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Gaussian Concentration Profile Modified by the Column-Inlet Concentration Profile and by an Additional Exponential-Decay Process

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Abstract

The chromatographic elution profile is described by the convolution of the Gaussian curve with the column-inlet concentration profile and with an additional exponential distribution. Two different column-inlet profiles are considered, viz., the rectangular and exponential-decay concentration profiles. The relationships obtained are used to show the effect of an extracolumn exponential-decay process on the peak height, and on the sensitivity of quantitative chromatographic analysis. A previously proposed criterion of the effect of column-inlet concentration profile on the peak height is also extended to accommodate the extracolumn exponential-decay process.

INTRODUCTION

Peak shape in elution chromatography may be significantly altered by the action of various extracolumn zone-broadening factors. The column-inlet concentration profile itself may be considered as one of these factors. In this paper the elution concentration profile in linear chromatography is expressed through the convolution of the Gaussian profile with the column-inlet concentration profile and with an additional extracolumn exponential-decay process. The original impetus for this work was the need to develop relationships describing the effects of extracolumn zone-broadening factors on the sensitivity of quantitative chromatographic analysis. Under certain conditions the sensitivity of chromatographic determination of the mass of analyte may be measured by the ratio of the maximum analyte concentration in the elution zone to the mass of analyte within the zone (*1*).

Recently, the dependence of the sensitivity of analyte-mass determination on the volume of sample charge was investigated (*2*). The treatment applied to the situation in which the mass of analyte introduced into the column was constant and independent of the sample-charge volume, i.e., the concentration of the analyte in the sample was inversely proportional to the sample-charge volume. Such a situation arises in trace analysis where it is often necessary to apply a sample-enrichment step prior to the chromatographic run proper. The concentration profile of the analyte at the column outlet was expressed through convolution (*3–5*) of the column-inlet analyte-concentration profile with the Gaussian curve. Hence, the variance of the column-inlet concentration profile was assumed to be the only extracolumn contribution to the total variance of the column-outlet concentration profile of the analyte.

In the present paper the previous treatment is extended to include the effect of the additional extracolumn exponential-decay process. An example of such a process is provided by the action of dead volumes within the chromatographic system, or, if the q's below are interpreted as detector responses rather than concentrations, by the action of the time constant of the detection system.

CONCENTRATION PROFILES

Throughout this treatment, reduced (dimensionless) variables will be employed. The reduced volume of the mobile phase passed through the column is given by

$$T = (V - V_{Ri,c})/\sigma_i \qquad (1)$$

where V is the volume of the mobile phase passed through the column, $V_{Ri,c}$ is the retention volume corresponding to a Gaussian concentration profile of analyte i at the column outlet, and σ_i is the volumetric standard deviation of the Gaussian concentration profile of analyte i. Hence, σ_i^2 gives the dispersion due to the intracolumn zone-broadening factors only. The quantity R_1 is the reciprocal of the reduced volume of sample charge (sample loop),

$$R_1 = \sigma_i/v \qquad (2)$$

where υ is the volume of sample charge. Similarly,

$$R_2 = \sigma_i/w = \sigma_i/(F\tau) \tag{3}$$

where τ is the time constant of the additional extracolumn exponential-decay process, w is the volume equivalent to τ, and F is the volumetric flow rate of the mobile phase.

All the concentration profiles will also be given in a reduced form,

$$\bar{q}_i(T) = q_i(T)/q^*_{i,c} \tag{4}$$

where $q_i(T)$ is the concentration (mass/volume) of analyte i at the column outlet as a function of the reduced volume of the mobile phase, and $q^*_{i,c}$ is the maximum concentration of the analyte in the Gaussian zone at the column outlet,

$$q^*_{i,c} = \frac{m_i}{\sigma_i\sqrt{2\pi}} \tag{5}$$

where m_i is the mass of analyte injected.

