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NOTE

Asymmetry and the Third Moment of Chromatographic Peaks

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Abstract

The skewness of a chromatographic peak can be characterized by simple parameters. The validity of these parameters is shown using model peaks.

Skewed peaks are often observed in chromatograms and can be the result of various mechanisms, e.g., multisite adsorption, nonlinear distribution isotherms, and inlet effects (e.g., Refs. *1–3*). Actually, all recorded peaks in chromatography are asymmetrical due to the fact that even the usual Gaussian peakforms are skewed when viewed as a time distribution. The present note is concerned with an analysis of the significance of the third moment, in reduced form, for characterizing asymmetry.

In statistical theory, the skewness S defined by (*4*)

$$S = \mu_3/\mu_2^{3/2}$$

is generally used as an asymmetry parameter. (All symbols are defined at the end of the paper). Grubner (*5*) has attached special importance to a parameter

$$Z = \mu_3/\mu_1^3$$

which he called the specific asymmetry. These reduced third moments may be inconvenient to apply in practice, however, since they are not easily measured. It can be demonstrated, however, that for a variety of skewed peak forms, and in general for slightly skewed peaks (*6*), μ_3 is functionally related to the lower moments and the mode Mo. This implies that an alternative set of basis parameters exists for the characterization of skewed peaks, viz., the moments up to and including the second plus Mo. We will first illustrate this for a number of peak forms and subsequently analyze Grubner's results on specific asymmetry in the light of these findings.

There is, unfortunately, no unique analytical expression for skewed chromatographic peaks so that one has to resort to an analysis of suitable fitting functions. For this purpose, three have been selected, viz.,

Poisson:

$$F(z) = \frac{1}{b^n(n!)} z^n \exp(-z/b) \qquad 0 \leq z < \infty$$

Bi-Gaussian:

$$G(z) = \begin{cases} \dfrac{m_1}{(2\pi)^{1/2}\sigma_1} \exp\left[-\dfrac{(z-\mathrm{Mo})^2}{2\sigma_1^2}\right] & -\infty < z \leq \mathrm{Mo} \\ \dfrac{m_2}{(2\pi)^{1/2}\sigma_2} \exp\left[-\dfrac{(z-\mathrm{Mo})^2}{2\sigma_2^2}\right] & \mathrm{Mo} \leq z < \infty \end{cases}$$

Pearson (Type III):

$$P(z) = X(z - z_0)^{n_1} \exp(-z/b_1) \qquad z_0 \leq z < \infty$$

The expressions for S are summarized in Table 1, from which it is clear that S is in all cases merely proportional to a parameter

$$\phi = (\langle z \rangle - \mathrm{Mo})/\sigma$$

This suggests the use of ϕ as an index of asymmetry for chromatographic peaks. Two aspects require comment:

(1) The parameter ϕ is less sensitive to details of peak shape than is S. This is seen by noting that the S values of Poisson and bi-Gaussian distributions with identical ϕ-values differ by a factor of 2. This does not

TABLE 1

	S
Poisson	$2(\langle z\rangle - \mathrm{Mo})/\sigma$
Bi-Gaussian	$\sim(\langle z\rangle - \mathrm{Mo})/\sigma$
Pearson	$2(\langle z\rangle - \mathrm{Mo})/\sigma$

disqualify ϕ as a skewness parameter, however, since the details to which S are numerically sensitive may be unimportant in a chromatographic sense. Indeed, the excessive sensitivity of S to details in distant parts of the distributions are well known in statistics (e.g., Ref. *7*) and has given rise to the introduction of alternative measures of skewness such as, for example, the quartile coefficient of skewness (*7, 8*) in which this dependence is removed.

(2) An even simpler parameter of skewness can be introduced provided that the fitting of chromatographic peaks by means of the bi-Gaussian distribution is considered satisfactory. It is easy to show that in such cases all of the more common measures of skewness can be functionally related to a single parameter $s = \sigma_2/\sigma_1$, e.g.,

$$S = \frac{\mu_3}{\mu_2^{3/2}} = \frac{\sqrt{2}(s-1)\{(4-\pi)s^2 + (3\pi-8)s + (4-\pi)\}}{\{(\pi-2)s^2 + (4-\pi)s + (\pi-2)\}^{3/2}}$$

$$\phi = \frac{\langle z\rangle - \mathrm{Mo}}{\sigma} = \frac{\mu_1 - \mathrm{Mo}}{\mu_2^{1/2}} = \frac{\sqrt{2}(s-1)}{\{(\pi-2)s^2 + (4-\pi)s + (\pi-2)\}^{1/2}}$$

