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Review

Is chromatography a separation process?

The zonoid answer

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ABSTRACT

The separation state of a physical system is defined as a geometric entity called a *zonoid* and a brief account of the mathematical properties of zonoids is given. Visual representations of (2-D and 3-D) zonoids enhance the intuitive grasp of the theory and calculation of their volume gives a useful (although degraded) measure of separation. The answer to the title question is then, on rigorous grounds, that chromatography is not a separation, but a "sepmix" process, *i.e.*, it is both a separation and a mixing process. In linear chromatography, loss in 2-volume of separation between a solute and carrier increases along the column approximately according to $\sqrt{N}$, where N is the number of theoretical plates. 3-Volume of separation between two solutes and carrier first increases and then decreases. More intricate topics such as selectivity of separation are defined and discussed. Examples of problem solving with zonoids are given and it is shown that Rony's extent of separation results from a problem of approximation and reflects only part of separation produced by the column.

CONTENTS

1. INTRODUCTION

This paper presents a brief account of a new geometric approach to separation engineering, called zonoid theory and shows its potential by application to chromato-

graphy. A small part of this theory has been presented elsewhere [1,2]. In order to be self-consistent, we recall and complete, in an abstract setting, relevant parts of the backbone of the theory, definitions and theorems without proofs or validity statements, in Section 2. Long or technical proofs are relegated to the Appendix. This will allow differently inclined categories of readers to linger on what they like most, without having to extract it painfully. Such an abstract setting is intended to ease application to other processes as well. Section 2 also develops further basic mathematical tools for comparison and classification of separation states.

Column chromatography makes a challenge to separation engineering, a key-stone to its methodology. It is a transient process since the flow-rate of species is a function of time t and abscissa z, which involves at least three species, *i.e.*, two solutes and a carrier. Any correct theory of separation must cope with these two basic facts without recourse to simplification *ab initio*. Conversely, if such a theory can treat chromatography successfully, it will presumably be able to do so for any other process.

Previous theories [3,4] on separation failed mainly on two grounds: first, they did not take in account the fact that, as stated above, the primary "product" of a column is, by nature, a flow, the composition of which is a *continuous* function of time. Failure occurred possibly because recovering and managing a large number of small samples would be "uneconomic", or even "unthinkable". Second, these theories concentrate on the separation of solutes, "forgetting" the eluent, which is however an essential part of the process and of its thermodynamic consistency.

The aim of this paper is to show that zonoid theory removes these limitations: the evolution of separation between three species in the column can be computed as a function of z, without the need to resort to any (arbitrary) "cut point".

The ability to cope with multi-component *differential* families is the core of the new separation theory presented here. In fact, a discretization of the outlet flow into "cuts" is unavoidable, but we must do it thoughtfully. Indeed, zonoid theory will give us a safe procedure: to minimize the loss of separation by mixing induced by the trapping procedure, after taking due account of the separation really produced by the column. This task will be addressed in further work.

Is chromatography a separation process? This seemingly strange question stands behind the interesting and paradoxical paper from Golay [5] on entropy (im)balance in chromatography, but has not, up to now, been considered in all of its aspects. We shall leave for further study the pinpointing of the reasons why Golay [5] finds a discrepancy between entropy balance in chromatography and the second law of thermodynamics, noting for the moment only that the solution to this problem would clarify our understanding of chromatography.

In contrast to entropic theories, a remarkable feature of the present theory is that *the very nature, or selectivity type, of a process can be established by pure observation of conserved species evolution*. It is *model independent*. It is also *independent of the nature of these conserved species* (including, *e.g.*, energy).

Section 3 identifies the chromatographic counterpart to the mathematical entities given in Section 2. It also states the methodology for the study of separation states.

Section 4 is a rather qualitative presentation of tools and geometric objects, using simple linear models of the process. The various degrees of selectivity of chromatographic separation are studied.

Section 5 deals with the title question not on "intuitive" grounds, but by a quantitative study of separation zonoids. As it becomes increasingly apparent in Section 4 that chromatography is not a separation process (at least according to the given definition), we must assess clearly which type of process really chromatography is. Here comes into play the new type of process called the "sepmix" process, coined in Section 3 for a process (or transformation) that is neither a separation nor a mixing process. Chromatography will be revealed to be the first example of a sepmix process.

Section 6 lists some other questions that the theory of zonoids asks (and requires answers for), in order of importance. It also shows how the extent of separation defined by Rony [3] fits into the scheme.

On a point of terminology, in the following, zonoids, convex sets of mixtures (CSM) and separation content are really the same object, they are all the embodiment (of the concept) of the separation state, seen from different points of view.

One could give many variant forms to the results of this paper, according to which parameters on which one wishes to make the separation state depend. We have chosen to use variables more natural to users of chromatography. Readers with a deeper interest in zonoids are referred to refs. 6–12.

2. THEORY OF ZONOIDS, A SUMMARY

We outline here, without an attempt to justify the concepts axiomatically, or to give proofs or make precise conditions of the validity of the theorems, as would require a correct mathematical exposition, the main concepts and results of zonoid theory, in a restricted frame suited to column chromatography. The mathematical theory of zonoids is treated in detail in refs. 6–12.

2.1. Systems, linear space E and differential families

A formalization of the concept of a (uniaxial) "physico-chemical system" leads to the following definition.

Definition
Given a vector space E of finite dimension n, state Σ of a system $\mathscr{S}$ is a 1-differential form on the real line R, with value in the positive orthant E^+, and such that coefficient $\mathbf{F}$ of Σ is a Lebesgue integrable vector valued function:

$$\Sigma = \mathbf{F}(t)\mathrm{d}t, \quad t \in \Delta t \subset R$$

E is called the space of (conservative) quantities, and a vector $\mathbf{N} \in E$ is called a quantity vector. E is referred to as an n-dimensional (n-D) space. In accordance with tensor notations, (contravariant) coordinates are indexed as superscripts.

E is given norm L_1, $\|\mathbf{N}\|_1 = \sum_{i=1}^{n} |N^i|$

A problem of evolution arises when $\mathbf{F}$ depends on a parameter z, *i.e.*, we consider the evolution of state of the system as a function of z. We note

$$\Sigma(z) = \mathbf{F}(z,t)\mathrm{d}t, \quad t \in \Delta t(z) \subset R, \quad z \in L \subset R$$

In the following, we consider $n = 3$, and diffuse, smooth states, *i.e.*,

$$\mathbf{F}(z,t) = (F^1(z,t), F^2(z,t), F^3(z,t)), t \in \Delta t, F^i \text{ of class } C^2(\Delta t) \cap C^1(L)$$

Let Δ_2 be the standard simplex of E:

$$\Lambda_2 = \{\mathbf{x} \in E^+ | x^1 + x^2 + x^3 = 1\}$$

Calling $F^0 = F^1 + F^2 + F^3$, $\|\mathbf{F}(z,t)\| > 0$ on $L \times \Delta t$, we associate to $\mathbf{F}$ the composition function $\mathbf{x}$ (point valued in Δ_2):

$$\mathbf{x}(z,t) = \left(\frac{F^1}{F^0}(z,t), \frac{F^2}{F^0}(z,t), \frac{F^3}{F^0}(z,t)\right), \quad t \in \Delta t, \quad z \in L$$

Formally (and for a better physical grasp), the 1-differential form Σ may be thought of as a set of "infinitesimal" quantity vectors "$\mathrm{d}\mathbf{N}$" in E,

$$\mathscr{F} = \{\mathrm{d}\mathbf{N}(t) | t \in \Delta t\} = \{\mathbf{F}(t)\mathrm{d}t\}_{t \in \Delta t}$$

which is called a 1-differential (1-d) family and generically noted $\mathscr{F}$. System state and families or 1-differential forms are therefore the same concept. A problem of evolution will therefore involve a 1-d family depending on a parameter, *e.g.*, $\mathscr{F}(z)$.

The concept of a family of vectors is central to zonoid theory as the family contains all the relevant information to characterize separation present in the system.

The mixing convention is that a state (family) is said to be reduced iff all its colinear vectors in E^+ have been added together. The mixing convention avoids trivial complications, and is natural as we are looking at separations. Note that many physically different systems can map into same reduced state.

Invariance of families or states by change of variables
    The change of variables follows a chain rule, or, more precisely, let $t = f(\tau)$, f, continuous, derivable, monotonic on segment Δt, $\tau = f^{-1}(t)$:

$$\{\mathrm{d}\mathbf{N}(t)\} t \in \Delta t = \{\mathbf{F}(t)\mathrm{d}t\} t \in \Delta t = \left\{\mathbf{F} \circ f(\tau) \left|\frac{\mathrm{d}f}{\mathrm{d}\tau}(\tau)\right| \mathrm{d}\tau\right\}_{\tau \in f^{-1}(\Delta t)} \tag{1}$$

This is really a property of differential forms. Note that inclusion of $\mathrm{d}t$ in the notation of differential families allows for the automatic use of the chain rule and that the absolute value is taken to conserve positivity in the case when f is decreasing. Eqn. 1 expresses conservation of quantity in the form of an invariant property associated with $\mathscr{F}$.

Integration of families

Any interval (or reunion of disjoint intervals, generically called a region), $\omega \subset \varDelta t$ generates a *quantity vector* by

$$\mathbf{N}(\omega) = \int_{\omega} \mathbf{F}(t)\mathrm{d}t = \int_{\mathbf{R}} \chi_{\omega} \mathbf{F}(t)\mathrm{d}t, \mathbf{N}(\omega) \in E \tag{2}$$

where the characteristic function, $\chi_{\omega} : \mathbb{R} \to \{0,1\}$ (or discrete sampling function) is defined by

$$\chi_{\omega}(t) = 1 \text{ if } t \in \omega$$
$$\chi_{\omega}(t) = 0 \text{ if } t \notin \omega$$

$\mathbf{N}_0 = \int_{0}^{\varDelta t} \mathbf{F}(s)\mathrm{d}s$ is called the sum (or distal) vector of family $\mathscr{F}$. In an evolution problem, a system is isolated iff $\mathbf{N}_0(z)$ is fixed.

Approximation of families

A partition of $\varDelta t$ into p intervals (or sub-regions) $\omega_1, ..., \omega_p$ defines a discrete sampling (approximation) of system state by the (discrete) family of quantity vectors:

$$\left\{ \mathbf{N}_j \right\}_J = \left\{ \mathbf{N}_j \in E \,|\, j \in J = \{1,2,...,p\} \right\} = \left\{ \mathbf{N}_1, \mathbf{N}_2, ..., \mathbf{N}_p \right\}$$

If needed, $\mathbf{N}_j$ can be looked at as columns of the non-negative quantity matrix $[N]$, whose entry N_j^i represents the quantity of species i in region j.

2.2. Zonotopes and zonoids (convex sets of mixtures)

Taking advantage of the vector space structure of E, we define a geometric operation on sets. The Minkowski sum of sets A and B is the set

$$A + B = \{\mathbf{M} + \mathbf{N} \,|\, \mathbf{M} \in A, \mathbf{N} \in B, A, B \subset E\} \tag{3}$$

with E considered as an affine (point) space.

To a quantity vector $\mathbf{N}$ we associate, in a straightforward way, a segment denoted $[0,N]$ or $\mathbf{N}$ for short, with $\mathbf{N} = \{\lambda \mathbf{N} \,|\, \lambda \in [0,1], \mathbf{N} \in E\}$. Here E is considered as a vector space.

Definition (Coxeter [6,7])

A zonotope Z is the Minkowski sum of a finite set (family) of segments of E:

$$\mathbf{Z} = \sum_{j=1}^{p} [0, \mathbf{N}_j]$$

Simple examples of zonotopes (zonohedra if $n = 3$) are a parallelogram, plane polygon with central symmetry, cube and parallelepiped.

Theorem 1
A zonoid Z is the limit (norm L_1, Hausdorff distance on the set of conpact convex polytopes induced by norm L_1 on E) of a convergent sequence of zonotopes.

Examples of zonoids are a circle, closed plane curve with central symmetry, sphere and ellipsoid.

Let $\mathbf{Z}$ be the closed set of n-dimensional zonoids. In fact, if $\mathbf{K}$ is the set of zonotopes in E, $\mathbf{Z}$ is the closure of $\mathbf{K}$.

2.2.1. Projections
Any partition of a base of E in two subsets and their spanned subspaces V, $V^\perp$, defines a canonical projection in E, that is, a projection parallel to $V^\perp$ onto V. The projected object inherits the indexes of base of V, *e.g.*, if $V = $ linear span $(\mathbf{e}_1, \mathbf{e}_2)$ then Z_{12} is the projection of Z onto $V^\perp = $ linear span $(\mathbf{e}_3)$.

Theorem 2
The image of a zonoid $Z\{\mathscr{F}\}$ by a linear transformation T (*e.g.*, projection), $T(Z)$, is the zonoid generated by the transformed family $T\mathscr{F}$, *i.e.*,

$$T(Z\{\mathscr{F}\}) = Z\{T(\mathscr{F})\} \tag{4}$$

Definition
The separation content Z of a system state Σ of system $\mathscr{S}$ is as follows:
for a discrete system state with p vectors, the zonotope

$$Z\{\mathbf{N}_1, \mathbf{N}_2, ..., \mathbf{N}_p\} = \left\{\mathbf{M} \in E \,|\, \mathbf{M} = \sum_{j=1}^{p} \lambda^j \mathbf{N}_j, \lambda^j \in [0,1], j = (1, ..., p)\right\} \tag{5}$$

for a diffuse system, the zonoid

$$Z\{\mathbf{F}(t)\mathrm{d}t\}_{\varDelta t} = \left\{\mathbf{M} \in E \,|\, \mathbf{M} = \int_{\varDelta t} \lambda(t)\mathbf{F}(t)\mathrm{d}t, \lambda \in [0,1]\right\} \tag{6}$$

$\lambda(t)$, called the sampling function, is a measurable function of t on $\varDelta t$.

If Σ is a discrete (diffuse) system state, its separation content $Z(\Sigma)$ is a zonotope (or zonoid) said to be generated by the discrete (or differential) family of quantity vectors. In both cases, $Z(\Sigma)$ is defined as the set of mixtures feasible by sampling from Σ.

Liapunov's convexity theorem asserts that Z is convex and closed. The Krein–Milman theorem shows that we may take sampling functions λ (eqn. 6) in the smaller (included) set χ_ω, that is, we may restrain the sampling function to be characteristic functions without loss in possible mixtures. Therefore, eqn. 6 can be restated as the following theorem.

Theorem 3

Z is the range of the vector measure μ, whose density is $F(t)$ relative to the Lebesgue measure on Δt.

From theorem 3 we obtain the fundamental property of zonoids.

Theorem 4

A necessary and sufficient condition for $M \in E$ to be feasible by sampling from a family $\mathscr{F}$ is that M belongs to zonoid $Z\{\mathscr{F}\}$.

2.2.2. *Exterior product of vectors*

Define the exterior (or cross) product of two vectors $N_1, N_2 \in E = R^2$ as

$$N_1 \wedge N_2 = \text{Det}\,[N_1, N_2] = N_1^1 N_2^2 - N_1^2 N_2^1 \tag{7}$$

and for $n = 3$, $N_1, N_2 \in E = R^3$ is a vector (in a 3-D space denoted $\Lambda^2 E$)

$$(N_1 \wedge N_2)^k = = N_1^i N_2^j - N_1^j N_2^i, 1 \leqslant i < j \leqslant 3, i,j \neq k, k = 1,2,3 \tag{8}$$

If $N_1, N_2, N_3 \in E = R^3$, the exterior (or mixed) product is

$$N_1 \wedge N_2 \wedge N_3 = \text{Det}\,[N_1, N_2. N_3] \tag{9}$$

The properties of an exterior product generalize those of determinants.

2.2.3. *Regular selectivity*

Definition

A family of p vectors in 3-D space E has the 3-regular selectivity property iff its elements can be linearly ordered in such a way that

$$N_{j_1} \wedge N_{j_2} \wedge N_{j_3} \geqslant 0, \;\forall\; 1 \leqslant j_1 < j_2 < j_3 \leqslant p \tag{10}$$

Similarly, a 1-differential family has the 3-regular selectivity property if a regular parameter exists such that

$$F(s) \wedge F(t) \wedge F(u) \geqslant 0, \;\forall\; 0 \leqslant s < t < u \leqslant \Delta t \tag{11}$$

Theorem 5

If F is two times differentiable, a local requirement for 3-regular selectivity is that the Wronskian determinant $W(F)$ be non-negative:

$$W(F) = F(t) \wedge F'(t) \wedge F''(t) \geqslant 0, \;\forall\; 0 \leqslant t \leqslant \Delta t \tag{12}$$

Selectivity can be monitored directly from the graph γ of $x(t)$ in simplex Δ_2, as shown by the following theorem.

Theorem 6

Selectivity is 3-regular iff γ is convex.

Selectivity between species $i, j, i \neq j$, is 2-regular iff one of the equivalent properties holds for any straight line KQ, K the vertex of Δ_2 (extremity of e_k), $k \neq i, j$, Q on γ:

(i) KQ rotates uniformly when Q follows γ uniformly;

(ii) no line KQ has another point on γ than Q.

Definition

A 1-differential family of n species has totally regular selectivity iff it has r-regular selectivity for any $1 \leqslant r \leqslant n$.

For $n = 3$, a study of selectivity involves study of 2×2 minors of Wronskian matrix 12.

Definition (Karlin [13])

A function $f: R \to R^+$ is a Polya frequency (PF) function iff all minors of the matrix $n \times p$ of elements K_j^i, $K_j^i = f(y_j - x_i)$, are positive for any two finite linearly ordered sequences: $x_1 < x_2 < \ldots < x_n, y_1 < y_2 < \ldots < y_n$; f is a Polya frequency density if further it is integrable on R.

