Short communication

Relationship between carbon number and peak width in gas chromatography

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Abstract

When the unadjusted width (w_R) is divided into hold-up width (w_M) and adjusted width (w_R'), a linear relationship between the natural logarithm of the width factor (p') and the carbon number (n) is demonstrated and can be described by: $\ln p' = a + bn$ where a and b are constants. The coefficients of variance (r^2) for n-alkanes, fatty acid methyl esters and fatty alcohols are 0.9997, 0.9996 and 0.9998, respectively. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Peak shape; Alkanes; Fatty acid methyl esters; Fatty alcohols

1. Introduction

It has been demonstrated that the extra-column band broadening is inversely proportional to the column length [1]. Thus, the contribution of extra-column band broadening is insignificant and ignored in long columns. However, extra-column band broadening will be very significant for improper column installation. Several methods for the estimation of the extra-column band broadening have been reported [2–4]. Kaiser [2] simply approached it by using the intercept of the plot between retention factor (k') and width at half height (w_h), but the plot was not linear at all values of k' [3]. Smuts et al. [4] proposed a plot between peak variance and $(1 + k')^2$, but it was shown that the plot was not strictly linear [5].

Gaspar et al. [1] used methane ($k' = 0$) together with a complicated mathematical calculation for the determination of the extra-column band broadening. Bemgård and Colmsjö [6] reported that the extensive computer optimization method of calculation of the extra-column band broadening gave a higher accuracy than the extrapolation to zero column length method.

In this paper, the concept of hold-up width (w_M) and width factor (p') is introduced. The measurement of w_M is much easier than that of extra-column band broadening. Also, the linear relationship between $\ln p'$ and carbon number (n) is demonstrated.

2. Experimental

Fatty acid methyl esters (FAMEs), fatty alcohols

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S. Lomsugarit et al. / J. Chromatogr. A 926 (2001) 337–340

and *n*-alkanes of various chain lengths were pur-
chased from Sigma Chemical Co. (St. Louis, MO,
USA).

GC analysis was carried out on a Shimadzu model
14A equipped with flame ionization detection (FID)
and thermal conductivity detection (TCD), split-
splitless injector, and a C-R4A data processor
(Kyoto, Japan). An HT-5 fused-silica capillary col-
umn (25 m×0.32 mm I.D.) (SGE, Australia) was
used with a helium carrier gas flow-rate of 0.85–1.15
ml/min. The TCD system was optimized for packed
columns and it was slightly modified. One of the
detector tips was threaded and a three-way connector
was connected. Helium make up gas was supplied
through this connector. The total flows of helium gas
through the reference and sample cells were approxi-
mately 25 ml/min each. The TCD current was
maintained at 100 mA. Injector and detector tem-
peratures were 230°C. Sample injection was per-
formed with a split ratio of 50:1.

3. Result and discussion

3.1. The linear relationship between ln p′ and carbon number of n-alkane

Fig. 1 shows a gas chromatogram of *n*-alkanes
printed out by the C-R4A data processor. Peak
widths are simply calculated from area and height
and summarized in Table 1. By analogy to retention
time, the width of each peak is divided into un-
adjusted width (w_R), adjusted width (w_R'), and hold-
up width (w_M). Their relationship is described in
Eqs. (1) and (2):

$$w_R'^2 = w_R^2 - w_M^2 \tag{1}$$

and

$$p' = \frac{w_R'}{w_M} \tag{2}$$

Hold-up width is the width of non-retained solute.
Neon gas that has been widely employed for the
measurement of the gas hold-up time (t_M) [7,8] is
adopted here for the measurement of w_M.

