

Critical capillary column examination of the relationship between separation number and height equivalent to a theoretical plate and their dependence on temperature

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ABSTRACT

Separation numbers (TZ values) for the homologous pair C_{11} – C_{12} were determined using a capillary column at 40, 60 and 80°C, as was the height equivalent to a theoretical plate, h , for each hydrocarbon at various linear velocities. Increasing temperatures produced both decreasing TZ and h values, indicating decreased column resolution but suggesting an increase in the number of theoretical plates and hence a contradictory improved column efficiency. The optimum linear velocity required for producing maximum TZ was shown to be the expected average of that required to produce h_{min} for C_{11} and C_{12} . Van Deemter-type plots further suggested an inverse relationship between h and TZ . The following equation was derived: $TZ = (L/5.54)^{1/2} \cdot [(t_r^a - t_r^b)/(t_r^b h_b^2 + t_r^a h_a^2)] - 1$, where t_r is the retention time of consecutive homologues a and b and L is the column length. Results using this equation were compared with those obtained with $TZ = [(t_r^b - t_r^a)/(w_{0.5}^a + w_{0.5}^b)] - 1$, where $w_{0.5}$ is the peak width at half-height. The excellent agreement using the data from this study and previous reports clearly shows the concept of TZ to be based on sound chromatographic principles.

INTRODUCTION

The concept of the separation number, TZ , was first proposed in 1962 [1] and incorporated the retention times and the peak widths at half-height ($w_{0.5}$) of two homologues, a and b , which differed by one CH_2 group:

$$TZ = \frac{t_r^b - t_r^a}{w_{0.5}^a + w_{0.5}^b} - 1 \quad (1)$$

Ettre [2] in a definitive paper on TZ and its relationship to other gas chromatographic parameters, viewed the relationship as an indication of column efficiency. He related TZ to the resolution R of the homologues a and b as defined by the equation

$$R_{b/a} = \frac{2(t_r^b - t_r^a)}{w_b^a + w_b^b} \quad (2)$$

where w_b is the base width. Substitution of the equality $w_{0.5} = w_b/1.699$ in eqn. 1 redefined TZ in terms of base widths:

$$TZ = \frac{1.699(t_r^b - t_r^a)}{w_b^a + w_b^b} - 1 \quad (3)$$

Substitution of eqn. 2 in eqn. 3 gave

$$TZ = 1.699 \left(\frac{R_{b/a}}{2} \right) - 1 = \frac{R_{b/a}}{1.177} - 1 \quad (4)$$

thus relating TZ and R . Assuming that homologues a and b eluted very close to one another, then the approximation can be made that $w_b^b \approx w_b^a$, which would reduce eqn. 2 to

$$R_{b/a} = \frac{t_r^b - t_r^a}{w_b^b} \quad (5)$$

By assuming that $TZ = 0$ for these homologues, it can be seen from eqn. 4 that $R_{b/a} = 1.177$ and therefore eqn. 5 becomes

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$$1.177 = \frac{\Delta t_r}{w_b} \quad (6)$$

As $w_b = 4\sigma$, $\Delta t = 4.7\sigma$, which gives rise to Ettre's statement [2] that TZ expresses the number of component peaks which are separated by a 4.7σ resolution that can be placed between the peaks of two consecutive alkanes with z and $z + 1$ carbon atoms. Interestingly, there is no inclusion of h (the height equivalent to a theoretical plate) in the relationship.

Subsequently, Jennings and Yabumoto [3] noted that as the column temperature is lowered, relative retentions and TZ increase, leading to the conclusion that the two are related. Rooney and Hartigan [4] showed that "the value of the separation number can be manipulated to give high results if desired". They proposed the approximation $w_{0.5}^b/w_{0.5}^a \approx \alpha$, which, when used in eqn. 1, gave rise to the equation

$$w_{0.5}^b = \frac{t_r^b - t_r^a}{(1 + 1/\alpha)(TZ + 1)} \quad (7)$$

By substitution of eqn. 7 in the equation defining N_{eff} :

$$N_{\text{eff}} = 5.54 \left(\frac{t_r^b}{w_{0.5}^b} \right)^2 \quad (8)$$

and utilization of the relationship $t_r^b/(t_r^b - t_r^a) = \alpha/(\alpha - 1)$, the following equation was obtained after several rearrangements:

$$TZ = 0.425 \left(\frac{\alpha - 1}{\alpha + 1} \right) (N_{\text{eff}})^2 - 1 \quad (9)$$

Important to this derivation is the fact that only the peak with the larger t_r or capacity factor is utilized, and again the assumption was made that the peak widths are "approximately" the same.