PF functions are stable by certain transformations:

(1) if $f(u)$ is PF, then $f(au + b)$ is PF, a, b given real numbers;

(2) if $f(u)$ is PF, $\psi(u)$ strictly increasing, then $f(\psi(u))$ is PF.

Theorem 6a

A family $F(t)$ such that $F^i = f(t - t_i)$, where f is a Polya frequency function, has totally regular selectivity.

These definitions generalize themselves to constant sign in eqns. 12. Note that selectivity is conserved for a family $\lambda(t) \mathscr{F}$, $\lambda \geqslant 0$, but not conserved in general linear operations.

2.2.4. Boundary of zonoids

Call ∂Z the boundary of zonoid Z and consider 3-D zonoids.

Lemma 6

Every tangent plane to Z is spanned by two vectors $F(t_1)$, $F(t_2)$, $t_1, t_2 \in [0, \Delta t]$.

Definition

A zone $L(t_1)$ is the set of points M on ∂Z, where the tangent (support) plane T_M contains direction of $F(t_1)$.

Theorem 7

$L(t_1)$ is a closed line and the set of tangent planes envelopes a cylinder whose generatrix is parallel to $F(t_1)$.

Theorem 8

In the case of 3-regular selectivity, ∂Z is split in two parts, ∂Z^+, ∂Z^- by the

cumulate curve. For ∂Z^+, called the "upper" (or "positive") part of ∂Z, we obtain a two-parameter expression of the surface:

$$\partial Z^+ : \mathbf{M}(t_1, t_2) = \int_0^{t_1} \mathbf{F}(\tau)d\tau + \int_{t_2}^{\Delta t} \mathbf{F}(\tau)d\tau, 0 \leqslant t_1 \leqslant t_2 \leqslant \Delta t \tag{13}$$

or

$$\partial Z^+ : \mathbf{M}(t_1, t_2) = \mathbf{N}_0 + \mathbf{N}(t_1) - \mathbf{N}(t_2), 0 \leqslant t_1 \leqslant t_2 \leqslant \Delta t$$

For the "lower" part, ∂Z^-, we obtain

$$\partial Z^- : \mathbf{M}(t_1, t_2) = \int_{t_1}^{t_2} \mathbf{F}(\tau)d\tau, 0 \leqslant t_1 \leqslant t_2 \leqslant \Delta t \tag{14}$$

Clearly points $\mathbf{M}$ with same arguments in eqns. 13 and 14 are antipodal (*i.e.*, they sum to $\mathbf{N}_0$) in line with central symmetry of Z.

In the general case we obtain an equation for any point on ∂Z^+:

$$\partial Z^+ : \mathbf{M}(t_1, t_2) = \int_{\omega^+(t_1, t_2)} \mathbf{F}(\tau)d\tau, 0 \leqslant t_1 < t_2 \leqslant \Delta t$$

$$\tag{15}$$

$$\omega^+(t_1, t_2) = \{\tau \in [0, \Delta t] \,|\, \mathbf{F}(t_1) \wedge \mathbf{F}(t_2) \wedge \mathbf{F}(\tau) \geqslant 0\}$$

where the integration domain is defined by the solution of a (non-linear) equation.

2.2.5. n-Volume of zonoids

Ξ, the volume of the n-dimensional body Z, provides a numerical value (in fact, an antisymmetric tensor) for separation, called the n-volume of separation. If one considers a separation between a subset of species, *e.g.*, 1, 2, the volume is labelled accordingly, Ξ_{12}.

The differential volume element is, for a 2-d zonoid,

$$d\Xi = |\mathbf{F}(s) \wedge \mathbf{F}(t)| dsdt$$

where we may drop the absolute value if

$$\mathbf{F}(s) \wedge \mathbf{F}(t) \geqslant 0, 0 \leqslant s < t \leqslant \Delta t$$

Theorem 9

The 2-volume of separation of the differential family **F** is given by

$$\Xi = \iint\limits_{0 \leqslant s < t \leqslant \Delta t} |\mathbf{F}(s) \wedge \mathbf{F}(t)| \, \mathrm{d}s \mathrm{d}t \tag{16}$$

In this case, multi-linearity of the exterior product gives, through integration, if selectivity is 2-regular:

$$\Xi = \int\limits_{0 \leqslant t \leqslant \Delta t} \mathbf{N}(t) \wedge \mathbf{F}(t) \mathrm{d}t \tag{17}$$

with cumulate vector $\mathbf{N}(t)$, defined as

$$\mathbf{N}(t) = \int\limits_0^t \mathbf{F}(s) \mathrm{d}s$$

Note that eqn. 17 is a classical expression for signed area (seen from the origin) generated by a plane curve given by parametric equations.

These equations extend readily to zonotopes and zonoids in spaces of higher dimension (compare eqns. 16 and 19).

In the discrete case, *i.e.*, for a 3-D zonotope, 3-volume is (from ref. 10)

$$\Xi = \sum_{1 \leqslant j_1 < j_2 < j_3 \leqslant p} |\mathbf{N}_{j_1} \wedge \mathbf{N}_{j_2} \wedge \mathbf{N}_{j_3}| \tag{18}$$

For a diffuse family, the equivalent of eqn. 18 is

$$\Xi = \iiint\limits_{0 \leqslant r < s < t \leqslant \Delta t} |\mathbf{F}(r) \wedge \mathbf{F}(s) \wedge \mathbf{F}(t)| \, \mathrm{d}r \mathrm{d}s \mathrm{d}t \tag{19}$$

2.3. Geometric comparison of separation contents

2.3.1. The existence ordering

Definition

A discrete system state Σ represented by family $\mathscr{F} = \{\mathbf{N}_j | j \in J\}$ is said to contain a greater separation than system state Σ', or $\mathscr{F}' = \{\mathbf{M}_k | k \in K\}$ iff family $\mathscr{F}'$ can be made by sampling from family $\mathscr{F}$, that is, iff a $J \times K$ matrix $[\mu]$ exists such as

$$\mathbf{M}_k = \sum_{j \in J} \mu_k^j \mathbf{N}_j, \, k \in K \tag{20}$$

$$0 \leqslant \mu_k^j, \quad j \in J, \quad k \in K, \quad \sum_{k \in K} \mu_k^j = 1, \quad j \in J \tag{20a}$$

As $N_0 = \sum_{k \in K} \mathbf{M}_k = \sum_{j \in J} \mathbf{N}_j$, families $\mathscr{F}$ and $\mathscr{F}'$ have the same sum vector, and therefore we compare two states of an isolated system. If $n = 1$, we recover the rule of conservation of quantity.

For diffuse systems represented by 1-differential families, we make the following definition.

Definition
A system state (family):

$$\mathscr{F}_2 = \{\mathbf{F}_2(\tau)\mathrm{d}\tau\}_{\tau \in [\tau_1, \tau_2] = I_2 \subset R}$$

has a greater separation content than a system state (family):

$$\mathscr{F}_1 = \{F_1(t)\mathrm{d}t\}_{t \in [t_1, t_2] = I_1 \subset R}$$

iff a non-negative function λ, called a sampling kernel, $\lambda: I_1 \times I_2 \to R^+$ exists such that

$$\mathbf{F}_1(t) = \int_{I_2} \lambda(t,\tau)\mathbf{F}_2(\tau)\mathrm{d}\tau, \; t \in I_1 \tag{21}$$

$$\int_{I_1} \lambda(t,\tau)\mathrm{d}t = 1, \; \tau \in I_2 \tag{21a}$$

Both eqns. 21 and 21a imply, through Fubini's theorem,

$$\int_{I_1} \mathbf{F}_1(t)\mathrm{d}t = \int_{I_2} \mathbf{F}_2(\tau)\mathrm{d}\tau = \mathbf{N}_0$$

Sampling kernels generalize sampling functions defined in eqn. 6.

Sampling kernels generate a partial order relation, called existence, on separation states or zonoids, *i.e.*, on $\mathbf{Z}$: one writes

$$Z(\Sigma') \prec Z(\Sigma) \tag{22}$$

and reads eqn. 22 as: separation state Σ' *exists* in separation state Σ. We have

$$Z(\Sigma') \prec Z(\Sigma) \text{ and } Z(\Sigma) \prec Z(\Sigma') \Rightarrow \Sigma = \Sigma'$$

By a theorem from Blackwell [12], if $\dim E = 2$, the existence order is equivalent to inclusion of zonoids, but is a stronger order in general.

The physical meaning of inequality 22 is that (the whole) system state Σ' can be made by sampling of system Σ.

As subtraction has no meaning for zonoids, we cannot simplify these as for scalar inequalities. However, we have a simplification property:

$$\text{If } Z' = Z'_1 + Z_2, Z = Z_1 + Z_2, \text{then } Z' \prec Z \Leftrightarrow Z'_1 \prec Z_1 \tag{23}$$

2.3.2. A classification of transformations

Definition

A transformation $T, \Sigma \to \Sigma' = T(\Sigma)$, occurring in a isolated system is qualified as:

a pure separation iff $(Z(T(\Sigma)) \prec Z(\Sigma)$, *i.e.*, separation content increases;
a pure mixing iff $(Z(\Sigma)) \prec Z(T(\Sigma))$, *i.e.*, separation content decreases;
a sepmix iff neither case holds, *i.e.*, separation contents are incomparable.

3. OVERALL SEPARATION BALANCE IN CHROMATOGRAPHY

Our primary interest will be in the overall separation balance and we shall not attempt here to go to the root of the process and discover how the separation evolution is governed by partial differential equations of propagation themselves, together with their initial and boundary conditions and their thermodynamic constraints.

3.1. Identification of flow families

The separation of two species by chromatography is basically a ternary process, as it involves necessarily some spending of a third species called carrier: space E of quantities is three-dimensional, $\dim E = 3$.

A natural base for E is formed on unit quantity of each pure species, *e.g.*, axes will be labelled in moles of species 1, 2 (solutes), 3, carrier. In this base we associate, for any mixture of carrier and solutes, a vector of components (N^1, N^2, N^3). Note the superscript species label. A formal distinction is that species will be all chemical components injected into the column and solutes will be only those one wishes to analyse or separate. We make the convention that solutes are numbered by increasing retention times and the carrier is put as the last species.

The composition of a mixture is now expressed by a molar fraction vector x and associate point in Δ_2, the molar fraction simplex.

From this point on, we shall use consistently notations linked with the physical nature of the represented entity: **F** for a (vector) flow of species, **N** for a (vector) quantity of species, **x** for a (vector) molar fraction.

A (hypothetical) selective detector placed at a fixed point on the abscissa z in the chromatographic column would record a chromatogram of concentrations of solutes in the mobile phase (and, consequently, flow-rates), from which we calculate the coefficient function **F** of 1-differential family of quantities:

$$\mathbf{F}(z,t) = (F^1(z,t), F^2(z,t), F^3(z,t)), \quad t \in \Delta t, \quad z \in R$$

Carrier flow is usually calculated by difference, from

$$F^3(z,t) = F^0(z,t) - F^1(z,t) - F^2(z,t)$$

where $F^0(z,t)$ is the total molar flow-rate, assumed to be known or to be measured.

A family is denoted $\mathscr{F}(z) = \{\mathbf{F}(z,t)dt\}_{t \in \Delta t}$

Alternatively, one may obtain a family by simulation through a differential model of the propagation involving a balance equation for all species, a necessity when only the sum $F^1(z,t) + F^2(z,t)$ is the one physical quantity that can be monitored.

Clearly we obtain a *diffuse* system (except at $z = 0$), as components of F, flow of species through the section of a column at abscissa z, are smooth functions.

3.2. Parameters and intervals

The natural parameter t of the family is time and the evolution problem has parameter z, abscissa in the column.

In principle, owing to the nature of diffusion, the cycle or interval of time of collection $\Delta t(z)$ (and therefore carrier quantity and zonoids) is unbounded. To avoid mathematical complications, we shall often consider that essentially all the injected feed is recovered in a finite time interval called a cycle, a good assumption since for all of our models, the solute i flow ($i = 1, 2$) will follow Gaussian or near Gaussian laws centred at $\bar{t}_i$, with variance σ_i^2. For rigorous study, we must take $\Delta t = (-\infty, +\infty)$. However, for most practical purposes

$$\Delta t = [\bar{t}_1 - 3\sigma_1, \bar{t}_2 + 3\sigma_2] \tag{24}$$

or

$$\Delta t = [0, \bar{t}_2 + 3\sigma_2] \tag{24a}$$

will be appropriate. In the last case we shall slightly abuse the notation by confusing the interval Δt with its upper bound. For an isovariant case, eqn. 24 defines an interval $6\sigma + \bar{t}_2 - \bar{t}_1$ centred on the mid-point between peak maxima.

A column is of bounded length L, so that we may put $0 \leqslant z \leqslant L$.

The system state is obtained from observation of flow-rates given by a detector located at z as a function of time, during time interval Δt. Passing to space of quantities E is straightforward since $dN(z,t) = \mathbf{F}(z,t)dt$ represents formally the (infinitesimal) quantity that would be collected in the mobile phase between t and $t + dt$ at z in the column.

A parallel theory could have been developed, reversing z and t, using lineic concentrations instead of flows, *i.e.*, considering the system (state) Σ as the content of a volume Ω of the column with the problem of evolution in time. However, it would be less natural for the present application.

Although flows are the more natural variables, we may also consider chromatography as a spatial process and, in a sense, this must always be ultimately so, thinking as if elements of the family were in different regions (or tanks), the produced family $\{\mathbf{F}(z,t)dt\}_{t \in \Delta t}$ going into a fraction collector which collects during a time interval dt

flow vector $F(z,t)$ passing through point z into a differential (volumic) region of volume dV, whose content has concentration $C(z,V)$. As we have

$$\{F(z,t)dt\}_{t \in \Delta t} = \{C(z,V)dV\}_{V \in \Delta V} \text{ with } dV = Qdt$$

this new family results from the flow family by a simple change of parameter and use of a chain rule and therefore is completely equivalent to it.

In elution chromatography, an inlet (discrete) family consists of two vectors:

$$\mathscr{F}(0) = \left\{ \begin{bmatrix} N_0^1 \\ N_0^2 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ F_0^3 \Delta t \end{bmatrix} \right\}$$

the former being the quantity of feed and the latter the quantity of pure carrier taken in by the column during the cycle time, taking the flow of carrier as $F^3(z,t) = F_0^3 =$ constant. The outlet family produced by the column is $\mathscr{F}(L) = \{F(L,t)dt\}_{t \in \Delta t}$. The overall species balance imposes that these two families acquire the same sum vector, at least to a reasonable approximation. However, the flow-rate of carrier F_0^3 must be such that solutes are sufficiently diluted in the column so that hypotheses of the model hold. In practice, taking in account the cycle time given by eqn. 24, this will impose a minimum quantity of carrier N_0^3. Using the simplification property given in eqn. 23, we see that any quantity of virtually pure carrier recovered at the column outlet can be "subtracted" from the pure carrier vector in the inlet family. This allows the minimum cycle time to be taken.

Fig. 1 shows chromatograms, the starting point of our investigation.

3.3. Problem of evolution

We identify now the problem of evolution: clearly we are interested in comparing separation states of flow families for increasing values of z, length along column and, especially, initial (inlet) and final (outlet) flow families. The inlet zonoid is generated by the (differential) family of inlet quantity vectors in the cycle and the outlet zonoid is
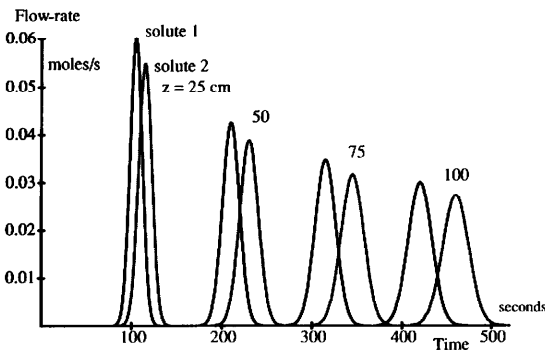

Fig. 1. Chromatograms at different locations in the column. $L = 25, 50, 75, 100$ cm. Conditions: HETP $= 0.1$ cm; $u = 5$ cm/s; $k^1 = 20$; $k^2 = 22$; $\alpha = 1.10$; quantity injected per cycle, 1, 1, 26 mol; carrier flow-rate, 0.2 mol/s; cycle time, $\Delta t = 130$ s.

generated by the family of outlet quantity vectors. From species conversion, these two zonoids have the same sum vector.

In other words, a cycle transforms a system state Σ into a system state Σ'. From this point of view, the inlet (or outlet) family can also be called the initial (or final) family.

For theoretical and design purposes, the evolution of a zonoid together with all of its canonical projections has to be considered, *i.e.*, projections on planes of coordinates (1,2), (2,3), (2,3), which indicate the binary separation evolution between solutes or a solute and the carrier. Note also that separation between linear combinations of species can be considered, *e.g.*, separation between carrier and total flow of solutes (1,2) will be monitored in the vertical bisector plane.

The above material is all we need in order to assess and compare, in two and three dimensions, separation states.

However, two intermediate geometric tools will be useful, namely, graph Γ of cumulated quantities, in E, for the construction of a zonoid, and, graph γ of molar fractions function, in Δ_2, for the study of selectivity.

3.4. Graph Γ of cumulated quantities

By time integration of $F(z,t)$ as shown in eqn. 2, from $\tau = 0$ to $\tau = t$, we obtain the cumulate family, $N(z,t)$, which is shown for $z = 25$ in Fig. 2.

