of some of the more common procedures based upon the linearity but, in so doing, attempts to put these on a proper statistical footing, commonly lacking in previous considerations.

2. Basic equations

The fundamental equation in gas–liquid partition chromatography relating the column contribution to a total retention parameter p_R for a particular compound and the corresponding hold-up parameter p_M is

$$p_{Rc} = p_{Mc}(1 + K/\beta) \quad (1)$$

In this equation, β is the column phase volume ratio (mobile/stationary) and K is the distribution constant (concentration in stationary/concentration in mobile) for the compound; the additional subscript c refers to column contributions. The parameter p_R can represent a variety of quantities: (i) retention volume (with or without compression factor correction), (ii) retention time, commonly for a constant carrier flow-rate, (iii) retention volume divided by mass of stationary phase. Eq. (1) assumes negligibility of surface adsorption on the stationary phase. It may be extended to include extracolumn factors as follows. Suppose that the extracolumn contributions are independent of compound, retained or otherwise, so that total retention and hold-up parameters (p_R and p_M) are given by

$$p_R = p_{Rc} + p_e \text{ and } p_M = p_{Mc} + p_e$$

the subscript e referring to the extracolumn contribution. Then, using Eq. (1),

$$p_R = p_e + p_{Mc}(1 + K/\beta) = p_M + p_{Mc}K/\beta$$

This equation may also be written

$$\ln k = -\ln \beta - \Delta G_m^\circ/RT + \ln(p_{Mc}/p_M) \quad (2)$$

where k = retention factor (formerly capacity factor) = $p_R/p_M - 1$, ΔG_m° = standard molar Gibbs energy of transfer (mobile to stationary), R = gas constant and T = thermodynamic temperature. Additional assumptions in Eq. (2) are those of ideal gas mixture and ideal dilute solution behaviour, not unreasonable for the usual concentrations involved;

(these assumptions imply independence of ΔG_m° on the choice of standard concentration). The final logarithmic term in Eq. (2) will generally be comparatively small, but need not be neglected completely.

Consider now a homologous series of compounds and suppose that (a) ΔG_m° is, to close approximation, a linear function of carbon number N when that number is not too small, i.e.,

$$\Delta G_m^\circ = A_0 + A_1N \quad (3)$$

and (b) $\ln(p_{Mc}/p_M)$ is a comparatively weak polynomial function of N , i.e., $\ln(p_{Mc}/p_M) = \sum_{i=0}^{\infty} B_i N^i$; A_0 , A_1 and B_i are constants for particular series, stationary phase and temperature. Eq. (2) can then be written

$$\ln k = a + bN + \sum_{i=2}^{\infty} B_i N^i \quad (4)$$

where $a = -\ln \beta - A_0/RT + B_0$ and $b = -A_1/RT + B_1$. At this stage, it will be assumed that the summation in Eq. (4) is negligible, so that

$$\ln k = a + bN \quad (5)$$

Even without experimental chromatographic evidence, the assumption of Eq. (3) is not unreasonable. Table 1 shows the standard molar Gibbs energies of gas formation and vaporisation at 25°C (standard pressure = 101 325 Pa) for a series of *n*-alkanes [4]; in each case, approximate linearity with N is clearly evident for the larger N , but with significant deviation for the lower N ; one might then reasonably extrapolate this behaviour to solution in stationary phase solvents. As stated above, there is substantial support for Eq. (5) when p_M has been determined by the direct method of injecting an unretained solute; this also applies to homologous series other than *n*-alkanes, e.g., methyl esters, alcohols, ketones). Furthermore, use of Eq. (5) for different homologous series has yielded very similar values of p_M , (e.g., [5]). The remainder of this paper will therefore proceed on the basis either of the absolute truth of Eq. (4) (when N is not too small) or with the possibility that better results could be obtained by extending the right side to a quadratic function, i.e.,