Among several treatments of peak widths (data in
Table 1), the plot between ln p' and n yields a
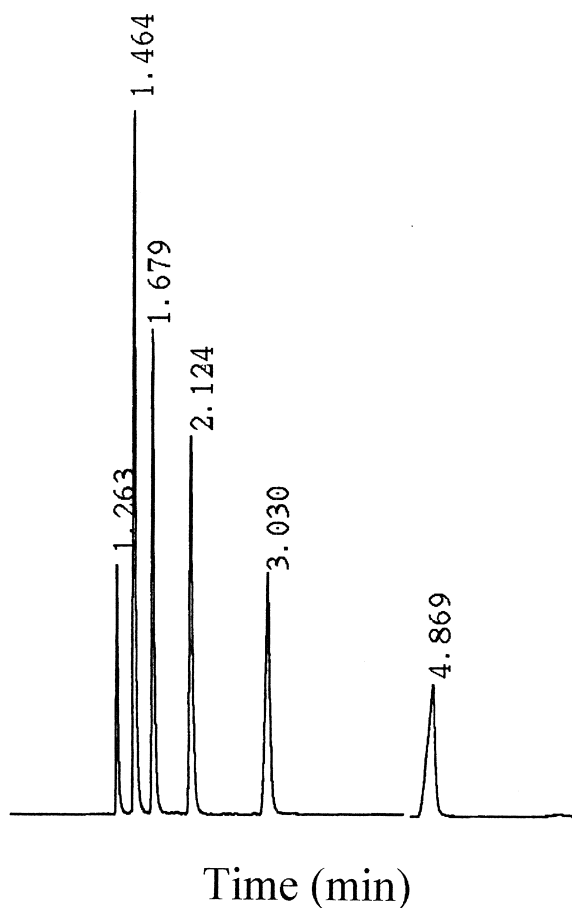

Time (min)

Fig. 1. Gas chromatogram of neon gas and *n*-alkanes (C$_8$–C$_{12}$) on
HT-5 (25 m×0.32 mm I.D.) at 90°C. Numbers on peak tops are
retention times in minutes.

straight line (Eq. (3)) with a coefficient of variance
(r^2) of 0.9997:

$$\ln p' = 0.659 - 6.652n \tag{3}$$

Also, data collected at temperatures between 80 and
100°C at 5°C intervals show a linear relationship
between ln p' and n with a coefficient of variance
better than 0.9995 (data are not shown). Thus, the
relationship between p' and n can generally be
described by Eq. (4):

$$\ln p' = a + bn \tag{4}$$

where *a* and *b* are constants. It is speculated that the

Table 1
Gas chromatographic peak information printed out from C-R4A data processor (Peak width=2*Area/Height)

Compounds	t_R (min)	Area (μV s)	Height (μV)	Width (s)	w_R^2
Neon	1.263	277	157	3.53	12.45
Octane	1.464	805	444	3.63	13.15
Nonane	1.679	596	306	3.90	15.17
Decane	2.124	581	239	4.86	23.64
Undecane	3.030	564	152	7.42	55.07
Dodecane	4.869	527	83	12.70	161.26

resolution of any solute pair would be easily estimated by Eqs. (4) and (5). However, the calculation is still limited to isothermal GC:

$$\ln t_R' = a + bn \qquad (5)$$

3.2. Calculation of hold-up width

Although neon gas has been widely accepted for the measurement of hold-up time (t_M), it does not cause a FID response (the most widely used detection method). Furthermore, at higher oven temperatures, neon tends to be co-eluted or is not well separated from the solvent peak. This would complicate the measurement of peak width. In the case of retention time, there are many mathematical methods of calculation of t_M [9–13]. These were excellently reviewed by Wainright and Haken [10]. The iterative method of Guardino et al. [9] was modified to calculate w_M based on Eq. (4). The calculated w_M (3.52 s) was 0.01 s less than the width of neon gas (3.53 s). The calculated w_M of *n*-alkanes at several temperatures between 80 and 100°C showed a highest deviation of less than 0.02 s (data are not shown). However, higher deviations would be expected for

chromatograms whose peaks eluted very fast or very slow.

The calculated w_M of FAMEs (C_{16}–C_{22}) and fatty alcohols (C_{12}–C_{20}) are summarized in Tables 2 and 3, respectively. Also, the plots between $\ln p'$ and n of these homologs yield straight lines with coefficients of variance of 0.9996 and 0.9998, respectively.

3.3. Analysis of data by Smuts et al. [5]

Table 4 summarizes the calculated t_M, w_M, k', w_R' and p' from data by Smuts et al. [5]. The plot between $\ln p'$ and n gives a straight line with coefficient of variance of 0.9975.

