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Variance of a zone migrating in a linear medium

II. Time-varying non-uniform medium

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ABSTRACT

A model of dispersion of a solute migrating in a non-uniform (coordinate-dependent) time-varying medium has been proposed. Only two quantities, plate height and velocity of the solute required for the complete model. Derivatives of the variance of the zone have been found for the general case of a linear (independent of solute concentration) medium, and for many special cases. For the practically important case where the local plate height and the local gradient of the solute velocity are nearly coordinate-independent within the zone, a simple model of the evolution of the variance of the zone has been derived. A consistent definition of the local plate height has been constructed. It has been shown that the currently accepted method of calculation of the variance of the zone is valid only under the certain conditions which were not known before.

INTRODUCTION

Chromatographic conditions may change during the analysis (*time-variance*) and/or along the column (*non-uniformity*), see Table I.

Many types of *temporal* and *spatial* variations of chromatographic conditions specific for particular chromatographic techniques have been analyzed in the literature [3–25]. However, no unified general theory describing the underlying effects of these changes is known.

Certainly, a specific study is well suited for the analyses of particular circumstances of a given technique. It can take into account all the details of the technique. A general theory, on the other hand, allows to see the broad picture of many separation techniques and provide the answers applicable to all of them. It can also serve as a framework and a guide for the more detailed studies. For instance, it has been recently shown [26] that, as long as a separation is *linear* (concentration independent) and *ideal* (infinitely short injection time, *etc.*), no focusing [15–26] can improve chromatographic resolution. If, on the other hand, the conditions were not ideal (which, in practice, is always the case) the focusing can recover [26] the losses in resolution. These conclusions were based on the theory described in this paper. They can guide a study of focusing in many separation techniques.

The purpose of this paper is to develop the foundation for the *kinetic* theory of separation in an arbitrary linear medium (time-varying and/or non-uniform). The study of the evolution of the variance of the zone is viewed as a corner stone for such theory. This paper is part 2 in the series dedicated to that study.

In the first part of the series [2], the theory for an arbitrary *time-invariant* medium (Table I), has been developed. The theory was derived from the basic principles of dispersion of migrating solutes.

In this paper, this theory has been further extended. Although the theory covers the entire

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TABLE I

CLASSIFICATION OF CHROMATOGRAPHIC MEDIA BY THE TYPES OF CHANGES

Media	Changes	Ref.	Examples
Time-invariant uniform	No changes	1[a]	Isocratic LC, isothermal GC with low-pressure drops
Time-invariant non-uniform	Changes in distance only	2[a]	Supercritical fluid chromatography (SFC), isoelectric focusing, isothermal GC
Time-varying uniform	Changes in time only	3–12	Programmed-temperature GC with low-pressure drops
Time-varying non-uniform	Changes in time and distance	13–25	Programmed temperature GC, chromathermography, gradient elution LC, programmed-pressure SFC

[a] And references cited therein.

Table I, its main focus has been the most complicated case of the *time-varying* non-uniform media.

Model

The model of a mass-conservative migration and dispersion of a solute in a time-varying non-uniform medium can be represented by the partial differential equation [2]

$$\frac{\partial m}{\partial s} = \frac{\partial^2}{\partial x^2}(D_{\text{eff}}m) - \frac{\partial}{\partial x}(um) \tag{1}$$

where x and s are, respectively, distance and time coordinates for the medium, m is *specific mass* (per unit length) of the solute, D_{eff} is local *effective diffusivity* [27] of the solute, and u is local *velocity* of the solute.

In this study, the scope of the model is limited by the following assumptions.

(C1) *Linearity* of the medium. Quantities $D_{\text{eff}} = D_{\text{eff}}(x, s)$ and $u = u(x, s)$ do not depend on m.

In addition, D_{eff} is not negative, and at any time, both D_{eff} and u are bounded within any bounded interval of x while their gradients are bounded when x approaches infinity. More specifically:

(C2) $0 \leqslant s < \infty$ implies: $0 \leqslant D_{\text{eff}} < \infty$ and $|u| < \infty$ when $|x| < \infty$; $|\partial D_{\text{eff}}/\partial x| < \infty$ and $|\partial u/\partial x| < \infty$ when $x \rightarrow \pm\infty$.

Finally, m is not negative, and the second moment of the zone is bounded at any time, *i.e.*

(C3) $m = m(x, s) \geqslant 0$, and $\int_{-\infty}^{\infty} x^2 m \, dx < \infty$ when $0 \leqslant s < \infty$.