$$\phi_M = \frac{\langle z\rangle - \mathrm{Med}}{\sigma} = \frac{\mu_1 - \mathrm{Med}}{\mu_2^{1/2}} = \frac{\sqrt{2}(s-1) - \sqrt{2}s\,\mathrm{erf}^{-1}\left(\frac{1}{2} - 1/2s\right)}{\{(\pi-2)s^2 + (4-\pi)s + (\pi-2)\}^{1/2}}$$

$$S_Q = \frac{(Q_3 - \mathrm{Med}) - (\mathrm{Med} - Q_1)}{Q_3 - Q_1} = \frac{A_1(s)s - 1}{A_2(s)s - 1}$$

where

$$A_1(s) = \frac{\mathrm{erf}^{-1}\left(\frac{3}{4} - 1/4s\right) - 2\,\mathrm{erf}^{-1}\left(\frac{1}{2} - 1/2s\right)}{\mathrm{erf}^{-1}\left(\frac{3}{4} - s/4\right)}$$

and

$$A_2(s) = \frac{\mathrm{erf}^{-1}\left(\frac{3}{4} - 1/4s\right)}{\mathrm{erf}^{-1}\left(\frac{3}{4} - s/4\right)}$$

TABLE 2

Model I	Model II[a]	Model III[a]
$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial z} + D\frac{\partial^2 C}{\partial z^2}$	$\frac{\partial C_1}{\partial t} = -u\frac{\partial C_1}{\partial z} + \frac{1}{\epsilon}Q_{\mathrm{II}}$	$\frac{\partial C_1}{\partial t} = -u\frac{\partial C_1}{\partial z} + D\frac{\partial^2 C_1}{\partial z^2} + \frac{1}{\epsilon}Q_{\mathrm{III}}$
	$\frac{\partial C_2}{\partial t} = -Q_{\mathrm{II}}$	$\frac{\partial C_2}{\partial t} = -Q_{\mathrm{III}}$
	$Q_{\mathrm{II}} = \Lambda_{21}C_2 - \Lambda_{12}\epsilon C_1$	$Q_{\mathrm{III}} = \Lambda_{21}C_2 - \Lambda_{12}C_1$
$\mu_1 = \frac{l}{u} + \frac{2D}{u^2}$	$\mu_1 = \frac{l}{u}(1 + k_{12}),$	$\mu_1 = \left[\frac{l}{u} + \left(\frac{2D}{u^2}\right)\right](1 + k_{12}),\ k_{12} = \frac{\Lambda_{12}}{\Lambda_{21}}$
	$k_{12} = \frac{\Lambda_{12}}{\Lambda_{21}}$	
$\mu_2 = \frac{2Dl}{u^3} + \left(\frac{8D^2}{u^4}\right)$	$\mu_2 = \frac{2l}{u}\frac{k_{12}}{\Lambda_{21}}$	$\mu_2 = \left[\frac{2Dl}{u^3} + \left(\frac{8D^2}{u^4}\right)\right](1 + k_{12})^2 + \left[\frac{2l}{u} + \left(\frac{4D}{u^2}\right)\right]\frac{k_{12}}{\Lambda_{21}}$

$\mu_3 = \frac{12D^2l}{u^5} + \left(\frac{64D^3}{u^6}\right)$	$\mu_3 = \frac{6l}{u}\frac{k_{12}}{\Lambda_{21}^2}$	$\mu_3 = \left[\frac{12D^2l}{u^5} + \left(\frac{64D^3}{u^6}\right)\right](1 + k_{12})^3 + \left[\frac{12Dl}{u^3} + \left(\frac{48D^2}{u^4}\right)\right]\frac{k_{12}}{\Lambda_{21}}(1 + k_{12})$ $+ \left[\frac{6l}{u} + \left(\frac{12D}{u^2}\right)\right]\frac{k_{12}}{\Lambda_{21}^2}$
$\frac{\mu_2}{\mu_1^2} l = \frac{2D}{u} = H_m$	$\frac{\mu_2}{\mu_1^2} l = \frac{2u}{k_{12}\Lambda_{21}} = H_s$	$\frac{\mu_2}{\mu_1^2} l = \left[\frac{2D}{u} + \frac{2u}{k_{12}\Lambda_{21}}\right] = H_m + H_s = H$
$\frac{\mu_3}{\mu_1^3} l^2 = 3\frac{4D^2}{u^2} = 3H_m^2$	$\frac{\mu_3}{\mu_1^3} l^2 = \frac{3}{2}\frac{4u^2}{k_{12}^2\Lambda_{21}^2}$ $= 3/2 H_s^2$	$\frac{\mu_3}{\mu_1^3} l^2 = \frac{3}{2}\frac{4D^2}{u^2} + \frac{3}{2}\left[\frac{2D}{u} + \frac{2u}{k_{12}\Lambda_{21}}\right]^2$ $= 3/2 H_m^2 + 3/2[H_m + H_s]^2$ $= 3/2[H_m^2 + H^2]$
$\frac{\mu_3}{\mu_2} = 3\frac{2D}{u^2}$	$\frac{\mu_3}{\mu_2} = \frac{3}{\Lambda_{21}}$	$\frac{\mu_3}{\mu_2} \approx 3\frac{2D}{u^2} + \frac{3}{\Lambda_{21}}$

[a] Two regions: 1, mobile; 2, stationary.