It is interesting to point out that the slope of the regression is the change in $\ln p'$ per the change of one carbon atom. This would directly or indirectly relate to the column efficiency.

4. Conclusion

A linear relationship between $\ln p'$ and n has been demonstrated and it would provide a convenient method for forecasting the peak widths of organic

Table 2
Gas chromatographic peak information of FAMEs on column coated with HT-5 at 200°C

Compound	t_R (min)	Area (μV s)	Height (μV)	Width (s)	$\ln p'$
C_{16}	4.959	25 178	7842	6.42	0.434
C_{17}	6.368	24 376	5555	8.78	0.836
C_{18}	8.439	27 388	4534	12.08	1.197
C_{19}	11.463	23 628	2701	17.50	1.591
C_{20}	15.900	28 631	2330	24.08	1.941
C_{22}	31.799	25 293	926	54.63	2.748
w_M	3.39 s				
t_M	1.90				

Table 3
Gas chromatographic peak information of fatty alcohols on column coated with HT-5 at 185°C

Compound	t_R (min)	Area (μV s)	Height (μV)	Width (s)	ln p'
C_{12}	2.996	19 362	11 196	3.46	−0.416
C_{14}	4.293	18 494	7054	5.24	0.416
C_{16}	7.263	18 568	3818	9.73	1.169
C_{18}	14.004	18 138	1680	21.59	2.003
C_{20}	29.176	20 042	831	48.24	2.814
w_M	2.79 s				
t_M	1.97				

Table 4
Re-analysis of data by Smuts et al. [7]

Compound	k'	w'_R	w'^2_R	p'	ln p'
Nonane	0.544	1.57	2.46	0.668	−0.403
Decane	0.840	2.64	6.95	1.123	0.116
Undecane	1.309	3.53	12.44	1.502	0.407
Dodecane	2.054	5.40	29.13	2.298	0.832
Tridecane	3.233	7.16	51.26	3.047	1.114
Tetradecane	5.076	10.82	116.97	4.604	1.527
Pentadecane	7.981	16.55	274.00	7.043	1.952
Hexadecane	12.538	25.32	641.26	10.774	2.377
Heptadecane	18.816	38.78	1504.15	16.502	2.803
t_M	208.65 s				
w_M	2.35 s				

compounds in the same homologous series. Also, it would undoubtedly provide a convenient and accurate means for the determination of w_M which may be employed for the estimation of the extra-column band broadening.

References

[1] G. Gaspar, R. Annino, C. Vidal-Madjar, G. Guiochon, Anal. Chem. 50 (1978) 1512.

[2] M.A. Kaiser, in: R.L. Grob (Ed.), Modern Practice of Gas Chromatography, Wiley, New York, 1985, p. 160.

[3] G. Guiochon, Chromatographia 11 (1978) 249.

[4] T.W. Smuts, T.S. Buy, K. de Clerk, T.G. du Toit, J. High Resolut. Chromatogr., Chromatogr. Commun. 1 (1979) 41.

[5] T.W. Smuts, T.S. Buys, K. de Clerk, T.G. du Toit, J. High Resolut. Chromatogr., Chromatogr. Commun. 4 (1981) 385.

[6] A.K. Bemgård, A.L. Colmjö, J. High Resol. Chromatogr. 13 (1990) 689.

[7] F. Parcher, D.M. Johnson, J. Chromatogr. Sci. 18 (1980) 267.

[8] F. Reido, D. Fritz, G. Tarján, E. sz Kováts, J. Chromatogr. 126 (1976) 63.

[9] X. Guardino, J. Albaigés, G. Firpo, R. Rodriguez-Viñal, M. Gassiot, J. Chromatogr. 118 (1976) 13.

[10] M.S. Wainright, J.K. Haken, J. Chromatogr. 184 (1980) 1.

[11] R. Lebrón-Aguilar, J.E. Quintanilla-López, J.A. García-Domínguez, J. Chromatogr. A 760 (1997) 219.

[12] F.R. Gonzalez, J. Chromatogr. A 832 (1999) 165.

[13] T. Watanachaiyong, N. Jeyashoke, K. Krisnangkura, J. Chromatogr. Sci. 38 (2000) 67.