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Calculation of programmed temperature gas chromatography characteristics from isothermal data
IV. Prediction of peak widths

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Abstract

Two alternative theoretical procedures are described for the calculation of peak widths in programmed temperature gas chromatograms from corresponding isothermal widths. The essential distinction between the procedures for the case of essentially temperature-independent column efficiency is noted. Application to a limited set of isothermal width and retention time data and comparison with experimental programmed temperature results reveals the unsatisfactory nature of one of the procedures. The other method is then applied to a more extensive set of compounds and programmed temperature conditions.

1. Introduction

Previous papers in this series [1–3] have been concerned with the prediction of retention times, elution temperatures, retention indices and equivalent temperatures in programmed temperature gas chromatography (PTGC) from experimental retention times obtained under isothermal conditions. In testing theory by experiment, the temperature programme considered was restricted to the single linear temperature–time ramp, although the theory presented covered more general situations (multiple plateaus and ramps). The present paper extends predictions to those of PTGC peak (time-)width from isothermal widths, again with application to

experiments involving a single linear ramp programme. [Since the experiments involve the use of (a) column temperatures above the boiling point of the sample diluent (dichloromethane), and (b) split injection mode, the effects of solvent condensation on the stationary phase have not been considered here.] Two distinct theoretical procedures are described for this purpose and tested on selected experimental data, with a view to choosing the best predictor and then applying this to a more extensive set of compounds and conditions. A further paper [4] will describe an extension of the chosen method to peak asymmetry. The composite calculation of retention times, peak widths and peak asymmetries then permits the prediction of overall shapes of chromatograms from injected mixtures, particularly those with components of similar retention time. Associated with this prediction will be the calculation of various numerical parame-

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ters, each (in its own way) a measure of either peak-pair or overall chromatographic resolution. Variation of PTGC conditions (in this work, only initial column temperature and rate of temperature increase) will then allow prediction of optimum resolution conditions ("optimization"). The calculations in this and subsequent papers have been performed without estimation of error.

2. First general procedure for PTGC width prediction

The following considerations are independent of (a) peak shape (Gaussian, triangular, etc; symmetrical or otherwise), (b) where peak width is measured (half-height, triangular base, etc).

It will be supposed that there are two additive contributions to peak width, w: (i) peak dispersion due to the characteristics of the column, w_c, and (ii) peak dispersion due to extracolumn factors (finite rates of injection, evaporation into the column, passage to the detector), w_e.

$$w = w_c + w_e \qquad (1)$$

For a particular chromatograph, carrier gas flow-rate, injected compound and injection technique, one might expect w_e to be independent of column temperature (or temperature programme). If, however, carrier gas pressure differential, rather than flow-rate, is kept constant (as is the practice of the authors), carrier gas flow-rate (and therefore column dead time) will depend in a small way upon column temperature/programme and this may have a corresponding small effect upon w_e. For the present purposes, it will be assumed that the effect on the overall w is negligible, i.e. w_e will be taken as independent of column temperature/programme.

For a particular injected compound, the column term w_c will certainly depend upon column temperature for isothermal runs and upon the temperature programme for non-isothermal runs. For isothermal runs, represent w_c as w_{ci}. The contribution to this for passage through an

infinitesimal fraction dF of the column is then $dw_{ci} = w_{ci}\, dF$. Now $dF = dt/t_{Ri}$, where dt is the corresponding infinitesimal time and t_{Ri} is the isothermal time (or strictly the column contribution to this) given by [1][2]

$$t_{Ri} = t_0[1 + k_1 \exp(k_2/T)] \qquad (2)$$

(t_0 = isothermal column dead time, a weak function of temperature [1]; k_1, k_2 = column characteristics for a particular compound and assumed as before [1] to be independent of thermodynamic temperature T). On the basis of these equations,

$$
\begin{aligned}
dw_{ci} &= w_{ci}\, dt/t_{Ri} \\
&= w_{ci}\, dt/\{t_0[1 + k_1 \exp(k_2/T)]\} \qquad (3)
\end{aligned}
$$

For a programmed temperature run, the value of w_c, w_{cp}, is obtained by integration of Eq. 3 between zero time and the programmed temperature retention time [1,2] t_R (again strictly the column contribution),

$$w_{cp} = \int_0^{t_R} w_{ci}\, dt/t_{Ri} \qquad (4)$$

w_{ci} and t_0 depend upon T, and T depends upon t according to the temperature programme used.