Table 1
Standard molar Gibbs energies of gas formation and vaporisation of *n*-alkanes at 25°C

| <i>n</i> -Alkane | $\Delta G_m^\circ / \text{kJ mol}^{-1}$ | | | |
|---------------------------------|---|----------|--------------|----------|
| | Formation | Interval | Vaporisation | Interval |
| CH ₄ | -50.8 | | | |
| | | 17.9 | | |
| C ₂ H ₆ | -32.9 | | | |
| | | 9.4 | | |
| C ₃ H ₈ | -23.5 | | | |
| | | 6.3 | | |
| C ₄ H ₁₀ | -17.2 | | | |
| | | 8.8 | | |
| C ₅ H ₁₂ | -8.4 | | 1.21 | |
| | | 8.1 | | 2.87 |
| C ₆ H ₁₄ | -0.3 | | 4.08 | |
| | | 8.3 | | 2.93 |
| C ₇ H ₁₆ | 8.0 | | 7.01 | |
| | | 8.4 | | 3.01 |
| C ₈ H ₁₈ | 16.4 | | 10.02 | |
| | | 8.4 | | 3.03 |
| C ₉ H ₂₀ | 24.8 | | 13.05 | |
| | | 8.4 | | 2.91 |
| C ₁₀ H ₂₂ | 33.2 | | 15.96 | |
| | | 8.4 | | 2.94 |
| C ₁₁ H ₂₄ | 41.6 | | 18.92 | |
| | | 8.4 | | 3.03 |
| C ₁₂ H ₂₆ | 50.0 | | 21.95 | |
| | | 8.5 | | 2.95 |
| C ₁₃ H ₂₈ | 58.5 | | 24.90 | |
| | | 8.3 | | 3.03 |
| C ₁₄ H ₃₀ | 66.8 | | 27.93 | |
| | | 8.4 | | 2.94 |
| C ₁₅ H ₃₂ | 75.2 | | 30.87 | |
| | | 8.6 | | 2.90 |
| C ₁₆ H ₃₄ | 83.8 | | 33.77 | |
| | | 8.3 | | 3.13 |
| C ₁₇ H ₃₆ | 92.1 | | 36.90 | |
| | | 8.4 | | 2.64 |
| C ₁₈ H ₃₈ | 100.5 | | 39.54 | |
| | | 8.5 | | 3.14 |
| C ₁₉ H ₄₀ | 109.0 | | 42.68 | |
| | | 8.3 | | 3.01 |
| C ₂₀ H ₄₂ | 117.3 | | 45.69 | |

Standard pressure = 101 325 Pa.

$$\ln k = \ln(p_R/p_M - 1) = a + bN + cN^2 \quad (6)$$

The problem is then to deduce a value of p_M from values of p_R for members of a homologous series. In the author's view, previous attempts (see [2] and [3]) have not always had a proper statistical basis, recognising here that measured retention parameters are subject to experimental error.

3. Computational procedures

Three general regression (functional relationship) approaches have been considered, in each case least squares being used as best fit criterion: (A) the solution of non-linear variants of Eqs. (5,6); (B) the use of trial values of p_M directly in the equations; (C) the use of equations developed by Al-Thamir et

al. [6]. None of these approaches are completely original in general terms (see Refs. [2] and [3]), but the present implementations are believed to have novel features. In each case, it is necessary to analyse n pairs of experimental data, retention parameter, p_{R_i} and carbon number, N_i ($i = 1$ to n), the latter often for consecutive N , but this is not essentially so. For procedure (c), regular (but not necessarily unit) N spacing is required.

(A) Eqs. (5,6) can be written

$$p_R = p_M [1 + \exp(a) \exp(bN)] \quad (5a)$$

$$p_R = p_M [1 + \exp(a) \exp(bN) \exp(cN^2)] \quad (6a)$$

In these forms, regression analysis, using either of the well-known non-linear iterative techniques of Gauss and of Marquadt/Levenberg, involves no weighting complications for the dependent variable p_R . The simpler Gauss approach [7] proved satisfactory for the application in hand. Using Eq. (5a) as example, this requires algebraic expressions for the first derivatives of p_R with respect to each of the unknowns p_M , a and b , say $D(p_M)$, $D(a)$ and $D(b)$. Following initial guesses of the unknowns (which generally can be quite poor), progression from iteration step j to step $j+1$ requires least squares solution of the matrix equation

$$\Delta p = \delta D \quad (7)$$

for δ , where

1. Δp is the row vector difference

$$(p_{R1} p_{R2} \cdots p_{Rn}) - (\hat{p}_{R1} \hat{p}_{R2} \cdots \hat{p}_{Rn})_j$$

members of the first and second vectors being, respectively, experimental and step- j -calculated values;

