CHROM. 10,444

Note

Resolution of overlapping asymmetrical chromatographic peaks

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(Received June 22nd, 1977)

Chromatographic peak profiles are generally asymmetric. However, for ease of resolution, overlapping peaks are usually considered to be symmetrical and described mathematically by gaussian curves[1], thus enabling standard computer programs for resolution of such curves to be used. If the real peak shapes are not close to gaussian this procedure introduces large errors. To increase the accuracy of peak areas determined after curve resolution procedures one needs a comparatively simple and versatile mathematical formula for asymmetrical peak shapes.

A number of functions have been proposed for asymmetric peaks[1–5], and the purpose of this paper is to introduce a new function for skewed gaussian band shapes:

$$Y = c_0 \exp(-L) \tag{1}$$

where Y is the peak height at the time t, c_0 is the maximum peak height, and

$$L = \frac{(t - c_2)^2}{c_1 + P(t - c_2)c_3} \tag{2}$$

where c_1, c_2, c_3 are constants, and

$$P = 0.5 + 0.5 \tanh[1000(t - c_2)] \tag{3}$$

If $t - c_2 < 0$, $P \approx 0$, and the leading edge of the peak has a gaussian shape. If $t - c_2 > 0$, $P \approx 1$, and the trailing edge has a tail because $c_1 + P(t - c_2)c_3 > c_1$. Instead of a simple function $P(t - c_2)c_3$, a more complicated function $P \cdot \varphi(t, c_2, \ldots c_n)$ may be used, but prolonged use of these equations in our calculations has shown that, in practice, the function $P(t - c_2)c_3$ is satisfactory.

If $c_3 = 0$ in eqn. 2, the peak has a gaussian shape. The flexibility of eqn. 1 is shown in Fig. 1. It should be noted that the shapes of the two peak edges given by eqn. 1 are not interdependent.

Eqn. 1 has been used for resolution of overlapping asymmetrical peaks (see Fig. 2). The respective computer program is based on the iteration procedure described in ref. 6. Using about 15 points per peak the computer calculates the sets of constants (c_0, c_1, c_2 and c_3) for each peak. The peak areas are obtained by numerical integration.
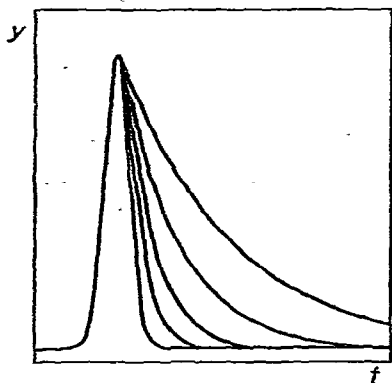
Fig. 1. Peak shapes calculated from eqn. 1. All peaks have the same leading edge. The only parameter changed to obtain different trailing edges is c_3.
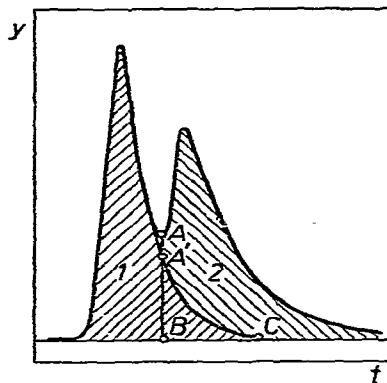
Fig. 2. Resolution of two asymmetrical peaks given by eqn. 1. The areas of first and second peak are 1 and 2, respectively. An electronic integrator divides the total area into two parts along the line AB, giving an error approximately A'BC.

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