Using Eq. 1, Eq. 4 may be rewritten as

$$w_{cp} = \int_0^{t_R} (w_i - w_e)\, dt/t_{Ri} = \int_0^{t_R} w_i\, dt/t_{Ri} - w_e$$

since [1] $\int_0^{t_R} dt/t_{Ri} = 1$; w_i is the total isothermal width (another function of T). Since w_p, the total programmed temperature width $= w_i + w_e$,

$$w_p = \int_0^{t_R} w_i\, dt/t_{Ri} \qquad (5)$$

If w_i and t_{Ri} are known as functions of T, these integrals may be evaluated, usually nu-

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[2] This is equivalent to stating that the logarithm of the capacity factor ($k' = t_{Ri}/t_0 - 1$) is a linear function of T^{-1}. Higher order functions will be considered at a later stage in this paper.

merically. The determination of t_R, required for the integration, has been described previously [1]. Several general possibilities for integral evaluation will be considered below.

For a temperature programme comprising a single linear ramp, $T = T_i + k_3 t$, $T_e = T_i + k_3 t_R$ and Eq. 5 becomes

$$w_p = k_3^{-1} \int_{T_i}^{T_e} w_c \, dT / t_{Ri}$$

$$= k_3^{-1} \int_{T_i}^{T_e} w_c \, dT / \{ t_0 [1 + k_1 \exp(k_2/T)] \} \quad (6)$$

(T_i is the initial column temperature, T_e is the temperature at elution and k_3 the heating rate, cf. Ref. 1).

As an example of a more complicated temperature programme consider an initial isothermal at T_i lasting for a time t_1 after injection, followed by a linear ramp (heating rate $= k_3$ as before). This merely exemplifies the procedure to be used for more elaborate programmes, but in fact the single ramp was used in the present experimental tests of the theory. Elution could occur either during the isothermal period (corresponding to a calculated isothermal retention time $= t_0[1 + k_1 \exp (k_2/t_i)]$ less than t_1) when the width will obviously be w_i (at T_i) —designated $w_i(T_i)$— or during the ramp period. For the latter situation, the integral of Eq. 5 is written as a sum of two integrals, i.e.

$$w_p = \int_0^{t_1} w_i \, dt / t_{Ri} + \int_{t_1}^{t_R} w_i \, dt / t_{Ri}$$

$$= w_i(T_i) t_1 / t_{Ri}(T_i) + \int_{t_1}^{t_R} w_i \, dt / t_{Ri}$$

$$= w_i(T_i) t_1 / t_{Ri}(T_i)$$

$$+ \int_{t_1}^{t_R} w_i \, dt / \{ t_0 [1 + k_1 \exp(k_2/T)] \}$$

with $T = T_i + k_3(t - t_1)$. The integral in the final expression could be written

$$\int_0^{t_R^*} w_i \, dt^* / \{ t_0 [1 + k_1 \exp(k_2/T)] \}$$

(with $t^* = t - t_1$ and $t_R^* = t_R - t_1$) or

$$k_3^{-1} \int_{T_i}^{T_e} w_i \, dT / \{ t_0 [1 + k_1 \exp(k_2/T)] \}$$

in which $T_e = T_i + k_3(t_R - t_1) = T_i + k_3 t_R^*$.

