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AN EMPIRICAL FORMULA FOR ASYMMETRIC GAS CHROMATOGRAPHIC PEAK

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It was found that the asymmetric gas chromatographic peak can be described as a normal distribution curve in oblique coordinates. By converting the curve into the rectangular coordinates, we obtained the empirical formula as shown by equation (1).

It is well known that at an optimum column temperature, the gas chromatographic peak can be expressed by the Gaussian or normal distribution curve, but as the column temperature becomes higher or lower than the optimum one, the shape of chromatogram becomes tailing or leading type, respectively[1]. As for the skew ratio of the peak, only a qualitative explanation on the basis of the nonlinear partition isotherm has been given.

Rudenko et al.[2] proposed a new method for determining the area of chromatographic peak that is based on the conversion of Gaussian curve into a linear plot. They successfully applied the method to the peak area measurement, even in the case that the peak top is not recorded by scale-out.

In this paper, we applied the linear plot method to the elucidation of the nature of an extremely tailing or leading gas chromatographic peak.

The gas chromatograph used was a Hitachi KGL-2A, equipped with a thermal conductivity detector. The column, 1 m in length and 0.4 cm in diameter, was a stainless steel tube packed with 25 % DNP on 60 - 80 mesh Shimalite. The flow rate of helium carrier gas was kept to 30 ml per minute.

Ten straight lines, which are parallel to the base line and divide the whole peak into eleven parts of the equal height, are drawn. Then the middle points of the segments cut off by the peak are connected together. In any chromatogram obtained with varying column temperatures and sample amounts injected, the middle points were found to be on a straight line, as shown in Fig. 1. Thus, as the y-axis in the oblique coordinates, one may suitably choose the middle point line.

