Dependence of the width of the chromatographic zone on retention time in capillary gas chromatography

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The dependence of the width of the chromatographic zone on retention time for capillary columns was studied theoretically and experimentally.

Key words: capillary gas chromatography, retention time, peak width.

Retention time (t_R) and peak width measured at half-height (ω_h) are the main parameters of a chromatographic peak that are widely used to characterize retention of a substance and peak broadening. Therefore, elucidation of the functional dependence between these parameters in capillary gas chromatography:

$$t_R = f(\omega_h). \tag{1}$$

is of certain theoretical and practical interest.

Previously, it has been found empirically that in the case of packed columns, dependence (1) is linear;[1] later, this dependence was used successfully in the studies of broadening of chromatographic zones for light and heavy impurities in gas chromatography.[2,3] However, in the published studies, the linear functional dependence was considered only for packed columns (for one nonpolar stationary liquid phase and for nonpolar sorbates, *viz.*, hydrocarbons), which casts doubts upon its universality.

The purpose of the present study is to identify the form of dependence (1) for capillary columns, when the main experimental parameters are varied. The study was carried out for columns containing two types of stationary liquid phase (SLP) (polar and nonpolar) and for three velocities of the carrier gas (larger, smaller, and equal to the optimal).

Dependence (1) is of interest, first, for determination of the widths of individual chromatographic zones when they are poorly separated from the neighboring peaks; second, as a characteristic that would make it possible to detect considerable changes in the mechanism of broadening of chromatographic zones for individual compounds (in this case, the point corresponding to a compound with specific properties markedly deviates from the general linear dependence (1)); third, for quantitative characterization of variation of the efficiency of a chromatographic column under various experimental conditions[3]).

Calculation and experimental techniques

Theory. The height equivalent to one theoretical plate (HETP, H) is known[4] to depend on the carrier gas velocity, according to the Golay equation:

$$H = \frac{1+6k+11k^2}{96(1+k)^2}\cdot\frac{d_c^2}{D_g}\cdot u + \frac{2k}{3(1+k)^2}\cdot\frac{d_f^2}{D_l}\cdot u + \frac{2D_g}{u}, \tag{2}$$

where k is the capacity factor, u is the linear velocity of the carrier gas, d_c is the diameter of the column, D_g is the coefficient of diffusion of the sorbate in the gas phase, d_f is the thickness of the SLP film; D_l is the coefficient of diffusion of the sorbate in the SPL.

After the change of variable $x = 1/k$ by $k = 1/x$, one can write:

$$H = \frac{11+6x+x^2}{96(1+x)^2}\cdot\bar{C}_g\cdot u + \frac{x}{3(1+x)^2}\cdot\bar{C}_l\cdot u + \frac{2D_g}{u}, \tag{3}$$

where $\bar{C}_g = d_c^2/D_g$; $\bar{C}_l = d_f^2/D_l$. It is known that[4]

$$H = \frac{L}{5.54}\cdot\left(\frac{\omega_h}{t_R}\right)^2, \tag{4a}$$

$$k = \frac{t_R - t_m}{t_m}, \tag{4b}$$

where L is the length of the column, ω_h is the width of the chromatographic zone measured at half-height, t_R is the retention time, and t_m is the "dead" time of the column. From relations (4a) and (4b), it follows that

$$\frac{\omega_h}{t_R} = \sqrt{\frac{5.54}{L}}\cdot\sqrt{H} = m\cdot\sqrt{H} \tag{5}$$

or

$$\frac{1}{m}\cdot\frac{\omega_h}{t_R} = \sqrt{H(x)}, \tag{6}$$

where $m = m = \sqrt{\frac{5.54}{L}}$.