In order to evaluate the integral of Eq. 5, it is desirable to express isothermal width in terms of isothermal retention time. Empirical polynomial functions, with best-fit parameters determined from experimental isothermal data, are considered here. Such functions have reasonable experimental support in the present applications. Fig. 1a shows the dependence of w_i upon t_R for n-octane on a capillary column coated with silicone elastomer for six temperatures ranging from 353 to 423 K. Fig. 1b shows the composite dependence for five homologous n-alkanes (C_8–C_{12}) at the same six temperatures. Both plots shows close approximation to linearity, and indeed to direct proportionality, the latter corresponding to column efficiency being temperature-independent (and by Fig. 1b solute independent also). For the present purpose, the simple linearity/proportionality will be extended to a low order polynomial, which could be applicable to a single compound, a homologous series or even a wider range of compounds, i.e.

$$w_i = \sum_{j=0}^{n} q_j t_{Ri}^j \quad \text{(with low } n) \quad (7)$$

Combination of Eqs. 5 and 7 then gives

$$w_p = \int_0^{t_R} \sum_{j=0}^{n} q_j t_{Ri}^{j-1} \, dt$$

$$= q_0 + q_1 t_R + \int_0^{t_R} \sum_{j=2}^{n} q_j t_{Ri}^{j-1} \, dt \quad (8)$$

by virtue of the fact that $\int_0^{t_R} dt / t_{Ri} = 1$. If q_j ($j \geqslant 2) = 0$, $w_p = q_0 + q_1 t_R$, exactly as for the isothermal case. Despite the near linearity shown in Fig. 1, this simple prediction is in fact *not*
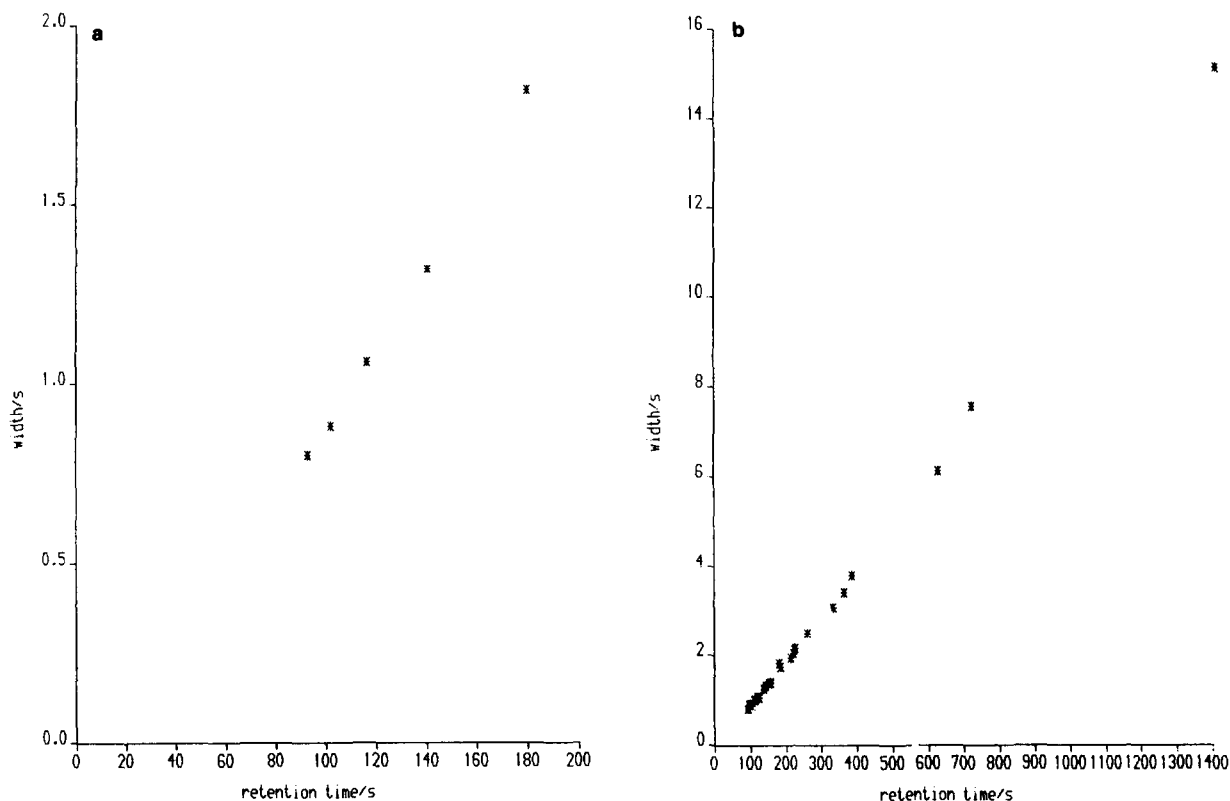
Fig. 1. Dependence of isothermal peak width upon retention time for (a) n-octane and (b) five n-alkanes (C_8–C_{12}) each at six temperatures (353, 373, 393, 403, 413, 423 K) (SE-54 column).

realised and this point will be considered further below.