Of these conditions, only C1 represents the practically meaningful limitation. It means, *e.g.*, that the results of this theory can not be applied to many cases of preparative chromatography [14] where frequently, due to the column overloading, the conditions are substantially *non-linear*. In the analytical chromatography, however, the overloading is typically avoided, and the results of the theory are valid. Also, only this condition is *substantially different* from its counterpart in ref. 2 reflecting the much broader scope of this treatment. Whereas in ref. 2, the quantities D_{eff} and u were only allowed to be functions of the distance, x, (*time-invariant non-uniformity*), here they can depend on the time, s, as well (medium can be *time-varying* and/or non-uniform).

Conditions in the collections C2 and C3 are either the statements of the physically existing facts (non-negative mass and effective diffusivity), or of the limitations which always exist in practice. Interpretation of all these conditions is obvious with the one possible exception of the bounded second moment of the zone. The latter means that the width of the zone expressed via the *standard deviation* of the zone is required to be bounded. A simple example of a zone with the non-bounded variance (see Appendix 1) is of certain theoretical interest.

THEORY

Many derivations in this section are similar to those in ref. 2. However, the possibility of the changes of the properties of the medium in time (excluded in ref. 2) requires special attention. As before [2], a distinction between an arbitrary coordinate x in the medium and the coordinate, z, of the center of mass of a migrating zone is carefully maintained. Additionally, here, similar distinction between an arbitrary time variable s and the migration time of the zone, t (the time when the center of mass of the zone is at z), is recognized.

Implications of conditions C1–C3

Conditions C3 imply that the amount, M, of the solute in the zone is bounded. Additionally, due to the mass conservative nature of the eqn. 1, M is constant [2]. In other words,

$$M = \int_{-\infty}^{\infty} m \, \mathrm{d}x = \text{constant} < \infty \tag{2}$$

The second of the conditions C3 also implies that at any instant, $s = t$, of time

$$z = z(t) = \frac{1}{M} \int_{-\infty}^{\infty} x m(x, t) \, \mathrm{d}x < \infty \tag{3}$$

i.e. the coordinate, z, of the center of mass of the zone is bounded as well. If necessary, the function $z = z(t)$ can be inverted[a] to $t = t(z)$. Relations $z = z(t)$ and $t = t(z)$ can be used to transform any function of z into a function of t and vice versa. Finally, together, eqns. 2 and 3 imply a known relation

$$\int_{-\infty}^{\infty} (z - x) m \, \mathrm{d}x = 0 \tag{4}$$

Modified model

Effective diffusivity, D_{eff}, in eqn. 1 represents the rate of diffusion of a solute per unit of time [27] (*temporal* rate of diffusion). Better known in chromatography is the rate of *dispersion* of the zone per unit of its displacement in the column (*spatial rate* of dispersion). In a uniform time-invariant chromatography that rate known as a column *plate height*, relates to the effective diffusivity as [27]

$$H = \frac{2D_{\text{eff}}}{u} \tag{5}$$

In an arbitrary medium, the quantity H in eqn. 5 represents the *local* rate of dispersion of the solute per unit of its displacement in the medium, and, therefore, can be identified with the *local plate height* in the medium [2] (see Discussion for the direct definition of the local plate height). Substitution of eqn. 5 in eqn. 1 yields

$$\frac{\partial m}{\partial s} = \frac{1}{2} \cdot \frac{\partial^2}{\partial x^2} (Hum) - \frac{\partial}{\partial x} (um) \tag{6}$$

This model describes the mass-conservative migration of a zone directly through the two best known basic concepts in chromatography: a column plate height and velocity of a solute.

Velocity of the zone

In a non-uniform medium, different parts of the zone can migrate with different velocities. Nevertheless, the concept of the single (*aggregate*) *velocity*, $\tilde{u}$, *of the zone* as a whole can be defined. If the location of the zone is identified with the coordinate, z, eqn. 3, of its center of mass, and t is the time required for the zone to migrate to z then the velocity of the zone becomes

$$\tilde{u} = \frac{\mathrm{d}z}{\mathrm{d}t} \tag{7}$$

It can be shown (see Appendix 2) that

$$\tilde{u} = \frac{1}{M} \left(\int_{-\infty}^{\infty} um \, \mathrm{d}x \right)_{s=t} = \frac{1}{M} \int_{-\infty}^{\infty} u(x, t) m(x, t) \, \mathrm{d}x \tag{8}$$

Evolution of the spatial variance of the zone

The changes in the *spatial variance*

$$\sigma^2 = \frac{1}{M} \int_{-\infty}^{\infty} (x - z)^2 m \, \mathrm{d}x \tag{9}$$

of the zone can be described by the derivative $\mathrm{d}\sigma^2/\mathrm{d}z$ [2]. It can be shown (see Appendix 3) that

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[a] If the velocity of the zone reverses direction, the relation $t(z)$ can become multi-valued.