The fact that the reduced third moment is not of basic significance in the above hypothetical cases suggests that a similar situation might apply in the case of actual skewed chromatographic peaks. An interesting case is provided by an analysis of Grubner's derivation of the statistical moments for a realistic model of an actual chromatographic situation. In order to facilitate the interpretation, however, three simpler models have been set up and solved by means of the Laplace transform technique. The results are summarized in Table 2. In all cases a finite degree of skewness is indicated by the occurrence of nonzero third moments. On referring back to the bi-Gaussian model, one finds a μ_3/μ_2 expression of the form

$$\frac{\mu_3}{\mu_2} = \langle t \rangle - t_m - (\pi - 3)\,\frac{(\langle t \rangle - t_m)^3}{\mu_2}$$

Since $(\langle t \rangle - t_m)$ is small, the second term may safely be neglected so that one expects μ_3/μ_2 to be proportional to a small time interval indicative of the deviation from symmetry. The expressions for the reduced third moments given in Table 2 have been obtained by neglecting the bracketed terms in the expressions for the moments and by assuming that $k_{12} \gg 1$. Inspection of Table 2 shows that the third moments are merely the product of two factors, viz., the second moment and a time interval, Δt, proportional to the time to pass through a theoretical plate. The nonzero value of the third moment is thus due exclusively to this time interval, Δt (e.g., $2D/u^2$ for Model I). It is also known (*9*), however, that this Δt stems from the finite time which the peak takes to move past the detector, during which time the later portions undergo greater spreading corresponding to the increased residence times. The third moment in Grubner's work is thus expected to be simply a measure of this inherent asymmetry of a concentration–time distribution multiplied by the second moment and is therefore not due to a significant new column contribution. This interpretation is only obscured and not altered by reducing μ_3 by μ_1^3 so that the u-dependence of Z, for instance, stems primarily from the plate-height dependence on u. This is illustrated in Table 2 where Grubner's definition for the plate height has been used.

The results obtained above can now be summarized:

(1) The parameter $\phi = (\langle z \rangle - \mathrm{Mo})/\sigma$ is suggested as a general measure for skewness in chromatographic peaks. In cases where a bi-Gaussian fit is adequate, the much simpler parameter $s = \sigma_2/\sigma_1$ may be used instead.

(2) The third moment need not be included in the set of basis parameters for the characterization of skewed peaks. The position of the peak maximum is practically more convenient and yields equivalent information when used in conjunction with the first and second moments.

SYMBOLS

$A_1(s)$	convenient parameter
$A_2(s)$	convenient parameter
b	parameter in $F(z)$
b_1	parameter in $P(z)$
C	solute concentration
C_1	solute concentration in Region 1 (mobile phase region)
C_2	solute concentration in Region 2 (stationary phase region)
D	effective diffusion coefficient
$F(z)$	Poisson distribution
$G(z)$	bi-Gaussian distribution
H	total plate height
H_m	mobile phase contribution to H
H_s	stationary phase contribution to H
k_{12}	$= \Lambda_{12}/\Lambda_{21}$, mass distribution coefficient
l	column length
Med	median
Mo	mode
m_1, m_2	mass parameters in $G(z)$
n	parameter in $F(z)$
n_1	parameter in $P(z)$
$P(z)$	Pearson's curve (Type III)
Q_1	first quartile
Q_3	third quartile
S	$= \mu_3/\mu_2^{3/2}$, coefficient of skewness
S_Q	quartile coefficient of skewness
s	$= \sigma_2/\sigma_1$, skewness parameter for bi-Gaussian distribution
t	time
t_m	maximum of concentration-time distribution
$\langle t \rangle$	mean (first moment) of concentration–time distribution
u	mobile phase linear flow velocity
X	parameter in $P(z)$
Z	$= \mu_3/\mu_1^3$, specific asymmetry

z	distance coordinate
z_0	parameter in $P(z)$
$\langle z \rangle$	mean (first moment) of concentration–distance distribution

Greek Letters

ϵ	void fraction
σ	standard deviation
σ_1, σ_2	standard deviation parameters in $G(z)$
Λ_{ij}	transition probability from region i to region j
μ_1	first moment
μ_2	second central moment
μ_3	third central moment
ϕ	$= (\langle z \rangle - \mathrm{Mo})/\sigma$, skewness parameter
$\phi\mathrm{P}$	$= (\langle z \rangle - \mathrm{Med})/\sigma$, skewness parameter

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