The integrals of Eq. 8 may be evaluated numerically; the Romberg method (see Ref. [5]) has been used in this work. Before integration is possible, the following information is required:

(a) The q coefficients of the equation. These are obtained by fitting least squares relationships between w_i and t_{Ri}; orders up to four have been considered. Relationships have been considered both for single compounds and for a homologous series of compounds (in each case at several temperatures).

(b) The relationship of t_{Ri} and thus of k' to T. In previous papers [1–3], this has been Eq. 2 and this is equivalent to

$$\ln k' = \ln k_1 + k_2 / T$$

i.e. the logarithm of capacity factor taken as a

linear function of reciprocal temperature —the thermodynamic significance of k_1 and k_2 has been given previously [1]. In the present work this has been extended to powers of reciprocal temperature up to four.

(c) The dependence of t_0 upon T. As previously [2], relationships of the type $t_0 = A + BT$ and $t_0 = A + B\sqrt{T}$ have been considered, with the parameters determined by least squares methodology. The differences between predictions from the two types of formulae are in fact small. For the predictions tested experimentally and presented in the present paper, only the second of the two formulae has been used.

(d) The temperature programme. For multiramp/multiplateau programmes, the integrals have to be written as sums of other integrals, one for each step; plateau integrals are then easily written —see above for an example involving a

single plateau followed by a single linear ramp. In the present work, experimental testing has been restricted to a programme comprising only a single linear ramp, whence the time integrals are easily converted into temperature ones by replacing dt by $k_3^{-1} \, dT$, and the integration limits 0 and t_R by T_i and T_e.

(e) t_R or equivalently T_e, the upper integration limit. This has been considered previously [1,2], where Eq. 2 was used for t_{Ri}. As in (b), this has been extended here to higher powers of T^{-1} in the expression for ln k'.

Two computer programmes in Turbo Pascal have been written, for use on an IBM-type microcomputer, to calculate programmed temperature widths; one of the programmes is for a single temperature ramp and the other for an initial isothermal followed by such a ramp. A combination of keyboard and filed input provides (a) selection facilities for (i) the type of dead time vs. temperature relationship, (ii) the orders of polynomials for both ln k' and w_i (limited to a maximum of one less than the number of points), (b) isothermal data for (i) the dead time vs. temperature relationship (or coefficients A and B directly), (ii) width vs. retention time for a set of compounds (as appropriate), (iii) retention time, dead time and width for a specific named compound, and (c) information about the temperature programme, i.e. initial temperature T_i, heating rate k_3 and (where appropriate) the duration of the initial isothermal t_1.

3. Second general procedure for PTGC width prediction

Another way of approaching the prediction of programmed temperature widths, completely different from the procedure described above, is based upon the use of two effective retention times for each isothermal peak; these times are $t_{Ri} \pm w_i/2$. Using procedures described previously [1], but now allowing the possibility in the polynomial relationship of ln k' to T^{-1} of an order higher than 1, each of the two sets of isothermal retention times (one compound, vari-

ous temperatures) has been used to predict a programmed temperature retention time. The difference between these has then been equated to the programmed temperature width. As before, width may be variously defined, e.g. at half height.

Two further microcomputer Pascal programmes (for a single temperature ramp and for an initial isothermal followed by a ramp) have been written to calculate programmed temperature widths by this alternative procedure. A combination of keyboard and filed input provides (a) selection facilities for the type of dead time vs temperature relationship, (b) isothermal data for (i) the dead time vs temperature relationship (or coefficients A and B directly), (ii) retention time, dead time and width for a specific named compound, and (c) information about the temperature programme. Programmed temperature widths are calculated for all ln k' vs T^{-1} polynomials up to order 4 (or for one less than the number of points for the compound when the latter is less than 5).