2. δ is the row vector difference

$$(p_M a b)_{j+1} - (p_M a b)_j$$

i.e., the difference between steps $j+1$ and j for the parameters to be determined;

3. D is the $3 \times n$ matrix

$$\begin{pmatrix} D(p_M)_1 & D(p_M)_2 & \cdots & D(p_M)_n \\ D(a)_1 & D(a)_2 & \cdots & D(a)_n \\ D(b)_1 & D(b)_2 & \cdots & D(b)_n \end{pmatrix}_j$$

where $D(p_M)_i$, $D(a)_i$, $D(b)_i$ are the values of

$D(p_M)$, $D(a)$ and $D(b)$ for $N=N_i$, and the matrix subscript j indicates the iteration stage for the parameters.

The least squares solution of Eq. (7) is then

$$\delta = \Delta p D^T (DD^T)^{-1} \quad (8)$$

where superscripts T and -1 indicate transpose and inverse.

The algorithm (8) has been incorporated into short Turbo C computer programmes, one for each of the Eqs. (5a) and (6a). Experimental data for a single chromatographic run are provided on file (the name of which is requested by the programme). Iteration continues until each equation parameter [p_M , a , b , c] changes by less than 0.01% at an iteration step. The residual variance $V(\text{res})$ of p_M values is checked at each step, i.e., after each δ determination by Eq. (8), and special provision is made in the programme when the variance increases (as opposed to the normal progressive decrease). The provision progressively halves the vector δ obtained as solution of Eq. (8) until the variance shows a decrease. Following this, the factors multiplying δ solutions are progressively increased back to one, by multiplying these factors by 2 once at each subsequent iteration step. Finally, after satisfactory completion of iteration, the estimated variance-covariance matrix V for the determined parameters is calculated by the equation

$$V = V(\text{res}) (DD^T)^{-1}$$

and $V(\text{res})$ estimates the (supposedly) common variance of the measured p_R (alternatively obtained by replication, of course). Normal distribution of measured retention parameters is a basic assumption here. As is often the case with iterative processes using initial guesses, poor initial guesses can lead to divergence of successive solutions or attainment of local rather than global variance minima. These possibilities generally increase as the number of parameters increase. Although these problems have been encountered to some extent here, they have certainly not proved troublesome with the test data used. The use of a single set of data at a time however recognises the existence of the potential problem.

(B) On the basis of the reasonable assumption of equal variances of measured p_R , it is essential to recognise the need for variable point weighting when using Eqs. (5,6) directly. In such applications, using least squares linear first order or linear second order regression (as appropriate), p_M is systematically varied so as to ultimately produce a minimum residual variance. Essentially each of the trial regressions treats p_M as a constant. So for the dependent variable transformation $p_R \rightarrow \ln(p_R/p_M - 1) = y$ (say), the variances of each y [$V(y)$] and of p_R [$V(p_R)$] will be related by

$$V(y) = (p_R - p_M)^{-2} V(p_R) \quad (9)$$

It is then normal practice to weight individual y values by something inversely proportional to the reciprocal of $V(y)$, whence the residual mean square for the weighted regression becomes an estimate of the proportionality constant. In conformation with this practice, a weighting of $(p_R/p_M - 1)^2 \{=V(p_R)/[V(y)p_M^2]\}$ by Eq. (9) has been used, making the residual variance estimate equal to $V(p_R)/p_M^2$, from which is derived $V(p_R)$. In this connection, p_M is treated as providing a unit deficiency of the degrees of freedom, giving totals of $n-3$ and $n-4$ for Eqs. (5,6). C programmes have been written to obtain optimum p_M values. The procedure used comprises the following steps:

1. A low value of p_M is progressively increased by a fixed increment until the residual mean square shows an increase rather than a progressive decrease;
2. p_M is then decreased by twice the increment and a new increment obtained as 10% of the old one;
3. Incrementation is then repeated until there is again an increase of residual mean square;
4. Steps (2) and (3) are repeated until the increment decreases below 0.001 retention parameter unit (s).