As a one-dimensional "object", Γ, the graph of $N(t)$, is a skewed curve (Fig. 2) and bears no evident connection with the three-dimensional zonoid Z it generates. When t increases, point N goes from the origin towards the distal point on Γ. Although it is clear that Γ belongs to Z, there is no guarantee that it belongs to ∂Z. Hence one needs either some algorithm to calculate and represent the zonoid from experimental data, or some equation to obtain the boundary if the model is known. Such an algorithm is currently under development. Here we adopt the second approach as equations are simple to conceive and implement, at least for some simple models considered below.

Remark
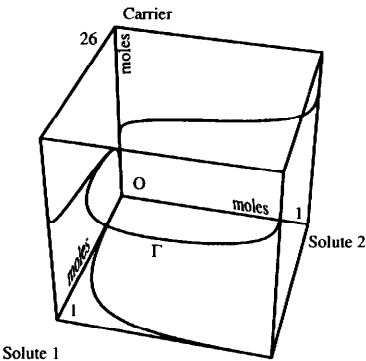In all 3-D drawings of zonoids or simplexes, the orientation will always be the

Fig. 2. Graph of cumulated quantity vector $N(t)$ with canonical projections. $z = 25$ cm; $F_0^3 = 0.2$ mol/s.
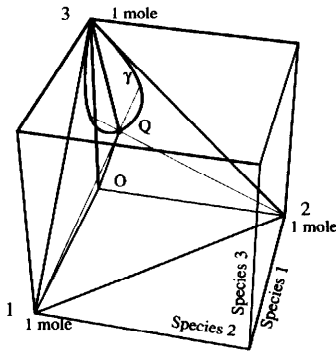
Fig. 3. Evolution of the composition $x(t)$ in Δ_2. Conditions as in Fig. 1, $L = 25$ cm.

same, namely with the origin at the lower, back and left vertex, with the species 1 (the less retained) axis pointing towards the front, the species 2 axis horizontal parallel to the plane of the drawing and the carrier axis vertical parallel to the plane of the drawing. The cube is assumed to be transparent and the vertical scale has been contracted by a factor of 26.

3.5. Graph γ of molar fractions family

Evolution of the composition [molar fraction vector, $x(t)$] of the outlet flow is represented by a curve $\gamma(t)$ in the molar fraction simplex Δ_2 on a cycle (Fig. 3). This curve belongs also to the hodograph cone of Γ (the set of rays starting at the origin, parallel to a tangent vector to Γ).

γ is a closed curve in Δ_2 if t is allowed to vary from $-\infty$ to $+\infty$. Note that γ is "nearly closed", *i.e.*, on most practical grounds if Δt is given by eqn. 24. In our convention that species 1 is less retained than species 2, point x rotates counterclockwise when t increases.

4. LINEAR MODELS OF CHROMATOGRAPHY

We shall consider two types of linear models of propagation of elution bands into the column. For ease of interpretation in zonoid theory, these models are written (a rather unusual feature) in terms of flow-rates, but they could be transformed easily into concentrations, since $C^i = QF^i$.

4.1. Basic hypotheses

Strong hypotheses are made to arrive at an explicit solution of the propagation model of chromatography.

By linearity of a process we mean that a linear combination of injection functions $\mathbf{F}^1(0,t)$, $\mathbf{F}^2(0,t)$ with positive coefficients a, b produces the same linear combination of outlet flow-rates function $\mathbf{F}^1(z,t)$, $\mathbf{F}^2(z,t)$:

$$a\mathbf{F}^1(0,t) + b\mathbf{F}^2(0,t) \text{ gives } a\mathbf{F}^1(z,t) + b\mathbf{F}^2(z,t) \quad \forall z \in R^+$$

Linearity allows us to normalize quantities of species, as zonoids will transform themselves by linearity and n-volumes will be multiplied by an appropriate scalar quantity. Therefore, a yield of 3-volume can be defined as

$$\zeta = \frac{\Xi}{N_0^1 N_0^2 N_0^3} \tag{25}$$

where $N_0^1 N_0^2 N_0^3$ represents the 3-volume of total separation between species.

The linearity hypothesis involves high dilution both in the stationary phase, *i.e.*, constant partition coefficients and the assumption of a small injection of solutes, both in quantity and in injection time, into the carrier (superscript 3). Then, we have

$$F^3(z,t) = F^0 - F^1(z,t) - F^2(z,t) \approx F^0 \tag{26}$$

where F^0, the flow-rate at the column inlet, is a known constant. In the following we admit also that the carrier is not adsorbed or absorbed on the stationary phase.

Anyway, this assumption is not necessary since a differential family with coordinate functions (F^1, F^2, F^0) results from (F^1, F^2, F^3) by a linear transformation, and the results upon separation can therefore be transposed immediately (Theorem 2) from one family to the other.

The solution of the balance equation of species, in the form of Partial Differential Equations in the case of superimposition of diffusion upon a plug flow (with suitable limit conditions), or of a discrete model of the column in the form of Ordinary Differential Equations (the plate model), leads in the former instance to an (approximate) Gaussian and in the latter to a Poisson distribution of flow-rate of a solute; see, *e.g.*, Villermaux [14] for a comparison of these models. From the central limit theorem in probability theory, both of them are asymptotically identical, that is, when the number of plates or, equivalently, the length of column approach infinity, a result which allows both of them to be expressed with the same parameters.

Hence parameters of the plate model, more acceptable to chromatographers, will be used throughout: a column is equivalent to N perfectly agitated vessels called theoretical plates, set in series. On the above asymptotic common solution, N and D, the dispersion coefficient (supposed to be identical for all the species), are related by

$$\text{HETP} = \frac{L}{N} = \frac{2D}{u} \tag{27}$$

where HETP (denoted H) is the height equivalent to a theoretical plate and u is the linear flow-rate of the carrier. σ_i, the standard deviation of the Gaussian distribution of the flow-rate (as a function of time), depends on the mean residence time $\bar{t}_i$ of solute i:

$$\sigma_i = \frac{\bar{t}_i}{\sqrt{N}} \tag{28}$$

Of course, more realistic expressions for H *vs.* u could be used, taking account different contributions to dispersion.

As $z = NH$, $\bar{t}_i$ at location z is given by

$$\bar{t}_i = \frac{z}{u}(1 + k^i) \approx \frac{(1 + k^i)NH}{u} \tag{29}$$

Although in the following, for the sake of simplicity, we adopt the "no pressure drop" hypothesis, such a requirement could be relaxed as far as separation between species is concerned. In the case of a moderate pressure drop, and for a carrier following the law of perfect gases, flow vectors do not depend explicity on pressure p, a distinct advantage of the present formulation, and we have simply to take into account the dependence of p and u on z. By straight integration of Darcy's law we obtain

$$u(z)p(z) = u(L), \quad p(0) = P, \quad p(L) = 1, \quad p^2 = P^2 - \frac{z}{L}(P^2 - 1)$$

which, by integration of eqn. 29, written in a differential form relating dz and $d\bar{t}_i$, gives the dependence of retention time on pressure:

$$\bar{t}_i = \frac{2}{3} \cdot \frac{P^3 - p^3}{P^2 - 1} \cdot \frac{1}{Lu(L)}(1 + k^i)$$

Similarly, eqn. 27 for the mean HETP (H) should be modified to

$$H = \frac{9}{8} \cdot \frac{(P^4 - p^4)(P^2 - 1)}{(P^3 - p^3)^2} \cdot \frac{2D(L)}{u(L)}$$

A complete study of separation would, however, take into account another conserved quantity, namely momentum, but, although feasible in principle, this would complicate the study tremendously.

4.2. Three linear models

4.2.1. Model I, asymptotic Gaussian
From the well known equation for Gaussian peaks, valid for a pulse injection of a small quantity of mixture into a column of infinite length (at both ends), we may deduce, using a staged model, asymptotically valid, i.e., for $N \to +\infty$, the following expression for the flow-rate of solute i:

$$F^i(N,t) = N_0^i \frac{\sqrt{N}}{\sqrt{2\pi t_i}} e^{-\frac{1}{2}N\left(1 - \frac{t}{\bar{t}_i}\right)^2}, \quad t \in R, \quad i = 1,2 \tag{30}$$

(note that in a strict sense, eqn. 30 cannot be valid for $t < 0$, as it would violate the principle of causality). $\bar{t}_i$ is equal to the retention time of the maximum of the peak.

4.2.2. Model II, Gaussian, isovariance assumption
For computational simplicity, and as interest in chromatography focuses mainly

on difficult separations, that is with differences between retention times much lower than the retention times themselves, we may assume that σ_i in eqn. 28 depends not on i, but on some mean retention time for the group of solutes. Physically, this means that although the two peaks translate at different speeds, they enlarge at the same rate, depending on z or N but not on the species. The injected quantity of species acts only through a vertical affinity on the peak. We shall set (although other mean values could be chosen)

$$\bar{t} = \frac{1}{2}(\bar{t}_1 + \bar{t}_2)$$

From eqn. 28, we obtain (isovariance assumption)

$$\bar{\sigma} = \frac{\bar{t}}{\sqrt{N}} = \frac{(\bar{t}_1 + \bar{t}_2)}{2\sqrt{N}} \tag{31}$$

Therefore, the flow-rate vector for solutes becomes

$$F^i(N,t) = N_0^i \frac{\sqrt{N}}{\sqrt{2\pi t}} e^{-\frac{1}{2}N\left(\frac{\bar{t}_i - t}{\bar{t}}\right)^2}, \quad i = 1,2 \tag{32}$$

4.2.3. Model III, Poisson

The final linear model considered is the plate model, a classical one in chemical engineering, the solution of which can also be derived by a probabilistic argument assuming for each species an independent Poisson law with parameter λ_i. Let $P(N,\lambda)$ be the probability for a molecule of given λ to be at stage N:

$$P(N,\lambda) = \frac{1}{N!} e^{-\lambda} \lambda^N \tag{33}$$

Parameter λ_i, depending on the species i, is

$$\lambda_i = \frac{u}{(1 + k^i)H} = \frac{N}{\bar{t}_i}$$

is the mean number of plates "seen" by a molecule of species i during the unit time interval if the molecules distribute themselves randomly upon the $t \geqslant 0$ axis. By replacement of λ_i with its above value, multiplied by t, the flow-rate vector acquires the form

$$F^i(N,t) = N_0^i \frac{N}{\Gamma(N)\bar{t}_i} e^{-\frac{Nt}{\bar{t}_i}} \left(\frac{Nt}{\bar{t}_i}\right)^{N-1}, \quad t \in R^+, \quad i = 1,2 \tag{34}$$

where we have extended to real (rather than integer) values of N using $\Gamma(N)$, the gamma function (recall $\Gamma(N) = (N - 1)!$ if N is an integer). For $t < 0$, $F^i(N,t) = 0$.

Note that if N is an integer, eqn. 34 is the solution for a Dirac injection at time $t = 0$ into the first cell of a series of N perfectly agitated cells (modelled by a system of ordinary differential equations). Therefore, the results of model III will be valid for a larger class of separation processes than chromatography, *e.g.*, liquid–liquid extraction.

All families resulting from these models are summarized in Table 1. According to our conventions, **F** is the flow-rate family and N is the quantity (cumulated starting from the initial time of the cycle). The following definition has been used:

$$N(u) = \mathrm{erf}(u) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{u} e^{-\frac{t^2}{2}} \, dt \tag{35}$$

Eqn. 35 is slightly different from the other definition of error function often used, *i.e.*,

$$\mathrm{Erf}(u) = \frac{2}{\sqrt{\pi}} \int_{0}^{u} e^{-t^2} \, dt$$

We have: $\mathrm{erf} = {}^1\!/_2(\mathrm{Erf} + 1)$.

The incomplete gamma function $\gamma(a,u)$ is defined as usual by

$$\gamma(a,u) = \int_{0}^{u} t^{a-1} e^{-t} \, dt, \, a > 0$$

$W(\mathbf{F})$ are the corresponding (Wronskian) matrices, *i.e.*, lines of the matrix are for species 1, 2, 3 and columns for time derivatives of order 0, 1, 2 of **F**.

4.3. A qualitative study of zonoids evolution

Unless specified otherwise, we shall use the Gaussian model I although other models would give similar results, except for some details. That we may study a 1-differential family and zonoid independently of the quantity and composition of injected mixture can be deduced from the following.

From linearity, **F**, or the 1-differential, family is proportional to the corresponding coordinate of $\mathbf{N_0}$, that is, the zonoid obtained from injected vector $\mathbf{N_0}$ is deduced from the zonoid calculated for the mixture (1,1,1) by the product of affinities N_0^i along axes e_i ($i = 1,2,3$). Also, canonical projection (1,2) does not depend on the dilution of the injection in the carrier, as long as injection time is short.

The curve $\Gamma = \mathbf{N}(t)$, as the primary ingredient for the zonoid construction, is drawn in Fig. 2. Direct examination of Γ and its projections on base planes reveals that the vertical projection of Γ on the ground plane (1,2) is convex, but projections on planes (1,3) and (2,3) are not. It suffices to note here that a plane arc of curve generates a two-dimensional zonoid and bounds it if the arc is convex. Therefore, canonical projection of Γ on the ground plane shows directly the projection of the 3-D zonoid.

Clearly there is a large difference between the separation of solutes 1 and 2 and

TABLE 1

FLOW-RATE VECTOR FUNCTION $\mathbf{F}(t)$ AND WRONSKIAN MATRIX

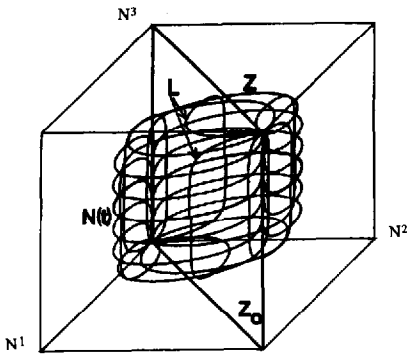| Model	$\mathbf{F}(N,t)\,dt$	$N(N,t)$	Wronskian matrix		
I	$N_0^1 \cdot \dfrac{\sqrt{N}}{\sqrt{2\pi \bar{t}_1}} \cdot e^{-\frac{N}{2}\left(1-\frac{t}{\bar{t}_1}\right)^2} dt$	$N_0^1 \mathrm{erf}\left(\sqrt{N}\cdot\dfrac{\bar{t}_1 - t}{\bar{t}_1}\right)$	1	$-\dfrac{t-\bar{t}_1}{\bar{t}_1^2}$	$\dfrac{1}{\bar{t}_1^2}\left\{N\left(\dfrac{t-\bar{t}_1}{\bar{t}_1}\right)^2 - 1\right\}$
	$N_0^2 \cdot \dfrac{\sqrt{N}}{\sqrt{2\pi \bar{t}_2}} \cdot e^{-\frac{N}{2}\left(1-\frac{t}{\bar{t}_2}\right)^2} dt$	$N_0^2 \mathrm{erf}\left(\sqrt{N}\cdot\dfrac{\bar{t}_2 - t}{\bar{t}_2}\right)$	1	$-\dfrac{t-\bar{t}_2}{\bar{t}_2^2}$	$\dfrac{1}{\bar{t}_2^2}\left\{N\left(\dfrac{t-\bar{t}_2}{\bar{t}_2}\right)^2 - 1\right\}$
	$F_0^3 dt$	$F_0^3 t$	1	0	0
II	$N_0^1 \cdot \dfrac{\sqrt{N}}{\sqrt{2\pi t}} \cdot e^{-\frac{N}{2}\left(\frac{\bar{t}_1 - t}{t}\right)^2} dt$	$N_0^1 \mathrm{erf}\left(\sqrt{N}\cdot\dfrac{\bar{t}_1 - t}{t}\right)$	1	$-(t-\bar{t}_1)$	$N\left(\dfrac{t-\bar{t}_1}{t}\right)^2 - 1$
	$N_0^2 \cdot \dfrac{\sqrt{N}}{\sqrt{2\pi t}} \cdot e^{-\frac{N}{2}\left(\frac{\bar{t}_2 - t}{t}\right)^2} dt$	$N_0^2 \mathrm{erf}\left(\sqrt{N}\cdot\dfrac{\bar{t}_2 - t}{t}\right)$	1	$-(t-\bar{t}_2)$	$N\left(\dfrac{t-\bar{t}_2}{t}\right)^2 - 1$
	$F_0^3 dt$	$F_0^3 t$	1	0	0
III	$N_0^1 \cdot \dfrac{N}{\Gamma(N)\bar{t}_1} \cdot e^{-\frac{Nt}{\bar{t}_1}} \cdot \left(\dfrac{Nt}{\bar{t}_1}\right)^{N-1} dt$	$N_0^1 \cdot \dfrac{\gamma\left(N,\frac{Nt}{\bar{t}_1}\right)}{\Gamma(N)}$	1	$-\dfrac{N}{\bar{t}_1} + \dfrac{N-1}{t}$	$\dfrac{N^2}{\bar{t}_1^2} - 2\cdot\dfrac{N}{\bar{t}_1}\cdot\dfrac{N-1}{t} + \dfrac{(N-1)(N-2)}{t^2}$
	$N_0^2 \cdot \dfrac{N}{\Gamma(N)\bar{t}_2} \cdot e^{-\frac{Nt}{\bar{t}_2}} \cdot \left(\dfrac{Nt}{\bar{t}_2}\right)^{N-1} dt$	$N_0^2 \cdot \dfrac{\gamma\left(N,\frac{Nt}{\bar{t}_2}\right)}{\Gamma(N)}$	1	$-\dfrac{N}{\bar{t}_2} + \dfrac{N-1}{t}$	$\dfrac{N^2}{\bar{t}_2^2} - 2\cdot\dfrac{N}{\bar{t}_2}\cdot\dfrac{N-1}{t} + \dfrac{(N-1)(N-2)}{t^2}$
	$F_0^3 dt$	$F_0^3 t$	1	0	0

Fig. 4. Injected and recovered 3-d zonoids. Two solutes + carrier; Gaussian model; $z = 25$ cm.

separation of the carrier with solute 1 or solute 2. We shall consider the meaning and significance of convexity in Section 5.5, under the heading "Selectivity" at the end of this section. A quantitative study of the growth and decrease or increase in separation in three-dimensional space and in ground planes will be given in Section 7.

