Journal of Chromatography, 154 (1978) 226–227

CHROM. 10,941

Note

Determination of the area of a tailing peak by mathematical integration

B. JÓVÉR and J. JUHÁSZ

Institute of Inorganic and Analytical Chemistry, L. Eötvös University, P.O. Box 123, H-1443 Budapest (Hungary)

(First received December 6th, 1977; revised manuscript received February 8th, 1978)

Determination of the peak area —this common and easy task in chromatography— becomes troublesome when the peak is tailing. Whatever method (*e.g.*, planimetry or electronic integration) is used, the determination will have an uncertainty, because the descending branch of the peak is hardly distinguishable from the base line, which itself is somewhat uncertain due to the noise level and possible slight drift.

It has been found in practice that the descending branch of a tailing peak can often be described by an exponential function:

$$h_t = h_0 \cdot e^{-kt}$$

or

$$h_L = h_0 \cdot e^{-k.L/v}$$

where h is the height of the peak (the signal), t is the time, L is the length along the peak (if $t = 0$, then $L = 0$), v is the speed of the recorder chart and k and h_0 are constants.

Tailing peaks are very common in gas–solid chromatography, and the procedure to be described below was applied, for example, to the peak for n-butylamine eluted from a short column of θ-alumina (see Fig. 1). The area of such a peak can easily be obtained as follows. Let us divide the peak into two parts at point L_1 (which

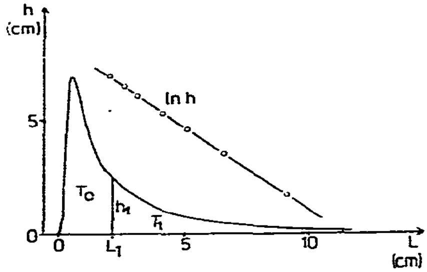

Fig. 1. Elution peak of n-butylamine from θ-alumina at 226°. Conditions: carrier gas, He (flow-rate 0.97 $cm^3\ sec^{-1}$); column (6 cm × 3 mm I.D.), 0.130 g of θ-alumina (surface area 7.8 m^2) diluted with 1.30 g of glass powder (particle size 0.16–0.40 mm); sample, 1 μl of n-butylamine introduced by syringe. Recorder-chart speed, 0.085 cm sec^{-1}.

must lie on the exponentially descending branch of the peak). The area of the first part (T_0) may be determined by any of the common methods, and that of the second part (T_1) by an integration utilising the exponential character of this part of the peak:

$$T_1 = \int_{L_1}^{\infty} h_L \mathrm{d}L = \int_{L_1}^{\infty} h_0 \cdot e^{-kL/v} \mathrm{d}L$$

It is well-known that

$$\int a e^{-bx} \mathrm{d}x = -\frac{a}{b} \cdot e^{-bx} + C$$

consequently:

$$T_1 = \left[-\frac{h_0}{k/v} \cdot e^{-kL/v} + C \right]_{L_1}^{\infty} = \frac{h_0}{k/v} \cdot e^{-kL_1/v} = \frac{h_1}{k} \cdot v$$

One needs only to check the exponential character of the descending branch of the peak (by plotting $\ln h_L$ or $\log h_L$ against L), and, if it is exponential, the slope of the line gives k; the other two parameters (h_1 and v) are easy to obtain. The sum of T_0 and T_1 gives the total area of the peak.

In this instance, the exponential character of the descending branch of the peak was checked by plotting $\ln h$ against L (see Fig. 1). The slope (k) was calculated by the method of least squares. The value of the correlation coefficient ($r = -0.998$) also shows that the degree of fit is acceptable. The results are as follows:

T_0 (by planimetry) $= 8.48$ cm^2

T_1 (by planimetry) $= 5.57$ cm^2

T_1 (by mathematical integration):

$$T_1 = \frac{h_1}{k} \cdot v = \frac{2.37 \text{ cm}}{0.03238 \text{ sec}^{-1}} \cdot 0.085 \text{ cm sec}^{-1} = 6.22 \text{ cm}^2$$

Comparing the two values of T_1 shows that taking account of the "non-detectable" part of the descending branch of the peak involves a significant correction.

In theory, this method is applicable to any other type of tailing peak, provided that one can establish the function $h(t)$ and that this function can be integrated in closed form.