Using Eq. (5) as example, variances and covariances for the derived parameters p_M , a and b are then obtained by (i) numerical estimation of the $3n$ partial derivatives $\partial p_M/\partial p_{Ri}$, $\partial a/\partial p_{Ri}$, $\partial b/\partial p_{Ri}$, $i=1$ to n – this requires small (usually 0.1% but sometimes 0.01%) individual increase of each p_{Ri} , followed by

repetition of p_M optimisation as above – and then (ii) solution of the equation

$$V = AA^T V(p_R)$$

where V is the required variance-covariance matrix and A is the matrix

$$\begin{pmatrix} \frac{\partial p_M}{\partial p_{R1}} & \frac{\partial p_M}{\partial p_{R2}} & \dots & \frac{\partial p_M}{\partial p_{Rn}} \\ \frac{\partial a}{\partial p_{R1}} & \frac{\partial a}{\partial p_{R2}} & \dots & \frac{\partial a}{\partial p_{Rn}} \\ \frac{\partial b}{\partial p_{R1}} & \frac{\partial b}{\partial p_{R2}} & \dots & \frac{\partial b}{\partial p_{Rn}} \end{pmatrix}$$

For comparison purposes, a C programme for processing Eq. (5) without the point weighting has also been prepared. For all three programmes, multiple homologous series data are provided in a single file. This contrasts with the (A) programmes.

(C) The well-known methodology for processing Eq. (5) due to Al-Thamir et al. [7] requires two linear first order regressions; for the present purpose, consecutive N data will be assumed. The two equations, easily derived from Eq. (5a), are

$$\begin{aligned} \ln[(p_{R,N+1} - p_{R,N})/p^\circ] &= z \text{ (say)} \\ &= \ln\{p_M \exp(a) [\exp(b) \\ &\quad - 1]/p^\circ\} + Nb \end{aligned}$$

$$p_{R,N}/p^\circ = p_M/p^\circ + [p_M \exp(a)/p^\circ] \exp(bN)$$

where p° is any unit of retention parameter p . A plot of z against N gives b as slope and then a plot of $p_{R,N}/p^\circ$ against $\exp(bN)$ gives $p_M \exp(a)/p^\circ$ as slope and p_M/p° as intercept, from the pair of which one can derive p_M and a . As in (b), one would criticise this approach on the grounds of the non-application of weighting. On the basis of equal variances of the p_R , the variable variance of $z[V(z)]$ is related to the p_R variance [$V(p_R)$] by

$$V(z) = 2(p_{R,N+1} - p_{R,N})^{-2} V(p_R)$$

Weighting points in the first plot by $[(p_{R,N+1} - p_{R,N})/p^\circ]^2$ then makes the residual mean square (degrees of freedom = $n-3$) an estimate of $2V(p_R)/(p^\circ)^2$, from which may be determined an estimate of $V(p_R)$. For the second plot, both variables are subject to error, $p_{R,N}/p^\circ$ having a constant standard deviation and

$\exp(bN)$ having a variable one, proportional to $N \exp(bN)$. Furthermore, since b is derived from the p_R , the errors are not independent. The procedure for handling the situation where both variables have constant, independent standard deviations is now established [8], but the situation here is more complicated and any procedure adopted must necessarily have subjective features. Generally, relative errors¹ are less for the p_R than for the $\exp(bN)$ values, substantially so for the larger values of N . On this basis, it was thought sensible (i) to weight points by $[N \exp(bN)]^{-2}$, and (ii) to regress $\exp(bN)$ upon p_R , rather than the reverse. Three C programmes have been written:

1. With no weighting for either plot and regressing p_R upon $\exp(bN)$; in fact, with this version, the first plot was *also* performed with weighting for the sole purpose of determining $V(p_R)$ but parameter b was obtained from the unweighted plot.
2. With weighting for the first plot and unweighted regression of p_R upon $\exp(bN)$ for the second.
3. With weightings for both plots and with the reversed regression for the second plot.

In each case, the variance-covariance matrix for the derived parameters was determined by the same procedure as for the first order method of (B).

4. Application to sample data

To test the above theories and computer programmes, these were applied to a limited set of data selected from the literature. Application to more extensive data is regarded as outside the scope of the paper. The data chosen as illustration were taken from a paper by Reddy et al. [9]. The paper gives data, inter alia, in the form of derived thermodynamic data for the transfer of various solutes (many forming homologous series) from mobile gas phase to a variety of stationary liquid phases. The primary retention time data and the derived retention volume data had been corrected for mobile phase compressibility; furthermore, gas hold-up time had

been obtained by injection of neon, unquestionably unretained by the stationary phases. On this basis, the column contribution to hold-up volume V_M becomes equivalent to column volume V_c .