We wish now to acquire some visual grasp of the 3-D zonoid itself, that is, we want to draw its boundary. Although different shapes of the boundary of the zonoid are possible, the simplest type of lines covering Z is provided by zonal lines or zones. Let us postpone the construction of such lines and suppose here that we have constructed a set of such lines.

We are in position to "see" the 3-D separation balance defined in Section 4. Recall the fundamental property of zonoids: M is feasible by mixing from the effluent of the column iff it belongs to Z.

The initial or injected zonoid, Z_0 (Fig. 4), is a vertical parallelogram constructed on the vectors $(1, 1, 0)$ and $(0, 0, 26)$. The final or outlet zonoid, Z, may be drawn as a slanted ovoidal box: the quasi-vertical part of Z corresponds to almost pure carrier (part in front, part to the rear of the peaks), and the top and bottom correspond to an effective separation between solutes.

Clearly zonoids Z_0 and Z intersect themselves (in the sense that they have common points although none is contained in the other), a general fact of great importance in view of the fundamental property of CSM: more precisely, mixtures $M \in Z$, $M \notin Z_0$, feasible from the final separation state are not feasible from the initial state because they do not have the initial composition in solutes and conversely, mixtures $M \notin Z$, $M \in Z_0$ feasible from the initial separation state are not feasible from the final state because they are too rich (or too poor) in carrier.

Finally, one may look at canonical projections of Z on coordinate planes, which of course are zonoids and therefore centrally symmetric convex sets (Fig. 5).

4.4. Drawing the boundary of a zonoid

We give a projective construction of zones using simplex Δ_2, which provides also a geometric rationale for eqns. 13–15.

Consider a plane Π_M passing through the origin. Π_M intersects simplex Δ_2 along
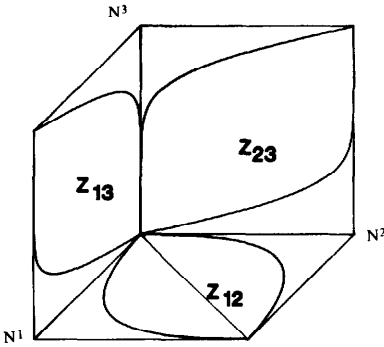
Fig. 5. Canonical projections of the zonoid Z on coordinate planes: Z_{12}, Z_{13}, Z_{23}. Conditions as in Fig. 4.

line PQ. Suppose P, Q are on γ, located at parameter values t_1, t_2, i.e., they have coordinates $\mathbf{x}(t_1)$, $\mathbf{x}(t_2)$. Therefore, Π_M is an oriented plane spanned by $\mathbf{F}(t_1)$, $\mathbf{F}(t_2)$.

As Z is convex, we associate to Π_M a pair of tangent (or, more generally, support) planes T_{M_1}, T_{M_2} with M_1, M_2 the contact point on ∂Z. Recall that domain of integration ω^+ for any point M on ∂Z is defined by a value τ such that eqn. 15 holds:

$$\mathbf{F}(t_1) \wedge \mathbf{F}(t_2) \wedge \mathbf{F}(\tau) \geqslant 0 \text{ or } \mathbf{x}(t_1) \wedge \mathbf{x}(t_2) \wedge \mathbf{x}(\tau) \geqslant 0 \tag{36}$$

Therefore, ω^+ is the set of the points of γ which are in the positive half simplex plane defined by PQ. ω^- would be defined symmetrically by inequalities $\leqslant 0$ in eqn. 36.

To generate zone $L(t_1)$ we just rotate line PQ in Δ_2 around fixed point P. We obtain two symmetrical points on the zone, M_1, $M_2 \in L(t_1)$ by integrating flow-rate family upon ω^+, ω^-. Now two cases arise:

(a) γ is a convex curve, i.e., selectivity is 3-regular: PQ has no other intersection point with γ. Letting $t = t_2$ vary, we obtain a parametric expression of zonal line $L(t_1)$ as the sum of the union of the two subfamilies:

$$\left\{ \{\mathbf{F}(\tau)d\tau\}_{\tau \in [0, t_1]} \cup \{\mathbf{F}(\tau)d\tau\}_{\tau \in [t, \Delta t]} \right\}$$

which is exactly eqn. 13. The first subfamily does not depend on t and its sum defines point $N(t_1)$ on the cumulate curve. When t varies, the sum vector of the second subfamily is just what is obtained by drawing, in the reverse order, this part of the initial family, going from Δt to t. The zonal line can be completed through symmetry about the centre of Z, or the above reasoning can be made, with $0 < t < t_1$ as the complementary subfamily defines the symmetrical part of $L(t_1)$.

(b) γ is not convex, i.e., selectivity is not 3-regular: the above construction has to be modified. For each position of line PQ one must look at all cut points of PQ with γ. If only one other than P exists, we obtain the same case as before and construct $M(t)$ accordingly. If more than one exists, e.g., of argument t_2, t_3, $M(t)$ is the sum of the union of all subfamilies whose elements point in the positive half-space defined by Π_M.

Indeed, γ need not to be a convex curve in Δ_2. In fact, convexity requires, as we

shall see in Section 5.5, $N \leqslant N_c$, where N_c is the critical number of plates, or, equivalently, $z \leqslant z_c$, where z_c is the critical abscissa in column.

Note the geometric rationale for eqn. 15: contact points M_1 or M_2 are attained when planes parallel to Π_M passing through M, the sum of any subfamily, cannot recede further from the origin. But the plane recedes or not on adding $F(\tau)d\tau$ to the subfamily according to the sign of the dot product $< \eta, F(\tau) >$, where η is the coefficient vector of plane Π_M. Now, in view of the well known fact that mixed product $F(t_1) \wedge F(t_2) \wedge F(\tau) = < \eta, F(\tau) >$, this amounts to including $F(\tau)dt$ in the subfamily according to the sign of the mixed product, which is exactly the meaning of eqn. 15.

Zones form a system of lines which cover ∂Z and do not intersect themselves, except trivially, at the origin and at S, the distal point of Z, and at two antipodal points. In Fig. 4, the shape of the zonoid corresponding to Fig. 1 is sketched, as a perspective view, by such zones. Each zone, such as L in Fig. 4, is defined by its starting point (and tangent vector) on Γ and therefore $\Gamma \in \partial Z$. It is smooth except at O, S and at points on Γ.

4.5. A study of 3-regular selectivity

One may note in Fig. 4 that every zone passes through O and $S = N_0$. Such a property is not guaranteed in general and results from what we have called the 3-regularity of the differential family. This is the first time that selectivity acquires an intrinsic (geometric) definition, that is, one independent of any model involving, e.g., affinity ratios. n-Regular selectivity (n-RS) is a rather intricate topic, but a crucial one in both

separation and zonoid theory. We leave a thorough study of selectivity for further work, noting only that one may conjecture that the "ordered" ion-exchange systems defined by Tondeur [15] exhibit n-RS [although not $(n + 1)$-RS, taking into account the carrier]. One could study also the "selectivity reversal" along the same lines. It will be more and more apparent that the properties of Z depend heavily on the convexity properties of the plane curve γ, in the molar simplex Δ_2 defined in Section 4. Here, we shall study selectivity from geometric, then algebraic, points of view and show how the loss of selectivity can be monitored directly on the chromatogram.

4.5.1. A general geometric condition

Selectivity can be monitored directly from γ in simplex Δ_2. Indeed, the physical meaning for 3-regular selectivity stems from Theorem 6:

Family $\mathscr{F} = \{F(t)dt\}_{t \in \Delta_t}$ is 3-regular iff $F(t)$ is extreme in $\mathscr{F}$, i.e., a mixture of composition $x(t)$ cannot be made by mixing from other elements of $\mathscr{F}$.

Therefore, in some way, each differential vector (or composition) delivered by a 3-regular process is "new". Looking at Fig. 3, we see that selectivity is 3-regular (or seems geometrically to be so). Taking each vertex of Δ_2 in turn we obtain that the selectivity between species 1, 2 is 2-regular: any $3Q$ line cuts the curve γ only once (from convexity of γ). In contrast, selectivity between species 1, 3 (or 2, 3) is not 2-regular: $2Q$ (or $1Q$) lines cut the curve γ (convex and closed) at two points.

It is now apparent that selectivity is not stable by projection. We may say that 3-regular selectivity reversal occurs at points (if any) where γ acquires an inflection tangent. However, selectivity (or, as we shall see, values of critical parameters for selectivity reversal) do not depend on the injected quantities of solutes as long as the model remains linear.
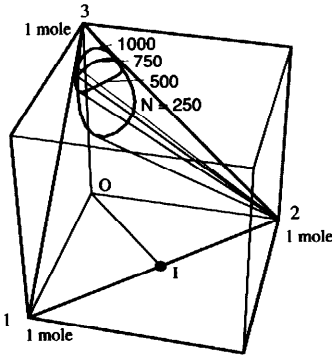
Fig. 6. Curves γ in Δ_2 in the case of 3-regular selectivity (N = 250), near 3-regular selectivity (N = 500) and non-3-regular selectivity (N = 750, 1000 plates).

To see the influence of the abscissa in the column on selectivity, the curves γ at different values of N are drawn in Fig. 6.

Notes

(1) The rule of decreasing maximum flow-rate (or concentration) of peaks on progressing along the column materializes into a monotonic rotation of tangents to γ around the vertices relative to pure species 1 or 2 in Fig. 6. γ shrinks to point 3 when N increases.

(2) The overall shape of γ depends on N: for $N \geqslant 500$, a depression appears on γ; γ is discontinuous for initial family $\mathscr{F}(0)$: it is composed of two points I, and vertex 3, which stresses the fact that the flow at the column inlet is not a smooth (and not even continuous) function of time.

4.5.2. An algebraic condition for 3-selectivity

The results will show the similarities and differences between models I, II and III. A study of the Wronskian matrix allows one to locate singularities in the plane of independent variables (N,t), for differential families (in the sense of 3-selectivity reversal), in terms of pairs (N_c, t_c), where N_c is the number of plates at which singularity occurs, t_c, the time of appearance, on the chromatogram taken at N_c.

$F(t)$ has continuous derivatives of any order, then, from Theorem 5, convexity of γ is equivalent to condition 13 involving the Wronskian matrix of the flow-rate $F^i(t)$, $i = 1,2,3$, $W(F)$ (in another context, see Karlin [13], Theorems 2-1 and 2-3).

Taking in turn matrices in the last column in Table 1 (where the maximum of possible factorization in lines or columns of (strictly) positive common terms comprising $F^1 F^2 F^0$ has already been made), we obtain, after expansion, the following.

The general idea is that, in view of the linearity in N of $W(F)$, we look for the maximum value of N such that $W(F)$ remains non-negative for all values of t. For different models, see the corresponding entries in Table 2.

Taking, for example, model II, selectivity is 3-regular iff $W(F) \geqslant 0$, *i.e.*,

$$N \leqslant N_c = \underset{t \in \,]t_1, t_2[}{\text{Max}} \left(\frac{-1}{\left(\dfrac{t}{t_1} - 1 \right)\left(\dfrac{t}{t_2} - 1 \right)} \right) \tag{37}$$

using linearity in N. Clearly, the product containing t in eqn. 37 is negative, and the minimum for $t = t_c$ with

$$t_c = \bar{t} = \frac{\bar{t}_2 + \bar{t}_1}{2} \tag{38}$$

Max is attained for t_c and leads to the following condition on N:

$$N_c = \frac{(\bar{t}_2 - \bar{t}_1)^2}{4\bar{t}^2} \tag{39}$$

We may rewrite the selectivity condition relevative to model II as a function of equilibrium parameters:

$$N \leqslant N_c = \left(\frac{\bar{t}_2 + \bar{t}_1}{\bar{t}_2 - \bar{t}_1}\right)^2 = \left(\frac{2 + k^1 + k^2}{k^2 - k^1}\right)^2 \approx \left(\frac{\alpha + 1}{\alpha - 1}\right)^2 \tag{39a}$$

Models I and III lead to a slightly more intricate Wronskian matrix and condition, but the method is similar and the results are given in Table 2.

Remarkably (see Table 2), N_c given by condition 39a appears to be model independent, *i.e.*, its value is the same for models I, II and III. However, the critical times t_c given in Table 2 differ slightly, reflecting the difference between the peak shapes in these models. A geometric interpretation will be given below.

Note that except for the leading factor $\bar{t}_2 - \bar{t}_1$ that is in line with the fact that $W(\mathbf{F})$ tends to 0 when α tends to 0 (solutes tend to be identical), $W(\mathbf{F})$ is, for all models, a second-degree polynomial in t, which means that γ will have two inflection points for $N > N_c$, the parameters of which are roots of these polynomials (see Fig. 6, case $N = 750$ and 1000).

Therefore, 3-regular selectivity inversion $N = N_c$ is just the condition for the existence of a "double" inflection point (*i.e.*, a point where the tangent has a contact of order 4) on γ and this point occurs at parameter t_c.

Under the conditions of Fig. 1, the formulae in Table 2 give for models I and III $N_c = 484$ plates and $t_c = 112$ s. With the isovariance assumption, $N_c = 484$ plates

TABLE 2

WRONSKIAN AND CRITICAL PARAMETERS

Model	$W(\mathbf{F})$	N_c	t_c
I	$N\left(\dfrac{t}{\bar{t}_1} - 1\right)\left(\dfrac{t}{\bar{t}_2} - 1\right)\left(\dfrac{t}{\bar{t}_1} + \dfrac{t}{\bar{t}_2} - 1\right) + 1$	$\left(\dfrac{\bar{t}_2 + \bar{t}_1}{\bar{t}_2 - \bar{t}_1}\right)^2$	$2 \cdot \dfrac{\bar{t}_1\,\bar{t}_2}{\bar{t}_2 + \bar{t}_1}$
II	$N\left(\dfrac{(t - \bar{t}_1)(t - \bar{t}_2)}{\bar{t}^2}\right) + 1$	$\left(\dfrac{\bar{t}_2 + \bar{t}_1}{\bar{t}_2 - \bar{t}_1}\right)^2$	$\dfrac{\bar{t}_2 + \bar{t}_1}{2}$
III	$Nt^2 - t(N - 1)(\bar{t}_2 + \bar{t}_1) - (N - 1)\bar{t}_2\bar{t}_1$	$\left(\dfrac{\bar{t}_2 + \bar{t}_1}{\bar{t}_2 - \bar{t}_1}\right)^2$	$2 \cdot \dfrac{\bar{t}_1\,\bar{t}_2}{\bar{t}_2 + \bar{t}_1}$

and $t = 110$ s, results not significantly different from the other (more rigorous) values. In any case, separation is far from complete at the critical number of plates.

If, for model I, II or III, the (unique) condition 39a is not fulfilled, *i.e.*, if the number of plates at the location of observation exceeds the critical number, γ is not convex and this introduces many complications in the study of zonoids and separation, including the fact that the volume of the zonoid must be computed as the integral of the absolute value of a function changing sign on a domain which may be intricate.

4.5.3. Comparing 2- and 3-selectivity for solutes

We may now compare algebraic conditions for 3- and 2-selectivity for solutes. In view of the constant carrier flow-rate, these two conditions involve only minors extracted from the two first lines of the Wronskian matrix relative to the model. Therefore, working on this sub-matrix gives all the information needed regarding selectivity for solutes.

For curve Γ_{12}, the canonical projection of the graph of $\mathbf{N}(t)$ into plane (1,2), *i.e.*, dropping the last coordinate in $\mathbf{N}$ and $\mathbf{F}$, 2-regular selectivity amounts to

$$\mathbf{N}'(t) \wedge \mathbf{N}''(t) = \mathbf{F}(t) \wedge \mathbf{F}'(t) > 0 \tag{40}$$

which simply means that the curvature vector always stands on the same side relative to the tangent vector, a classical condition for convexity.

It is clear that the 3-regular selectivity condition $W(\mathbf{F}) \geqslant 0$ reduces and implies, in the case of a constant total flow-rate, a higher order (stronger) condition on derivatives of flow of solutes only, namely

$$\mathbf{N}''(t) \wedge \mathbf{N}'''(t) = \mathbf{F}'(t) \wedge \mathbf{F}''(t) \geqslant 0 \tag{41}$$

These conditions are linked geometrically: if condition 42 is fulfilled, Γ_{12}, or the curve γ_{12} defined by $(F^1(t), F^2(t))$, in plane (1,2) is convex. The vertical translate of γ_{12} with length F^3 (which means dilution by a constant flow of carrier) defines a convex cone with apex O, the intersection of which with Δ_2 is γ. Therefore, γ must be convex in Δ_2: we recover the condition of constant sign for the Wronskian determinant in three dimensions.

4.5.4. Reading 3-selectivity condition on chromatogram

In practice, it is very easy to monitor the loss of 3-selectivity for model I, II or III (which is usually the one flow or concentration experimentally monitored). Indeed, a sufficient condition for following eqn. 42 to be satisfied as an equality at the limit of $t = t_c$

$$\mathbf{F}'(t_c) \wedge \mathbf{F}''(t_c) = 0 \tag{42}$$

is clearly $\mathbf{F}''(t_c) = 0$. As, in fact, $\mathbf{F}''$ depends on N, we simply obtain, for two solutes, two non-linear equations in two unknowns, t_c and N_c:

$$F^{1''}(t_c, N_c) = 0, \quad F^{2''}(t_c, N_c) = 0 \tag{43}$$

where derivatives are understood to be relative to t. Dimensionally, there is room for a solution of this system. Indeed, a solution of the system of eqn. 43 gives back those found through annulation of the Wronskian determinant.