Rectangular Profile at the Column Inlet

The convolution of the Gaussian profile with the rectangular column-inlet concentration profile (*5*) may be written as

$$\bar{q}_i(T) = R_1\sqrt{2\pi}\left[Q\left(T - \frac{1}{R_1}\right) - Q(T)\right] \tag{6}$$

where $Q(u)$ is the area under the normalized normal distribution curve between u and ∞,

$$Q(u) = \frac{1}{\sqrt{2\pi}}\int_u^\infty \exp\{-x^2/2\}\,dx \tag{7}$$

Several numerical approximations are available (*6*) to calculate $Q(u)$. To solve the convolution integral (*3*) of the profile given by Eq. (6) with an additional exponential distribution, the Q's in Eq. (6) may be replaced by the error functions using the identity

$$Q(u) = (1 - \mathrm{erf}\,[u/\sqrt{2}])/2 \tag{8}$$

Also, the original volume variables should be introduced. The convolution integral is then solved by per partes integration. After switching back from erf to Q, and to the reduced variables, the final result is

$$\begin{aligned}\bar{q}_i(T) = R_1\sqrt{2\pi}\Bigg[&Q\left(T - \frac{1}{R_1}\right) - Q(T) - \exp\left\{R_2\left(\frac{R_2}{2} - T\right)\right\}\\ &\times \left[Q(R_2 - T) - \exp\left\{\frac{R_2}{R_1}\right\}Q\left(R_2 + \frac{1}{R_1} - T\right)\right]\Bigg]\end{aligned} \tag{9}$$

Figure 1 shows the shapes of this concentration profile for several values of R_1 and R_2.

Taking the derivative $d\bar{q}_i(T)/dT$ and setting it equal to zero, one can show that the concentration-maximum reduced retention volume obeys the relation

$$Q(R_2 - T_{\max}) - \exp\left\{\frac{R_2}{R_1}\right\}Q\left(R_2 + \frac{1}{R_1} - T_{\max}\right) = 0 \tag{10}$$

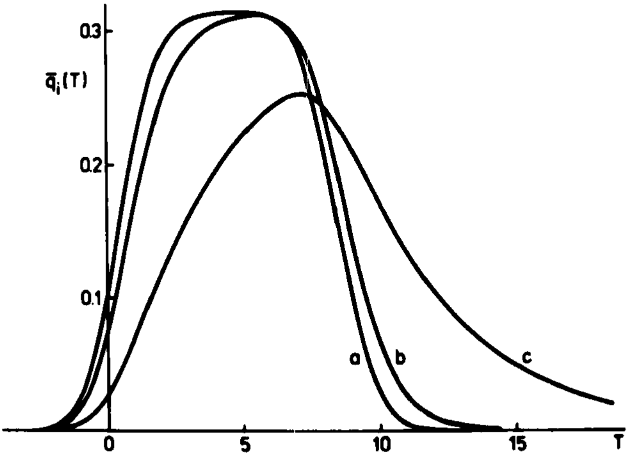

FIG. 1. Column-outlet concentration profile given by Eq. (9). (a) $R_1 = \frac{1}{8}, R_2 = 2$; (b) $R_1 = \frac{1}{8}$, $R_2 = 1$; (c) $R_1 = \frac{1}{8}, R_2 = \frac{1}{4}$.

To solve for $T_{\max}$ from Eq. (10), a secant method is preferred to the Newton-Raphson tangent method since the latter fails to converge unless the initial guess of $T_{\max}$ is very good. It is apparent from Eqs. (9) and (10) that, at the concentration maximum,

$$\bar{q}_i(T_{\max}) = R_1\sqrt{2\pi}\left[Q\left(T_{\max} - \frac{1}{R_1}\right) - Q(T_{\max})\right] \tag{11}$$

Exponential-Decay Profile at the Column Inlet

The convolution of a Gaussian profile with two or more exponential distributions was discussed by Delley (*7*). He showed that it is a relatively simple matter to solve the respective convolution integral since the convolution of two or more exponential distributions gives a weighted sum of these distributions. For the case of two exponential distributions, one obtains

$$\bar{q}_i(T) = \frac{R_1R_2\sqrt{2\pi}}{R_1 - R_2}\exp\left\{-\frac{1}{2}T^2\right\}\left[\exp\left\{\frac{1}{2}(R_2 - T)^2\right\}Q(R_2 - T) - \exp\left\{\frac{1}{2}(R_1 - T)^2\right\}Q(R_1 - T)\right] \tag{12}$$