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z} = \frac{1}{\tilde{u}M}\left(\int_{-\infty}^{\infty} Hum\,\mathrm{d}x + 2\int_{-\infty}^{\infty}(x-z)um\,\mathrm{d}x\right)_{s=t(z)} = \tilde{H} + \frac{2}{\tilde{u}M}\left(\int_{-\infty}^{\infty}(x-z)um\,\mathrm{d}x\right)_{s=t(z)} \tag{10}$$

where

$$\tilde{H} = \frac{1}{\tilde{u}M}\left(\int_{-\infty}^{\infty} Hum\,\mathrm{d}x\right)_{s=t} \tag{11}$$

is the *zonal* plate height, *i.e.* the (*aggregate*) plate height for the entire zone [2].

Special cases

So far, no limits to the degree of the variation of H and u in distance or time were imposed. For example, the gradient of velocity of the solute was allowed to change its sign *within* the zone. That can significantly distort the shape of the zone and even split a zone of a pure solute in several pockets. In analytical chromatography, however, efforts are made to avoid such extremes and keep the variation of the gradients

$$g_H = g_H(x,s) = \frac{\partial H}{\partial x} \quad \text{and} \quad g_u = g_u(x,s) = \frac{\partial u}{\partial x} \tag{12}$$

within the zone at the low level. Under such conditions, eqn. 10 can be simplified.

(C4) *Moderate media.* Within the zone located at z, the plate height and the solute velocity are linear functions of x:

$$H(x,t(z)) = H(z,t(z)) + g_H(z,t(z))(x-z),$$

$$\text{for all } x \text{ where } m(x,t(z)) \neq 0\,; \tag{13}$$

$$u(x,t(z)) = u(z,t(z)) + g_u(z,t(z))(x-z),$$

$$\text{for all } x \text{ where } m(x,t(z)) \neq 0 \tag{14}$$

For a moderate medium, eqn. 10 can be rewritten (see Appendix 4) as

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z} = H + \frac{2\sigma^2}{u}\cdot\frac{\partial u}{\partial x}\left(1+\frac{1}{2}\cdot\frac{\partial H}{\partial x}\right) \quad \text{or}$$

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z} = H + \frac{2\sigma^2 g_u}{u}\left(1+\frac{g_H}{2}\right) \tag{15}$$

(C5) *Partially moderate media.* Within the zone located at z, the solute velocity is linear functions of x, eqn. 14 (while the plate height can change arbitrarily).
In this case[a] (see Appendix 4),

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z} = \tilde{H} + \frac{2\sigma^2}{u}\cdot\frac{\partial u}{\partial x} \quad \text{or} \quad \frac{\mathrm{d}\sigma^2}{\mathrm{d}z} = \tilde{H} + \frac{2\sigma^2 g_u}{u} \tag{16}$$

(C6) *Smooth media* (a stronger case of the moderate media). Within the zone located at z, the solute velocity is a linear function of x, eqn. 14, while the plate height does not depend on x:

$$H(x,t(z)) = H(z,t(z))$$

$$\text{for all } x \text{ where } m(x,t(z) \neq 0 \tag{17}$$

This is the simplest of the time-varying non-uniform media (see Discussion). Due to $g_H = 0$, eqn. 15 becomes

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z} = H + \frac{2\sigma^2}{u}\cdot\frac{\partial u}{\partial x} \quad \text{or} \quad \frac{\mathrm{d}\sigma^2}{\mathrm{d}z} = H + \frac{2\sigma^2 g_u}{u} \tag{18}$$

(C7) *Uniform media.* Within the zone located at z, the plate height and the solute velocity do not depend on x, *i.e.* along with eqn. 17, one has:

$$u(x,t(z)) = u(z,t(z))$$

$$\text{for all } x \text{ where } m(x,t(z)) \neq 0\,. \tag{19}$$

Eqns. 15 and 18 become

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z} = H \tag{20}$$

Notice, that this familiar relation [28,29] remains valid even if the medium changes in time (time-variance).