A geometric interpretation of this result is the proposition that if inflection points on the chromatogram of solutes appear at the same time t at location x in the column, 3-selectivity reversal occurs at (x,t). Clearly this holds for any model with a constant flow of carrier. Therefore, any composition of injected quantities will satisfy eqn. 43 and especially $(F^1 + F^2)'' = 0$.

On the chromatogram of total flow-rate of solutes, $F^1 + F^2$, such a point of coincidence will correspond to a tangent of order 2 at the 3-regular selectivity reversal time, since clearly $(F^1 + F^2)'' = 0$. Further, in any linear model, the coincidence point will stay fixed for any composition (or quantity) of injected mixture.

For model II, at time t_c, the tangent will have a slope proportional to

$$-N_0^2 \cdot \frac{t - \bar{t}_2}{\bar{t}} - N_0^1 \cdot \frac{t - \bar{t}_1}{\bar{t}} \text{ or } (x_0^2 - x_0^1)\frac{t_c - \bar{t}_1}{\bar{t}} \text{ or } (x_0^2 - x_0^1)\frac{\bar{t}_2 - \bar{t}_1}{\bar{t}_2 + \bar{t}_1} \approx (x_0^2 - x_0^1)\frac{\alpha - 1}{\alpha + 1}$$

Therefore, half-way between the maxima of peaks, an inflection tangent begins to appear at 3-selectivity reversal on the total flow-rate $F^1 + F^2$ (Fig. 7; see Fig. 1 for chromatogram of individual species, especially the corresponding chromatograms for $z = 50$ cm, and conditions).

It should be noted that the simple expression of ∂Z in Section 4.4 as a parameterized surface does not hold true in the case of non-3-regular selectivity: some depressions would appear on the surface given by equation 13 which therefore could not be the boundary of a convex body.

The link with the bitangent line and the depression nascent between peaks and non-3-regular selectivity shows that the *loss of 3-regular selectivity is a necessary phenomenon to obtain a good separation*. This could be expected from the simplest translation model of rectangles, the study of which is left to the reader.

Hence the effect of diffusion is twofold: diffusion smooths out discontinuities in γ, and ensures a progressive shrinking of γ into vertex 3 of Δ_2 when z increases.

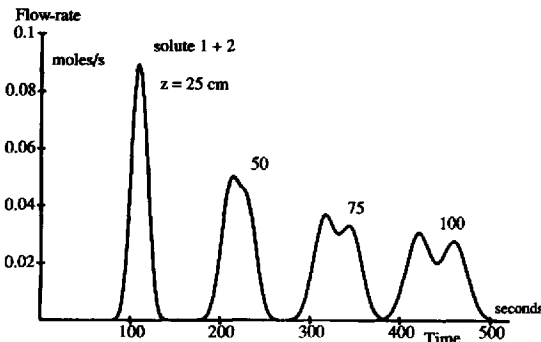We shall return to the study of zonoid projections and evolution in Section 6.

Fig. 7. Total flow-rate of solutes in the case of 3-regular selectivity ($z = 25$ cm), just after selectivity inversion ($z = 50$ cm), in the case of non-3-regular selectivity ($z = 75, 100$ cm).

4.6. Generalizations and comments

Canonical projections of zonoids give the separation state of subsets of species. The number of such canonical projections depends on n. For $n = 3$, we may group canonical projections into four subsets with (1 3 3 1) elements, that is, one 3-d zonoid (ternary separation), three 2-d zonoids (binary separations) and three 1-d zonoid (segments on the axes). Adding further the "dummy" 0-d zonoid, reduced to the origin point, we complete the variety of zonoids necessary to obtain a full picture of a ternary separation. It is significant that for 1-d zonoids, the separation balance reduces to a species balance; therefore, the latter appears as a special case (in one dimension) of the former.

This leads us to infer that, in general, the number of r-d zonoids to study for the separation of n species is the kth coefficient of the binomial expansion of nth order, which is indeed true. Hence there are $2^n - 1$ non-zero zonoids to study in the general case. These should be completed by the choice of appropriate projections or intersection with planes to fit special problems if needed.

Even in the simple models presented here, one finds complex features for selectivity, including changes along the column:

(1) 3-regular selectivity or not;
(2) absence of 2-selectivity between carrier and any solute;
(3) 2-selectivity between the two solutes.

Combined with the above comment, this gives a hint of how intricate and rich the study of separations can be for even a moderate number of species.

5. IS CHROMATOGRAPHY A SEPARATION PROCESS?

A quantitative (although not scalar) assessment of separation evolution in chromatography involves the evolution of zonoids "passing through" the abscissa z in the column, in addition to its canonical projections as a function of z.

The motivation for the study of projections comes from the following: a canonical projection has physical meaning; we neglect the content of species along which we project and consider only (partial) separation associated with remaining species. Therefore, although we are "interested" only in separation between solutes, we must consider in turn the three canonical projections of $Z(z)$, then the 3-d zonoid itself.

5.1. Separation between a solute and carrier

5.1.1. 2-Selectivity and convexification in the plane

The condition for 2-selectivity of separation of a solute i and a carrier is

$$\text{proj}_{i3}\mathbf{F}(t) \wedge \text{proj}_{i3}\mathbf{F}'(t) \geqslant 0$$

and the left-hand member is the corresponding minor on the Wronskian matrix $W(\mathbf{F})$. For model I, II or III, we obtain (see first two columns in square matrices, Table 1)

$$t_i - t \geqslant 0$$

Therefore, 2-selectivity reversal occurs at the maximum of the peak of the solute. As we consider only two species, we can apply the mixing convention (which would not be possible in three dimensions). That 2-selectivity between a solute and carrier is not regular could be anticipated by comparing projections of cumulated curves on planes (1,3) and (2,3) in Fig. 2 with corresponding projections of Z in Fig. 5.

Instead of a canonical projection of ∂Z to obtain, $e.g.$, ∂Z_{13}, we may construct ∂Z_{13} directly from the chromatogram of solute 1 in species 3 or from its cumulate curve C, using a method that we shall call convexification. Customizing eqn. 15 for 2-d space, we obtain

$$\partial \mathbf{Z}^+ : \mathbf{M}(t_1) = \int_{\omega^+(t_1)} \mathbf{F}(\tau) d\tau, \ 0 \leqslant t_1 \leqslant \Delta t$$

$$\omega^+(t_1) = \{\tau \in [0, \Delta t] \,|\, \mathbf{F}(t_1) \wedge \mathbf{F}(\tau) > 0\}$$

(44)

Eqn. 44 can be recast, using a new (reduced) family $\mathscr{F}^*$ obtained through use of the mixing convention on $\mathscr{F}$, both of these generating same separation state. Although in essence the mixing convention amounts on the chromatogram of the sum of the flow-rates at same molar ratio of species i to the carrier, care must be taken of the very nature of a 1-differential family (which contains dt). In the following, boundaries 0 and Δt are assumed to be taken such that the molar flow-rate of solutes are equal (and arbitrary near to zero).

Reduction of family $\mathscr{F}$

Let t_{max} be the retention time of the peak maximum and consider $\mathscr{F}$ as the union of two sub-families,

$$\mathscr{F} = \mathscr{F}_1 \cup \mathscr{F}_2, \mathscr{F}_1 = \{\mathbf{F}(t)dt\}_{t \in [0, t_{max}]}, \mathscr{F}_2 = \{\mathbf{F}(t')dt'\}_{t' \in [t_{max}, \Delta t]}$$

Given $t \in [0, t_{max}]$, we consider the solution $t' \in [t_{max}, \Delta t]$ of the equation

$$\mathbf{F}(t) \wedge \mathbf{F}(t') = 0$$

As $\mathbf{F}(t) = (F^1(t), F^3)$, and $F^3 = $ constant, this amounts to the scalar condition

$$F^1(t) = F^1(t')$$

For any "peaked model", this implicit equation defines a monotonically decreasing function $t' = f(t)$ of class C^1. We may therefore apply eqn. 1 for change of variable in $\mathscr{F}_2$, noting that $f^{-1}([t_{max}, \Delta t]) = [0, t_{max}]$, and we obtain

$$\mathscr{F}_2 = \left\{ -\mathbf{F} \circ \mathbf{f}(t) \frac{df}{dt} \cdot dt \right\}_{t \in [0, t_{max}]}$$

Owing to the definition of function f, $\mathbf{F} \circ f(t) = \mathbf{F}(t)$. Evaluation of the derivative is straightforward by use of the implicit function theorem

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\dfrac{\mathrm{d}F^{1}}{\mathrm{d}t}(t)}{\dfrac{\mathrm{d}F^{1}}{\mathrm{d}t}(t')}$$

Adding sub-families $\mathscr{F}_{1}$ and $\mathscr{F}_{2}$, which are now expressed with the same parameter t, we obtain identification

$$\mathbf{F}^{*}(t) = \mathbf{F}(t)\left(1 - \frac{\dfrac{\mathrm{d}F^{1}}{\mathrm{d}t}(t)}{\dfrac{\mathrm{d}F^{1}}{\mathrm{d}t}(t')} \right), \quad t \in [0, t_{\max}] \tag{45}$$

$\mathscr{F}^{*} = \{\mathbf{F}^{*}(t)\mathrm{d}t\}\, 0 \leqslant t \leqslant t_{\max}$ is called the reduced family and allows one to construct ∂Z_{i3} directly by drawing the cumulate curve of $\mathscr{F}^{*}$ through

$$\partial \mathbf{Z}^{+} : \mathbf{M}(t) = \int_{t}^{t_{\max}} \mathbf{F}^{*}(\tau)\mathrm{d}\tau, \ 0 \leqslant t \leqslant t_{\max} \tag{46}$$

$$\partial \mathbf{Z}^{-} : \mathbf{M}(t) = \int_{0}^{t} \mathbf{F}^{*}(\tau)\mathrm{d}\tau, \ 0 \leqslant t \leqslant t_{\max}$$

In the case when F^{i} is even (e.g., models I and II), symmetry around $t_{\max}$ implies $t' = 2t_{\max} - t$, and therefore eqn. 45 reduces to an explicit result: $\mathbf{F}^{*} = 2\mathbf{F}$. However, it is not so in more general cases (e.g., model III) and t' is, in general, not known explicitly.

Fig. 8 shows how points A and A' on cumulated curve C with parallel tangents map onto a unique point A^{*} on the convexified curve $C^{*} = \Gamma$.
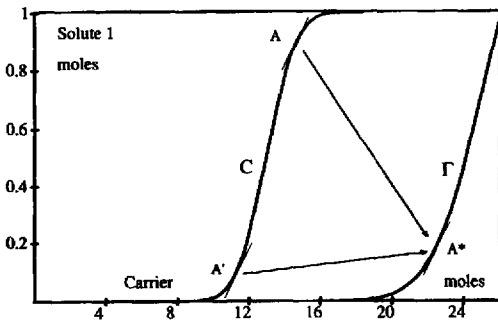

Fig. 8. Sigmoid curve C of cumulated quantities (solute, carrier). Convex boundary curve $\Gamma = C^{*}$.

This method extends itself readily to a non-unimodal chromatogram of solute i (including more than one cycle, for example) but is, in general, not valid in n-D space, $n > 2$.

5.1.2. Construction of 2-D zonoid

Let $\mathbf{F}$ be given by eqn. 30. Then, for a unique solute i and carrier 3, we obtain the equation of Γ_{i3} in the parameterized form (for model I or II):

$$
\left| \begin{array}{l}
N^i(N,t) = 2N_0^i \, \mathrm{erf}\!\left(\sqrt{N} \cdot \dfrac{\bar{t}_i - t}{\bar{t}_i} \right), \quad i = 1,2 \quad -\infty < t < \bar{t}_i \\[2em]
N^3(N,t) = 2F^3(\bar{t}_i - t)
\end{array} \right.
\tag{47}
$$

Convexity of Γ_{i3} stems from construction and can be shown directly through convexity of the function $\mathrm{erf}(x)$ for $x \in [-\infty, 0]$.

Some remarks are in order:

(a) The mixing convention is applied here only to the projected family: in the complete family, the simultaneous presence of solute j prevents colinearity occurring at times $t_i - \Delta$, $t_i + \Delta$. Therefore, it is clear that the mixing convention will give, in general, different results depending on the canonical projection, that is, on the species i.

(b) $Z(z)$ is unbounded in the time axis direction as support of the solution of the diffusional model extends to the whole time axis (or the positive axis R^+ for the Poisson model). As already noted, we restrict ourselves to an interval Δt of R^+ supporting "essentially" all the peak. Note that a rigorous study would involve unbounded zonoids. It is not too difficult to show by extending the boundaries of segment $[0, \Delta t]$ that this would not change the final conclusions concerning separation evolution (inclusion), but would give a useless (infinite) 2-volume of separation, thus showing a major drawback of use of these volumes as an index of separation.

Applying this to model II (isovariance assumption), we obtain a simple result (which was to be expected as in model II peaks of solutes at given z deduce themselves by translation).

The separation zonoid between species and carrier is independent of species (for model II):

$$
Z_{12} = Z_{13}
$$

[except for a trivial linear dependence (linearity) on injected quantity of species, and as long as the time interval is sufficient].

5.1.3. Evolution of separation state

Making first a geometric study, let us compare families of curves $\Gamma_{i3}(N)$, $i = 1, 2$. One uses the geometric invariance of Γ_{i3} in a regular change of parameter (depending on species i). Then (Gaussian model I or II), taking $\theta_i = t_i - t$ leaves Γ invariant; this
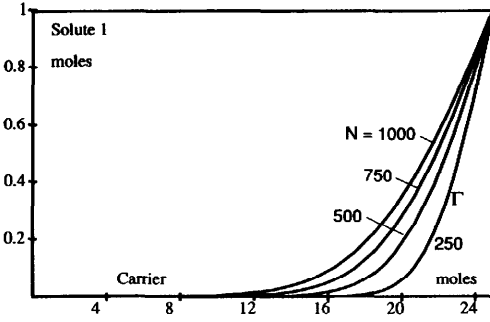
Fig. 9. Evolution of 2-d zonoid (solute 1, carrier) lower boundary. $z = 25, 50, 75, 100$ cm.

amounts to set time zero at the peak maximum and to reverse orientation of the time line (F is an even function).

In a second parameter change, $\tau_i = \sqrt{N}\dfrac{\theta_i}{t_i}$, eqn. 47, of Γ_{i3} becomes

$$N^i(\tau_i) = 2N_0^i \, \mathrm{erf}(\tau_i), i = 1 \text{ or } 2, \; 0 < \tau_i < \infty \tag{48}$$

$$N^3(\tau_i) = 2F_0^3 \cdot \dfrac{\bar{t_i}}{\sqrt{N}} \tau_i$$

That is, all curves Γ_{i3} map onto the graph of $\mathrm{erf}(x)$ over R^- by a linear application of diagonal matrix $[A]$ with elements $\left(\dfrac{1}{2N_0^i}, \dfrac{1}{2F_0^3 \dfrac{\bar{t_i}}{\sqrt{N}}} \right)$. Then curves Γ_{i3} do not intersect (except at the origin; note that this precludes these curves from having exactly the same sum vector) and lie above one another for increasing values of N. A decrease of the 2-d zonoid Z_{13} is clearly visible in Fig. 9.

We have thus established inclusion (recall $\mathrm{proj}_{i3} Z = Z_{i3}$)

$$Z_{i3}(z') \supset Z_{i3}(z) \text{ if } z' < z, \; i = 1,2$$

which amounts here to be *existence* order between canonical projections of $Z(z)$ and $Z(z')$ on planes (1,3) or (2,3).

$$Z_{i3}(z) \prec Z_{i3}(z') \text{ if } z' < z, \, i = 1,2$$

This leads us to an important and simple conclusion: *linear diffusional chromatography is a mixing process between carrier and a solute.*

5.1.4. Mixing kernel

Making now an analytical study, we give direct proof that solute propagation is a mixing process between solute and carrier by exhibiting a sampling kernel.

In view of the definition of a mixing process given in Section 2.3, we may enquire directly about the nature of the process. We must exhibit a mixing kernel λ according to eqn. 21 and 21a which allows one to obtain a differential family of flow-rate vectors obtained at $N + \Delta N$ plates from that obtained at N plates.

Looking, e.g., at solute 1, the flow-rate family at N (see Table I) is similar for models I or II:

$$\mathscr{F}(N) = \left[\begin{array}{c} N_0^1 \cdot \dfrac{\sqrt{N}}{\sqrt{2\pi \bar{t}_1}} \cdot e^{-\frac{1}{2}N\left(1 - \frac{t}{\bar{t}_1}\right)^2} dt \\ F_0^3 \, dt \end{array} \right]_{-\infty < t < +\infty}$$

As the second component of flow is constant, eqn. 21a will directly ensure the mixing properties for carrier species. Therefore, we need only to study the flow of the solute.