The key relations here are

$$\Delta H_m^\circ - T \Delta S_m^\circ = RT \ln(g/\text{atm kg mol}^{-1}) \quad (10)$$

$$V_R = V_{Mc}(1 + RTw_s/gV_c) + V_e \quad (11)$$

where ΔH_m° and ΔS_m° = standard molar enthalpy and entropy of transfer of a solute from mobile phase (standard pressure = 1 atm) to stationary phase (standard molality = 1 mol kg⁻¹) at thermodynamic temperature T , g = Henry constant (partial pressure/molality), R = gas constant, V_R = retention volume, V_e = extracolumn contribution to V_R and w_s = mass of stationary phase. Using $V_{Mc} = V_c$ and $V_R = V_{Mc} + V_e$, Eqs. (10,11) combine as

$$V_g \equiv V_R/w_s - V_M/w_s \\ = RT \exp(\Delta S_m^\circ/R - \Delta H_m^\circ/RT) \quad (12)$$

V_g being the specific retention volume for the particular solute. In the paper, ΔH_m° and ΔS_m° values are given for a temperature of 130°C, as are standard molar isobaric heat capacities, permitting conversion to other temperatures using Kirchhoff relationships. For the present purpose, Eq. (12) was used to convert selected thermodynamic data to corresponding V_g values for 130°C. The latter values are characteristics of solute and stationary phase only and are given in Table 2. The relationship between retention volume, hold-up volume and specific retention volume is simply $V_R/w_s = V_M/w_s + V_g$. To illustrate the present theories/programmes, a value of 100 cm³ g⁻¹ was chosen for V_M/w_s (representing an arbitrary chromatographic system), so that the illustrating parameter p_R is V_R/w_s and its values are 100 cm³ g⁻¹ greater than those of Table 2. The derived hold-up parameter is V_M/w_s and ought to be 100 cm³ g⁻¹. It is important to recognise that a different choice for V_M/w_s , say 100 cm³ g⁻¹ + X , would merely increase derived values of (i) this parameter by X and (ii) a by $\ln[100 \text{ cm}^3 \text{ g}^{-1}/(X + 100 \text{ cm}^3 \text{ g}^{-1})]$. Consequently, the arbitrary choice is inconsequential when comparing the various methods of calculation.

Results of analysis using the various computer

¹Errors in general x values are taken as a ratio to the square root of $\sum_i (x_i - \langle x \rangle)^2$, $\langle x \rangle$ being the mean of the values.

Table 2
Specific retention volumes appropriate to 130°C for *n*-alkanes and 1-alkynes with C78 and POH stationary phases (derived from thermodynamic data of Reddy et al. [9])

| Carbon number | Stationary phase ^a | Specific retention volume/cm ³ g ⁻¹ | |
|---------------|-------------------------------|---|-------|
| 6 | C78 | - | 18.4 |
| 7 | C78 | - | 35.6 |
| 8 | C78 | 73.5 | 68.0 |
| 8 | POH | 64.9 | - |
| 9 | C78 | 138.8 | 128.7 |
| 9 | POH | 122.0 | - |
| 10 | C78 | 261.2 | 242.5 |
| 10 | POH | 228.6 | - |
| 11 | C78 | 489.5 | - |
| 11 | POH | 426.1 | - |
| 12 | C78 | 914.3 | - |
| 12 | POH | 792.2 | - |
| 13 | C78 | 1705.3 | - |
| 13 | POH | 1469.9 | - |
| 14 | C78 | 3180.9 | - |
| 14 | POH | 2727.2 | - |

^a See [9] for details of stationary phases C78 and POH.

programmes are given in Table 3; estimated parameter covariances, calculated by the programmes, are not included in the table. Three and four parameter determinations are listed separately. Certainly, poor initial guesses for the A methods could lead to divergence or to local rather than global residual variance. However, this proved to be little of a problem with present data, particularly with some guidance from the results of B and C methods. For the B methods, it was sometimes found that too low an initial p_M could lead to false results for central values and/or for standard deviations. Apparently, this was caused by an initial increase of residual variance with increasing p_M . The initial value was set by a #define statement within the programme and was therefore easily adjustable to overcome this problem.