Krupcik *et al.* [5], using similar substitutions, derived the following equation for the resolution between homologues with $z + 1$ and z carbon atoms:

$$R_{(z+1)/z} = \frac{\alpha - 1}{2} \cdot \frac{(N_z N_{z+1})^{\frac{1}{2}}}{\alpha(N_z)^{\frac{1}{2}} + (N_{z+1})^{\frac{1}{2}}} \quad (10)$$

Then, approximating the number of effective plates by the equation

$$N = \left(N_\infty + \frac{b}{k'} \right) \left(\frac{k'}{1 + k'} \right)^2 \quad (11)$$

where k' is for the later eluting peak of the two homologues, and substituting in eqn. 10, the equation

$$R_{b/a} = \frac{N_\infty^{\frac{1}{2}}}{2} \cdot \frac{\alpha - 1}{\alpha + 1} \quad (12)$$

was obtained. Substituting this equation in eqn. 4 gave the TZ relationship

$$TZ = \frac{N_\infty^{\frac{1}{2}}}{2.35} \cdot \frac{\alpha - 1}{\alpha + 1} - 1 \quad (13)$$

It should be noted that none of the above derivations includes the column length, an important chromatographic parameter.

Both of these groups warned that the temperature dependence makes TZ a value that should be utilized with caution. Indeed, it was described as a "rubber ruler" [5] which should be used carefully or avoided.

We have studied the relationship between TZ and the average carbon number of the two homologues used, \overline{CH} [where $\overline{CH} = (C_b + C_a)/2$] using various temperature-programmed gas chromatographic (TPGC) conditions with various starting temperatures and column flow-rates. Under isobaric conditions (constant head pressure) and using an SP 2100-coated fused-silica capillary column, it was found that TZ was related to \overline{CH} by the equation

$$TZ = a(\overline{CH}) + b \quad (14)$$

for a homologous series of n -alkanes, carboxylic acids, methyl esters and alcohols with correlation coefficients > 0.95 [6]. The same relationship holds for the TPGC of C_{12} - C_{16} n -alkanes at starting temperatures of 40, 50 and 60°C under constant flow conditions (maintained by pressure programming) and isobaric flow. The differences in the two flow conditions resulted in a less negative slope value a under isobaric flow than under constant flow [7]. A plot of the experimentally determined maximum TZ values obtained at a starting temperature of 40°C and the lowest temperature programming rate (TPR) for all \overline{CH} s (12.5, 13.5, 14.5, 15.5 and 16.5) vs. the starting flow-rates (both constant and isobaric flows) produced an inverse Van Deemter plot. The visualized optimum starting flow-rate of ca. 0.9 ml/min at a TPR between 0.86 and 1.35°C/min with a starting temperature of 40°C produced the maximum TZ values for all \overline{CH} s, although there was

some evidence that lower flow-rates would be required for the higher molecular weight homologues.

As this suggested the possibility that an inverse relationship between TZ and the height equivalent to a theoretical plate (HETP), h , might exist, an investigation was initiated to study the changes in TZ and h as a function of different isothermal temperatures and at various constant flow-rates, and the results are presented in this paper.

EXPERIMENTAL

A Hewlett-Packard Model 5880A gas chromatograph equipped with a Model 7671 autosampler, a flame ionization detector, an electronic flow controller and a split-splitless injector set for a splitting ratio of 200:1 was used. A Level IV microprocessor with an alphanumeric keyboard controlled the temperature programming rates and the column head pressure of the helium carrier gas. Electronically measured retention times (± 0.10 min) and peak width at half-height ($w_{0.5}$), repeatable to $\pm 1\%$, were recorded in the "report annotation" mode [6]. On completion of the gas chromatogram, a specifically designed BASIC program listed the GC parameters for that analysis, giving the oven temperature, the column head pressure and the calculated TZ value for the two alkanes. The alkanes used in this study were 99+% pure undecane (C_{11}) and dodecane (C_{12}), obtained from Alltech (Applied Science Labs., Deerfield, IL, USA). These alkanes (ca. 300 mg of each) were made up to 10 ml with high-performance liquid chromatographic grade chloroform and 1 ml of this solution was diluted to 50 ml to give a solution that produced on-scale peaks (attenuation 0) for 5–10- μ l injections, depending on the column temperature and flow-rate.

A cross-linked DB-5 fused-silica column (25 μ m film thickness) (15 m \times 0.248 mm I.D.) was used (J&W Scientific, Rancho Cordova, CA, USA) and conditioned for 2 days by microprocessor-controlled repetitive TPGC runs from 100 to 200°C at 10°C/min at an initial helium flow-rate of 1.10 ml/min. The maximum column temperature was never allowed to exceed 250°C, although the manufacturer's recommended T_{\max} is 325°C for isothermal operation. When not in use, the column temperature was maintained at 250°C with a continuous helium purge of ca. 0.5 ml/min. All runs were

performed with injection port and detector temperatures of 275°C. Flow-rates were calculated in triplicate from the electronically determined retention time (t_r) of injected butane using the equation $F = \pi r^2 L/t_r$, where r (cm) is the radius of the column and L (cm) the column length.