The single ramp programme was also adapted for use on an Amdahl 5890-300E mainframe computer. This adaptation allowed calculation in a single run for several compounds and for all combinations of initial temperatures of 333.2, 353.2, 373.2, 393.2, 413.2 K and heating rates of 5.0, 7.0, 10.0, 15.0 K min^{-1}.

4. Comparison of general procedures for special case of columns with essentially temperature-independent efficiencies

For the case of columns which show a near linear dependence of width upon retention time under isothermal conditions (and this includes direct proportionality), it has already been shown that the first procedure gives the same linear relationship between width and retention time under programmed temperature conditions. A different situation will now be demonstrated for the second general method when there is direct proportionality, i.e. temperature-independent efficiency.

If the two subtracted retention times, leading

edge and trailing edge, are represented by t_{RL} and t_{RH}, with corresponding isothermal retention times of $t_{Ri} - w_i/2$ and $t_{Ri} + w_i/2$, then

$$1 = \int_0^{t_{RL}} dt/(t_{Ri} - w_i/2) = \int_0^{t_{RH}} dt/(t_{Ri} + w_i/2)$$

If now $w_i = q_i t_{Ri}$

$$1 - q_i/2 = \int_0^{t_{RL}} dt/t_{Ri} = \int_0^{t_R} dt/t_{Ri} - \int_{t_{RL}}^{t_R} t_R \, dt/t_{Ri}$$

$$= 1 - \int_{t_{RL}}^{t_R} t_R \, dt/t_{Ri}$$

and

$$1 + q_i/2 = \int_0^{t_{RH}} dt/t_{Ri} = \int_0^{t_R} dt/t_{Ri} + \int_{t_R}^{t_{RH}} dt/t_{Ri}$$

$$= 1 + \int_{t_R}^{t_{RH}} dt/t_{Ri}$$

whence $q_1 = \int_{t_{RL}}^{t_{RH}} dt/t_{Ri}$. Because the integration range is now very narrow and of magnitude equal to the programmed temperature width w_p, the integrand may be assumed constant and equal to the reciprocal of t_e, the isothermal retention time *corresponding to the elution temperature*. As a consequence of this, $w_p = q_1 t_e$ equal to the peak width for an isothermal run at the programmed temperature elution temperature T_e. This is a quite different prediction to that of the first procedure, where t_e in the proportionality relationship would be replaced
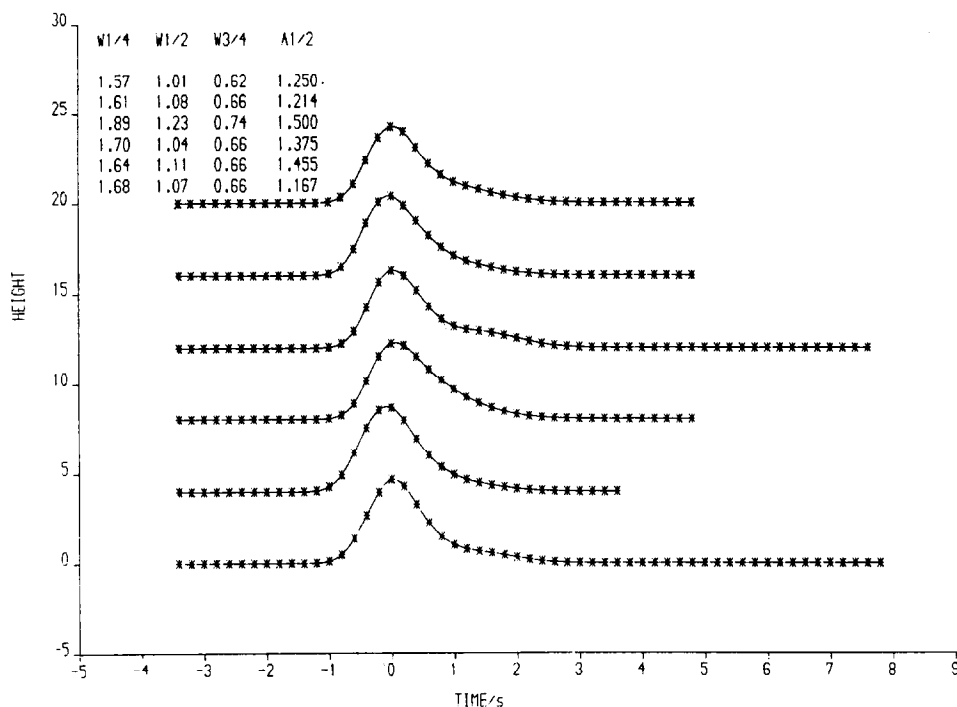