(C8) *Moderate time-invariant media.* During the passage of the center of mass of the zone through the coordinate z, the medium remains moderate, C4, and time-invariant. The latter means that

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[a] Eqn. 16 was instrumental for the derivations in ref. 26.

$$\left.\frac{\partial H}{\partial s}\right|_{s=t(z)}=0 \quad \text{and} \quad \left.\frac{\partial u}{\partial s}\right|_{s=t(z)}=0$$

$$\text{for all } x \text{ where } m(x, t(z)) \neq 0\,. \tag{21}$$

As partial derivatives of H and u over s vanish due to this condition, the partial derivatives of these quantities over x become the same as the full derivatives over x. Furthermore, since only $x = z$ is considered in eqn. 15 (see notations in Appendix 4), the derivatives over x are the same as the derivatives over z. Eqn. 15 becomes

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z}=H+\frac{2\sigma^2}{u}\cdot\frac{\mathrm{d}u}{\mathrm{d}z}\left(1+\frac{1}{2}\cdot\frac{\mathrm{d}H}{\mathrm{d}z}\right) \tag{22}$$

The quantity

$$\tau^2=\frac{\sigma^2}{u^2} \tag{23}$$

can be referred to as a *temporal variance of the zone*[a]. After the substitution of eqn. 23 into eqn. 22, the latter becomes (see Appendix 5)

$$\frac{\mathrm{d}\tau^2}{\mathrm{d}z}=\frac{H}{u^2}+\frac{\tau^2}{u}\cdot\frac{\mathrm{d}u}{\mathrm{d}z}\cdot\frac{\mathrm{d}H}{\mathrm{d}z} \tag{24}$$

Significance of eqns. 22 and 24 is discussed in the next section.

(C9) *Smooth time-invariant media* [2]. During the passage of the center of mass of the zone through the coordinate z, the medium remains smooth, C6, and time-invariant, eqn. 21.

This case has been studied in ref. 2. The same arguments which led from eqn. 15 to eqns. 22 and 24, lead [2] to

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z}=H+\frac{2\sigma^2}{u}\cdot\frac{\mathrm{d}u}{\mathrm{d}z}, \tag{25}$$

$$\frac{\mathrm{d}\tau^2}{\mathrm{d}z}=\frac{H}{u^2} \tag{26}$$

The latter allows to calculate the net temporal variance of the zone at any z as

$$\tau^2=\int \mathrm{d}\tau^2=\int\frac{H\,\mathrm{d}z}{u^2} \tag{27}$$

Other forms of eqns. 26 and 27 (see Discussion) were known before [35–38].

(C10) *Gaussian zone.*

$$m(x, t(z))=\frac{M}{\sigma\sqrt{2\pi}}\cdot\exp\left(-\frac{(x-z)^2}{2\sigma^2}\right)$$

is a Gaussian function of x when the zone is at z. For the Gaussian zone, eqn. 10 can be rewritten (see Appendix 6) as[b]

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z}=\tilde{H}+\frac{2\sigma^2}{\tilde{u}}\tilde{g}_u \tag{28}$$

where

$$\tilde{g}_u=\frac{1}{M}\left(\int_{-\infty}^{\infty} g_u m\,\mathrm{d}x\right)_{s=t}$$

is the average gradient of velocity of the solute in the zone.

This concludes the analysis of the special cases. Notice the structural similarity of eqns. 15 and 22, and eqns. 16, 18, 25 and 28. It is also worth mentioning that the special cases C4–C9 prescribe their conditions only in the vicinity of the certain coordinate z, and only at the time when the zone is there. In that sense, the conditions can be viewed as the zonal and the instantaneous ones. Obviously, the results are valid when the conditions are broader. For example, a certain region in the medium can be always smooth; or, at a given time, the entire medium can be smooth; and, finally, the entire medium can be always smooth.

DISCUSSION

The theory developed in the previous section is founded on the two basic principles of chromatographic separation in any medium: migration and dispersion of the zones. The small number of elements in the foundation of the theory assures broad application of its results

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[a] When $t^2(z) \gg \tau^2$ (large values of z), the temporal variance of the *zone*, eqn. 23, is a good approximation to the temporal variances of the *solute mass-flow* or the *concentration-time curve* at z [30–34].

[b] Eqn. 28 was the basis for the formulation of the generalized conclusion in ref. 26.

[2,26]. Some implications of the theory are discussed below.

Implications of the time-variance

The time-variance enters into the relations for $d\sigma^2/dz$ (see Theory) in a subtle way. For instance, integration in eqn. 10 is done only over the distance variable x with the fixed s, and the equation itself is very similar to its time-invariant counterpart [2]. In the equations describing the special cases, variable t is even less visible (all quantities σ^2, H, $\tilde{H}$, u, g_H, g_u, $\tilde{g}_u$ in these equations are functions of the single variable z). Nevertheless, the influence of the time-variance is significant.

First of all, full derivatives over dz in the time-invariant equations are replaced with partial derivatives over ∂x in their time-varying counterparts. What is more, the time-varying equations are more complex because parameters H, u, *etc.* in these equations are not as directly related to their counterparts in the model eqn. 6, as they are in a time-invariant medium.