RESULTS AND DISCUSSION

The effects of a change in carrier gas flow-rate at three different column temperatures (40, 60 and 80°C) on the h values of undecane and dodecane were determined in triplicate and, from the same GC runs, the TZ values were determined for the C_{11} – C_{12} homologous pair. The value of h (in mm) was calculated for each n -alkane from the equation

$$h = \frac{L}{5.54} \left(\frac{w_{0.5}}{t_r} \right)^2 \quad (15)$$

where L (mm) is the column length, $w_{0.5}$ the peak width at half-height and t_r (min) the retention time, *i.e.*, the time required for the alkane to elute from the column after injection.

Table I gives the TZ and h values calculated from the data generated. Several important facts are apparent. First, as the column temperature increases, the overall TZ values decrease, and the maximum TZ for each temperature group decreases with increasing temperature. Second, as the column temperature increases, the overall h values for each temperature group decrease (reflecting a decrease in t_r and a concomitant decrease in peak broadening), as do the minimum values of h for each temperature studied. Although this decrease in h would suggest improved column efficiency, the decreasing values of TZ indicate that the column resolving power is diminishing.

The Golay equation for a capillary column [8,9] is given by the equation

$$h = \frac{B}{\mu} + C\mu \quad (16)$$

where h is the height equivalent to a theoretical plate and μ the linear flow velocity. Using this equation, the data from Table I were used to model the relationships between both h and TZ and the velocity and/or flow.

$$h = \frac{B}{\mu} + C\mu + D \quad (17)$$

TABLE I

AVERAGE OF TRIPPLICATE DETERMINATIONS AT 40, 60 AND 80°C OF h , t_r , FLOW-RATE, μ , AND TZ FOR C_{11} AND C_{12} ALKANES ON A DB-5 FUSED-SILICA CAPILLARY COLUMN (15 m \times 0.25 mm I.D.) WITH $d_f = 0.25 \mu\text{m}$

Column temperature (°C)	Flow-rate (ml/min)	μ^a	C_{12}			C_{11}			TZ^e
			t_r^b	$w_{0.5}^c$	h^d	t_r^b	$w_{0.5}^c$	h^d	
40	0.516	17.52	179.31	2.218	0.414	72.88	0.867	0.383	33.51
	0.687	23.33	139.34	1.653	0.381	56.69	0.647	0.352	34.94
	1.10	37.35	85.29	1.087	0.440	34.67	0.431	0.419	32.34
	1.50	50.93	62.86	0.999	0.684	25.56	0.384	0.611	25.98
60	0.409	13.89	63.44	0.758	0.387	29.16	0.345	0.378	30.08
	0.503	17.08	55.22	0.602	0.322	25.34	0.295	0.368	32.30
	0.670	22.75	42.78	0.493	0.360	19.60	0.218	0.334	31.62
	1.08	36.67	26.49	0.303	0.355	12.15	0.145	0.386	31.00
80	1.46	49.57	19.44	0.262	0.491	8.91	0.118	0.475	26.73
	0.489	16.60	20.46	0.232	0.349	10.68	0.121	0.350	16.83
	0.651	22.10	15.69	0.160	0.349	8.18	0.083	0.279	29.96
	1.05	35.65	9.84	0.108	0.326	5.11	0.053	0.295	28.30
	1.42	49.57	7.19	0.086	0.391	3.73	0.045	0.394	25.32

^a Linear velocity (cm/s).

^b Retention time (min) S.D. < 6 parts in 1000.

^c Peak width at half-height (min) S.D. < 3 parts in 100.

^d Height equivalent to a theoretical plate (mm), S.D. < 2 parts in 1000.

^e TZ values calculated from eqn. 1, S.D. < 20 parts in 1000.

$$TZ = A - \frac{B}{\mu} - C\mu \quad (17a)$$

It has been shown [10] that the optimum flow-rate, F_{opt} , or velocity, μ_{opt} , can be determined by differentiating eqn. 17 (or 17a) and setting $dh/d\mu$ (or $dTZ/d\mu$, eqn. 17a) equal to zero, giving rise to the equation

$$\mu_{\text{opt}} = (B/C)^{\frac{1}{2}} \quad (18)$$

The minimum value of h and the maximum value of TZ can be calculated from the equations

$$h_{\text{min}} = D + 2(BC)^{\frac{1}{2}} \quad (19)$$

and

$$TZ_{\text{max}} = A - 2(BC)^{\frac{1}{2}} \quad (20)$$

respectively, which are obtained by substituting eqn. 18 into 17 and 17a. These equations were used to calculate the optimum flow-rate or linear velocity necessary to produce the maximum TZ or minimum h at the specified column temperatures used in this study.

Table II gives the coefficients and precision for the relationship between h_{min} and μ_{opt} or F_{opt} (eqns. 18 and 19).

The h values for undecane (C_{11}) and dodecane (C_{12}), obtained at column temperatures of 40, 60 and 80°C, were plotted *versus* the measured linear velocities and are shown in Figs. 1 and 2, respectively. The plots are in accord with those obtained by Desty and Goldup [11] in the definitive 1960 report on their study of coated capillary columns. As they observed, an increase in temperature produces a decrease in h and a small increase in μ_{opt} and/or F_{opt} (Table II). They noted that these temperature changes produced a slight reduction in the resistance to mass transfer or C term (eqn. 13), and also noted the flattening of the curve at low linear velocities in the longitudinal diffusion area with a corresponding decrease in the B term.