Fig. 2. Typical replicate record of peaks (393 K isothermal for *n*-nonane, SE-54 column) with cubic spline curves and statements of peak widths (at quarter, half and three quarter heights) and asymmetry [4]. Originals have replicate curves (and points) and results of analysis in corresponding colours —here lowest curve corresponds to highest analysis line. In this example, there is a vertical offset of replicates but no horizontal one.

by t_R, the programmed temperature retention time.

The computer programmes for the second procedure also calculate the programmed temperature width as the width for an isothermal run at T_e. This has been done by interpolation in a least squares linear plot of isothermal width vs. retention time, both with and without origin forcing. Proximity of these calculated programmed temperature widths and $t_{RH} - t_{RL}$ reflects proximity to proportionality of isothermal width and retention time over the temperature range of interest. As Fig. 1 shows, this is close in the present experimental studies.

5. Experimental testing of predictive procedures

The general experimental procedure has been described previously [2]; two Hewlett-Packard coated capillary columns (25 m × 0.2 mm I.D., 33 μm film thickness), types SE-54 (5% phenyl-

Table 1
Comparison of experiment and half height width predictions: initial testing, all methods, n-decane and n-dodecane (SE-54 column)

(a) Isothermal data (specific compounds only)

	Temperature/K	Retention time/s	Dead time/s	Width/s
Decane	353.2	387.0	67.9	3.80
Dodecane		1411.2		15.14
Decane	373.2	225.8	71.2	2.16
Dodecane		629.5		6.14
Decane	393.2	156.9	74.1	1.40
Dodecane		335.1		3.08
Decane	403.2	138.5	75.6	1.26
Dodecane		261.5		2.50
Decane	413.2	125.8	77.1	1.06
Dodecane		212.9		1.94
Decane	423.2	116.8	78.9	1.06
Dodecane		179.8		1.82

(b) Predicted programmed temperature widths/s

Methods: (1a) Eq. 5 + isothermal width = polynomial function of retention time, single compound (n-decane or n-dodecane); (1b) Eq. 5 + isothermal width = polynomial function of retention time, set of compounds (n-alkanes C_8–C_{12}); (2a) two-retention-time method: $t_{RH} - t_{RL}$; (2b) isothermal width at T_e, linear regression through origin; (2c) isothermal width at T_e, linear regression not through origin. The polynomial order is shown in [ ] for ln (capacity factor) vs. reciprocal temperature, and in { } for width vs. retention time.

Method	Decane	Dodecane	Method	Decane	Dodecane
(1a)[1]{1}	1.71	3.26	(2a)[2]	1.39	2.04
(1a)[1]{2}	1.72	3.19	(2a)[3]	1.42	2.02
(1a)[2]{1}	1.70	3.24	(2b)[1]	1.48	2.25
(1a)[2]{2}	1.70	3.17	(2b)[2]	1.47	2.27
(1b)[1]{1}	1.72	3.35	(2b)[3]	1.47	2.27
(1b)[1]{2}	1.71	3.25	(2c)[1]	1.41	1.94
(1b)[2]{1}	1.70	3.33	(2c)[2]	1.41	1.96
(1b)[2]{2}	1.69	3.23	(2c)[3]	1.40	1.96
(2a)[1]	1.60	2.21	Experiment	1.41	2.03

Temperature programme: single ramp, initial temperature 373.2 K, heating rate 7.0 K min^{-1}.