Consider, *e.g.*, the plate height in the time-invariant eqns. 22, 24–27. Notice, that the plate height in eqn. 6 is a function $H = H(x)$ of a single variable x [2]. Substitution of $x = z$ results in the function $H = H(z)$ for all eqns. 22, 24–27. In other words, quantity H eqns. 22, 24–27 is **the same function** as the one in eqn. 6. In the time-varying eqns. 15, 16, 18 and 20, the plate height is also a function of the single variable z, but now it is defined as $H = H(z, t(z))$ (see Appendix 4). To derive $H(z, t(z))$, the function $t = t(z)$ (see comments to eqn. 3) must be known. To find $t = t(z)$, notice that $\tilde{u} = u(z, t)$ for all eqns. 15, 16, 18 and 20 (see Appendix 4). Therefore, eqn. 7 becomes

$$\frac{dz}{dt} = u(z, t) \tag{29}$$

where the function $u(x, s)$ is known from eqn. 6. The function $t = t(z)$ can be found by solving eqn. 29 for $z = z(t)$ and inverting the latter relation to get $t = t(z)$, or by solving equation

$$\frac{dt}{dz} = \frac{1}{u(z, t)} \tag{30}$$

directly for $t = t(z)$. These manipulations are not as trivial (see Appendix 7) as the substitution $x = z$ which is valid only for the time-invariant media.

Comparison of new and previously known results

It is important that the previously known special cases follow from the broader theory. If that does not occur, the sources of the inconsistency must be identified.

Notice that eqn. 10 developed here for an arbitrary medium has its narrower precedent in the theory developed before [2] for the time-invariant medium. It has also been shown above that the new and broader relations such as eqns. 16, 18 and 28 converge to the previously known [2] eqn. 25 while eqn. 24 converges to the previously known [2] eqn. 26 when the appropriate conditions [2] are reproduced.

Eqn. 26 was also previously known [35–38] in its approximate form

$$\tau_i^2 = \frac{H_i z_i}{u_i^2} \tag{31}$$

where H_i and u_i were, respectively, the plate height and solute velocity in a short column segment z_i, and τ_i^2 was the contribution of that segment to the total τ^2. The latter was calculated as

$$\tau^2 = \sum \tau_i^2 = \sum \frac{H_i z_i}{u_i^2} \tag{32}$$

Previously [35–38], eqn. 32 was viewed as the **self-evident** rule of addition of the small contributions, τ_i^2, to the total τ^2 in **any** time-invariant medium. The theory developed in the previous section provides an example of a time-invariant medium where the rule is **not valid**. Indeed, eqns. 31 and 32 are approximations of eqns. 26 and 27. As eqn. 24 indicates, eqns. 26 and 27 are not valid when $dH/dz \neq 0$. Invalid as well become their respective approximations eqns. 31 and 32. Discovery of the unknown limitations of the currently accepted techniques is one of the important results of the theory.

As the discussion in ref. 2 indicates, previous theories can justify eqns. 31 and 32 for the time-invariant medium which has *nearly constant* *solute velocity* and plate height within the zone. The discussion in the previous paragraph, on the other hand, justifies eqns. 31 and 32 for the much broader class of the time-invariant medium, the one where the solute velocity *does not have to be nearly constant* within the zone. In other words, the theory developed in the previous section, not only reveals the limitations of the previously accepted techniques but also provides the less restrictive justifications for such techniques than the previous theories do.

For the time-invariant smooth media, all eqns. 25–27, 31 and 32 are valid. However, eqns. 31 and 32 still remain approximations of the exact and mathematically more manageable eqns. 26 and 27 which were deduced from eqn. 25. Therefore, eqn. 25 seems to be a better alternative as a starting point in the analysis of chromatography in a smooth, time-invariant medium. Eqn. 25 itself is a special case of eqn. 18 which describes the variance of the zone in *any* (not necessarily time-invariant) *smooth medium* and provides the most consistent starting point for the analysis of such medium[a]. The use of the smooth model, C6, and eqn. 18 for the analysis of many practical cases of a non-uniform chromatography can be justified by the following.

In many cases of a non-uniform chromatography [13–25, 37–40] the local plate height, H, is a much weaker function of a distance than the local solute velocity, u, is. Also, typically, in chromatography with a reasonably high efficiency (more than a hundred of plates), the largest portion of the migration of the zones from the inlet to the outlet takes place under the conditions where the widths of the zones are much narrower than the column length. As a result, typically, H and the gradient of u do not change significantly within the zone[b]. Finally, eqn. 18 is the simplest among the equations describing the time-varying non-uniform medium. (Eqn. 15 is more complicated, eqns. 16 and 28 require zonal parameters $\tilde{H}$ and $\tilde{u}$ instead of local H and u, other special cases deal only with the time-invariant medium.)