For these data, one can make several generalisations as follows, but it must be emphasised that other data might well lead to different conclusions.

(i) Part 2 of Table 3 generally shows large estimated standard deviations for the c parameter. Two-sided 20% points of the t statistic for one and three degree of freedom are 3.08 and 1.64, respectively. On this basis, one would with high confidence reject the inclusion of the quadratic term in all cases.

This provides support for the common practice of using Eq. (5), rather than extending to Eq. (6) or beyond. Therefore, there will be no further reference to Part 2.

(ii) Part 1 shows that, for particular column and homologous series, there is good agreement between both central values and standard deviations from non-linear (A1), corresponding weighted logarithmic (B2) and weighted A1-Thamir et al. (C3) methods; in the comparison of standard deviations, one should note the two-sided 20% points of the F statistic for two/two and four/four degrees of freedom are 9.00 and 4.11, respectively.

(iii) Agreement between corresponding weighted and unweighted methods will depend on how closely data fits Eq. (5) or Eq. (6); this is reflected in the estimated standard deviation of the V_M/w_s values.

(iv) Weighting of the second graph in the C methods has little effect, apparently.

(v) Derived values of V_M/w_s are generally significantly different from the nominal value of 100 cm³ g⁻¹ in most cases even at the 1% level (2-sided $t_4 = 4.60$, $t_2 = 9.92$). Exceptions to this rule occur for the C1 method, where standard deviations are significantly larger than for other methods. Conspicuously, derived values are always lower than 100 cm³ g⁻¹.

(vi) Common method values of V_M/w_s , for the C78 stationary phase but with different homologous series (*n*-alkanes and 1-alkynes), may be compared by pooling corresponding variances (4 and 2 degrees of freedom) and applying the well-established t -test for comparison of means [10]. For all except the C1 method, F -tests show no significant difference at the 5% level (one-sided $F = 10.6$, $F = 39.2$) between corresponding standard deviations, and the t -tests are each based on 6 degrees of freedom; in each case there is significant difference at the 5% level between V_M/w_s values. For the C1 method, where there is significant difference between standard deviations and where the alkane standard deviation is particularly large, the number of degrees of freedom is calculated as 4.11 by the more complicated formula appropriate to this situation [10], and here there is no significant difference between V_M/w_s values. However, this should not be regarded as evidence for superiority of the C1 method, since the absence of weighting is statistically unsound.