The exponential terms in Eq. (12) could certainly be collected. However, there is some computational advantage to Eq. (12) since certain expansions of the function exp $\{u^2/2\}Q(u)$ are simpler than the corresponding expansions of $Q(u)$ (*6, 8*). At first glance, the shape of the profile given by Eq. (12) does not differ from a Gaussian curve modified by a single exponential-decay process (*7*).

From the condition $d\bar{q}_i(T)/dT = 0$, the following relation for $T_{\max}$ results,

$$R_1 \exp\{\tfrac{1}{2}(R_1 - T_{\max})^2\}Q(R_1 - T_{\max}) - R_2 \exp\{\tfrac{1}{2}(R_2 - T_{\max})^2\}Q(R_2 - T_{\max}) = 0 \tag{13}$$

The maximum concentration is then given by

$$\bar{q}_i(T_{\max}) = R_1\sqrt{2\pi}\exp\{-\tfrac{1}{2}T_{\max}^2\}\exp\{\tfrac{1}{2}(R_1 - T_{\max})^2\}Q(R_1 - T_{\max})$$

$$= R_2\sqrt{2\pi}\,\exp\{-\tfrac{1}{2}T_{\max}^2\}\,\exp\{\tfrac{1}{2}(R_2 - T_{\max})^2\}Q(R_2 - T_{\max}) \qquad (14)$$

In the case where $R_1 = R_2$, Eq. (12) reduces to an indefinite expression (*7*). Taking the limit as $R_2 \to R_1$, one obtains

$$\bar{q}_i(T) = R_1^2\exp\{-\tfrac{1}{2}T^2\}[1 - (R_1 - T)\sqrt{2\pi}\,\exp\{\tfrac{1}{2}(R_1 - T)^2\}Q(R_1 - T)] \qquad (15)$$

The value of $T_{\max}$ is then calculated from the relation

$$\left(R_1 + \frac{1}{R_1} - T_{\max}\right)\sqrt{2\pi}\,\exp\left\{\frac{1}{2}(R_1 - T_{\max})^2\right\}Q(R_1 - T_{\max}) - 1 = 0 \qquad (16)$$

and the maximum concentration is again given by Eq. (14).

PEAK HEIGHT

Effect of the Volume of Sample Charge

Suppose that the partition coefficient of the analyte is constant during migration of the analyte through the column, and that the maximum concentration of the analyte in the mobile phase at the column outlet is within the range of dynamic linearity of the detector. The peak height reduced by its value corresponding to the total absence of any extracolumn zone-broadening factors is then given by

$$\bar{\varphi}_{mi} = \bar{q}_i(T_{\max}) \qquad (17)$$

If the above term "additional extracolumn exponential-decay process" refers to the action of a nonzero time constant of the detection system, the detector-response profile is delayed and distorted with respect to the concentration profile. In such a case, Eq. (17) still applies provided the above relations for $\bar{q}_i(T)$ are understood to represent reduced-response rather than reduced-concentration profiles. In addition, $T_{\max}$ in this case refers to the maximum response rather than to maximum concentration.

The reduced peak height, $\bar{\varphi}_{mi}$, is identical to the reduced sensitivity of analyte-mass determination. In Fig. 2 the dependence of $\bar{\varphi}_{mi}$ on the

