Journal of Chromatography, 114 (1975) 179–183

CHROM. 8462

Note

Study on the effect of detector dynamics on the peak height in quantitative gas chromatography

H. KRZYŻANOWSKA
Institute of Heavy Organic Synthesis, Blachownia, Kędzierzyn (Poland)
(First received February 17th, 1975; revised manuscript received May 27th, 1975)

The purpose of the present analysis is to determine quantitatively the error on the measurements resulting from the effect of detector dynamics. In this study, the dynamics of the chromatography column is not analysed. A definite form of output signal is assumed to come from the column and enter the detector, the signal being consistent with the concentration of a particular component in a mixture with the carrier gas. The signal is assumed to have the form of an exact triangle. Owing to the non-negligible volume of the detector cell, the concentration profile is not exactly triangular and the peak height is decreased. We assume that the detector is of a catharometer type[1], *i.e.* that the concentration in the detector cell is proportional to the electric signal.

To make the analysis feasible, it is necessary to assume some mathematical correlation between the concentration of the gas that streams from the column into the detector cell and the gas concentration inside the cell. In this study, the correlation is expressed by a first-order linear differential equation in time. Problems of transient phenomena have been dealt with in detail by Sternberg[2]. Hana has also discussed these problems from a somewhat different point of view, but employing the same logical approach[3].

METHOD

Concentration response of the detector cell

The detector cell is regarded as a tank of volume V. It is assumed that the gas in the cell is perfectly mixed[4] and that the flow-rate, F, of the mixed gas (including the carrier gas) is constant. The assumption of perfect mixing is satisfied for the case where the detector cell is of flow-cell type in which the tube-enlargement results in an improved mixing performance. With these assumptions, the material balance equation is as follows:

$$F \cdot x - F \cdot y = V \cdot \frac{dy}{dt} \tag{1}$$

A perfectly mixed tank responds like a first-order system to changes in input concentration[5]. Because the correlation between the concentration x of the gas coming out of the column into the detector cell and the concentration y inside the detector cell is expressed by a linear differential equation, the superposition principle may be applied. Eqn. 1 is transformed by using the Laplace transform method and rearranged to give the transfer function $y(s)/x(s)$, where

$$\frac{y(s)}{x(s)} = \frac{1}{Ts+1} \tag{2}$$

and $T = V/F$ is the time constant.

Response of a detector cell to the assumed input

The input signal to the detector cell, being an output signal from the column, is assumed to have the form of an exact triangle. This signal represents a chromatographic peak. The following graphical notation is used: τ = time of the impulse (peak) increase, and $k = \tan \alpha$. The input signal may be resolved into three component signals x_1, x_2, x_3 (Fig. 1), whence the following dependence is valid: $\tan \beta = 2 \tan \alpha$. Thus, the input signal x consists of an algebraic sum of mathematic functions that represent the component signals x_1, x_2, x_3. This is expressed by eqn. 3 in an untransformed form and by eqn. 4 in a transformed form:

$$x(t) = ktu(t) - 2\,k(t-\tau)u(t-\tau) + k(t-2\tau)u(t-2\tau) \tag{3}$$

$$x(s) = \frac{k}{s^2} - \frac{2k}{s^2}\,\mathrm{e}^{-s\tau} + \frac{k}{s^2}\,\mathrm{e}^{-2s\tau} \tag{4}$$

$u(t)$ is a function[6] that assumes the value:

$$\begin{aligned} u(t) &= 1 \quad \text{if} \quad t > 0 \\ u(t) &= 0 \quad \text{if} \quad t \leqslant 0 \end{aligned}$$