Table 2
Comparison of experiment and half-height width predictions

Compound	Width/s					
	Heating rate = 5 K min^{-1}		Heating rate = 10 K min^{-1}		Heating rate = 15 K min^{-1}	
	Predicted[a]	Observed[b]	Predicted[a]	Observed[b]	Predicted[a]	Observed[b]
Initial temperature = 353.2 K						
n-Octane	1.08	1.07 (0.01)	1.04	0.92 (0.02)	1.02	0.87 (0.03)
	1.13		1.03		0.96	
n-Nonane	1.48	1.42 (0.01)	1.32	1.10 (0.03)	1.20	1.00 (0.07)
	1.49		1.24		1.10	
n-Decane	2.06	1.92 (0.05)	1.62	1.38 (0.04)	1.38	1.13 (0.05)
	1.96		1.47		1.25	
n-Undecane	2.66	2.45 (0.04)	1.84	1.54 (0.06)	1.46	1.24 (0.03)
	2.42		1.69		1.39	
n-Dodecane	3.08	2.57 (0.16)	1.94	1.66 (0.05)	1.48	1.26 (0.05)
	2.76		1.86		1.52	
Initial temperature = 393.2 K						
n-Octane	0.94	0.90 (0.03)	0.90	0.89 (0.04)	0.86	0.87 (0.03)
	0.88		0.86		0.84	
n-Nonane	1.08	0.97 (0.02)	1.00	0.92 (0.02)	0.92	0.87 (0.02)
	1.00		0.94		0.90	
n-Decane	1.34	1.15 (0.07)	1.16	1.02 (0.06)	1.02	0.92 (0.03)
	1.23		1.11		1.03	
n-Undecane	1.66	1.40 (0.06)	1.32	1.16 (0.03)	1.12	1.02 (0.04)
	1.55		1.32		1.18	
n-Dodecane	2.06	1.87 (0.10)	1.50	1.37 (0.09)	1.20	1.13 (0.04)
	1.98		1.58		1.36	

Two-retention-time method, *n*-alkanes (SE-54 column), single ramp temperature programme
[a] First line of each pair: first order in ln k' vs. T^{-1}. Second line of each pair: second order in ln k' vs. T^{-1}.
[b] Estimated standard error of mean based upon six replicates.

methylsilicone coating) and SE-30 (100% methylsilicone) were used (arranged in parallel configuration). Two solutions of mixed solutes in dichloromethane —50 mm^3 of each solute in 25 cm^3 of solvent— were subjected to chromatographic separation: (i) a mixture of normal hydrocarbons (C_8–C_{13}), together with three ketones (nonan-5-one, *n*-propanoylbenzene and *n*-butanoylbenzene), (ii) a mixture of methyl carboxylic esters (C_8–C_{12}). The chromatograph was connected via an analogue-to-digital converter to a computer integrator (Trilab 2500). This instrument maintained, for each chromatographic run, a record of bunch-averaged intensity against incremental time. It also had a programmed facility for analysing these data to

obtain, for each peak, retention time, effective start and finish times (determined by successive significant gradient methodology) and area. A BBC Basic computer programme (written by Mr. G.O. Hughes) then processed the composite of primary and derived data and also activated transmission to a BBC Model B computer, via an RS232 serial link, of peak data between start and finish times but with the addition of a few pre-start and post-finish points. Data were accumulated for sets of six chromatograms, obtained under identical isothermal or programmed temperature conditions. The accumulated data were then transferred via a KERMIT communication package to a file on an Amdahl 5890 mainframe computer. A Pascal programme on