Table III gives the coefficients and precision of the relationship between TZ_{max} and μ_{opt} or F_{opt} (eqns. 18 and 20).

The plots for the combined data for TZ and $h(C_{11})$

TABLE II

COEFFICIENTS FOR THE EQUATION $h = B/\mu + C\mu + D$ FOR THE C₁₁ AND C₁₂ ALKANES FOR COLUMN TEMPERATURES OF 40, 60 AND 80°C

Alkane	Temperature	B	C	D	R ²	μ_{opt}^a	F_{opt}^b	h_{min}^c
C ₁₁	40	10.962	0.019	-0.568	0.994	24.118	0.699	0.341
	60	4.446	0.009	-0.058	0.973	22.342	0.648	0.340
	80	9.178	0.013	-0.411	0.999	27.068	0.785	0.267
C ₁₂	40	13.958	0.023	-0.780	0.982	24.530	0.711	0.358
	60	5.320	0.010	-0.146	0.846	22.554	0.654	0.326
	80	6.742	0.010	-0.227	0.927	26.199	0.759	0.288

^a Optimum linear velocity (cm/s) calculated from eqn. 18.

^b Optimum flow-rate (ml/min) calculated from $\mu = 34.502 F$.

^c Minimum h as calculated from eqn. 19.

and C₁₂) at 40, 60 and 80°C versus μ are shown in Figs. 3, 4 and 5, respectively. A comparison of the B and C terms in eqns. 17 and 17a (Tables II and III) show the trend that, with increasing column temperature, both terms decrease. The TZ_{max} values also decrease with increasing column temperature, indicating that the column resolving power or separation capability is being reduced. This reduction in TZ values has been reported previously [3,4,7] and is consistent with the fact that increased temperatures

result in decreased t_r and $w_{0.5}$ values owing to an increase in the solute molecular diffusion coefficients in the mobile and stationary liquid phases (D_G and D_L , respectively), particularly for low-molecular weight C₄-C₉ solutes [11].

An examination of plots of TZ and h versus measured column linear velocities or flows-rates at 40°C (Fig. 3), 60°C (Fig. 4) and 80°C (Fig. 5) shows that the TZ curve is very nearly the mirror image of the h curve. The optimum flow-rates or velocities for

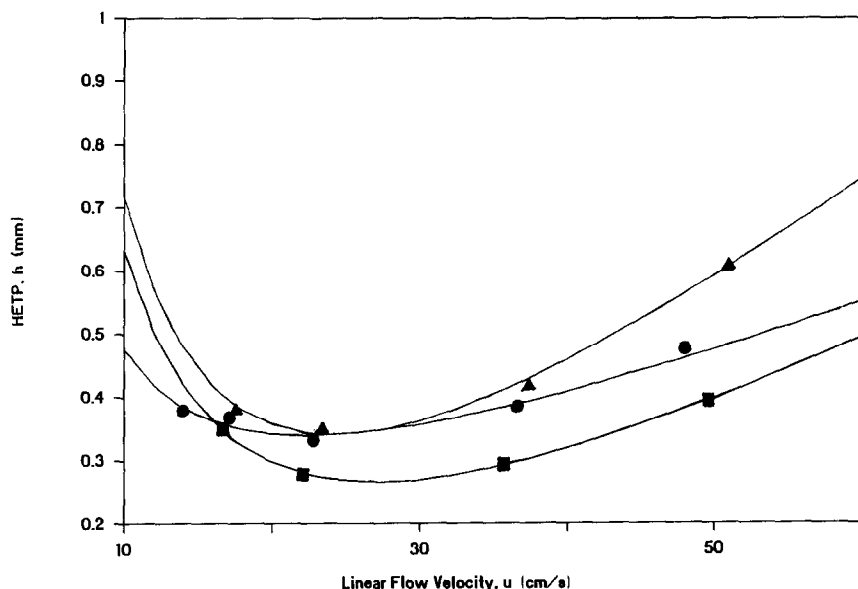


Fig. 1. Undecane: computer-generated (Lotus 1-2-3, version 2.2) plot of the height equivalent to a theoretical plate, h , versus linear flow velocity, μ , using a DB-5 fused-silica column, 25 μ m film thickness (15 m \times 0.248 mm I.D.) with helium as carrier gas. Column temperature: \blacktriangle = 40; \bullet = 60; \blacksquare = 80°C. Data from Table I.