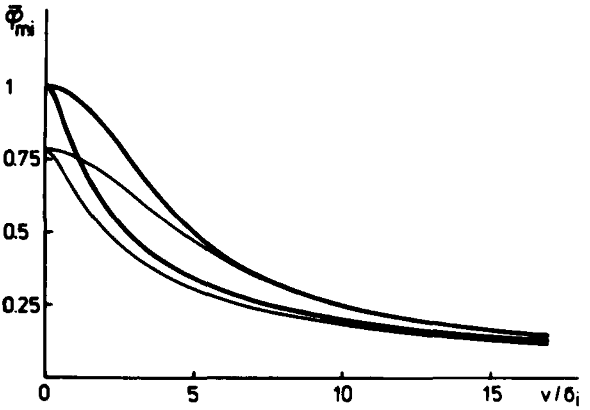

FIG. 2. Dependence of the reduced peak height on the reduced volume of sample charge. Thick lines: $w = 0$; upper line, rectangular inlet profile; lower line, exponential-decay inlet profile. Thin lines: $w = \sigma_i$; upper line, rećtangular inlet profile; lower line, exponential-decay inlet profile.

reduced volume of sample charge is shown. The pair of thick lines show the situation when $w = 0$ ($R_2 \rightarrow \infty$), i.e., when the variance of the column-inlet concentration profile is the only extracolumn contribution to the variance of the column-outlet profile (*2*). The upper thick line applies to a rectangular inlet profile, and the lower thick line to an exponential-decay inlet profile. When $w \neq 0$, the additional contribution to the variance of the column-outlet profile causes a general decrease in $\bar{\varphi}_{mi}$. The pair of thin lines in Fig. 2 refer to the case when $R_2 = 1$. For any value of R_2, the limiting value, ϕ, of $\bar{\varphi}_{mi}$ as $v/\sigma_i \rightarrow 0$ may be obtained from

$$\exp\{-\tfrac{1}{2}(R_2 - \underline{Y})^2\} - R_2\sqrt{2\pi Q}(R_2 - \underline{Y}) = 0 \qquad (18)$$

$$\phi = \exp -\tfrac{1}{2}\underline{Y}^2$$

It is seen from Fig. 2 that, for a rectangular concentration profile at the column inlet, the curves for $w = 0$ and $w = \sigma_i$ quickly converge, and become indistinguishable for $v/\sigma_i \approx 8$. This is readily understood, because large values of v/σ_i correspond to a transition from elution to frontal chromatography, and, in frontal chromatography, a small value of w is no longer significant.

Effect of the Column-Inlet Concentration Profile

From the point of view of both the sensitivity of chromatographic analysis and the separation efficiency, the two column-inlet concentration profiles considered above represent extreme alternatives. The rectangular inlet profile is certainly the best way to introduce a sample of volume v into the column, and the exponential-decay inlet profile with a characteristic volume equal to v may reasonably be considered as the worst way. Hence, for any value of v/σ_i, the relative span of a pair of curves in Fig. 2 shows the effect of the column-inlet profile on the peak height (or on the sensitivity of analysis). This criterion may be expressed as (*9*)

$$\bar{S}_a = (\bar{\varphi}^r_{mi} - \bar{\varphi}^e_{mi})/\bar{\varphi}^e_{mi} \tag{19}$$

where the superscripts r and e denote the rectangular and exponential-decay inlet profiles, respectively. The value of $-\bar{S}_a/(\bar{S}_a + 1)$ gives a quantitative assessment of the damage to peak height caused by distorting the column-inlet concentration profile from a rectangular pulse to an exponential decay. In a previous communication (*9*), criterion $\bar{S}_a$ was evaluated for the case when $w = 0$. The result is shown by the thick line in Fig. 3. When $w = 0$ ($R_2 \rightarrow \infty$), the maximum value of $\bar{S}_a$ is about 0.5178, and it occurs at $v/\sigma_i \approx 3.2529$. The equations derived above are used here to evaluate the effect of the additional extracolumn exponential-decay process on the position and value of the maximum in the dependence of $\bar{S}_a$ on v/σ_i. The results are given in Table 1. It appears that an additional exponential-decay process tends to increase the maximum

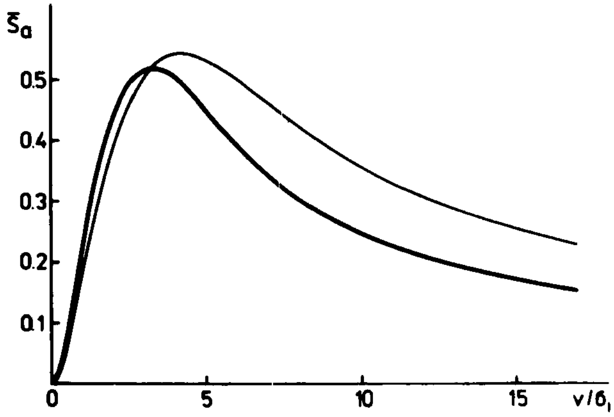

FIG. 3. Criterion given by Eq. (19) as a function of the reduced volume of sample charge. Thick line, $w = 0$; thin line, $w = \sigma_i$.