Starting from the following identity, which expresses the classical property of additivity of variances (see Appendix for a proof using Fourier transformation):

$$\frac{1}{\sqrt{2\pi}\sqrt{\sigma^2 + \sigma'^2}} e^{-\frac{\tau^2}{2(\sigma^2 + \sigma'^2)}} = \int_{-\infty}^{+\infty} \frac{e^{-\frac{w^2}{2\sigma^2}}}{\sqrt{2\pi}\sigma} \cdot \frac{e^{-\frac{(w-\tau)^2}{2\sigma'^2}}}{\sqrt{2\pi}\sigma'} \cdot dw$$

we obtain, on identification of the left-hand term with the flow-rate at $N + \Delta N$ plates, calling σ'' the square root of variance at this location, and use of eqns. 27 and 29,

$$\sigma = \frac{(1 + k^1)\sqrt{N}H}{u}, \qquad \sigma'' = \frac{(1 + k^1)\sqrt{N + \Delta N}H}{u}$$

hence

$$\sigma' = \sqrt{\sigma''^2 - \sigma^2} = \frac{(1 + k^1)\sqrt{\Delta N}H}{u}$$

Therefore, family $\mathscr{F}(N + \Delta N)$ (up to translations of time scale to obtain centred distributions, i.e., $w = t - \bar{t}_1$, $\tau = t' - \bar{t}_2$) results from family $\mathscr{F}(N)$ by a mixing process with the mixing kernel:

$$\lambda(t - \bar{t}_1, t' - \bar{t}_2) = \frac{e^{-\frac{(t - t' + \bar{t}_2 - \bar{t}_1)^2}{2\sigma'^2}}}{\sqrt{2\pi}\sigma'} = \frac{1}{\sqrt{2\pi}}\sqrt{\frac{N + \Delta N}{\Delta N}} \cdot \frac{1}{\bar{t}_2} \cdot e^{-\frac{N + \Delta N}{\Delta N} \cdot \frac{(t - t' + \bar{t}_2 - \bar{t}_1)^2}{2\bar{t}_2^2}}$$

and property 21a stems from normalization of the area under a Gaussian curve.

Note that the above mixing kernel derives also from a Gaussian function and is a convolution kernel. Also, the above result holds for an unbounded quantity of carrier, *i.e.*, for $t \in R$.

Of course, the existence of a mixing kernel is linked with the fundamental fact that diffusion (as represented here by the increase in variance of a Gaussian curve) is basically a mixing process, a fact that can be traced back to the diffusion equation and will be emphasized in future work.

5.1.5. 2-Volume of separation between solute and carrier

Although a direct integration can be made using eqn. 48, it is simpler to use the linear transformation T of matrix $[A]$ defined in Section 5.1.3.

In view of the fact that for the unbounded (rigorous) case, when the quantity of carrier is infinite, the area in the rectangle of total separation, under the curve Γ_{i3}, stays finite, we introduce the following.

Definition

The loss of 2-volume is the area ζ_{i3} of the complement of 2-d zonoid to the rectangle of total separation.

Let ζ be the area under the graph of $\mathrm{erf}(x)$ over R^-, *i.e.*, $\zeta = \displaystyle\int\limits_{-\infty}^{0} \mathrm{erf}(s)\mathrm{d}s =$

$\dfrac{1}{\sqrt{2\pi}}$. Through transformation T^{-1}, ζ will be multiplied by dat $[A]^{-1}$, so that we obtain

$$\zeta_{i3} = 8\zeta N_0^i F_0^3 \cdot \dfrac{\bar{t}_i}{\sqrt{N}} = 8\zeta N_0^i F_0^3 \sigma_i$$

Therefore, for separation 2-volume (pairs 1,3 or 2,3) we obtain

$$\Xi_{i3}(N) = \Xi_0 - \dfrac{8}{\sqrt{2\pi}} N_0^i F_0^3 \sqrt{N} \cdot \dfrac{1 + k^i}{u} \cdot H \tag{49}$$

as long as sufficient carrier is allowed to contain virtually all the solute. Recall that area $\Xi_0 = N_0^i F_0^3 \varDelta t$ is unbounded if $\varDelta t \to \infty$.

At a given retention time for solute i, we obtain ζ_{i3}, proportional to $\bar{t}_i/\sqrt{N}$, *i.e.*, the loss of 2-volume diminishes if we increase the number of plates or, for a given z, if we decrease the HETP.

Eqn. 49 may be given in a different form: introducing τ_1^i, the residence time of solute per plate, $\tau_1^i = H \cdot \dfrac{1 + k^i}{u}$, an interesting statement can be made: in linear diffusional chromatography, ζ_{i3}, the loss in 2-volume of separations between carrier and solute i, increases as the square root of the number of plates and as the residence time of solute per plate. The rate of decrease in 2-volume of separation between solute i and carrier is given by

$$\Xi_{i3}(N) = \Xi_0 - 8\zeta N_0^i F_0^3 \sqrt{N} \tau_1^i$$

A conclusion may be drawn in another way: although the separation between a solute and a given quantity of carrier decreases when z increases, $i.e.$, zonoids become smaller as the column length increases, nevertheless, a given increment of length has less and less influence on mixing; this can be related to Fick's law, which states that the flux is proportional to the gradient of concentration. Indeed, the effect of a constant increment of column length on the mixing is clearly visible in Fig. 9, as the relative loss area ratios are 1, 1.41, 1.73 and 2.

These conclusions all fit fairly well the "intuitive" (qualitative) thinking about what the effect of these parameters on separation should be.

5.2. Separation between two solutes

Consider now the separation between solutes 1 and 2, that is, the canonical projection on the plane (1,2) of the three-dimensional zonoid. We must first construct proj(Z) and then study its variation with N.

5.2.1. Study of 2-selectivity

Model I: taking the leading minor in $W(F)$ in Table 1, we obtain the 2-selectivity condition

$$\text{sgn}(\text{proj}_{12}F(t) \wedge \text{proj}_{12}F'(t)) = \text{sgn} \begin{vmatrix} 1 & -\dfrac{(t - t_1)}{(\bar{t}_1)^2} \\[4mm] 1 & -\dfrac{(t - \bar{t}_2)}{(\bar{t}_2)^2} \end{vmatrix} \tag{50}$$

$$= \text{sgn}(\bar{t}_1 - \bar{t}_2)\left(t - \frac{\bar{t}_1 \bar{t}_2}{\bar{t}_1 + \bar{t}_2}\right) = -1 \text{ for } t > \frac{\bar{t}_1 \bar{t}_2}{\bar{t}_1 + \bar{t}_2} > \frac{\bar{t}_1}{2}$$

The sign is constant for any practical conditions, as the above inequality in t is always satisfied when a non-negligible flow of solute 1 or 2 occurs, for sufficiently high N. This means that, on the cumulate curve Γ_{12}, the inflection point is very near to the origin. Presumably this inflection point is an artefact of the approximation of the peak shape by a Gaussian curve.

To make this point precise, let us make a comparison with model II. Now $W(F)$ leads to the 2-regular selectivity condition taken from Table 1, or just equating denominators to $\bar{t}$ in the determinant of eqn. 50. Similarly, model III leads to a 2-regular selectivity condition also taken from Table 1:

$$1 = \text{sgn} \begin{vmatrix} 1 & -\dfrac{N}{\bar{t}_1} + \dfrac{N-1}{t} \\[4mm] 1 & -\dfrac{N}{\bar{t}_2} + \dfrac{N-1}{t} \end{vmatrix} = \text{sgn}(\bar{t}_2 - \bar{t}_1) \tag{51}$$

which is clearly always satisfied since $\bar{t}_2 > \bar{t}_1$.

The family of flow-rate vectors (models II and III) therefore possesses 2-regular selectivity properties. Then, from the chromatogram, the construction of a convex set of mixtures is very simple: integrate F from 0 to t, to obtain ∂Z^-. The tangent to Z at point $N(t)$ is parallel to $F(t)$.

Returning to model I, we can trace the lack of 2-regular selectivity to the following: the peak of species 2 is slightly more diffuse than that of species 1 ($\bar{t}_2 > \bar{t}_1$), and indeed this stems from the influence of retention time on the variance in eqn. 28. Therefore, at some early value of t, species 2 will supersede species 1. In fact, model I is valid only asymptotically for the Dirac inlet distribution and high N. This view is confirmed by the fact that, if we equate the variances of the two peaks, that is, if we pass to model II, Γ is convex on R as the factor containing t in eqn. 50 drops out. Hence a lack of 2-regular selectivity points to a discrepancy between the model and physical reality, a satisfactory result.

Physically, 2-selectivity for species 1, 2, means that in the flow passing through location z, species 2, the more retained species, increases in purity as time goes on.

5.2.2. Construction of 2-D zonoid

Consider, e.g., the Gaussian model I, neglecting the above-mentioned inversion of selectivity. Projection Γ_{12} of the cumulate curve $N(t)$ is a convex curve. Therefore, the (half) boundary of Z_{12} has a parametric equation:

$$
\left|
\begin{array}{l}
N^1(N,t) = N_0^1 \operatorname{erf}\left(\sqrt{N}\cdot\dfrac{\bar{t}_1 - t}{\bar{t}_1}\right), \quad t \in [0, \Delta t] \\[4mm]
\\[2mm]
N^2(N,t) = N_0^2 \operatorname{erf}\left(\sqrt{N}\cdot\dfrac{\bar{t}_2 - t}{\bar{t}_2}\right)
\end{array}
\right.
\tag{52}
$$

Convexity of Γ_{12} is towards the axis of the more retained species.

5.2.3. Evolution of separation state

A quantitative study of the growth of zonoid Z_{12} with z covers both relative positions of Z and area growth. Through a change of parameters (already done in Section 6.1.3.),

$$
\tau = \sqrt{N}\cdot\frac{t}{\bar{t}}, \quad \bar{t} = \frac{\bar{t}_1 + \bar{t}_2}{2}
$$

we obtain

$$
N^i(\tau) = N_0^i \operatorname{erf}(\tau_i - \tau), \tau \in \left[0, \sqrt{N}\cdot\frac{\Delta t}{\bar{t}}\right], \quad i = 1,2
$$

Accordingly, the peaks representing the flow-rate are translates of affine Gaussian curves with δ, the reduced translation parameter:

$$
\delta = \tau_2 - \tau_1 = \sqrt{N}\cdot\frac{\bar{t}_2 - \bar{t}_1}{\bar{t}} \approx 2\cdot\frac{\alpha - 1}{\alpha + 1}\cdot\sqrt{N}
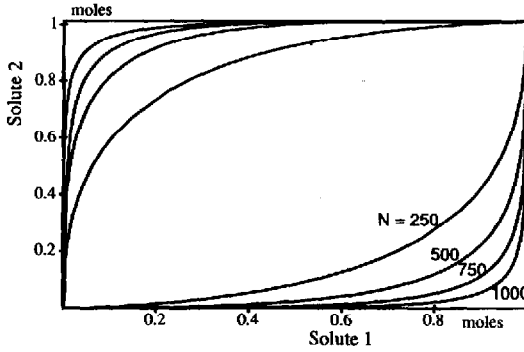\tag{53}
$$

Fig. 10. Growth of separation, zonoid Z_{12}. $L = 25, 50, 75, 100$ cm.

Evolution of the zonoid of separation is therefore a function of δ, valued in the set of zonoids (of given sum vector in 3-D space) (Fig. 10).

Inclusion is then simple to show: at any given τ, increasing δ makes the second peak recede from the first, thus $N^2(\tau)$ decreases. The point on ∂Z^- moves towards axis 1 on the vertical above $N^1(\tau)$, thus proving inclusion. Note that slope of the tangent at $N^1(\tau)$ decreases if $\tau < \tau_1 + \delta$ and increases if $\tau > \tau_1 + \delta$.

5.2.4. 2-Volume of separation

Calculation of the law of increase of 2-volume of separation with δ is less easy (see Appendix) but gives a simple result, both as a first-order expansion of Ξ and in general.

From eqn. (A5) (see Appendix), we obtain for the Gaussian isovariant model

$$\Xi_{12} = 2\,\mathrm{erf}\left(\frac{\delta}{\sqrt{2}}\right) - 1 \tag{54}$$

and at first order, for small δ (i.e., for $N \ll N_c$)

$$\Xi_{12} \approx \frac{\delta}{\sqrt{\pi}} = \frac{1}{\sqrt{\pi}}\,\sqrt{N}(\alpha - 1)$$

where the last inequality amounts to $N \leqslant N_c$. Therefore, at incipient separation, 2-volume increases as only as $\sqrt{N}$ or, conversely, the rate of growth of 2-volume is infinite at $N = 0$, and decreases as $1/\sqrt{N}$ because

$$\frac{d\Xi_{12}}{dN} = -\frac{1}{\sqrt{\pi}} \cdot \frac{1}{2\sqrt{N}}(\alpha - 1)$$

This relative inefficiency of theoretical plates in the process can be traced back to the fact that separation is produced only in part of the column, the width of the signal being approximately proportional to $\sqrt{N}$. Remarkable also is the grouping of α and

N into a single factor, which is indeed linked with resolution $R = R_{12} = 2\left(\dfrac{\bar{t}_2 - \bar{t}_1}{w_1 + w_2}\right)$ (where w_i is the distance between the intercept of the inflection tangents with the baseline), since (for two Gaussian peaks of equal area) $\delta = 4R$, we obtain

$$\Xi_{12} \approx \frac{4R}{\sqrt{\pi}}$$

However, the use of these approximations is severely restricted, as first-order expansion (eqn. A8) is valid only in the cases of difficult separation ($\alpha \approx 1$) and incipient separation $[\sqrt{N}(\alpha - 1) \ll 1]$. That condition of incipient separation is usually not satisfied in practice as one aims for a resolution of about unity between peaks. However, R is restricted to be lower than about 5 if the above equation is to have any chance of being valid, *i.e.*, to give a value lower than 1 (and, in this instance, it is hardly measurable from the chromatogram). Finally, as concerns resolution, it is not difficult to prove that at the 3-selectivity inversion point, N_c, $R = 0.5$ for model II.

We may state that for a difficult separation, when peaks are not too well separated, the rate of 2-volume production for solutes 1, 2 is proportional to $\sqrt{N}$. Note, however, that area is of limited interest here and can even be misleading; a complete study should encompass growth of the zonoid itself.

The study of canonical projections of Z leads to a remarkable conclusion concerning binary separations, namely that linear chromatography (models II and III) with diffusion is a separation process between two solutes, a mixing process between a solute and carrier. As linear diffusional chromatography is neither a pure separation nor a pure mixing process, it must be a sepmix process. Note that, although drawn from studies of binary separations, this conclusion also holds for ternary separations. Indeed it is a sufficient condition for a process to be sepmix that two 2-D projections exist in which the initial and final zonoids are not ordered in the same way.

5.2.5. A generalization to n solutes

We generalize the results in Section 5.2.1. to the separation of any number of solutes: using Polya's frequency functions (PF) we obtain the following general theorem, holding for any number of solutes.

Theorem

Gaussian isovariant and Poisson models give rise to 1-differential families endowed with regular selectivity of any order between solutes.

Proof

Refer to Section 2.2.3. on PF functions. Clearly K_j^i may depend on i and j through constant multipliers, *e.g.*, N_i^0.

Take model II. We show first that $e^{-\frac{\eta^2}{2}}$ is a PF density. Let $L(x,y) = e^{xy}$. Clearly all minors of the generalized Vandermonde matrix $n \times p$ of elements L_j^i, $L_j^i = e^{x_i y_j}$ are positive for any two finite linearly ordered sequences: $x_1 < x_2 < \ldots < x_n$,

$y_1 < y_2 < \dots < y_n$. Therefore, through multiplication of lines and rows by constant factors,

$$e^{-\frac{y_j^2}{2}} e^{x_i y_j} e^{-\frac{x_i^2}{2}} = e^{-\frac{(x_i - y_j)^2}{2}}$$

enjoys the same property and is of the required form for a PF function. As it is integratable on the real line, it is a PF density. Use of transformation property 1 of PF functions given under Theorem 6 gives immediately the desired result that F^i, for model II, *i.e.*, for a fixed variance (eqns. 31 and 32) is generated by the PF function

$$f(\eta) = \frac{1}{\sqrt{2\pi}\sigma} \cdot e^{-\frac{\eta^2}{2\sigma^2}}$$

For model III, we show first that $P(N,\lambda) = \frac{1}{\Gamma(N)} \cdot e^{-\lambda}\lambda^N$ is a totally positive kernel. Starting anew from the generalized Vandermonde matrix generated (this time directly) by λ^N, we obtain the result by multiplication with $1/\Gamma(N)$ and $e^{-\lambda}$. F^i in eqn. 34 is a PF function replacing y_j with $\ln t_j$, x_i with $\ln \bar{t_i}$.

5.3. Separation between solutes and carrier

An overview of the character of chromatographic separations is gained by a three-dimensional representation of the zonoid rather than from the two-dimensional projections, as done above. 3-Selectivity was studied in Section 4.4, as it was necessary to draw the boundary of Z. Calculation of the volume of the zonoid is not a simple matter, so we shall attempt first to draw qualitative "visual" conclusions.

5.3.1. 3-d Zonoid comparison

The influence of z for given operating conditions can be seen in Fig. 11. Only the bottom half of the zonoid boundary has been represented.

At $z = 0$, the injected zonoid is a vertical parallelogram, as the mixture of solutes and the pure carrier are separately available. Therefore, clearly, if solutes are to be separated to some extent, the resulting zonoid must not project on a segment, *i.e.*, no inclusion property between zonoids can hold: the process must be a sepmix. In fact, the construction of zones used assumed 3-regular selectivity, which is true in the cases in Fig. 11a and b, approximately true in Fig. 11c and false in Fig. 11d.

Note that increasing the time cycle Δt by δt would add a vector $(\varepsilon_1, \varepsilon_2, F^3 \delta t)$ with small $\varepsilon_1, \varepsilon_2$ to the initial and final families, or, equivalently, expand all zonoids with an (almost) vertical cylinder of length $F^3 \delta t$ without adding any really interesting information. The 3-volume of Z would then increase by $\Xi_{12}F^3\delta t$.