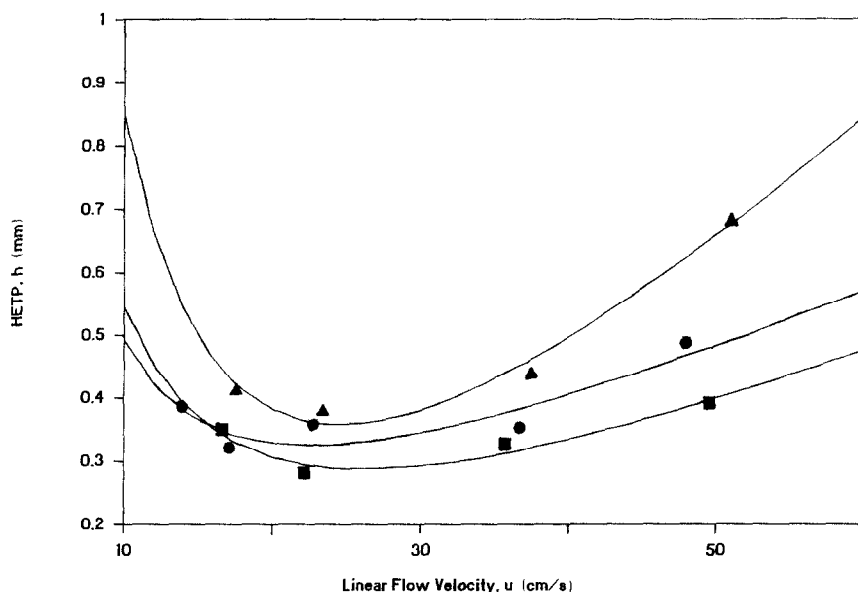


Fig. 2. Dodecane: computer-generated (Lotus 1-2-3, version 2.2) plot of the height equivalent to a theoretical plate, h versus linear flow velocity, μ , using a DB-5 fused-silica column, 25 μm film thickness (15 m \times 0.248 mm I.D.) with helium as carrier gas. Column temperature: \blacktriangle = 40; \bullet = 60; \blacksquare = 80°C. Data from Table I.

maximizing TZ values can be seen to be very nearly the average of the μ_{opt} or F_{opt} of the h_{min} for C_{11} and C_{12} , respectively. Therefore, TZ would have a theoretical t_r equal to the average of the t_r values of C_{11} and C_{12} $[(t_r^{11} + t_r^{12})/2]$ and μ_{opt} can be calculated for these two alkanes. The average F_{opt} of these two homologues should approximate the calculated F_{opt} producing TZ_{max} . From Table III, the F_{opt} producing TZ_{max} at 40°C is 0.704 ml/min and the average of F_{opt} for C_{11} and C_{12} (Table II) is 0.705 ml/min. At 60°C, the F_{opt} for TZ_{max} is 0.661 ml/min

and the C_{11} - C_{12} average F_{opt} is 0.651 ml/min. Performing the same comparison for 80°C, the TZ_{max} F_{opt} is 0.774 ml/min and the C_{11} - C_{12} average F_{opt} is 0.772 ml/min. The excellent agreement between the average F_{opt} values determined for h and the flow-rate determined for TZ_{max} suggests that there is a relationship between TZ and h . Further, Figs. 3-5 and the equations generated (eqns. 17 and 17a, Tables II and III) indicate that they are inversely related.

The is an equivalence relative to eqn. 1 that can be

TABLE III

COEFFICIENTS FOR THE EQUATION $TZ = A - B/\mu - C\mu$ FOR THE C_{11} - C_{12} ALKANE HOMOLOGUE PAIR FOR COLUMN TEMPERATURES OF 40, 60 AND 80°C

Temperature (°C)	B	C	A	R^2	μ_{opt}^a	F_{opt}^b	TZ_{max}^c
40	385.842	0.653	66.902	0.998	24.301	0.704	35.146
60	196.518	0.378	49.648	0.926	22.804	0.661	32.412
80	317.385	0.446	53.605	0.942	26.689	0.774	29.821

^a Optimum linear velocity (cm/s) calculated from eqn. 18.

^b Optimum flow-rate (ml/min) calculated from $\mu = 34.502F$.

^c Maximum TZ calculated from eqn. 20.