The response $y(t)$ of the detector cell to the input signal $x(t)$ expressed by eqn. 3 is obtained by substituting the transform of the input signal $x(s)$ expressed by eqn. 4 into eqn. 2 and taking the inverse transform of the resulting expression for $y(s)$:

$$y(s) = \frac{k}{s^2\,(Ts+1)} - \frac{2k}{s^2\,(Ts+1)}\,\mathrm{e}^{-s\tau} + \frac{k}{s^2\,(Ts+1)}\,\mathrm{e}^{-2s\tau} \tag{5}$$

$$\begin{aligned} y(t) = {} & \left[kt - kT\left(1 - \mathrm{e}^{-\frac{t}{T}}\right)\right] u(t) - \left[2k(t-\tau) - 2kT\left(1 - \mathrm{e}^{-\frac{t-\tau}{T}}\right)\right] u(t-\tau) + \\ & + \left[k(t-2\tau) - kT\left(1 - \mathrm{e}^{-\frac{t-2\tau}{T}}\right)\right] u(t-2\tau) \end{aligned} \tag{6}$$

The output signal $y(t)$ according to eqn. 6 is an algebraic sum of mathematic functions that represent the component signals y_1, y_2, y_3 in response to the input signals x_1, x_2, x_3; this is shown in Fig. 1.