Local plate height

The concept of the plate height is one of the key concepts in chromatography. Previously known definitions of the local plate height [11,27,29,35] in a non-uniform chromatography have internal inconsistencies [11]. A new definition, free from the known inconsistencies is constructed below.

Notice, that in eqn. 5, the local plate height, H, was introduced via the local effective diffusivity, D_{eff}, and the local solute velocity. Eqn. 5 for the time-invariant uniform [27] and non-uniform [2] medium was known before.

Typically, in chromatography, H is a better known quantity than D_{eff}. A direct definition of H which does not require a knowledge of D_{eff} can be (see Appendix 8 and ref. 2):

$$H = \lim_{\sigma^2 \to 0} \frac{\mathrm{d}\sigma^2}{\mathrm{d}z} \tag{33}$$

CONCLUSIONS

The plate height and the solute velocity based model of a chromatographic medium has been proposed. Eqn. 10 describing evolution of the variance of the zone in any linear medium (possibly time-varying and/or non-uniform), and many special cases of that equation have been derived. When the medium is smooth (local plate height and gradient of the solute velocity are nearly coordinate-independent within the zone), the evolution of the variance of the zone is governed by the newly derived ordinary linear differential equation, eqn. 18, which can be used as the simplified model for the majority of the known non-uniform time-varying separation techniques.

Among other important results, it has been

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[a] Previously [26], eqn. 18 was introduced without the derivation.

[b] This may not be true in the vicinity of joints of columns with inlets, detectors, retention gaps, *etc.* where significant upsets of velocity of solutes and/or plate height can occur *within* the zone. The non-uniformity can also be severe in case of the thick-film GC with the vacuum outlet [41]. Analysis of the extremes of the non-uniformity is also within the scope of this theory, eqn. 10. However, it is beyond the scope of this paper.

shown that the previously accepted rule of calculation of the temporal variance of the zone in an arbitrary non-uniform time-invariant medium, eqn. 32, is valid only if the medium is smooth. Also a definition, eqn. 33, of the local plate height free from the previously known inconsistencies has been constructed.

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APPENDIX

1. An example of the zone with unbounded variance

A zone which at a certain time, t, has specific mass

$$m = m(x, t) = \begin{cases} m_o, & |x| \leq 1 \\ m_o|x|^{-3}, & |x| > 1 \end{cases}$$

where m_o is a constant, has bounded zeroth moment (the *total amount* of solute), M, and bounded first moment (the *center of mass* of the zone), z. Its half-height width, w, is also bounded, but its second central moment (the *variance* of the zone), σ^2, is infinite. Indeed,

$$M = \int_{-\infty}^{\infty} m \,\mathrm{d}x = 3m_o\,, \quad z = \frac{1}{M}\int_{-\infty}^{\infty} xm \,\mathrm{d}x = 0\,,$$

$$w = 2(1 + \sqrt[3]{2}) \approx 4.52\,,$$

$$\sigma^2 = \frac{1}{M}\int_{-\infty}^{\infty} (x-z)^2 m \,\mathrm{d}x = \frac{2}{3}\left(1 + \int_1^{\infty} x^{-1}\,\mathrm{d}x\right) = \infty$$

2. Derivation of the velocity of the zone

Due to eqn. 3 and the constancy of M one has

$$\tilde{u} = \frac{\mathrm{d}z}{\mathrm{d}t} = \left(\frac{1}{M}\cdot\frac{\mathrm{d}}{\mathrm{d}s}\int_{-\infty}^{\infty} xm\,\mathrm{d}x\right)_{s=t}$$

$$= \left(\frac{1}{M}\int_{-\infty}^{\infty} x\frac{\partial m}{\partial s}\,\mathrm{d}x\right)_{s=t}$$

The integral in the right-hand side of this expression can be replaced [2] with $\int_{-\infty}^{\infty} um\,\mathrm{d}x$ yielding eqn. 8.