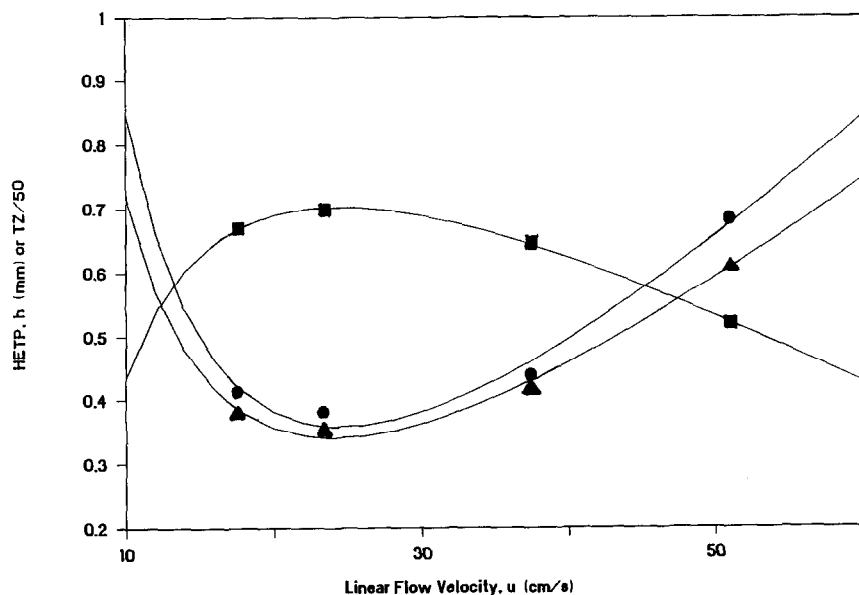


Fig. 3. Computer-generated (Lotus 1-2-3, version 2.2) plot of the height equivalent to a theoretical plate, h , for (\blacktriangle) C_{11} and (\bullet) C_{12} and (\blacksquare) TZ (C_{11} - C_{12}) versus linear flow velocity, u , using a DB-5 fused-silica column, 25 μm film thickness (15 m \times 0.248 mm I.D.) with helium as carrier gas. Column temperature, 40°C.

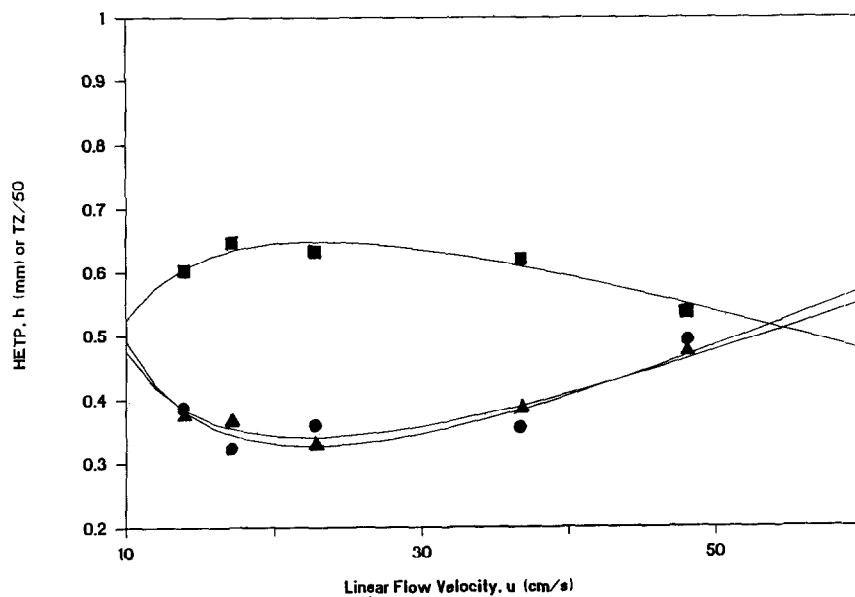


Fig. 4. Computer-generated (Lotus 1-2-3, version 2.2) plot of the height equivalent to a theoretical plate, h , for (\blacktriangle) C_{11} and (\bullet) C_{12} and (\blacksquare) TZ (C_{11} - C_{12}) versus linear flow velocity, u , using a DB-5 fused-silica column, 25 μm film thickness (15 m \times 0.248 mm I.D.) with helium as carrier gas. Column temperature, 60°C.

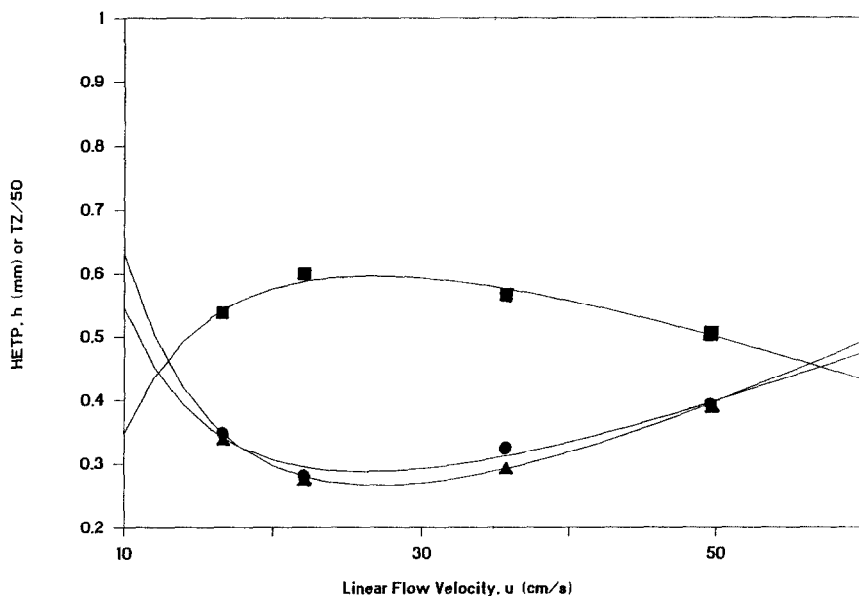


Fig. 5. Computer-generated (Lotus 1-2-3, version 2.2) plot of the height equivalent to a theoretical plate, h , for (\blacktriangle) C_{11} and (\bullet) C_{12} and (\blacksquare) TZ (C_{11} - C_{12}) versus linear flow velocity, μ , using a DB-5 fused-silica column, 25 μ m film thickness (15 m \times 0.248 mm I.D.) with helium as carrier gas. Column temperature, 80°C.