Table 3
Values of parameters using various methods of determination

| (1) Three parameter calculations | | | | | | | |
|--|--------|------------------|--------|--------|--------|--------|--------|
| Parameter | Method | A1 | B1 | B2 | C1 | C2 | C3 |
| <i>n-Alkanes with C78 and POH stationary phases</i> | | | | | | | |
| (V_M/w_s) ($\text{cm}^3 \text{g}^{-1}$) | C78 | 97.39 | 97.62 | 97.39 | 98.10 | 97.64 | 97.55 |
| | | 0.25 | 0.16 | 0.25 | 1.35 | 0.44 | 0.47 |
| a | POH | 97.44 | 97.76 | 97.44 | 98.23 | 97.59 | 97.59 |
| | | 0.20 | 0.18 | 0.20 | 1.10 | 0.36 | 0.36 |
| a | C78 | -5.228 | -5.236 | -5.228 | -5.244 | -5.233 | -5.233 |
| | | 0.005 | 0.005 | 0.005 | 0.030 | 0.009 | 0.008 |
| b | POH | -5.307 | -5.318 | -5.307 | -5.326 | -5.311 | -5.311 |
| | | 0.004 | 0.005 | 0.004 | 0.026 | 0.008 | 0.008 |
| b | C78 | 0.6225 | 0.6229 | 0.6225 | 0.6231 | 0.6227 | 0.6227 |
| | | 0.0002 | 0.0002 | 0.0002 | 0.0011 | 0.0003 | 0.0003 |
| S^a ($\text{cm}^3 \text{g}^{-1}$) | POH | 0.6171 | 0.6177 | 0.6171 | 0.6179 | 0.6173 | 0.6173 |
| | | 0.0002 | 0.0003 | 0.0002 | 0.0010 | 0.0003 | 0.0003 |
| With given data, number of degrees of freedom = 4 in each case | | | | | | | |
| <i>1-Alkynes with C78 stationary phase</i> | | | | | | | |
| $(V_M/w_s)/\text{cm}^3 \text{g}^{-1}$ | | 98.66 | 98.74 | 98.66 | 98.78 | 98.66 | 98.66 |
| | | 0.05 | 0.18 | 0.05 | 0.16 | 0.09 | 0.09 |
| a | | -5.383 | -5.392 | -5.383 | -5.393 | -5.383 | -5.383 |
| | | 0.004 | 0.017 | 0.004 | 0.014 | 0.007 | 0.007 |
| b | | 0.6288 | 0.6296 | 0.6288 | 0.6296 | 0.6287 | 0.6287 |
| | | 0.0004 | 0.0015 | 0.0004 | 0.0011 | 0.0006 | 0.0006 |
| S ($\text{cm}^3 \text{g}^{-1}$) | | 0.03 | 0.07 | 0.03 | 0.03 | 0.03 | 0.03 |
| With given data, number of degrees of freedom = 2 in each case | | | | | | | |
| (2) Four parameter calculations | | | | | | | |
| Parameter | Method | Stationary phase | | | | | |
| | | C78 | | POH | | | |
| | | A2 | B3 | A2 | B3 | | |
| (V_M/w_s) ($\text{cm}^3 \text{g}^{-1}$) | Alkane | 98.64 | 96.86 | 97.29 | 97.30 | | |
| | | 0.71 | 0.70 | 0.60 | 0.60 | | |
| a | Alkyne | 98.91 | 98.91 | - | - | | |
| | | 0.21 | 0.21 | - | - | | |
| a | Alkane | -5.191 | -5.192 | -5.296 | -5.297 | | |
| | | 0.045 | 0.044 | 0.042 | 0.042 | | |
| b | Alkyne | -5.452 | -5.452 | - | - | | |
| | | 0.058 | 0.058 | - | - | | |
| b | Alkane | 0.6179 | 0.6180 | 0.6157 | 0.6158 | | |
| | | 0.0055 | 0.0054 | 0.0053 | 0.0053 | | |
| $1000 c$ | Alkyne | 0.6418 | 0.6419 | - | - | | |
| | | 0.0109 | 0.0109 | - | - | | |
| S^a ($\text{cm}^3 \text{g}^{-1}$) | Alkane | 0.169 | 0.164 | 0.052 | 0.048 | | |
| | | 0.201 | 0.200 | 0.194 | 0.194 | | |
| S^a ($\text{cm}^3 \text{g}^{-1}$) | Alkyne | -0.649 | -0.651 | - | - | | |
| | | 0.542 | 0.543 | - | - | | |
| S^a ($\text{cm}^3 \text{g}^{-1}$) | Alkane | 0.29 | 0.29 | 0.24 | 0.24 | | |
| | Alkyne | 0.03 | 0.03 | - | - | | |

With given data, number of degrees of freedom = 3 in each alkane case and 1 in each alkyne case.

Methods: A1. Non-linear 3 parameter; A2. Non-linear 4 parameter; B1. Unweighted logarithmic linear first order; B2. Weighted logarithmic linear first order; B3. Weighted logarithmic linear second order; C1. Unweighted Al-Thamir et al.; C2. Partially weighted Al-Thamir et al.; C3. Fully weighted Al-Thamir et al. Estimated standard deviations are given just below each value.

^a S = estimated common standard deviation of experimental V_M/w_s values.

5. Conclusions

As far as the present data is concerned, unweighted linear first-order regression methods appear to give no less satisfactory values of gas hold-up parameters than the more statistically sound procedures. Direct measurement of gas hold-up time using a gas insoluble in the stationary phase is clearly to be preferred. However, it seems that homologous series methodology generally gives hold-up parameters fairly close to (albeit significantly lower than) true values, and despite the opening statement of this paragraph, one ought to use correct statistical methods (non-linear or weighted linear) when processing the homologous series data. Generally, there appears to be no grounds for extending beyond first order the relation of the logarithm of retention factor to carbon number in a homologous series.

6. Computer programmes

Copies of the programmes are available on request to the author.

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