TABLE 1
Percentage Increases in the Position and Value of the Maximum in the Dependence of $\bar{S}_a$ on v/σ_i (relative to the case where $w = 0$)

w/σ_i	Position (%)	Value (%)	w/σ_i	Position (%)	Value (%)
0.1	0.491	0.0255	1.1	32.2	5.40
0.2	1.89	0.169	1.2	36.5	6.14
0.3	3.99	0.461	1.3	40.9	6.89
0.4	6.61	0.879	1.4	45.4	7.63
0.5	9.61	1.39	1.5	50.1	8.37
0.6	12.9	1.97	1.6	54.6	9.11
0.7	16.4	2.60	1.7	59.4	9.84
0.8	20.1	3.27	1.8	64.1	10.6
0.9	24.0	3.96	1.9	69.0	11.3
1.0	28.0	4.68	2.0	73.9	12.0

value of $\bar{S}_a$, and to shift the maximum toward larger values of the reduced volume of sample charge. On increasing the time constant of the additional exponential-decay process, the maximum in the dependence of $\bar{S}_a$ on v/σ_i becomes flatter, as shown by the thin line ($w = \sigma_i$) in Fig. 3.

CONCLUSION

With the above equations, the effects of an extracolumn exponential-decay process on the peak height and on the sensitivity of chromatographic analysis may be evaluated. An extracolumn exponential-decay process amplifies the discrepancy between the rectangular and exponential-decay column-inlet profiles as measured by the maximum value of the criterion $\bar{S}_a$. However, for small values of the time constant of the extracolumn exponential-decay process (say, $w/\sigma_i < 0.4$), the amplification is negligible (<1%).

SYMBOLS

$\mathrm{erf}(u)$	error function, $(2/\sqrt{\pi})\int_0^u \exp\{-x^2\}\,dx$
F	volumetric flow rate of the mobile phase
m_i	mass of analyte i injected into the column
$q_i(T)$	concentration (mass/volume) of analyte i at the column outlet
$\bar{q}_i(T)$	reduced concentration of analyte i

$q^*_{i,c}$	maximum concentration of analyte *i* in the Gaussian zone at the column outlet
$Q(u)$	integral of the normalized normal distribution from *u* to $+\infty$
R_1	reciprocal of the reduced volume of sample charge
R_2	reciprocal of the reduced characteristic volume of the additional extracolumn exponential-decay process
$\bar{S}_a$	criterion defined by Eq. (19)
T	reduced volume of the mobile phase passed through the column
$T_{\max}$	reduced retention volume corresponding to the maximum concentration of the analyte
V	volume of the mobile phase passed through the column
$V_{Ri,c}$	retention volume corresponding to the Gaussian concentration profile of analyte *i* at the column outlet
υ	volume of the sample charge
w	characteristic volume ($= F\tau$) of the additional extracolumn exponential-decay process
$\underline{Y}$	auxiliary parameter in Eq. (18)

Greek Letters

σ_i	volumetric standard deviation of the Gaussian concentration profile of analyte *i*
τ	time constant of the additional extracolumn exponential-decay process
$\bar{\varphi}_{mi}$	reduced peak height of analyte *i* = reduced sensitivity of chromatographic determination of the mass of analyte *i*
ϕ	limiting value of $\bar{\varphi}_{mi}$ as $\upsilon \rightarrow 0$

Superscripts

e	exponential-decay concentration profile at the column inlet
r	rectangular concentration profile at the column inlet

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