Table 3
Comparison of experiment and half-height width predictions

Compound	Width/s					
	Heating rate = 5 K min^{-1}		Heating rate = 10 K min^{-1}		Heating rate = 15 K min^{-1}	
	Predicted[a]	Observed[b]	Predicted[a]	Observed[b]	Predicted[a]	Observed[b]
Initial temperature = 373.2 K						
Methyl octanoate	1.66	1.90 (0.04)	1.34	1.40 (0.08)	1.14	1.10 (0.05)
	2.00		1.42		1.20	
Methyl nonanoate	2.24	2.26 (0.10)	1.54	1.54 (0.05)	1.22	1.20 (0.01)
	2.44		1.60		1.28	
Methyl decanoate	2.52	2.62 (0.13)	1.58	1.67 (0.01)	1.18	1.26 (0.04)
	2.56		1.64		1.32	
Methyl undecanoate	2.72	2.94 (0.09)	1.62	1.73 (0.13)	1.18	1.35 (0.04)
	2.76		1.74		1.38	
Methyl dodecanoate	2.78	2.88 (0.18)	1.58	1.78 (0.17)	1.12	1.51 (0.09)
	2.84		1.70		1.28	
Initial temperature = 413.2 K						
Methyl octanoate	1.20	1.08 (0.11)	1.02	1.14 (0.13)	0.90	0.92 (0.10)
	1.16		1.04		0.96	
Methyl nonanoate	1.40	1.32 (0.07)	1.12	1.21 (0.11)	0.94	0.96 (0.08)
	1.38		1.18		1.06	
Methyl decanoate	1.64	1.64 (0.07)	1.20	1.28 (0.06)	0.96	1.06 (0.04)
	1.66		1.32		1.14	
Methyl undecanoate	1.96	1.98 (0.07)	1.30	1.42 (0.06)	1.00	1.18 (0.05)
	2.04		1.48		1.24	
Methyl dodecanoate	2.18	2.34 (0.10)	1.36	1.57 (0.08)	1.00	1.44 (0.09)
	2.26		1.50		1.18	

Two-retention-time method, methyl carboxylic esters (SE-30 column), single ramp temperature programme.
[a] First line of each pair: first order in ln k' vs. T^{-1}. Second line of each pair: second order in ln k' vs. T^{-1}.
[b] Estimated standard error of mean based upon six replicates.

this computer sorted the data into a new file so that data for successive runs were contiguous *for each compound*. This new file then became the input of a FORTRAN programme which, for each compound, (a) plotted the peak data points for successive runs (with vertical and horizontal offset as desired and using a different colour for each run), (b) joined the points with cubic spline curves, and (c) computed peak widths at quarter, half and three-quarter-heights (and peak asymmetries —to be considered in a subsequent publication [4]). Features (a) and (b) required GINOF plotting and NAG subroutines, available on the Amdahl computer. A typical plot (rendered here in monochrome) is shown in Fig. 2. Averages and standard deviations of sets of six

corresponding heights could then be obtained. Only the widths at half-height were used in comparisons of observation and prediction.

For the purpose of the predictions, column dead times were required at various temperatures. These were determined by the method of Al-Thamir et al. [6], using retention times for successive members of homologous series [n-alkanes for the components of solution (i) and methyl carboxylic esters for the components of solution (ii)].

As an initial test, the predictions from the two procedures were compared with one another and with experiment for two hydrocarbons, n-decane and n-dodecane for a single ramp temperature programme with an initial temperature of 373.2

K, a heating rate of 7.0 K min^{-1} and the SE-54 column. This is shown in Table 1. The general conclusions here are as follows.

(a) The second procedure, including the use of isothermal width at T_e, gives significantly better predictions than the first procedure, particularly when second and third order polynomials are used in ln k' vs. T^{-1} relationships.

(b) The first procedure, however, significantly overestimates the width (at least for these test compounds and certainly more so for dodecane than for decane). The reason for this is not apparent to the authors. Furthermore, progressing from first to second or third order polynomials for ln k' vs. T^{-1} has little effect on predicted widths.

As a consequence of this initial testing, all further comparisons between theory and experiment were performed on the basis of the two-retention-time method, i.e. $t_{RH} - t_{RL}$. Typical results are shown in Tables 2 and 3. Other results are available [7]. Agreement is generally satisfactory; certainly some cases are better than others and there are a few cases where agreement is poor.

Copies of computer programmes referred to above are available from the authors. The Pascal data sorting programme will probably not be of general utility.

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