The effect of detector dynamics on the peak height

Owing to the appreciable volume of the detector cell, the output signal $y(t)$,

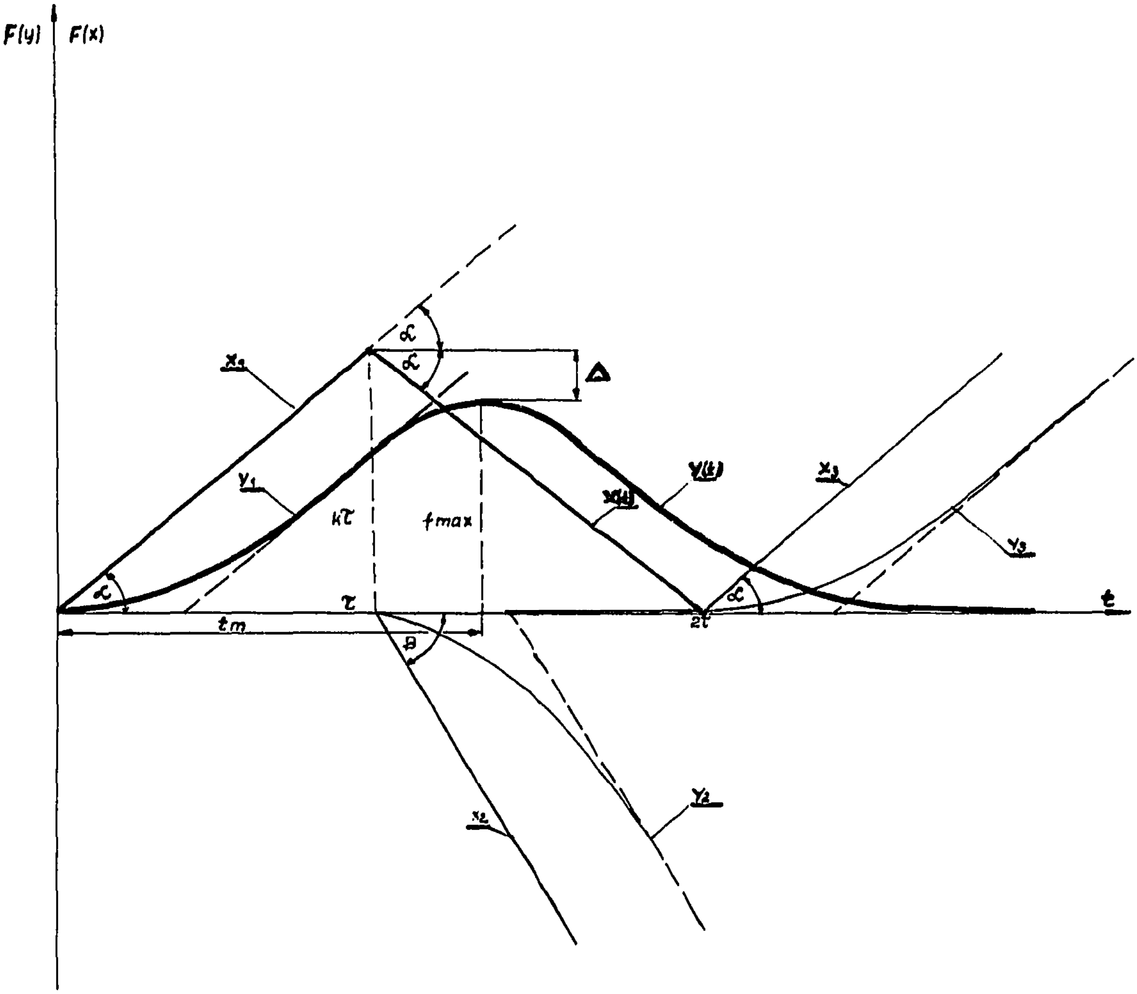

Fig. 1. Input and output signals, x and y, of the detector cells.

which expresses the gas concentration in the detector cell, is not exactly triangular. The height of the peak expressing the concentration in the detector cell is decreased. Fig. 1 shows the assumed input signal represented by eqn. 3 and the response of the detector cell according to eqn. 6. The amount by which the output signal y is decreased as compared with the input signal x, will be denoted by Δ:

$$\Delta = x(\tau) - y(t_m) \tag{7}$$

where t_m = time to obtain the maximum level of the signal $y(t)$, *i.e.* $y(t_m) = f_{max}$. It can be easily proved, for any values of T/τ, that t_m will be contained within the following interval:

$$\tau \leqslant t_m \leqslant 2\tau \tag{8}$$

We now determine the maximum of the function that denotes the signal $y(t)$ within the interval $\tau \leqslant t \leqslant 2\tau$:

$$y(t) = -kt + kT + 2\,k\tau + kT\,\mathrm{e}^{-\frac{t}{T}}\left(1 - 2\,\mathrm{e}^{\frac{\tau}{T}}\right) \tag{9}$$

Eqn. 9 was obtained by substituting $\tau \leqslant t \leqslant 2\tau$ into eqn. 6. We examine the first and the second derivative of this function:

$$\frac{\mathrm{d}\,y(t)}{\mathrm{d}t} = k\left[\left(2\,\mathrm{e}^{\frac{\tau}{T}} - 1\right)\mathrm{e}^{-\frac{t}{T}} - 1\right] \tag{10}$$

By equating the first derivative to zero, we obtain, for $k \neq 0$,

$$\mathrm{e}^{-\frac{t_m}{T}} = \frac{1}{2\,\mathrm{e}^{\frac{\tau}{T}} - 1} \tag{11}$$

or

$$t_m = T\ln\left[2\,\mathrm{e}^{\frac{\tau}{T}} - 1\right] \tag{12}$$

On examining the second derivative at a point t_m, we obtain $\mathrm{d}^2y/\mathrm{d}t^2 < 0$ for $t = t_m$, the latter condition requiring that it is a maximum. By substituting eqns. 11 and 12 into eqn. 9 we obtain

$$y(t_m) = f_{max.} = 2\,k\tau - kT\ln\left[2\,\mathrm{e}^{\frac{\tau}{T}} - 1\right] \tag{13}$$

$$f_{max.} = f(T)$$

Substituting eqn. 13 into eqn. 7 we obtain

$$\Delta = kT\ln\left[2\,\mathrm{e}^{\frac{\tau}{T}} - 1\right] - k\tau \tag{14}$$

Eqn. 14 may be expressed in the non-dimensional form:

$$\delta = z\ln\left[2\,\mathrm{e}^{\frac{1}{z}} - 1\right] - 1 = f(z) \tag{15}$$

where $\delta = \Delta/k\tau$ is the relative decrease of the peak height, and $z = T/\tau$ is the ratio of the time constant of the detector cell to the time of the peak increase. The dependence represented in eqn. 15 is shown in Fig. 2 in the form of a plot of $\delta = f(z)$ using a semi-logarithmic scale, where δ is expressed in percent.