The general deformation trends are as follows when z increases:

(1) Z becomes thinner (maximum vertical width decreases): for a given carrier quantity, this means a more homogeneous medium as a given mixture of solutes 1, 2 can be made with less and less different minimal and maximal quantities of carrier;
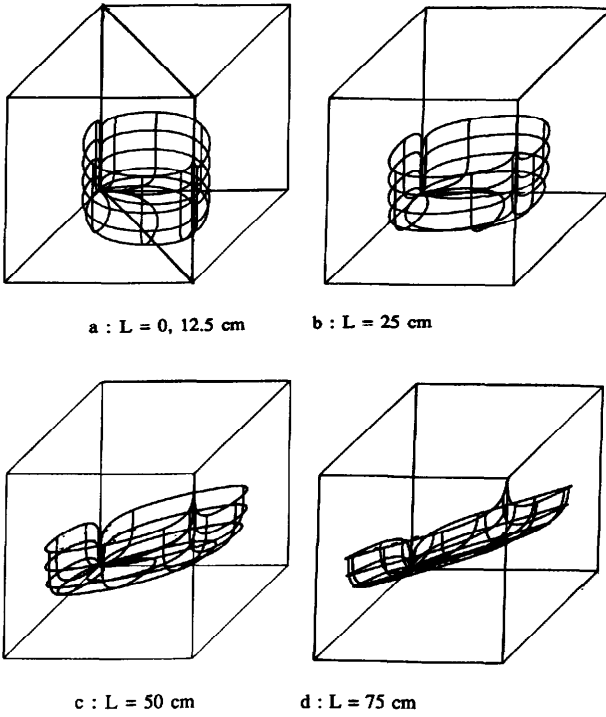
a : L = 0, 12.5 cm   b : L = 25 cm

c : L = 50 cm   d : L = 75 cm

Fig. 11. Evolution of three-dimensional zonoid along the column. Axes labelling and orientation are similar to those in Fig. 4.

(2) Z becomes larger in horizontal projection (the smallest vertical cylinder containing Z grows).

5.3.2. Evolution of 3-volume

We first give a remarkable expression for 3-volume.

Theorem

For a family $\mathscr{F}$ given by model II or III, when $N < N_c$, *i.e.*, for 3-regular selectivity,

$$\Xi = N_0^1 N_0^2 N_0^3 \left\{ \xi_{12} - \frac{(\bar{t}_2 - \bar{t}_1)}{\Delta t} \right\}$$

Proof

As selectivity is 3-regular, one may drop absolute values and sum for r, in eqn. 19, which gives

$$\Xi = \iint_{0 \leqslant s < t \leqslant \Delta t} \mathbf{N}(s) \wedge \mathbf{F}(s) \wedge \mathbf{F}(t)\, \mathrm{d}s\mathrm{d}t \tag{55}$$

Similarly, summing on t from s to Δt,

$$\varXi = \int\limits_{0 \leqslant s \leqslant \Delta t} \mathbf{N}(s) \wedge \mathbf{F}(s) \wedge (\mathbf{N}(\Delta t) - \mathbf{N}(s)) \mathrm{d}s$$

Using linearity and antisymmetry properties of the exterior product we obtain

$$\varXi = \mathbf{N}(\Delta t) \wedge \int\limits_{0 \leqslant s \leqslant \Delta t} \mathbf{N}(s) \wedge \mathbf{F}(s)\, \mathrm{d}s \tag{56}$$

We need simply to integrate the three components of the integrand (in $\Lambda^2 E$) and then to make the exterior product with the sum vector $\mathbf{N}(\Delta t) = \mathbf{N}_0$.

For the separation of two solutes with carrier by chromatography, the selectivity is 2-regular for pair (1,2) but is not so for pairs (1,3) and (2,3). Therefore, eqn. 56 leads to

$$\varXi = N_0^1 \phi_{23} - N_0^2 \phi_{13} + N_0^3 \varXi_{12} \tag{57}$$

where

$$\phi_{13} = \int\limits_{0 \leqslant s \leqslant \Delta t} \begin{pmatrix} \mathbf{N}^1(s) \\ \mathbf{N}^3(s) \end{pmatrix} \wedge \begin{pmatrix} \mathbf{F}^1(s) \\ \mathbf{F}^3(s) \end{pmatrix} \mathrm{d}s \qquad \phi_{23} = \int\limits_{0 \leqslant s \leqslant \Delta t} \begin{pmatrix} \mathbf{N}^2(s) \\ \mathbf{N}^3(s) \end{pmatrix} \wedge \begin{pmatrix} \mathbf{F}^2(s) \\ \mathbf{F}^3(s) \end{pmatrix} \mathrm{d}s$$

Integrands do not have a fixed sign in these expressions. They also depend on Δt. A geometrical interpretation of these expressions is that they give the algebraic area of curve $\mathbf{N}(s)$ seen from the origin, in plane (1,3) or (2,3). However, a remarkable feature is that $N_0^1 N_0^2$ can be put into the first two terms of eqn. 57, in such a way that $N_0^1 N_0^2 (\varphi_{23} - \varphi_{13}) \cdot \varphi_{13}, \varphi_{23}$ are mapped on $[0,1] \times R$ to form a curve closed at infinite [$i.e.$, with $\varphi_{13}(-\infty) = \varphi_{23}(-\infty) = 0$ and $\varphi_{13}(\infty) = \varphi_{23}(\infty) = 1$]. Then $\varphi_{23} - \varphi_{13}$ is the area inside this curve. As in model II peaks are translated by $\bar{t}_2 - \bar{t}_1$, and so are $\varphi_{13}, \varphi_{23}$, this oriented area is finite and equal to $\varphi_{23} - \varphi_{13} = -(\bar{t}_2 - \bar{t}_1)[\varphi_{23}(\infty) - \varphi_{23}(-\infty)] = -(\bar{t}_2 - \bar{t}_1)$. Therefore, as long as $N < N_c$ holds,

$$\varXi = N_0^1 N_0^2 F^3 \Delta t \xi_{12} - N_0^1 N_0^2 F^3 (\bar{t}_2 - \bar{t}_1) \tag{58}$$

or

$$\xi = \left\{ \xi_{12} - \frac{(\bar{t}_2 - \bar{t}_1)}{\Delta t} \right\} \tag{59}$$

which concludes the proof since $N_0^3 = F^3 \Delta t$.

Geometrically, one may understand this result as follows. Let us split eqn. 58

into two terms, in same way as in eqn. 49. $N_0^1 N_0^2 F^3 \Delta t \xi_{12}$ is 3-volume of a vertical cylinder with base Z_{12}, height $N_0^3 = F^3 \Delta t$, which would be obtained if the carrier was not an integral part in the process and could be spared (of course a hypothetical case). Note that this 3-volume is unbounded when $\Delta t = \infty$.

$N_0^1 N_0^2 F^3 (\bar{t}_2 - \bar{t}_1)$ is, dimensionally, a (bounded) 3-volume. Formally, this term represents 3-volume of total separation between pure solutes and the quantity of carrier which flows between the retention times of the peaks. It does not depend on either Δt, and therefore it is finite, or directly on the efficiency of the process (HETP or N). As this term is subtracted from the first term in eqn. 58, it can be appropriately called *loss of 3-volume*.

Finally, one obtains for the Gaussian isovariant model, $N < N_c$,

$$\xi = \left\{ 2\,\text{erf}\left(\sqrt{\frac{N}{2}} \cdot \frac{\bar{t}_2 - \bar{t}_1}{\bar{t}_1} \right) - 1 - \frac{(\bar{t}_2 - \bar{t}_1)}{\Delta t} \right\} \tag{60}$$

where t_i can be evaluated using eqn. 29. Therefore, the yield of 3-volume is given by (Fig. 12)

$$\xi = \left\{ 2\,\text{erf}\left(\sqrt{\frac{N}{2}}(\alpha - 1) \right) - 1 - \frac{(\alpha - 1)}{\Delta t} \cdot \frac{(1 + k^1) N H}{u} \right\} \tag{61}$$
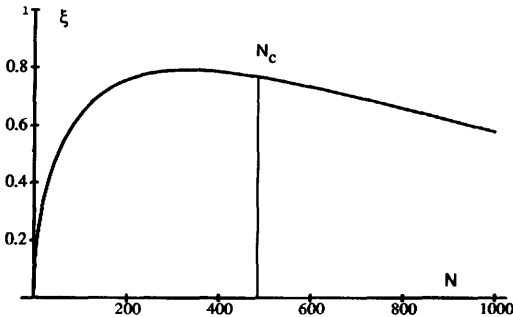

Fig. 12. 3-Volume yield *vs.* number of plates. Conditions as in Fig. 1, $\Delta t = 100$ s.

Especially interesting is the rapid (in $\sqrt{N}$) increase in 3-volume creation at the beginning, followed by a step-up and a decrease. The mean rate of creation of 3-volume per plate, ξ/N, goes to zero at a certain number of plates. Clearly, the existence of such a maximum on ξ is a very important feature for optimization: it indicates that one should consider some way of enhancing the efficiency of the process beyond this point.

5.3.3. Evolution of 3-volume for three solutes

For 3 solutes, in the special case of totally regular selectivity, we recognize that the components in eqn. 56 are exactly the 2-volumes of canonical projections of Z and,
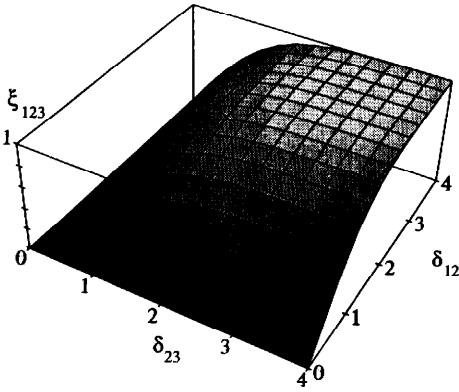
Fig. 13. 3-Volume yield between three solutes *vs.* translation parameters.

therefore, we derive the simple and useful expression that 3-volume is a linear function of 2-volumes:

$$\Xi = N_0^1 \Xi_{23} - N_0^2 \Xi_{13} + N_0^3 \Xi_{12} \tag{62}$$

which can also be recast yields in 3- and 2-volume (eqn. 25), with coefficients independent of quantities of species:

$$\xi = \xi_{23} - \xi_{13} + \xi_{12} \tag{63}$$

Combining the results in Section 5.2.4. and the generalization in Section 5.2.5. we obtain for the Gaussian isovariant model the expression of 3-volume of separation between three solutes:

$$\xi = 2\left\{ \mathrm{erf}\left(\frac{\delta_{23}}{\sqrt{2}}\right) - \mathrm{erf}\left(\frac{\delta_{13}}{\sqrt{2}}\right) + \mathrm{erf}\left(\frac{\delta_{12}}{\sqrt{2}}\right) \right\} - 1 \tag{64}$$

where δ_{ij}, given by eqn. 53, is the translation parameter between peaks of solutes i and j. As $\delta_{13} = \delta_{12} + \delta_{23}$, ξ is a symmetric function of two independent variables (Fig. 13).

6. PROBLEM SOLVING WITH ZONOIDS

A good theory should first integrate previous knowledge and then ask new questions whose answers open new avenues. Many separation problems can be recast geometrically and given innovative answers. We consider below five problems, in order of increasing complexity, but clearly they only scratch the surface of a vast subject. For many of these problems, the fundamental property of a convex set of mixtures will be the critical property. Meanwhile, we shall encounter the extent of separation, proposed by Rony [3], and show how well it fits into zonoid theory. Although economy (*e.g.*, marginal costs and linear programming) is assumed to give answers to these problems, this is not so in most instances owing to the overwhelming complexity of the calculations. We then need first to answer on a technical basis, and zonoid theory gives the answer.

6.1. A problem of recovery with minimum dilution

Given a process delivering a family of mixtures by use of a (conservative) separation agent, and a mixture of solutes, find the sampling (if any) which will allow them to be recovered with minimum dilution in separation agent.

It is not commonly considered that a sampling function λ may, in principle, oscillate wildly between 0 and 1. There is no real reason why only "gentle" sampling procedures should be the best.

The answer is given below for $\dim E = 3$, but can be generalized.

Consider a family $\mathscr{F}$ and $\mathbf{M} = (M^1, M^2)$, a mixture of solutes. If $\mathbf{M} \in Z_{12}(\mathscr{F})$, $\mathbf{M}$ is feasible, and the problem amounts to determining geometrically the point on the boundary ∂Z^- above $\mathbf{M}$. In the case of 3-regular selectivity, in view of eqn. 14, it is equivalent to finding t_1, t_2 such that

$$\mathbf{M} = \int_{t_1}^{t_2} \mathbf{F}(\tau)d\tau, 0 \leqslant t_1 \leqslant t_2$$

or, a segment equipollent to $\mathbf{M}$ can be put as a chord on ∂Z_{12}.

The minimum quantity of separation agent will then be

$$M_{\min}^3 = \int_{t_1}^{t_2} F^3(\tau)d\tau$$

If selectivity is not 3-regular, a more complicated sampling function (deduced from a variant of eqn. 15) will be necessary, but it remains gentle.

6.2. A problem of yield

Given a family $\mathscr{F}$, characterize all mixtures $\mathbf{M}$ with a given content M^i of a given solute i (i.e., all mixtures with a given yield of solute i). Geometrically, this is equivalent to finding the intersection of Z_{12} ($\mathscr{F}$) by a plane, the equation of which is $N^i = M^i$, and must be solved by computer to be represented graphically.

Strongly related is the problem of chromatographic design. Let us consider the existence of a real problem in preparative chromatography (overlooked until now). To choose the sampling valves for continuous outlet flow $\mathbf{F}(t)$, the designer must answer first the question: Is it best to actuate the sampling valve through an "all or nothing" command (called bang–bang in control theory) or through an arbitrary, bounded command? In the first instance the sampling function is as in eqn. 2 and in the second as in eqn. 6. In other words, are they mixtures which can be sampled in the latter (and more general) way but not in the former? A sideways question is whether the answer depends on the number of chemical species in the flow. The answer is (through the Krein–Milman theorem, referred to in Section 2; see comments on Theorem 3) that any mixture which can be made by the general sampling approach can also be made by, at least, one bang–bang command, a result which justifies everyday practice.

6.3. A problem of approximation

Given a family $\mathscr{F}$, find a criterion for the optimum recovery of a fixed number p of cuts and find the corresponding set of optimum p-1 cut-points.

The answer is to take the p cuts to minimize loss of n-volume.

This is a problem of approximation of a differential family by a discrete family. Clearly we may consider the approximation in the full space in n dimensions (*i.e.*, take into account the separation agent), or a projected subspace defined by r "preferred species", *e.g.*, solutes. We must have $p \geqslant n$ or $p \geqslant r$ depending on the case.

With $n = 3, r = 2$, the second procedure would involve minimizing 2-volume lost in the plane of solutes 1,2. Let us consider in the following $p = 2$. We have to find one cut-point.

Now, recall that for a binary mixture N_0 split into two mixtures, N_1, N_2, Rony [3,4] has defined the extent of separation as

$$\xi = \mathrm{Abs}\left(\frac{1}{N_0^1 N_0^2}\begin{vmatrix} N_1^1 N_2^1 \\ N_1^2 N_2^2 \end{vmatrix}\right) = \frac{1}{N_0^1 N_0^2}|N_1 \wedge N_2|$$

and this definition has been generalized by Valentin [2] to a vector extent of separation. We shall take $N_0 = (1,1)$. In the present theory we should call ξ a yield of 2-volume. Zonoid theory gives a physical interpretation which was lacking in Rony's index. ξ is the yield of 2-volume of $Z\{N_1, N_2\}$ (a parallelogram). Now, it is natural, if N_1 and N_2 are obtained from a 1-differential family of parameter t by a 1-cut point sampling at τ, to ask for ξ^*, the maximum $\xi(\tau)$. Clearly, ξ^* is the 2-volume of a (best) approximation of Z_{12} by a parallelogram.

In the case of linear chromatography (model II), Rony [4] showed that the optimum cut point is located at $\tau^* = \delta/2$ and

$$\xi^* = 2\,\mathrm{erf}\left(\frac{\delta}{2}\right) - 1 \tag{65}$$

From the corresponding eqn. 54 it is clear that loss of 2-volume induced by the two-cut trapping procedure is then independent of δ, as long as the linear expansion is valid, and therefore,

$$\frac{\xi^*}{\Xi} = \frac{1}{\sqrt{2}} = 0.707$$

Eqns. 54 and 65 set in perspective the effect of recovering only two cuts on the length of the column: to obtain the same 2-volume of separation between solutes in chromatography with 1-cut point, as in differential chromatography, one needs a two times longer column.

Thus ξ^*, the extent of separation, as defined by Rony [3,4], reflects only part of the separation produced by the column. Further, returning to the full dimensional approximation, one may take into account dilution of the solutes in the carrier, *i.e.*, a ternary separation. Now it is clear that a 2-cut procedure cannot be optimal as the

3-volume recovery would be zero. This strongly suggests that optimizing a 3-cut recovery should be considered for recovering a better part of the separation produced by the column and that classification of processes by Rony [17] should be re-worked accordingly.

6.4. A problem of basestock management

Given a family of mixtures, what should be the criterion for fabrication of a required mixture if the next mixture to be made is unknown?

This problem, also called the paint dealer problem, has been elegantly solved [16] using the fact that the probability of hitting a zonoid by a point is proportional to its n-volume (for a uniform density of probability of demand).

6.5. A problem in design

This last problem is certainly the most difficult and rewarding: how can one match a given separation (*e.g.*, by purity and yield) with some set of elementary devices (*e.g.*, equilibrium stages)?