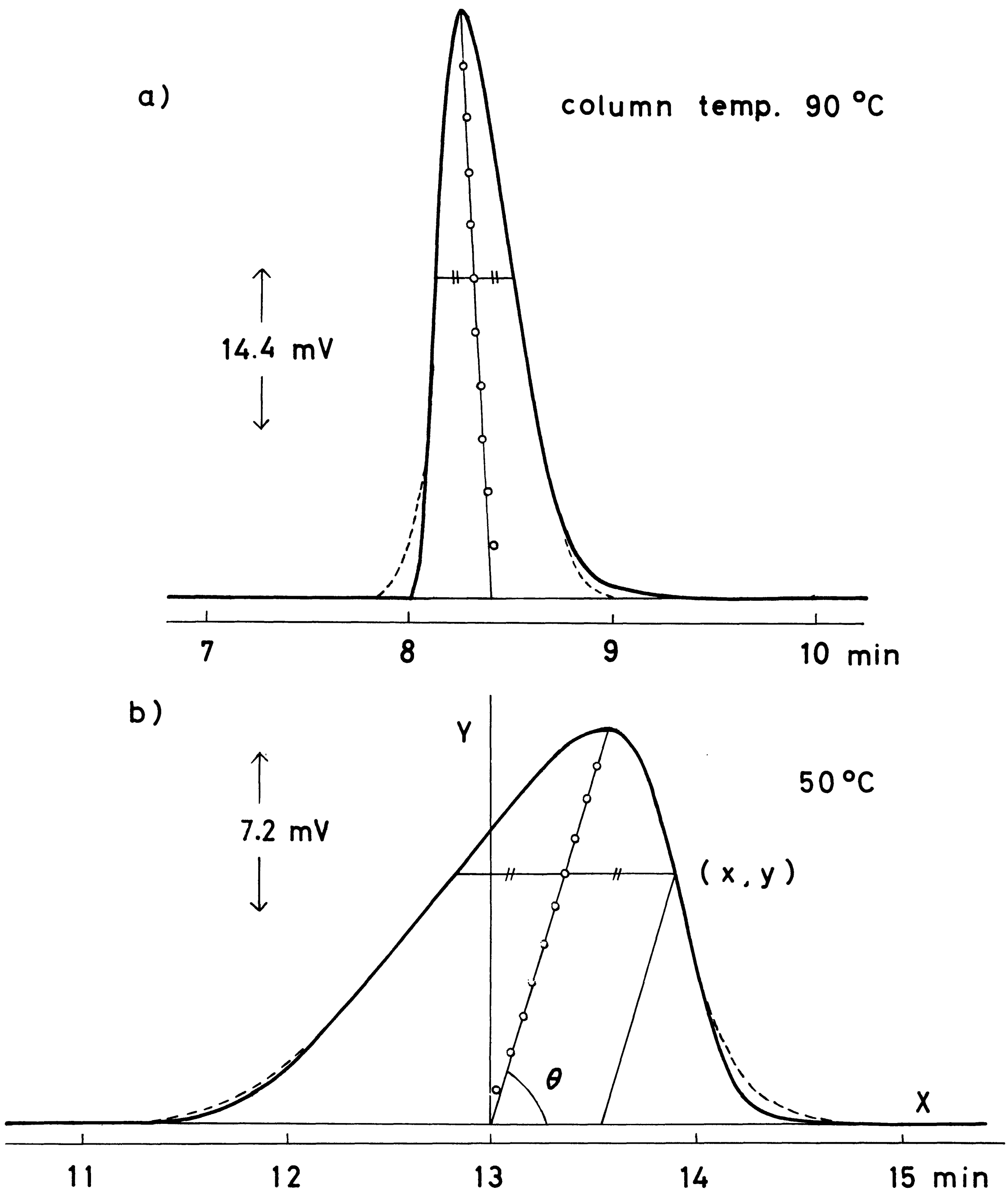

Figure 1. Gas chromatograms of 5-μl benzene with (a) trailing and (b) leading shape
Open circle denotes the middle point of segment. Dotted line indicates the theoretical Gaussian curve which is constructed by superposing the inflection points and the vertex on those of the experimental gas chromatogram.

Next, the correlation coefficient of the plot of log y vs. x^2 of the peaks with various skewnesses was calculated. The skewness of the peak was expressed by the degree of asymmetry defined by the logarithm of skew ratio[1]. The linearity was confirmed at the significant level of 1 %, as shown in Table 1.

Table 1 Correlation coefficient of the plot of log y vs. x^2 of the peak with various skewnesses obtained by changing column temperature and sample amount injected.

Column temp. °C	Sample amount μl	Correlation coefficient, r	t_0	Degree of asymmetry
40	3	0.992	21.5	0.484
50	3	0.997	39.1	0.352
60	3	0.998	47.1	0.202
80	3	0.999	66.6	- 0.163
90	3	0.999	55.3	- 0.435
100	3	0.983	15.0	- 0.453
110	3	0.999	68.5	- 0.544
50	1	0.999	50.9	0.158
	3	0.997	39.1	0.352
	5	0.998	42.0	0.503
	7	0.996	30.0	0.628
80	1	0.999	62.9	- 0.068
	3	0.999	66.6	- 0.163
	5	0.992	22.2	- 0.256
	7	0.991	29.7	- 0.324

$t_0 = \dfrac{r(n - 2)^{1/2}}{(1 - r^2)^{1/2}}$, n = 10 (number of data), $t_0 \gg t_8(0.01) = 3.355$

Furthermore, we constructed the skewed normal distribution curve on the experimentally recorded gas chromatogram, in such a manner that the peak top and the two inflection points of the two curves are coinciding, as shown in Fig. 1. Chi-square test was applied to evaluate the goodness of fit of the empirical curve to the theoretical one and it was found that there was no difference between two curves at significant level of 1 per cent.

Therefore, the asymmetrical peak in gas chromatography can be expressed by the normal distribution curve on the inclined y-axis as obtained by plotting the middle points of segments of lines parallel to the base line.

Converting the skewed axes (x, y) into the rectangular coordinates (X, Y) one derives the empirical formula:

$$Y = \frac{h_0 \sin \theta}{(2\pi \sigma^2)^{1/2}} \exp \frac{-(X - Y \cot \theta)^2}{2 \sigma^2} \qquad (1)$$

where θ is axial angle, and h_0 peak height along the skewed axes. When $\theta = 90^\circ$, the above equation is reduced to the familiar normal distribution curve on the rectangular coordinates.

References

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