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Table 1. Dependence of the width of a chromatographic peak (ω_h/s) on the retention time (t_R/min) at various linear velocities of carrier gas (u/cm s^{-1} = 11.0 (I), 21.4 (II), 35.7 (III), 12.0 (IV), 20.0 (V), 33.3 (VI))

Compound	I*		II*		III*		IV**		V**		VI**	
	ω_h	t_R	ω_h	t_R	ω_h	t_R	ω_h	t_R	ω_h	t_R	ω_h	t_R
Ethyl acetate	3.17	5.30	2.00	3.01	1.31	1.70	3.07	4.50	1.66	2.76	1.34	1.90
1-Pentanol	4.84	6.60	2.26	3.50	1.51	2.00	8.66	12.90	3.36	6.87	2.54	4.76
m-Xylene	6.92	10.50	2.29	4.30	1.89	3.01	6.97	11.01	3.19	6.40	2.12	3.60
n-Decane	9.48	17.00	3.24	8.55	2.58	4.80	4.82	8.10	1.92	4.00	1.49	2.27

Note. Parameters of Eq. (8): I. a = 1.092, b = 0.51, R = 0.981; II. a = 1.415, b = 0.213, R = 0.992; III. a = 0.676, b = 0.398, R = 0.998; IV. a = 0.16, b = 0.662, R = 0.991; V. a = 0.335, b = 0.439, R = 0.990; VI. a = 0.536, b = 0.426, R = 0.998.

* For capillary columns with the nonpolar SLP SE-30.

** For capillary columns with the polar SLP PEG-20M.

Now we expand the function $\sqrt{H}$ into the Maclaurin series with respect to x and write down the first two terms:

$$\frac{1}{m}\cdot\frac{\omega_h}{t_R} \approx \left(\frac{2D_g}{u}+\frac{11}{96}\overline{C}_g\cdot u\right)^{1/2} + \left(\frac{1}{12}\frac{C_l u - C_g u}{\sqrt{\frac{11}{96}C_g u+\frac{2D_g}{u}}}\right)x\ . \qquad (7)$$

After transformations of Eq. (7), we obtain the following expression

$$\omega_h = a + b\cdot t_R, \qquad (8)$$

where

$$a = m\left(\frac{1}{12}\frac{2C_l u - C_g u}{\sqrt{\frac{11}{96}C_g u+\frac{2D_g}{u}}}\right)x\ , \qquad (9)$$

$$b = m\left(\frac{2D_g}{u}+\frac{11}{96}\overline{C}_g\cdot u\right)^{1/2}\ . \qquad (10)$$

Since $t_R = t'_R + t_m$, then

$$\omega_h = \bar{a} + b\cdot t_R, \qquad (11)$$

where $\bar{a} = a - b\cdot t_m$.

Thus, using the known Golay equation, which describes the broadening of a chromatographic band as a function of the linear velocity of the carrier gas for open tubular capillary columns, one can show that the width of a chromatographic zone depends linearly on the retention time. Since the forms of dependence of the HETP on the linear velocity of the mobile phase in gas and liquid chromatography are similar, Eq. (8) is likely to be also valid for liquid chromatography, although this requires an additional verification.

Experimental procedure. The experiments were carried out on an LKhM-8MD instrument (the 5th modification) using a flame ionization detector. Quartz capillary columns (30 m×0.25 mm) with SE-30 and PEG-20M (Restek Corporation) as liquid stationary phases were used; the SLP film was 0.5 mm thick.

The conditions of the analysis were the following: helium as the carrier gas; temperature of the vaporizer 250 °C; temperature of the column 100 °C; sensitivity $50\cdot10^{-12}$ Å, flow ratios, 1 to 70. A mixture of ethyl acetate, 1-pentanol, *m*-xylene, and *n*-decane was used as the model mixture.

Results and Discussion

Previously,[1] the linear dependence between ω_h and t_R (see Eq. (8)) was established only for particular experimental conditions. Therefore, it was of interest to verify whether or not dependence (8) holds for capillary chromatography with various experimental parameters. Table 1 presents the experimental values of a and b in Eq. (11) as well as the correlation coefficients (R) that reflects the agreement between Eq. (8) and experimental data.

It follows from Table 1 that Eq. (8) describes quite adequately the set of experimental data obtained when the type of SLP, experimental conditions, and the type of compounds under analysis were varied over wide ranges.

Thus, the linear dependence between the width of the chromatographic zone and retention time is also valid for capillary chromatography, and this dependence holds irrespective of the type of SLP, the velocity of the carrier gas, and the type of compound subjected to analysis.

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