3. Derivation of $\mathrm{d}\sigma^2/\mathrm{d}z$

Due to the definition eqn. 9, one has:

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}t} = \frac{1}{M}\cdot\frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{\infty} (x-z)^2 m\,\mathrm{d}x$$

$$= \left(\frac{1}{M}\int_{-\infty}^{\infty} (x-z)^2\frac{\partial m}{\partial s}\,\mathrm{d}x\right)_{s=t}$$

$$-\frac{1}{M}\int_{-\infty}^{\infty} 2(x-z)\frac{\mathrm{d}z}{\mathrm{d}t}m\,\mathrm{d}x$$

In the second integral in the right-hand side of the last expression, the velocity, $\tilde{u} = \mathrm{d}z/\mathrm{d}t$, of the zone is not a function of x, and can be moved outside of the integral. The integral then vanishes due to the eqn. 4. The entire expression becomes

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}t} = \left(\frac{1}{M}\int_{-\infty}^{\infty} (x-z)^2\frac{\partial m}{\partial s}\,\mathrm{d}s\right)_{s=t}$$

The integral in the right-hand side of this expression can be replaced [2] with

$$\int_{-\infty}^{\infty} Hum\,\mathrm{d}x + 2\int_{-\infty}^{\infty} (x-z)u\,\mathrm{d}x$$

which yields

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}t} = \frac{1}{M}\left(\int_{-\infty}^{\infty} Hum\,\mathrm{d}x + 2\int_{-\infty}^{\infty} (x-z)um\,\mathrm{d}x\right)_{s=t}$$

Due to eqn. 7, one has $\mathrm{d}\sigma^2/\mathrm{d}z = \tilde{u}^{-1}\cdot(\mathrm{d}\sigma^2/\mathrm{d}t)$ which, due to the previous expression, can be re-written as eqn. 10.

4. Derivation of $\mathrm{d}\sigma^2/\mathrm{d}z$ *for the moderate medium*

Under the condition C4, eqn. 8 becomes

$$\tilde{u} = \frac{u(z, t(z))}{M}\int_{-\infty}^{\infty} m\,\mathrm{d}x$$

$$+ \frac{g_u(z, t(z))}{M}\int_{-\infty}^{\infty} (x-z)m\,\mathrm{d}x = u(z, t(z))$$

The second integral in that expression vanished due to the eqn. 4. The result indicates that the zone velocity becomes the same as the local velocity of the center of mass of the zone. That and condition C4 imply that eqn. 10 can be rewritten as

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z} = \frac{1}{uM}\left(\int_{-\infty}^{\infty} (H + (x-z)\cdot g_H)\right.$$

$$\cdot(u + (x-z)g_u)m\,\mathrm{d}x$$

$$+2\int_{-\infty}^{\infty}(x-z)(u+(x-z)g_u)m\,\mathrm{d}x\Big)_{s=t(z)}$$

where

$$H=H(z,t(z))\,,\quad u=u(z,t(z))\,,$$

$$g_H=g_H(z,t(z))=\left.\frac{\partial H(x,t(z))}{\partial x}\right|_{x=z}\,,$$

$$g_u=g_u(z,t(z))=\left.\frac{\partial u(x,t(z)}{\partial x}\right|_{x=z}$$

All these quantities are not functions of x. Taking that into account along with the eqn. 4, one finally has:

$$\frac{\mathrm{d}\sigma^2}{\mathrm{d}z}=H+\frac{1}{uM}\Big(g_Hg_u\int_{-\infty}^{\infty}(x-z)^2m\,\mathrm{d}x$$
$$+2g_u\int_{-\infty}^{\infty}(x-z)^2m\,\mathrm{d}x\Big)_{s=t(z)}$$
$$=H+\frac{\sigma^2}{u}g_u(2+g_H)$$

If this entire derivation was applied only to the integral term in the right-hand side of eqn. 10, the result would be eqn. 16.

5. *Derivation of* $\mathrm{d}\tau^2/\mathrm{d}z$ *for the time-invariant moderate medium*

From eqn. 23, one has

$$\frac{\mathrm{d}\tau^2}{\mathrm{d}z}=\frac{\mathrm{d}}{\mathrm{d}z}\left(\frac{\sigma^2}{u^2}\right)=\frac{1}{u^2}\left(\frac{\mathrm{d}\sigma^2}{\mathrm{d}z}-\frac{2\sigma^2}{u}\cdot\frac{\mathrm{d}u}{\mathrm{d}z}\right)$$

After the replacement of $\mathrm{d}\sigma^2/\mathrm{d}z$ in the right-hand side of this expression with eqn. 22 one has:

$$\frac{\mathrm{d}\tau^2}{\mathrm{d}z}=\frac{1}{u^2}\left[H+\frac{2\sigma^2}{u}\cdot\frac{\mathrm{d}u}{\mathrm{d}z}\left(1+\frac{1}{2}\cdot\frac{\mathrm{d}H}{\mathrm{d}z}\right)-\frac{2\sigma^2}{u}\cdot\frac{\mathrm{d}u}{\mathrm{d}z}\right]$$
$$=\frac{1}{u^2}\left(H+\frac{\sigma^2}{u}\cdot\frac{\mathrm{d}u}{\mathrm{d}z}\cdot\frac{\mathrm{d}H}{\mathrm{d}z}\right)$$
$$=\frac{H}{u^2}+\frac{\tau^2}{u}\cdot\frac{\mathrm{d}u}{\mathrm{d}z}\cdot\frac{\mathrm{d}H}{\mathrm{d}z}$$