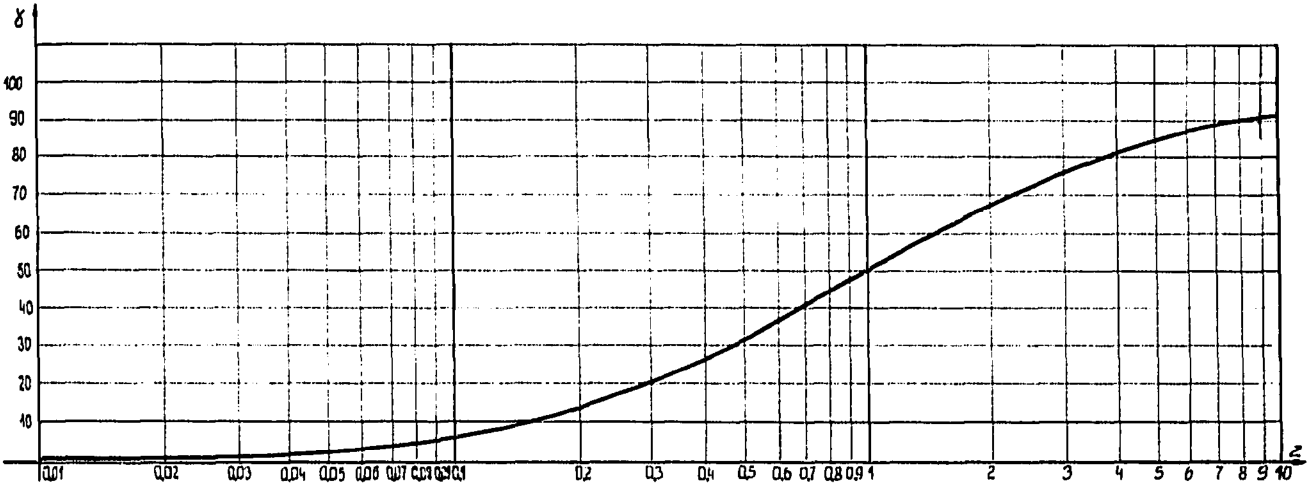

Fig. 2. A plot of the function $\delta = f(z)$ against z.

CONCLUSIONS

From Fig. 6, the following conclusions may be drawn on the effect of detector dynamics, resulting from a non-negligible detector cell volume, on the peak height in quantitative gas chromatography. Below a value of $z = T/\tau = 0.005$, *i.e.* when the time constant of the detector cell is less than the 1/200 of the time of the peak increase, there is no need to use the correction δ, as the accuracy of the catharometer (and of any other detector type) is usually decreased. Within the range of z values from 0.1 to 1, it is necessary to use the correction δ, as a sound decrease of the peak height occurs, *e.g.* when $z = 0.1$, $\delta = 6.93\%$, and when $z = 1$, $\delta = 49\%$. In this range, the detector cell volume very effectively influences the peak height. This dependence can be determined by means of equilibration of the apparatus.

However, for some higher values of z, the detector cell volume results in a decrease in the peak of such a degree that the sensitivity of the quantitative gas chromatography may prove to be too low. Detectors with cell volumes of this magnitude should not be used.

ACKNOWLEDGEMENT

I am grateful to Mr. Jerzy Bobiński for his help in drafting this paper in English.

REFERENCES

1 M. Geodert and G. Guiochon, *J. Chromatogr. Sci.*, 7 (1969) 323.
2 J. C. Sternberg, *Advan. Chromatogr.*, 2 (1966) 248.
3 K. Hana, *Collect. Czech. Chem. Commun.*, 32 (1967) 968.
4 H. W. Johnson, F. H. Stross, *Anal. Chem.*, 32 (1959) 357.
5 P. Harriott, *Process Control*, McGraw-Hill, New York, 1964, Ch. 3.
6 R. H. Cannon, Jr., *Dynamics of Physical Systems*, McGraw-Hill, New York, 1967.