shown by rearranging eqn. 15 to give $w_{0.5}$ as a function of h and the column length L as in the equation

$$w_{0.5} = \left(\frac{5.54}{L}\right)^{\frac{1}{2}} h^{\frac{1}{2}} t_r = 1.92 \cdot 10^{-2} h^{\frac{1}{2}} t_r \quad (21)$$

Substituting this $w_{0.5}$ expression for each homologue in eqn. 1 and solving gives the equation

$$TZ = C \cdot \frac{t_r^b - t_r^a}{t_r^b h_b^{\frac{1}{2}} + t_r^a h_a^{\frac{1}{2}}} - 1 \quad (22)$$

where $C = (L/5.54)^{\frac{1}{2}}$ or 52.035 for the 15 000-mm column length used in this study.

This is the first time that an equation has been derived for TZ in which the h value for both homologues and the column length are incorporated. Using this relationship and the experimentally determined t_r and h values for C_{11} and C_{12} , as shown in Table I, new TZ values were calculated from eqn. 22 and are compared with those calculated from eqn. 1 in Table IV. The TZ values from eqns. 1 and 22 agree extremely well with each other, as they should since eqn. 21 is simply an alternative definition of $w_{0.5}$.

To test further the derived relationship (eqn. 22),

the data reported by Ettre [2] were used for calculation. With a reported column length of 20 m, the constant C becomes 60.080, and utilizing the re-

TABLE IV

TZ VALUES CALCULATED FROM EQN. 1 COMPARED WITH TZ VALUES CALCULATED FROM EQN. 22 FOR COLUMN TEMPERATURES OF 40, 60 AND 80°C FROM THE DATA IN TABLE I

Column temperature (°C)	Flow-rate (ml/min)	TZ (eqn. 1)	TZ (eqn. 22)
40	0.516	33.51	33.51
	0.687	34.94	34.95
	1.10	32.34	32.33
	1.50	25.98	25.97
60	0.409	30.08	30.08
	0.503	32.30	32.29
	0.670	31.62	31.60
	1.08	31.00	30.98
80	1.46	26.73	26.73
	0.489	26.83	26.65
	0.651	29.96	29.95
	1.05	28.30	28.34
	1.42	25.32	25.33

TABLE V

TZ VALUES CALCULATED FROM EQN. 1 COMPARED WITH TZ VALUES CALCULATED FROM EQN. 22 USING ETTRE'S [2] DATA FOR A COLUMN 20 m \times 0.24 mm I.D. COATED WITH CARBOWAX 20M AT 80°C

Argon flow-rate (ml/min)	Compounds	Carbon No.	t_r (min)	h (mm)	TZ (eqn. 22) ^a	TZ (eqn. 1) ^b
0.291	<i>n</i> -Alkanes	C ₁₂	7.07	0.243	22.47	22.50
		C ₁₃	10.45	0.245	26.39	26.40
		C ₁₄	16.64	0.256		
	<i>n</i> -Alkanols	C ₅	9.24	0.232	26.45	26.50
		C ₆	14.51	0.239	29.85	29.80
		C ₇	24.32	0.244		

^a TZ value calculated from eqn. 22, C term = 60.080.

^b TZ value calculated [2] from eqn. 1.

ported t_r and $w_{0.5}$ values, the data in Table V were used to calculate the TZ values from eqn. 22, and demonstrated again that using the expression for TZ that includes h and column length L , the values obtained are essentially the same as those from eqn. 1.

Table VI compares the previously reported TZ values of Krupcik *et al.* as calculated with eqn. 1 [5], the values calculated by the combination of eqns. 4 and 10 [5] and those calculated by eqn. 22. In general, the agreement between the eqn. 22 TZ values and those determined from eqns. 4 and 10 [5] was better than 99%. However, for those values calculated for the C₈-C₉ homologues with the 19.5-m SE-30 column, large differences existed between the calculated TZ value of 13.1 (eqn. 22), the TZ value of 16.4 determined from eqns. 4 and 10 [5], and the eqn. 1 TZ value of 15.9 [5]. On examining the published data, it was determined that the α -value was 1.82, and not the reported value of 2.10 [5]. Recalculating TZ according to their method (eqns. 4 and 10) using this α -value yielded a TZ value of 13.07 or 13.1, rather than the reported value of 16.4.

As our method of calculation (eqn. 22) also produced a TZ value of 13.1, attention was directed to the validity of the reported TZ value of 15.9 for C₈-C₉ [5] obtained from eqn. 1. Given in their Table

III [5] were the α -values, the k' values and n (the number of plates) calculated for the hydrocarbons C₈, C₉, C₁₀, C₁₁ and C₁₂ for selected column lengths and the carrier gas velocity for each of these columns was contained in Table II in the same paper [5]. The velocity given for the column used for the above TZ determination (19.5 m \times 0.25 mm I.D. SE-30 coated capillary) was 37.1 cm/s, which when substituted in the equation [12]

$$t_0 \text{ (min)} = 1.67 \cdot \frac{L \text{ (m)}}{\mu \text{ (cm/s)}} \quad (23)$$

gave $t_0 = 0.878$ min. With this value and the relationship $t_r = k't_0 + t_0$, the t_r values for C₈ and C₉ were found to be 1.66 and 2.31 min, respectively.