The problem can be recast in term of zonoids, as the required separation can be represented by a convex set of mixtures Z_0 (or a set of these if the separation is not fully specified). Therefore, the problem is to find an arrangement of these stages which produces a zonoid Z_1 such that

$$Z_0 \prec Z_1$$

A simpler form of the problem is to determine the minimum number of stages in a column to obtain products $N_1, \ldots, N_p$. Formalization of this problem is

$$\underset{N}{\text{Min}} \left\{ Z(N) \mid N = 1, 2, \ldots, Z(N) \prec Z_0 \right\}$$

with

$$Z_0 = Z\{N_1, \ldots, N_p\} \text{ and } Z(N) = Z\left\{ \{F(N,t)dt\}_{t \in \Delta t} \right\}$$

7. CONCLUSIONS

Zonoid theory has been applied to very simple types of models of chromatography, namely the linear diffusional models. The results apply, of course, to all processes that can be modelled in this way, *e.g.*, liquid–liquid extraction. The method is general and should be a safe guide to the optimization or design of any process, including those which deliver families diffuse in 3-D space and time. Although the tools may seem very sophisticated and the applications remote at this stage, one must stress the probable long-term importance of this theory. Mathematical foundations and developments reflect an inherently complex situation and shed light on the specific features of chromatography.

Chromatography is not a separation process but a sepmix process. From this example, one may infer the importance of taking into account properly all the species involved, not forgetting the carrier. We have been able to study the three-dimensional zonoid of separation and its projections. The separation between species or mixing between one species and the carrier depends on the square root of the length of the column or of the number of theoretical plates, and is proportional to $\alpha - 1$. Chromatography exhibits how the interplay between separations and mixing operations may be a delicate one. Indeed, each species mixes with the carrier at the same time as it separates from other species. The important concept of r-regular selectivity has been defined.

The same methodology will be used in subsequent work to study non-linear effects on separations in chromatography where the power of the theory will be at its best; even though the inclusion of a zonoid of separation between solutes is valid in the simple model used, there are hints that the general situation is much more intricate. It certainly may happen that, owing to different diffusion or strong specific interaction effects, one species is better separated from the others when the feed quantity is increased. Then no inclusion property of zonoids will hold true and, *a fortiori*, no existence property.

This study has shown also that fundamental definitions in separation science are independent of concepts specific to thermodynamics. The former must define and study separation on a "stand-alone" basis. Then the latter may indicate subsequently how much separation production can occur, due to restraints imposed by the laws of thermodynamics (and also other sciences of matter, such as mass transfer kinetics). Basic independence will provide a firm ground for linking the evolution of separation in a system with the second principle of thermodynamics; more precisely, this will be made through a new general theorem expressing that separation between a carrier and solutes cannot increase (in the sense given by zonoid theory) in an isothermal, isobaric chromatographic column.

Among the fundamental questions to be investigated for a foundation in separation science along the lines developed here is the following: what are the springs of the separation and mixing creation hidden in the equations of motion in fluid mechanics and thermodynamics? In this respect the basic simplicity and the global nature of zonoids should allow one to concentrate only on salient features of solutions.

8. SYMBOLS

C	Concentration (mol/cm^3)
D	Diffusion or dispersion coefficient (cm^2/s)
E	Vector space of quantities (mol)
e	Base vector of E
$\mathbf{F}$	Flow-rate vector
H (HETP)	Height equivalent to a theoretical plate (cm)
I	Interval of natural numbers $\{1, \ldots, n)$
i	Chemical species
J	Interval of natural numbers
k	Equilibrium coefficient, ratio of number of moles
L	Length of a column

N	Number of theoretical plates
M,N	Quantity vector
N_0	Overall (or sum) quantity vector or distal point
n	Dimension of the space E; number of species
O	Origin
P	Hyperplane, point; relative inlet pressure
p	Number of regions or of cuts; relative pressure at location z
Q	Volume flow-rate (cm^3/s)
R	Vector space of real numbers ($-\infty, +\infty$)
R	Resolution
R^3	Usual Euclidean space
t	Time, retention time; current parameter on a curve
$\bar{t}$	Arithmetic mean of retention times
$\bar{t}_1$	Retention time of species 1
u	Speed of carrier
x	Molar fraction vector
Z	Zonoid, convex set of mixtures
Z	Set of Zonoids in R^n
z	Spatial coordinate in R or R^3

Greek letters

α	Relative volatility, $\alpha = k^2/k^1$
Γ, γ	Curve, boundary of a convex
Δ_{n-1}	$n-1$ Dimensional simplex (of molar fractions in E, $\dim E = n$)
δ	Dirac measure; dimensionless translation operator, $\delta = \sqrt{N} \cdot \dfrac{\bar{t}_2 - \bar{t}_1}{\bar{t}}$
∂	Operator taking boundary of an open set
Ξ	n-Volume of Z, ($Z \subset E$, $\dim E = n$) $(mol)^n$
ξ	Extent of separation
Σ	System state
σ	Reduced variance
τ	Reduced time, parameter on a curve

Superscripts

i,k	Chemical species
$+$	Positive orthant, upper part

Subscripts

j	Region
0	Entering in the system

Symbols

$[\ ]$	Matrix
$\{...\}$	A set of elements
$\circ$	Composition of functions: $f \circ g(x) = f(g(x))$
$+$	Sum or Minkowski sum

$\wedge$	Exterior product of vectors
n-D	n-Dimensional (space)
1-d	1-Differential (family)
sgn(x)	$+1$ if $x > 0$, -1 if $x < 0$
$\prec$	Exists in
O	Of the order of

9. ACKNOWLEDGEMENTS

10. APPENDIX: CALCULATION OF 2-VOLUME OF SEPARATION

We give a general expansion for Ξ_{12} for the case when $F(t)$ is generated by a Polya frequency (PF) function (in fact 2-selectivity would be sufficient here) and obtain an explicit equation in the special case of a Gaussian isovariant model.

10.1. A general expansion for Ξ

In the case of a Polya frequency function let us write

$$F^1(u) = F(u), F^2(u) = F(u - \delta)$$

dropping the indexes of solutes and taking unit total quantities of each solute, from eqn. 19, using Theorem 6a to discard absolute values:

$$d\Xi = \begin{vmatrix} N(u) & F(u) \\ N(u - \delta) & F(u - \delta) \end{vmatrix} du \tag{A1}$$

We also make the hypothesis that $N(u)F(u)$ and $N(u)F^{(k)}(u), k \geqslant 1$, is zero for $u = \pm\infty$.
We insert the Taylor development of F and N around u:

$$F(u - \delta) = F(u) - \delta F'(u) + (1/2)\delta^2 F''(u) - (1/6)\delta^3 F^{(3)}(u) + \ldots$$

$$N(u - \delta) = N(u) - \delta F(u) + (1/2)\delta^2 F'(u) - (1/6)\delta^3 F''(u) + \ldots$$

taking into account $N'(u) = F(u)$ in eqn. A1 and develop $d\Xi/du$ in powers of δ. From the multi-linearity property of determinants, we obtain

$$d\Xi = \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \cdot \delta^k \begin{vmatrix} N(u) & F(u) \\ F^{(k-1)}(u) & F^{(k)}(u) \end{vmatrix} du$$

where the superscripts in parentheses represent derivation. On integration on R we obtain the Taylor expansion of Ξ in powers of δ. From integration by parts of the general determinant, we obtain

$$\int_{-\infty}^{+\infty} \begin{vmatrix} N(u) & F(u) \\ F^{(k-1)}(u) & F^{(k)}(u) \end{vmatrix} du = \int_{-\infty}^{+\infty} N(u)F^{(k)}(u) - F(u)F^{(k-1)}(u)du$$

$$= -2\int_{-\infty}^{+\infty} F(u)F^{(k-1)}(u)du + [N(u)F^{(k-1)}(u)]_{-\infty}^{\infty}$$

where the last term is zero in view of the hypothesis. The general expansion can be written as

$$\Xi = 2\sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \cdot \delta^k \int_{-\infty}^{+\infty} (F(u)F^{(k-1)}(u))du \tag{A2}$$

Each coefficient in eqn. A2 is a well behaved integral which can be calculated numerically fairly easily and reduces the calculation of Ξ to quadratures. However, the series is slowly convergent for values of δ over 2.

For any even Polya frequency function, expression A2 loses its terms with even k, as $F^{(k-1)}(u)$ is odd.

Limiting eqn. A2 to its first terms, we obtain

$$\Xi = 2\delta \int_{-\infty}^{+\infty} F(u)^2 du - \delta^2 \int_{-\infty}^{+\infty} F(u)F'(u)du + \frac{1}{3}\delta^3 \int_{-\infty}^{+\infty} F(u)F''(u)du + O(\delta^4)$$

Applying eqn. A2 to the Gaussian isovariant model, we obtain the seven-term expansion, without even terms as $F(u)$ is even:

$$\Xi = \frac{1}{\sqrt{\pi}} \cdot \delta - \frac{1}{12} \frac{1}{\sqrt{\pi}} \cdot \delta^3 + \frac{1}{80} \cdot \frac{1}{\sqrt{\pi}} \cdot \delta^5 - \frac{1}{672} \cdot \frac{1}{\sqrt{\pi}} \cdot \delta^7 + O(\delta^9)$$

In view of the classical expansion of the error function around $x = 0$:

$$\text{erf}(x) = \frac{1}{2} + \frac{1}{\sqrt{2\pi}}\left(x - \frac{x^3}{3} + \frac{x^5}{2!5} - \frac{x^7}{3!7} + \cdots\right) \tag{A3}$$

rewriting eqn. A2 with $x = \frac{\delta}{\sqrt{2}}$:

$$\Xi = \frac{2}{\sqrt{2\pi}}\left[\frac{\delta}{\sqrt{2}} - \frac{1}{3}\left(\frac{\delta}{\sqrt{2}}\right)^3 + \frac{1}{2!5}\left(\frac{\delta}{\sqrt{2}}\right)^5 - \frac{1}{3!7}\left(\frac{\delta}{\sqrt{2}}\right)^7 + \cdots\right] \tag{A4}$$

gives through identification the final expression of 2-volume for the Gaussian isovariant model:

$$\Xi = 2\,\mathrm{erf}\left(\frac{\delta}{\sqrt{2}}\right) - 1 = \mathrm{Erf}\left(\frac{\delta}{\sqrt{2}}\right) \tag{A5}$$

10.2. Fourier transformation

Eqn. A5 may also be derived through the use of Fourier transformation, which proves to be an interesting tool for the calculation of volumes of zonoids. Starting from eqn. A1, we note that, on integration on R,

$$\Xi = \int_{-\infty}^{+\infty} [N(u)F(u - \delta) - N(u - \delta)F(u)]du \tag{A6}$$

Integrating by parts the second term in eqn. A6, we obtain

$$\Xi = 2\int_{-\infty}^{+\infty} N(u)F(u - \delta)du - 1$$

As we may write this as

$$\Xi = 2\int_{-\infty}^{+\infty} N(u)F(-(\delta - u))du - 1 \tag{A7}$$

Using the definition of the convolution integral

$$f*g(v) = \int_{-\infty}^{+\infty} f(u)g(v - u)du \tag{A8}$$

we recognize from eqn. A8 that Ξ results from convolution of $N(u)$ with $F(-u)$. Alternatively, this can be recast, using the correlation integral

$$h(v) = \int_{-\infty}^{+\infty} f(u)g(u + v)du$$

to say that $\Xi(-\delta)$ results from correlation of $N(u)$ with $F(u)$. Indeed, eqn. A8 reduces, if F is even, i.e., $F(u - \delta) = F(\delta - u)$, to the convolution

$$\Xi(\delta) = 2N * F - 1$$

Ξ, as a function of δ, results from a convolution between N and F.

Now we consider classical results linking Fourier transforms and convolution. Call $J(f;z)$ the Fourier transform J of f, and $J^{-1}(f;z)$ the inverse Fourier transform:

$$J(f;z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(u)\,e^{-iuz}\,du, \quad J^{-1}(f;u) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(z)\,e^{iuz}\,dz \tag{A9}$$

Let us introduce explicit (heavy) notations about the Fourier transform specifying the initial function, its variable and the variable of the transform, *i.e.*, $J(f(u);z)$. We write classical properties, *e.g.*,

$$J\!\left(f\!\left(\frac{u}{\sigma}\right);z\right) = |\sigma| J(f(u);\sigma z)$$

the equation for the Fourier transform of a derivative:

$$J(f'(u);z) = iz J(f(u);z)$$

and the equation for the Fourier transform of a convolution:

$$f*g(u) = \sqrt{2\pi}\, J^{-1}(J(f(u);z)\, J(g(u);z);u) \tag{A10}$$

The equation for the Fourier transform of a correlation involves the conjugate of the Fourier transform of one function (and is not symmetric):

$$h = \sqrt{2\pi}\, J^{-1}(J(f;z)\,\overline{J(g;z)};u)$$

The convolution equations apply to $F(u)$ and $N(u)$ as defined in model II, as $F(u)$ is even. Now, it is well known that a normal centred distribution is stable by operator J, *i.e.*,

$$J(F(u);z) = F(z)$$

From the derivation rule,

$$J(N;z) = \frac{1}{iz} J(F;z) = \frac{1}{iz} F(z)$$

Then we obtain, from eqn. A7

$$\Xi(\delta) + 1 = 2 J^{-1}(\sqrt{2\pi}\, J(F;z)\, J(N;z);\delta) \tag{A11}$$

from which follows eqn. A5 through

$$\Xi(\delta) + 1 = 2 J^{-1}\!\left(\frac{1}{\sqrt{2\pi}} \cdot \frac{1}{iz} \exp(-z^2);\delta\right)$$

$$= 2 J^{-1}\!\left(J\!\left(N\!\left(\frac{u}{\sqrt{2}}\right);z\right);\delta\right) = 2\,\mathrm{erf}\!\left(\frac{\delta}{\sqrt{2}}\right)$$

as

$$\frac{1}{\sqrt{2\pi}} \cdot \frac{1}{iz} \exp(-z^2) = \sqrt{2} \cdot \frac{1}{\sqrt{2\pi}} \cdot \frac{1}{is} \exp\left(-\frac{s^2}{2}\right) \text{ with } s = \frac{s}{\sqrt{2}}$$

$$= J(\sqrt{2}\,N(u);s) = J(\sqrt{2}N(u);z\sqrt{2}) = J\left(N\left(\frac{u}{\sqrt{2}}\right);z\right)$$

10.3. A basic equation for Gaussian mixing kernel

Let

$$f(\tau) = \int_{-\infty}^{+\infty} \frac{e^{-\frac{w^2}{2\sigma^2}}}{\sqrt{2\pi\sigma}} \cdot \frac{e^{-\frac{(w-\tau)^2}{2\sigma'^2}}}{\sqrt{2\pi\sigma'}} \, dw \text{ and } g(\eta) = \frac{e^{-\frac{\eta^2}{2}}}{\sqrt{2\pi}}$$

We apply Fourier transformation to f, seen as a convolution equation of simple normalized transforms of g

$$J(f(\tau); z) = \sqrt{2\pi}\, J\left(g\left(\frac{\tau}{\sigma}\right);z\right) J\left(g\left(\frac{\tau}{\sigma'}\right);z\right)$$

$$= \sqrt{2\pi}\, J(g(\tau); \sigma z)\, J(g(\tau);\sigma'z)$$

$$= \frac{1}{\sqrt{2\pi}} \cdot g(\sqrt{\sigma^2 + \sigma'^2}\, z) = \frac{1}{\sqrt{\sigma^2 + \sigma'^2}} \cdot J\left(g\left(\frac{\tau}{\sqrt{\sigma^2 + \sigma'^2}}\right);z\right)$$

Hence

$$f(\tau) = \left(\frac{1}{\sqrt{\sigma^2 + \sigma'^2}}\right) g\left(\frac{\tau}{\sqrt{\sigma^2 + \sigma'^2}}\right)$$

Therefore, a Gaussian mixing kernel, applied to a Gaussian family, gives a Gaussian family whose variance is the sum of variances.

REFERENCES

1 P. Valentin, Cours de Génie de la Séparation. Ecole Polytechnique. Paris. 1977.
2 P. Valentin, in A. Rodrigues and D. Tondeur (Editors), Percolation Process and Applications (NATO ASI Series, E33), Sijthoff and Noordhoff. Netherlands. 1980. pp. 141–195.
3 P. R. Rony, Sep. Sci., 3 (1968) 239.
4 P. R. Rony, Sep. Sci., 3 (1968) 357.
5 M. J. E. Golay, in D. Goldup (Editor), Gas Chromatography 1964, Institute of Petroleum, London. 1965, p. 2.

6 H. S. M. Coxeter, *J. Math. Pures Appl.*, 41, No. 9, (1962) 137.

7 H. S. M. Coxeter, *Regular Polytopes*, Macmillan, New York, 2nd ed., 1963.

8 E. D. Bolker, *Trans. Am. Math. Soc.*, 145 (1969) 323.

9 P. McMullen, *Trans. Am. Math. Soc.*, 159 (1971) 91.

10 G. C. Shephard, *Can. J. Math.*, 26 (1974) 302.

11 R. Schneider and W. Weil, *Applications of Convexity*, Birkhauser, Basle, 1982, pp. 296–317.

12 D. Blackwell, in *Proceedings of the Second Berkeley Symposium on Mathematical Statistics and Probability* (1950, Berkeley), Berkeley University Press, Los Angeles, 1951, pp. 93–102.

13 S. Karlin, *Total Positivity*, Stanford University Press, Stanford, CT, 1968.

14 J. Villermaux, in A. Rodrigues and D. Tondeur (Editors), *Percolation Process and Applications (NATO ASI Series*, E33), Sijthoff and Noordhoff, Netherlands, 1980.

15 D. Tondeur, *Ph.D. Thesis*, University of Nancy, 1969.

16 D. Girard and P. Valentin, in J. P. Penot (Editor), *New Methods in Optimization and Their Industrial Uses*, (*International Series of Numerical Mathematics*, Vol. 87), Birkhauser, Basle, 1989 pp. 57–71.

17 P. R. Rony, *AIChE Symp. Ser.*, 68, No. 120 (1972) pp. 89–104.