6. *Derivation of* $\mathrm{d}\sigma^2/\mathrm{d}z$ *for a Gaussian zone*

For a Gaussian zone, condition C10, $\partial m/\partial x=-[(x-z)/\sigma^2]m$. That allows to rewrite the second integral in the right-hand side of eqn. 10 as

$$\int_{-\infty}^{\infty}(x-z)um\,\mathrm{d}x=-\sigma^2\int_{-\infty}^{\infty}u\,\mathrm{d}m$$
$$=\sigma^2\left(-(um)|_{-\infty}^{\infty}+\int_{-\infty}^{\infty}\frac{\partial u}{\partial x}m\,\mathrm{d}x\right)$$

Due to the combination of conditions C2 and C3 which force $u(\infty,s)\cdot m(\infty,s)\cdot m(-\infty,s)=0$ for any s, the term $-(um)|_{-\infty}^{\infty}$ vanishes yielding

$$\int_{-\infty}^{\infty}(x-z)um\,\mathrm{d}x=\sigma^2\int_{-\infty}^{\infty}\frac{\partial u}{\partial x}m\,\mathrm{d}x$$

That along with the notations eqn. 12 allows to rewrite eqn. 10 as eqn. 28.

7. *Example derivation of* $z(t)$

A focusing by the constant negative gradient of a magnitude g_o which travels along the column with the constant speed [16,26] can be provided by the velocity function $u=u(x,s)=u_o+as-g_ox$ where initial velocity, u_o, and local acceleration, a, are constants. Eqn. 29 becomes $\mathrm{d}z/\mathrm{d}t=u_o+at-g_oz$. Its solution for $z(0)$ is

$$z=\frac{u_og_o}{g_o^2}(1-e^{-g_ot})+\frac{at}{g_o}$$

Inversion of this expression is not simple. However, in the special case, the expression can be significantly simplified. Notice that regardless of the initial velocity, u_o, the zone asymptotically approaches velocity $u_c=a/g_o$. If $u_o=u_c$, the previous expression for z becomes $z=u_ct$, *i.e.* the zone migrates with the constant velocity u_c. Assumption $u_o=u_c$ also simplifies eqn. 18. After the substitution $u=u_c=a/g_o$ and $g_u=-g_o$, eqn. 18 becomes $\mathrm{d}\sigma^2/\mathrm{d}z=H-2\sigma^2g_o^2/a$ where both g_o and a are constants.

8. *Definition of the local plate height*

A non-uniform medium can be nearly uniform within a small segment of its length. Indeed, other than at the points of discontinuity of the properties of the medium, there always exist such a short segment, Δx, in the path of the zone that the medium is nearly uniform within Δx. If the largest fraction of the zone is located within Δx then the migration of the zone in the vicinity of Δx is almost unaffected by the non-uniformity of the medium. The latter conditions are met when $\sigma^2\rightarrow 0$. Further, as m is not negative, it follows from the eqn. 9 that for a non-zero amount of the solute in the zone, $\sigma^2 \to 0$ implies $m(x, t(z)) \to M\delta(x - z)$ where $\delta(x - z)$ is a Dirac's delta-function. Substitution of the last implication in eqns. 8 and 10 yields $\tilde{u} = u$ and $d\sigma^2/dz = H$ indicating that H can be measured as prescribed by eqn. 33.

SYMBOLS

D_{eff}	local effective diffusivity in the medium (length^2/time)
g_H	local gradient of plate height
g_u	local gradient of velocity of the solute (time^{-1})
$\tilde{g}_u$	average gradient of velocity in the zone (time^{-1})
H	local plate height in the medium (length)
$\tilde{H}$	plate height for the entire zone (length)
M	total mass of the solute in the zone (mass)
m	specific mass of a solute (mass/length)
s	time coordinate (time)
t	migration time of the zone (time)
u	local velocity of a solute (length/time)
$\tilde{u}$	velocity of the zone (length/time)
x	distance coordinate (length)
z	coordinate of the center of mass of the zone (length)
σ^2	spatial variance of the zone (length^2)
τ^2	temporal variance of the zone (time^2)

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