For C₈ the number of plates reported (Table III, in ref. 5) was 36 800 and for C₉ 46 600, which for a column length of 19.5 m gave h values of 0.530 and 0.418 mm, respectively. Rearranging eqn. 15, these values were used to calculate the $w_{0.5}$ values to three significant figures; C₈ was found to have a $w_{0.5}$ value of 0.020 min and C₉ 0.025 min. Rounding these off to 0.02 and 0.03 min gave a TZ of 12.0 whereas using the original values gave a TZ of 13.1, identical with that calculated above by eqn. 20 and eqns. 4 and 10. It is apparent that $w_{0.5}$ values accurate to three significant figures are necessary for meaningful separation numbers.

TABLE VI

TZ VALUES CALCULATED FROM EQN. 1 COMPARED WITH TZ VALUES CALCULATED FROM EQN. 22 USING DATA OF KRUPCIK *et al.* [5]

Flow-rate (ml/min)	Column ^a	Alkane	t_r (min)	h (mm)	TZ (eqns. 4 and 10) ^{b,c}	TZ (eqn. 22)	TZ (eqn. 1) ^c
1.25	A ^d	C ₈	1.80	0.547	19.0 (18.8)	19.0	19.0 (19.0)
		C ₉	2.62	0.344	30.1 (30.2)	30.2	30.2 (30.3)
		C ₁₀	4.31	0.270	38.4 (38.0)	37.9	37.2 (37.7)
		C ₁₁	7.64	0.230	43.6 (44.4)	44.4	42.8 (44.3)
		C ₁₁	14.59	0.229			
1.09	B ^e	C ₈	1.16	0.530	16.4 (13.1)	13.1	15.9 (13.2)
		C ₉	2.30	0.418	24.6 (24.7)	24.8	24.7 (24.9)
		C ₁₀	3.83	0.280	32.4 (32.4)	32.4	32.5 (32.4)
		C ₁₁	6.90	0.272	34.8 (34.9)	35.0	35.0 (35.0)
		C ₁₂	13.11	0.270			
1.17	C ^f	C ₈	3.44	0.322	31.7 (30.9)	31.1	31.2 (31.6)
		C ₉	5.07	0.283	41.2 (41.3)	41.2	41.3 (41.3)
		C ₁₀	8.37	0.284	48.1 (48.1)	48.3	48.3 (48.2)
		C ₁₁	15.06	0.281	51.2 (51.3)	51.3	51.3 (51.4)
		C ₁₂	28.64	0.304			

^a Column A: 27 m × 0.25 mm I.D. SE-30-coated capillary; temperature 83°C. Column B: 19.5 m × 0.25 mm I.D. SE-30-coated capillary; temperature 83°C. Column C, 46.5 × 0.25 mm I.D. SE-30-coated capillary; temperature 83°C.

^b Calculated from eqns. 4 and 10 [5].

^c Values in parentheses are recalculated; see text.

^d In eqn. 22, C term = 69.81.

^e In eqn. 22, C term = 59.33.

^f In eqn. 22, C term = 91.62.

Having found such large discrepancies, the data in Table III in ref. 5 were recalculated in the manner described and the recalculated values are given in parentheses in the appropriate columns in Table VI. Some of the errors in utilizing eqns. 4 and 10 [5] were found to be related to incorrect calculations of α , whereas errors in the use of eqn. 1 arose from the rounding out off $w_{0.5}$ values.

As was previously noted in the reported derivations of eqns. 4 [2], 9 [4] and 10 [5], all were based on

approximations such as equating the $w_{0.5}$ for the two homologues [2], the $w_{0.5}$ fraction of the two homologues being equal to α [4] or the utilization of only the larger k' of the homologous pair in the derivation of eqn. 11. It is apparent from Table I that the $w_{0.5}$ values of a homologous pair are not "approximately" equal. The same can be said for the h values and/or the h values and/or the number of plates. As has been shown, the casual approximating or rounding off of $w_{0.5}$ values can cause a 9% error

in reported values. The excellent agreement between TZ values determined using eqn. 1 with $w_{0.5}$ values accurate to three significant figures and eqn. 20, which utilizes h , is obvious.

The procedure for determining the optimum flow-rate for h_{\min} is the same that provides the optimum flow-rate for TZ_{\max} and the inverse relationship between h and TZ only emphasizes the fact that the concept of TZ incorporates proven chromatographic principles. As in any chromatographic study, control of column length and diameter, coating, phase thickness, flow-rate and temperature will control retention time, peak width at half-height (the foundation of plate theory) and, as has been shown, the separation number.

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